



Faculty of Resource Science and Technology

**Cold Flow Behaviour of Esterified Palm Olein with TiO_2 Nanoadditive
for Green Lubricant**

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Cold Flow Behaviour of Esterified Palm Olein with TiO₂ Nanoadditive for Green Lubricant

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A thesis submitted

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

The poor cold flow properties of natural palm olein (PO_o) limits its application as a lubricant in low-temperature industrial fluids. To address this, PO_o was converted into large-branched esters via epoxidation, alcoholysis, and esterification. Epoxidation of PO_o with performic acid produced epoxidized palm olein (EPO_o) with a 90.65% yield and 98.14% oxirane conversion, followed by the glycerol-based alcoholysis that incorporated three hydroxyl groups for branching at 85.93% yield. Esterification with oleic, linoleic, and salicylic acids at 140°C for 4 h produced large-branched oleic acid-esterified palm olein (OA-EPO), linoleic acid-esterified palm olein (LA-EPO), and salicylic acid-esterified palm olein (SA-EPO) with excellent yields of 97.46%, 96.19%, and 99.29%, respectively. The Fourier Transformation Infra-Red (FTIR), proton (¹H) and carbon (¹³C) Nuclear Magnetic Resonance (NMR) spectroscopy analysis confirmed the compound structures. The results showed significant improvement ($P < 0.05$) in cold flow of all large-branched EPO, with pour point values ranging from -12 to -7°C relative to PO_o at 6°C. SA-EPO demonstrated the lowest pour point value of -12°C followed by LA-EPO (-11°C) and OA-EPO (-7°C). The addition of 0.1% (w/w) titanium dioxide (TiO₂) nanoadditive to LA-EPO further improved its pour point from -11°C to -12°C. These findings suggest the potential of large-branched esterified palm olein as sustainable feedstock for the development of green lubricant. By exhibiting good performance under cold condition with incorporation of nanoadditive technology, this formulation might be suitable in various sectors supporting the advancement and practical implementation of sustainable lubrication technology.

Keywords: Epoxidation, alcoholysis, esterification, TiO₂ nanoadditive, green lubricant

Kelakuan Aliran Sejuk Olein Sawit Terester dengan TiO₂ Nanoadditif bagi Pelincir Hijau

ABSTRAK

Sifat aliran sejuk olein kelapa sawit asli (PO_o) yang lemah menghadkan penggunaannya sebagai pelincir dalam cecair industri suhu rendah. Untuk mengatasinya, PO_o telah ditukar kepada ester bercabang besar melalui epoksida, alkoholisis, dan pengesteran. Epoksida PO_o dengan asid performik menghasilkan olein kelapa sawit terepoksida (EPO_o) dengan hasil 90.65% dan penukaran oksirana 98.14%, diikuti alkoholisis berasaskan gliserol yang menggabungkan tiga kumpulan hidroksil bagi bercabang pada hasil 85.93%. Pengesteran dengan asid oleik, linoleik, dan salisilik pada 140°C selama 4 jam menghasilkan olein kelapa sawit bercabang besar diesterkan asid oleik (OA-EPO), linoleik (LA-EPO), dan salisilik (SA-EPO) dengan hasil cemerlang 97.46%, 96.19%, dan 99.29% masing-masing. Spektroskopi Transformasi Fourier Infra-Red (FTIR), proton (¹H) dan karbon (¹³C) Resonan Magnetik Nukleus (NMR) mengesahkan struktur kompaun. Keputusan menunjukkan penambahbaikan ketara ($P < 0.05$) dalam aliran sejuk semua EPO bercabang besar, dengan nilai titik tuang antara -12 hingga -7°C berbanding PO_o pada 6°C. SA-EPO menunjukkan nilai titik tuang terendah -12°C diikuti LA-EPO (-11°C) dan OA-EPO (-7°C). Penambahan nanoadditif 0.1%(w/w) titanium dioksida (TiO₂) kepada LA-EPO meningkatkan lagi titik tuangnya daripada -11°C kepada -12°C. Penemuan ini mencadangkan potensi olein sawit terester bercabang besar sebagai bahan suapan yang mampan untuk pembangunan pelincir hijau. Dengan mempamerkan prestasi yang baik dalam keadaan sejuk dengan penggabungan teknologi nanoadditif, formulasi ini mungkin sesuai dalam pelbagai sektor yang menyokong kemajuan dan pelaksanaan praktikal teknologi pelinciran mampan.

Kata kunci: *Epoksida, alkoholisis, pengesteran, TiO₂ nanoadditif, pelincir hijau*

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LIST OF ABBREVIATIONS

Abs	Absorbance
ANOVA	Analysis of Variance
ASTM	American Society for testing Materials
ATR	Attenuated Total Reflectance
AV	Acid value
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	Boron trifluoride diethyl ether complex
$^{\circ}\text{C}$	Degree Celsius
C	Carbon
CaCl_2	Calcium chloride
CAGR	Compound Annual Grow Rate
CDCl_3	Deuterated chloroform
cm	Centimetre
cm^{-1}	Wavenumber
^{13}C -NMR	Carbon Nuclear Magnetic Resonance
df	Degree of Freedom
DMSO	Dimethyl sulfoxide
EPO _o	Epoxidized palm olein
equiv	Equivalent
EV	Ester value
FTIR	Fourier Transformation Infra-red
g	Gram
g/mol	Gram per mol

h	Hour
HCl	Hydrochloric acid
HCOOH	Formic acid
$^1\text{H-NMR}$	Proton Nuclear Magnetic Resonance
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
<i>In-situ</i>	In the place
<i>In vacuo</i>	In vacuum
IV	Iodine value
KOH	Potassium hydroxide
LA-EPO	Linoleic acid-esterified palm olein
LA-EPO-TiO ₂	Linoleic acid-esterified palm olein with titanium dioxide
mbar	Millibar
mg	Milligram
MgSO ₄	Magnesium sulphate
MHz	Megahertz
min ⁻¹	Per minute
min	Minutes
ml	Millilitre
mmol	Millimole
mol	Mole
MoS ₂	Molybdenum disulfide
MS	Mean of squares
MW	Molecular weight
N	Normality

NaCl	Sodium chloride
NaHCO ₃	Sodium bicarbonate
nm	Nanometre
OA-EPO	Oleic acid-esterified palm olein
OA-EPO-TiO ₂	Oleic acid-esterified palm olein with titanium dioxide
OH	Hydroxyl
OOC	Oxirane oxygen content
pH	Potential of hydrogen
pKa	Acid dissociation constant
PO _o	Palm olein
PP	Pour point
ppm	Parts per million
p-TSI	p-Toluene sulfonyl isocyanate
rpm	Revolutions per minute
SA-EPO	Salicylic acid-esterified palm olein
SA-EPO-TiO ₂	Salicylic acid-esterified palm olein with titanium dioxide
SEM	Scanning Electron Microscopy
SiO ₂	Silica
SS	Sum of squares
SV	Saponification value
T	Temperature
TiO ₂	Titanium dioxide
TiO ₂ -CuO	Titanium dioxide-Copper(II) oxide
μL	Microlitre
U.S.	United States

vol%	Percent by volume
ZnO	Zinc Oxide
% (w/w)	Weight by weight concentration percentage
β	Beta
$^{\circ}$	Degree
%	Percentage

CHAPTER 1

INTRODUCTION

1.1 Study Background

Since the industrial revolution, the global economic relies mostly on the factory manufacturing products such as lubricating oils. In industrial era, lubricant becomes demanding in the use of machines to optimize the energy consumption, reduce the friction, mechanical wear, and also corrosion which is expected for an extended period of use (Deuraseh & Deuraseh, 2023). Approximately 37 million tonnes of lubricants from the fossil oil resources are exploited globally every year due to increasing of the demand and population (Unugul et al., 2020). It is estimated to increase to 38.1 million tonnes by 2028.

In lubricant market, most of the lubricants are supplied to the countries in the Asia-Pacific (35%) followed by European regions (23%), North America (22%), Latin America (10%), Africa (6%), and Middle East (4%) (Pinheiro et al., 2021). In general, the lubricant formulation exists in liquid, solid, and gaseous states that mainly comprise of 70% to 99% of base oil. It is ranged at nearly 85% to 90% of lubricants are generated from the non-renewable fossil energy source which known as mineral oils. However, this emerges a huge environmental issue as approximately 50% of the toxic petroleum-based lubricants are discharged into our environment especially the water and soils due to the oil spillage and the accident loss that emerging the environmental pollutions and health problem as one kilogram of carcinogenic acids in the crude oils could damage a million litres of potable water (Almasi et al., 2021).

In fact, the development of today's modern machines still be subjected to the lubricating oils based on mineral oils due to their high operating efficiency. Nevertheless,

these mineral based lubricants are hazardous, non-renewable, and low biodegradability that cause a lot of environmental damage which it discharges more than 24 million tonnes of waste oil in global every year (Suhaimi et al., 2022). To concern the sustainability issue, the crude oils which are extracted from the earth's crust may face depletion in one day due to the high industrial demand on the supply of lubricants. That is the reason why the natural compounds are developed to replace the petroleum products nowadays.

From the research view, the vegetable oil-based bio-lubricant is a suitable candidate to supersede the petroleum-based lubricant due to its high biodegradability and low toxicity (Aziz et al., 2020). Oleochemical-based lubricants are environmentally benign which suit for different applications. The advantages of using bio-lubricants derived from the vegetable oils are their high availability meaning in an abundant resources which are more sustainable in the storage and shipping as well as their intermediate products are reusable for the application of biorefineries (Nogales-Delgado et al., 2021).

We can see that the global bio-lubricant market is growing as it is expected to increase from 1.9 billion in year 2020 to 2.5 billion by 2026 in U.S. lubricant market with a 5.2% of Compound Annual Grow Rate (CAGR) (Nurazira et al., 2022). This is caused by the enforcement of government regulations that restrict the use of petroleum-graded lubricants in some regions. To explore a new sustainable lubricant, the researchers start to focus their attention on the use of different vegetable oils to be their raw materials in the design of research. In this new trend, the explorations of plant oil-oriented lubricants have been initiated actively but not yet in an extensive application as some research gaps still be able to discover in the research area of vegetable oils especially on palm olein.

Palm olein is one of great potential sources to be developed as an alternative green lubricant through chemical modification techniques. From the oil palm tree, the edible semi-

solid crude palm oil is mainly extracted from the fleshy orange-red mesocarp of oil palm fruits. Palm olein (PO_o), a refined crude palm oil, is the liquid fraction derived from the industrial fractionation process (Syarifah-Noratiqah et al., 2020). PO_o is selected instead of conventional palm oil because PO_o shows better fatty acid configuration with higher contents of oleic acid (43.9%) and linoleic acid (13%) with more unsaturated double bonds than palm oil (Jadhav et al., 2021). The amphiphilic molecules in the PO_o belongs to the polar ester groups associated at the non-polar hydrocarbon chains. This amphiphilic characteristic satisfies the required requirements as the boundary and hydrodynamic lubricants. PO_o is renewable and less hazardous so it is forecasted to replace 90% of the petroleum oil to reduce the production of non-recyclable waste (Hussein et al., 2021).

In environmental and sustainability concerns, PO_o has high biodegradability that more than 95% so it can degrades in a rapid rate that ranged at 20% to 30% faster than the mineral oil-based lubricants (Owuna et al., 2020). PO_o is renewable, less hazardous, and also cheaper in price (Hambali & Puspita, 2021; Tajau et al., 2020). Moreover, Suhami and her research partners have reported that palm oil is more sustainable compared to the mineral oil because mineral oil has a relatively poor biodegradability between 0% and 40% (Suhaimi et al., 2022). Thus, PO_o stands as a promising substitute to the petroleum oils that also demonstrating a stable thermo-viscosity property with high flash and fire points which is safe over the temperature change (Rahman et al., 2023).

Besides, Malaysia is ranked as the second leading country in the worldwide production of the palm oil which owned 5.9 million hectares of oil palm trees and 423 palm oil operating factories (Abubakar et al., 2021). The yield of oil palm tree per unit land area in Malaysia is relatively high that up to 10 times more than other crops (Loh & Muzzammil, 2021). It is known that the palm oil production has reached as high as 75 million tons in

2020 (Almeida et al., 2021). Therefore, PO_o is eligible to become the replenishable feedstock to be manufactured into the bio-lubricant in order to support the growing market demand of lubricants for lubrication, abrasion resistance, and the formation of strong protecting films between the contacting surfaces in the machines.

Although these outstanding advantages are mentioned as above, the vegetable oils including PO_o share a major drawback of poor cold flow behaviour. This weakness will restrict the direct application of PO_o as the lubricant in the refrigeration system of food industry as well as its usage in the seasonal countries as it tends to solidify at low temperature (Norhayati et al., 2022). Solidification is commonly happened at the linear triacylglycerols of the lubricating oil because of the uniform shape which allows the individual molecules to link the network together into the crystal lattice via nucleation or crystallization at cold condition. Saturated fatty acid in the oil is susceptible to clump faster than the unsaturated fatty acid into the macro-crystals (Salih & Salimon, 2021). To summarize, the molecular structure and the presence of saturated fatty acids are the main concern to affect the fluidity of plant oils at low-temperature applications.

For the molecular structure, there are some reactive functional groups polymerized in the fatty acid chains of plant oils but with very low functionalities that limit the application. The triglyceride structure of PO_o comprises of a mixture of ester moiety derived from the glycerol and the free fatty acid chains mainly with the saturated palmitic and stearic acids together with the unsaturated fatty acid chains like linoleic and oleic acids (Shahdan & Hirzin, 2021). To synthesize the bio-lubricant, the chemical modification action is required on the reactive sites of the triglycerides such as the carbon-carbon double bonds of the plant oils (Li et al., 2020). The unstable double bonds in the triglycerides can be actively converted into high reactivity of oxirane ring which is a beneficial functional group suitable

for further functionalization (Stavila et al., 2023). The unsaturation can be used to react with the reactive peracid reagents of performic or peracetic acid via epoxidation.

Epoxidation is a well-known strategy to model the epoxide groups due to its simple and low-cost production with a high level of selectivity. However, epoxidation is an exothermic reaction that may causes thermal runaway so the experimental temperature should be controlled by the cooling medium with the chemical dosing in the dropwise rate (Dominguez-Candela et al., 2022). The thermal runaway may causes the collapse of the oxirane rings that impact the quality and the yield of products due to the presence of protons during the epoxidation (Meng et al., 2023).

Although there are some molecular structure changes by the epoxidation, the epoxidized plant oils still cannot completely substitute the mineral-processed lubricating oils because it lacks of promising lubricating performance (Sarma et al., 2021). To improve the oil's performance, the ring-opening reaction via alcoholysis is conducted after the epoxidation. The oxirane ring opening of epoxidized fatty acids can be carried out by various nucleophiles such as alcohols with the catalysts to generate valuable ring-opening intermediates (Sharma et al., 2022). By the way, the hydroxyl groups are inserted into the active sites of plant oil to synthesize the bio-polyols. The bio-polyols behaves low acid value, low viscosity, and with small molecular weight distribution (Stavila et al., 2023).

Even though the epoxidation and the ring opening reactions have enhanced some chemical properties of the starting oil but its damaging characteristic of poor cold flow behaviour still exists so it should proceed with the esterification reaction. The purpose is to correct the unstable β -hydrogen atom in the structure. This is declared by Almasi and other researchers in 2021. During the esterification reaction, the alkoxy group of ester acts as a good leaving group in the nucleophilic substitution mechanism (Soodoo et al., 2023). The

ester creates the lubricity feature by presenting the strong dipole moments at the polar sites that adhere strongly to the moving contact surfaces which can reduce the friction and wear.

Besides the friction-reducing ability, the synthetic esters also display a low-temperature property and high oxidative stability after increasing the oil's branch length and molecular weight through esterification (Raof et al., 2022). The fatty acid-based esters are proven to be versatile lubricant alternatives to the standard petroleum based-lubricant. However, there is still no much exploration using the solvents of toluene and acetonitrile during esterification reaction between oleic acid, linoleic acid, and salicylic acid with polyol intermediates respectively. In this study, the ester moiety was incorporated into the structure of PO_o using different reagents and solvents in the presence of catalyst to increase its mid-chain length between the fatty acid backbones.

In addition, the utilization of suitable nano-additive technology is allowed to develop an excellent nano-additive based lubricant which is significantly more effective than traditional bio-based lubricants to reduce the friction. The selection of a proper lubricant additive depends mostly on the additive's ability to compatible with the lubricating oils to perform the desired function. This can be seen from the hardness, concentration, and the particle size of the nano-additive (Zilabi et al., 2022). Theoretically, the addition of nanoparticles into the lubricating oils enhance the lubricating performance by acting as a nano-ball bearing to roll between two contacting surfaces or by forming a triple protective film to reduce the coefficient of friction (Yunus et al., 2020).

To design a nano-additive based lubricant, it is prepared by a small amount of nanoparticles from 0.2% to 0.5% to disperse with the vegetable oil derivatives using the ultrasonic and mechanical agitation methods (Karmakar et al., 2020). The inorganic nanoparticles are difficult to create a stable suspension in the vegetable oil due to its high

surface activity (Waqas et al., 2021). In this sense, it is assisted by the presence of surfactants to link with the hydroxyl and carboxyl groups on the surface of lubricating oil to stabilize the structure. In this manner, the dispersion of nano-powders in the non-polar mediums become more stable (Abdel-Rehim et al., 2021).

Additionally, the conditions of nano-dispersions are strongly correlated on the concentration of nano-powders as an insufficient amount could affect the lubricating property while an excess amount could form the discontinuous oil film (Río et al., 2022). The tribological behaviour of the nano-lubricant is controlled by the shape and the size of nanoparticles as spherical shaped nanoparticles result in higher load-bearing capacity. This can be observed from earlier research findings that the titanium dioxide (TiO_2) nano metal oxide particles by 0.01% of volume have improved the load-bearing strength by 40% (Singh et al., 2020). Other than the tribological performance, the oxidative and thermal stability are also improved by the dispersion of nano-particles in the vegetable oil derived lubricants (Sadiq et al., 2022). The metal oxide (TiO_2) nanoparticles are suggested in this study as the pour point improver due to its benefits of easily obtainable, non-toxic, and also considered as non-hazardous for human handling (Shashavali et al., 2021).

From the particular point of view, the yield of the intermediates and products are controlled predominantly by the operating reaction conditions (Zora et al., 2021). The reaction temperature and the reaction time are chosen as the variable controls in the experiment. This study could explore the potential of chemically modified PO_6 as a green lubricant to replace the conventional petroleum-based lubricants that not just limited to engines but also relevant for textile industries, food industries, hydraulic fluids, metalworking lubricants, greases, machinery and many others. Most research investigations have concluded the effectiveness of TiO_2 nano-additive in the tribology property of the

lubricant but there still lacks of information about its effect on the pour point of bio-based lubricant in literature. For this reason, the expected cold flow behaviour improvement of bio-lubricant through proposed epoxidation, alcoholysis, and esterification pathways with the incorporation of nano-additive will be evaluated in this study.

For example, green lubricants have been used in textile and fibre industries to lubricate fibre in order to withstand the weaving and spinning process. The use of green lubricant would be in a great demand to lubricate different types of machinery used in food processing and production industries due to non-toxic, non-petroleum smelling and biodegradable.

1.2 Problem Statement

Approximately 37 million tonnes of fossil-based lubricants are consumed globally each year due to rising demand and population, with its usage projected to reach 38.1 million tonnes by 2028 (Unugul et al., 2020). Petroleum-derived lubricants are extensively used in manufacturing, automotive, and industrial fluids due to their effective performance in reducing friction. However, their continued use poses significant environmental and health risks due to their toxicity and non-renewable nature. This also poses a major environmental threat, as around 50% of toxic petroleum-based lubricants are released into the water and soil through spills and accidents, with one kilogram of crude oil's carcinogenic acids capable of polluting a million litres of potable water (Almasi et al., 2021). Another problem is that the long-term sustainability of mineral oil is uncertain due to the possible future depletion.

To reduce the reliance on petroleum-based lubricants, biodegradable alternative lubricants derived from vegetable oils have been recently studied due to their renewability, non-toxicity, and environmental compatibility. Researchers have identified the vegetable oil of palm oil as a promising renewable feedstock for bio-lubricant production, particularly due

to its high productivity and availability in Malaysia. Previous studies primarily focused on optimizing the epoxidation reaction in palm oil or creating a small gap between fatty acid backbones (Nor and Salimon, 2019; Derawi and Salimon, 2013). According to their results, epoxidized palm oil exhibited a higher pour point of 18°C compared to the natural palm oil of 7°C. This indicates that the major drawback of palm oil with its tendency to solidify at low temperatures remains unresolved, as the initial epoxidation step does not improve the oil's cold flow properties, thereby limiting its application in cold environments.

Furthermore, the epoxide ring opening via water hydrolysis or decanolysis could only substitute one or small ester at the olefinic sites (Derawi and Salimon, 2013). The small gap formed between fatty acid backbones following these approaches would not efficiently reduce the pour point of epoxidized palm oil. Recent studies have suggested performing alcoholysis after epoxidation as a promising route to achieve a stable molecular structure of polyols. However, most studies employ mono-alcohols or diols, resulting in bio-polyols that contain only secondary hydroxyl groups (from mono-alcohols) or a mixture of both primary and secondary hydroxyl groups (from diols). When diols such as ethylene glycols were used, the resulting polyols exhibited relatively low hydroxyl numbers, typically ranging from 70 to 90 mg KOH/g (Musik et al., 2021). One key gap in the literature is the limited investigation of trihydric alcohols for epoxide ring opening reactions, which could potentially enhance the hydroxyl functionality and properties of resulting polyols.

Additionally, previous research on the subsequent esterification reaction had primarily focused on the palm oil-based bio-lubricants rather than the palm olein based bio-lubricants. Palm oil-based bio-lubricants still exhibited poor pour points of 10°C (Nurazira et al., 2022) and 17°C (Nurazira and Salimon, 2023) after the esterification reaction, although their lubrication performances were improved.

To address these limitations, this study proposes the chemical modification of palm olein by introducing ester moieties through a sequence of epoxidation, alcoholysis, and esterification reactions. The key step involves the use of glycerol in the alcoholysis reaction that incorporate three hydroxyl groups and enable the installation of large branched esters into the molecular structure. This is effective because palm olein, with its high degree of unsaturation, generates a high content of hydroxyl groups during the ring opening reaction with glycerol, which subsequently promotes the formation of large branched esters through esterification. Furthermore, the use of linoleic and oleic acids in the esterification reaction offers a low-cost and biodegradable approach, making the resulting bio-lubricants more sustainable compared to mineral-based lubricants. These modifications aim to increase the mid-chain length between the fatty acid backbones, which is expected to reduce the pour point of the bio-lubricant and to inhibit its easy crystallization at low temperatures.

Moreover, the literature offers limited information on the incorporation of titanium dioxide (TiO_2) nano-additives into the palm olein- based lubricant formulations as pour point improvers, as most studies had focused solely on their tribological performance. Therefore, this study investigates the development of a palm olein-based bio-lubricant with an improved pour point as a sustainable alternative to petroleum-based lubricants. This work aims to advance the understanding of the relationship between esterified palm olein and its cold-flow behaviour, along with the effect of incorporating TiO_2 nano-additives, thereby contributing to the development of sustainable and eco-friendly lubricants that reduce dependency on fossil-based lubricants.

1.3 Objectives

The objectives of this research study were listed below:

- i. To modify the chemical composition of palm olein via epoxidation, alcoholysis, and esterification reactions.
- ii. To evaluate the cold flow behaviour of esterified palm olein based on pour point value.
- iii. To investigate the effect of different concentrations of TiO_2 nano-additive to cold flow behaviour of esterified palm olein.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Palm Olein

Malaysia is one of the leading countries in Asia to cultivate the oil palm trees dominantly with 5.87 million hectares (Naidu & Moorthy, 2021) that is able to produce approximately 19.5 million metric tonnes (Chong et al., 2021) of palm oils per year. Palm oil of Malaysia has contributed to 10% of the country's gross domestic product that supports more than half of the worldwide palm oil (Chew et al., 2021; Salih & Salimon, 2021). Consequently, the palm oil market shows a strong and consistent expansion at a rate of around 2% annually (Parsons et al., 2020).

Palm oil is extracted from the mesocarp, the inner layer of the palm tree fruit. Palm oil is refined and dry fractionated into low melting point liquid fraction which is PO_o with a high conversion of 80% (Ishola et al., 2020). The fractionation involves the crystallization to separate and eliminate the solid crystals (stearin) from the less-dense upper layer of liquid (olein) via filtration. There is 80% of PO_o and 20% of palm stearin produced from a batch of palm oil extraction. The liquid portion, PO_o looks clear, light yellow, and odourless at room temperature with melting point between 18 and 20°C (Yılmaz & Ağagündüz, 2022).

For the structure of PO_o, it comprises of triglycerides with the component of three long-chains of fatty acids and glycerol in a *cis*-configuration. Fundamentally, triacylglycerol is a chemical compound that grouped by three main elements which are carbon, hydrogen, and oxygen to form the fatty acids and glycerol (Suhaimi et al., 2022). There is 85% of the unsaturation are discovered at the position SN-2 of the triacylglycerols (Absalome et al., 2020). The crude palm oil is normally packed with 80 to 85% of triacylglycerols,

diacylglycerols (3-8%), free fatty acids (3-4%), and below 3% of monoacylglycerols (Bahadi, Salih, et al., 2021). The structure of palm oil is packed with the ester group, beta-hydrogen, saturated, and unsaturated fatty acid chains with the double bonds. The saturated fatty acid chains are linear with sp^3 hybridized carbon-carbon (C-C) single bonds. Its molecular geometry is tetrahedral with the bond angle of 109.5° . Meanwhile, the unsaturation site is sp^2 hybridized C=C double bonds in trigonal planar at 120° of bond angle. The double bonds are joined by a strong sigma-bond and a weak pi-bond which control the relative chemical reactivity. The *cis* C=C double bond is kinked for fluid structure by adopting a bent shape. The ester group is constructed by a carbonyl (C=O) group and an alkoxy (C-O-C) group which can rotate easily so the flexibility of the molecule increases. It is flat trigonal planar in 120° of bond angle with the carbonyl carbon in sp^2 hybridized orbitals (Soodoo et al., 2023). To summarize, PO_o as a biodegradable vegetable oil with the polar ester group and non-polar hydrocarbon chains present the amphiphilic property.

The study shows that PO_o contains a high amount of oleic acid (43.9%) with one unsaturation and also linoleic acid (13%) with at least two unsaturation along with 40.8% of saturated palmitic acid (Jadhav et al., 2021). This is consistent with another study (Nainggolan & Sinaga, 2021) declaring that PO_o is made up of 41.58% oleic acid (C: 18-1), 10.71% linoleic acid (C: 18-2), and 42.23% palmitic acid (C: 16-1) where C denotes the carbon chain length. The proportions of saturated and unsaturated fatty acids are balanced at a ratio of almost 50% to each (Jaratrotkamjorn & Tanrattanakul, 2020). The additional benefit of PO_o is it has less palmitic acid (40%) than palm oil (44%). In contrast, PO_o has higher contents of oleic acid (43%) and linoleic acid (13%) (Jadhav et al., 2021) than conventional palm oil of 39% oleic acid and 9% linoleic acid (Padial-Jaudenes et al., 2020;

Wang et al., 2020). This is why that palm olein is selected in this study instead of using regular palm oil to be chemically modified into green lubricant.

Other than that, crude palm oil has low saponification value (Jakune et al., 2023) that ranged at 196 to 205 mg KOH/g due to the structure consists of long-chain fatty acid chains in high molecular weight. Iodine value (IV) defines the unsaturation degree of the oils that the crude palm oil is ranged at 51 to 53 mg/g (Suryani et al., 2020) which is lower than PO_o that more than 56 mg/g (Gibon & Danthine, 2020). PO_o has higher IV because of the withdrawal of saturated fractions when refining (Gomez et al., 2021). IV reflects the quantity of the double bonds in the oil as well as the oil's susceptibility to the oxidation (Omowonuola et al., 2023). PO_o is considered as a non-drying oil relative to its IV that less than the reference of 90 mg/g so it remains liquid state in the exposure to air (Stavila et al., 2023). PO_o has a high stock availability in Malaysia (Ayompe et al., 2021) due to the large-scale production of average 4 to 4.5 tonnes of palm oil per hectare in the cultivated regions throughout the year (Kaniapan et al., 2021) so the price of PO_o is considerably cheaper than the other plant oils (Yang et al., 2022). In the sense, the maximum product output of PO_o is much higher than the other crops (Oo et al., 2021). PO_o is derived from the renewable resources of palm oil with a high biodegradability (Shah et al., 2021) and less toxicity so it contributes to no volatile organic chemical compounds that can minimize the environmental and health issues. At the room temperature, palm oil behaves a semi-solid state while PO_o is more liquid form so it is easier to be chemically modified. Thus, PO_o with a high degree of unsaturation is considered as a better choice compared to palm oil.

However, vegetable oil is not suitable to be directly registered as a lubricant. This is because most of the plant oils hold an undesirable physical characteristic of poor cold flow property (Maleki et al., 2022) that it tends to crystallize after the cooling at low temperature.

This is caused by the conjugated *cis* double bonds distributed in the triglycerides that encourages the crystallization (Xu et al., 2021). According to the past research work, the presence of bis-allylic protons and the hydrogen atoms in the beta position of the glycerol in the triglyceride carbon skeleton provides the oxidation active sites to cause the structure becomes more unstable at the high temperature which impacts the lubrication performance (Ma et al., 2021). It is explained as a poor thermo-oxidative stability. Besides that, the double bonds in the fatty acid chains tend to react with the oxygen in the air that result in the oxidation reaction and also cause the deposition of the insoluble contaminants which degrade the oils (Esmaeili et al., 2022). These limitations can be moderated by the particular chemical modification processes of epoxidation, alcoholysis, and the esterification plus the addition of nano-additive to amend the functional group of double bonds into a green lubricant.

2.2 Epoxidation

Epoxidation is defined as the transformation of unsaturated carbon-carbon double bond into the epoxide which looks like a cyclic ether. There is an oxygen atom connected by two single bonds to the respective carbon atoms to form the highly reactive oxirane ring. The oxirane ring is absolutely stressed with a bond angle of 60 degrees (Mahadi et al., 2022). The epoxides are colourless, volatile, non-polar, and with low molecular weight. From the earlier research study, the epoxidation reaction is able to improve the oxidative stability of the vegetable oils and also reduce its acidity (Bashiri et al., 2021). It is reacted to the double bonds of the oil's long chain olefins to form the environment-friendly oxirane rings. This could reduce the active sites for the oxidation to radical attack. In the oil, the oleic and linoleic acids which contain the double bonds are usually used to undergo free radical polymerization to transform the unsaturated double bonds into the polymeric structures such as epoxy groups which increase the cross-link density and also improve the chemical

functionalities (Saraswat et al., 2024). From the epoxidation reaction, the resulting epoxide is highly reactive and suitable as the intermediates for the consequent organic synthesis.

Epoxidation is carried out by mixing the performic acid with the vegetable oil in a liquid-liquid phase (Sawitri et al., 2020). This process is called *in-situ* peracid epoxidation that the performic acid comes from the mixing of short-chain carboxylic acid, HCOOH and H₂O₂. HCOOH acts as the oxygen carrier while the H₂O₂ is the oxygen donor so the high reactivity and solubility of HCOOH is more preferred than H₂O₂ in the oil (Ashine et al., 2023). HCOOH has the simplest hydrocarbon chain that attend a large positive charge with the inductive effect which can release the proton easier to enhance the generation of epoxide (Zin et al., 2020). The epoxidation process implies the electrophilic addition mechanism that it starts from H₂O₂ to donate an oxygen element to the carboxylic acid of HCOOH to form the peracid and water. At the same time, the unsaturated double bonds of the oils receive the extra oxygen from the weak bond of peracid then the original carboxylic acid is released back to the liquid phase to complete the epoxidation reaction (Ju et al., 2020). After that, the reaction cycle restarts again. The epoxidation phase is rate-limiting and reversible (Ho et al., 2022).

Furthermore, the addition of performic acid into the vegetable oil is an exothermic reaction that releases extra heat so the process should be managed with the cooling medium. The performic acid must be added slowly to control the increment of temperature. This is to avoid the excessive decomposition of the thermally unstable H₂O₂ into the oxygen and water which degrade the product and also to prevent the formation of explosive mixture (Budiyati et al., 2020). The concentrated peracids are unstable that the performic acid itself may decomposes into the carbon dioxide and water which can be discovered indirectly from the stoichiometric mass balance between the H₂O₂ and HCOOH (Santacesaria et al., 2020).

The research paper confirms that the performic acid is better than peracetic acid to be the oxidant in the epoxidation reaction because the performic acid is easily formed from the H_2O_2 and HCOOH . H_2O_2 has a high content of active oxygen together with the HCOOH which is highly reactive and electrophilic that do not need any catalyst to make the reaction system safer and cheaper (Ho et al., 2022). The epoxidation is not suggested to use the mineral acids such as sulphuric acid and hydrochloric acid as the catalysts due to its high corrosion that may damage the apparatus and also form the undesirable by-products (Afifah et al., 2021). With the use of catalyst H_2SO_4 , the molar ratio of PO_6 : HCOOH : H_2O_2 at 1: 1: 1.5 has achieved high yield of 95% at 55°C in 25 min while the molar ratio of 1: 1.64: 2 at 45°C in 45 min has yielded 80%. Without the catalyst, the highest epoxidation yield is 88% (Rahman et al., 2020).

H_2O_2 , a peroxide is listed as an economical and environmentally friendly organic oxidizing agent (Fukuzumi et al., 2021) due to its lower price (Agu et al., 2022), less hazardous, easily handle, and safe operation (Azmi et al., 2022) that produce the water as the main side product (Targhan et al., 2021). The research study (Marriam et al., 2023) has suggested the use of versatile H_2O_2 to react with the carboxylic acid due to its highly efficiency to connect all the molecular junctions in the transition state of epoxidation to make the production yield greater. The study (Jalil et al., 2021) has examined that higher mole ratio of H_2O_2 can increase the epoxidation reaction rate as the molar ratio of 1.5 has gained 85.6% of yield which is higher than 0.5 and 1 molar ratio as well as the another study (Derahman & Abidin, 2022) with 2.19 mol ratio that reached 90.98% of epoxide yield. Besides the raw material of PO_6 , one university research has indicated that the epoxidation using the palm kernel oil under the reaction conditions of 7.67 mol of H_2O_2 and 5 mol of HCOOH at 51.85°C among 1.62 h is capable to obtain 92.5% of epoxide yield (Salimon &

Salih, 2023). Another study using the palm oil as the raw sample to react with 20 wt.% of acetic acid and 60 wt.% of H_2O_2 in the presence of 2% H_2SO_4 at 70°C in 90 min gives the highest oxirane conversion of 87.59% (Hartawan et al., 2022).

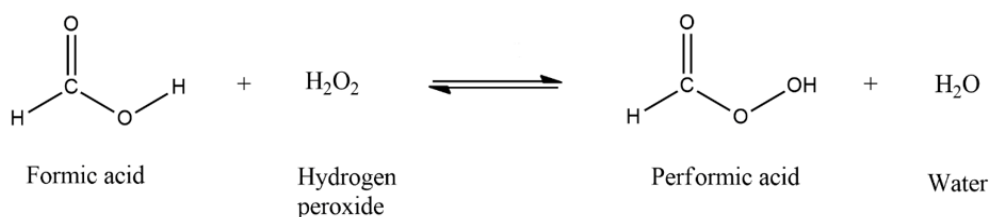
An university research study has investigated that the optimum reaction condition of epoxidation is controlled at 5.91 mole ratio of HCOOH with 3.60 mole of H_2O_2 at 40°C for 2.55 h that showed 86% of epoxide yield with a high relative oxirane conversion of 99.43% (Nurazira & Salimon, 2022). This is consistent to another study that using molar ratio of 5:4 for the HCOOH and H_2O_2 at 45°C which give 90% of yield and 95.5% of oxirane conversion (Hasnan et al., 2020). The research paper (Rasib et al., 2023) has reported that 150 min of epoxidation reaction time can attain 95.5% of oxirane conversion. Concurrently, a good performance is constructed at 40°C to give more than 95% of double bond conversions with 90% of epoxide selectivity (Cogliano et al., 2024). At higher temperature of 75°C , the maximum relative oxirane conversion is 86% (Yeop et al., 2024). The oxirane oxygen content drops after the reaction time of 3 h because the longer reaction times create larger molecular collisions that collapse the oxirane groups via the undesirable ring-opening reaction which result in more diols and glycols as the side outcomes (Pongmuksuwan et al., 2023).

For the main points, higher concentration of HCOOH can facilitate the epoxidation rate in shorter reaction time (Hambali & Puspita, 2021) but it should be controlled at the optimal amount to avoid the epoxides to become unstable. This is because excess concentration of HCOOH is qualified to destroy the weak π bond connected between the epoxides to form the diols as the side products (Jalil et al., 2021). In parallel, excess concentration of H_2O_2 also generates more water as the by-products to destabilize the oxirane rings (Hájek et al., 2023). For the reaction temperature, high temperature yields less

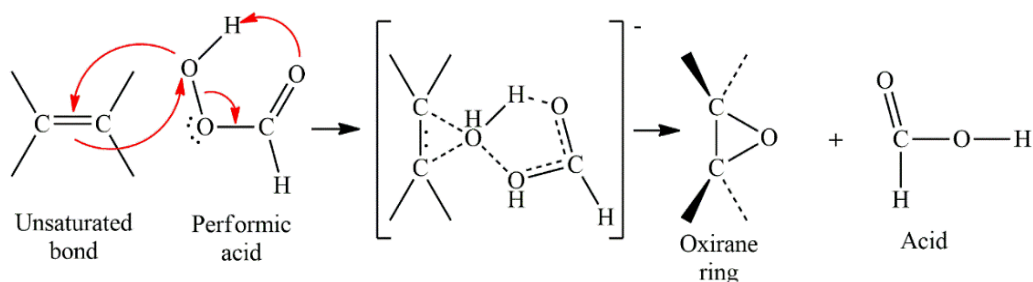
epoxy content even though the epoxidation happens but it undergoes partially hydrolysis that degrades the epoxy groups and may cause explosion due to the vigorous exothermic reaction. According to the Le Chatelier's principle, high reaction temperature can raise the epoxidation rate but it may also reverse the equilibrium of the reaction (Raofuddin et al., 2023). Increasing temperature and reaction time is allowed to amplify the kinetic energy of the oil particles which accelerate the molecular collisions to deteriorate the chemical bonds between the carbon and oxygen in the epoxide so the colour of product may look darker (Neswati & Nazir, 2021). The darkening of reaction product by the oxidation decreases the purity of epoxides. In contrast, low temperature can form a stable oxirane ring with less epoxide degradation. It is concluded that improper reaction conditions that beyond the optimal parameter values diminish the epoxide yield due to the effect of oxirane cleavage that form high peroxide values of epoxides and more by-products (Alsofiany & Resul, 2021).

The epoxidation reaction is a pseudo-homogeneous kinetic model which routes in only one phase that firstly formation of performic acid which is a reversible reaction (Scheme 2.1) then followed by the irreversible reaction between unsaturated fatty acids and performic acid (Budiyati et al., 2020). The mechanism for epoxidation reaction between PO_o and performic acid is illustrated in Scheme 2.2. Epoxidation implies the one-step electrophilic addition mechanism without releasing any intermediate to convert unsaturated double bonds into epoxide. The oxygen in the performic acid is electron deficient so it is attacked by the pi-electrons in the carbon-carbon double bonds of PO_o by breaking its O-O bond to build a new carbonyl bond. At the same time, the lone pair of the oxygen in the performic acid acts as the nucleophile to attack one of the carbon atoms of the alkene in PO_o to displace the carboxylate as a good leaving group. In this reaction, it is transferred by the farthest oxygen atom from the carbonyl group of the performic acid to the alkene of PO_o with syn

stereochemistry that both C-O bonds are added on the same side of the double bonds. In this experiment, performic acid is selected as the epoxidation agent because it gives the best benefit on its structure with an extra oxygen atom that presents between the carbonyl group and the acidic hydrogen atom that it also behaves electrophilic at the oxygen atom. In scheme 2.2, there is a transition state which shows clearly how the bond breaking and the new bond formation during the epoxidation reaction. It shows the work of electrophilic attack by firstly nucleophilic pi-bond donates its electrons to that specific oxygen atom in order to break the O-O bond. The electrons from the old O-H bond forms a new C-O bond and the original carbonyl group uses its electrons to pick up the proton so this results in the oxirane ring and also regenerates the formic acid. Thus, oxirane ring of EPO₀ is absolutely formed from the addition of the oxygen atom to the alkene of PO₀ by the epoxidation reaction.



Scheme 2.1: The formation of performic acid (Budiwati et al., 2020)



Scheme 2.2: The epoxidation reaction mechanism (Budiwati et al., 2020)

2.3 Alcoholysis

Ring-opening reaction via alcoholysis is organized for the purpose of attaching the hydroxyl groups into the oils' composition by chemically modifying the oxirane ring. Ring opening process is conducted to cleave the carbon-oxygen bonds of the epoxide. The highly reactive epoxide rings are subscribed to the nucleophilic attack so the hydroxyl groups added from the alcohols are able to attach to the aliphatic fatty acid chains via the chemical modification method (Singh et al., 2020). The trihydric organic alcohol of glycerol consists of three hydroxyl (OH) groups where two primary hydroxyl groups at each end and a secondary hydroxyl group in the middle. The primary hydroxyl groups on the both ends of the glycerol have greater ability to react with the oil to form the bio-polyols. Glycerol is a non-toxic polar compound (Nitbani et al., 2020) with a long hydrocarbon chain which contains a hydrophilic head that connected with a non-polar hydrophobic tail. Glycerol is a low-cost renewable resource derived from the biomass. The multiplex long-chained glycerol with high molecular weight and high boiling point is thermally stable (Kosamia et al., 2020) which is appropriate to design the lubricants while the short-chains alcohols are used to manufacture the biofuels. Nevertheless, alcohol with high molecular weight is less reactive than those with low molecular weight (Kuranska & Malewska, 2021). Polyhydric alcohols are ideal due to the absence of beta-hydrogen which can boost the thermal and oxidative stability of the product to suffer higher temperature (Murru et al., 2021).

The ring opening process is favoured with higher concentration of nucleophilic reagent of glycerol up to 1: 10 for the molar ratio of EPO₀: glycerol. The process at 90°C has produced the polyols with 208 mg KOH/g of hydroxyl value in the presence of 1.0% of catalyst (Kamairudin et al., 2021). The research has mentioned that the hydroxyl values of polyols rise with the increasing mole ratio of glycerol. Based on the literature of Prociak et

al. (2021), the bio-polyols synthesized with hydroxyl values beyond 250 mg KOH/g is characterized as high viscosity. The another study has declared that lower temperature of 55°C in shorter time of 120 minutes can only achieve low polyol conversion of 51.99% (Hartawan et al., 2022). During the ring-opening reaction, it is performed at high temperature of more than 100°C which more activation energy is provided to form the crosslinked products via the intermolecular dehydration (Ulanova et al., 2022). By the heat, there is a colour change of sample from clear yellow to brownish-yellow colour. An eco-friendly catalyst is needed in the ring-opening polymerization for lower reaction temperature and shorter reaction time. By the way, the hydroxyl value of polyol decreases when the reaction time beyond the optimum because the bio-polyols formed in the reaction react again with the remaining oxirane rings to form the undesirable dimers which has higher molecular weight and viscosity but with decreased hydroxyl value. Also, inappropriate ring opening reaction temperature and time may result in side product of acetate crystals (Neswati et al., 2022). The common side reaction is occurred by the free fatty acids to deactivate the hydroxyl groups so the product has poor hydroxyl value and acid value. Another type is the oligomerization reaction that happens during the epoxy ring-opening to form the dimers. The glycol chain relatively integrates into the bio-polyol molecules and lead to cyclization of fatty acids (Borowicz et al., 2024). The resulting polyols show quality of low acid value, small molecular weight distribution, and low viscosity (Stavila et al., 2023).

Hydroxyl value is used to measure the amounts of free hydroxyl groups formed in the polyols. Hydroxyl value, a basic characterization number is determined by the American Society for Testing and Materials (ASTM) methods such as ASTM E222 of acetylation by the acetic anhydride and pyridine and ASTM E1899, a potentiometric titration technique using p-TSI and tetrabutylammonium hydroxide. The limitation of ASTM E222 is longer

reaction time, intense heat, and utilize great amount of toxic pyridine chemical compounds. This restriction can be recovered by ASTM E1899 but it also introduces inaccurate and imprecise test results due to the impurities generated from the acids or bases making the pKa values move more towards to the acidic carbamate leading to much higher or lower hydroxyl values (Ghodke et al., 2021).

Most researchers have suggested the ring-opening reaction after the epoxidation reaction. It is investigated as the safest and cheapest route (Jalil et al., 2022) that promise the practical molecular structure (Tajau et al., 2020). Homogeneous or heterogeneous catalysts are selected to enhance the ring-opening reaction. In theory, the homogeneous catalyst stands in the same phase with the reactants so the catalysts collide more frequent with the reactants to introduce greater interactions. The homogeneous catalysts also disperse uniformly all over the reaction mixtures. In opposite, the heterogeneous catalyst participates in different phases with the reactants so it needs to align itself in a suitable orientation to collide with the reactant molecules. Moreover, the active centres for the homogeneous catalyst are opened for all atoms but the heterogeneous catalyst is only for surface atoms so it occupies limited surface area accessibility so the reaction is stopped when the catalysts are fully saturated with the reactants molecules and it is able to reattached again with new reactants once the products leave the catalyst surface. Homogeneous catalyst is generally with higher cost but it has defined structure with higher selectivity than heterogeneous catalyst (Norhayati et al., 2022). It is known that the alkaline homogeneous or heterogeneous catalysts are better because the reaction is conducted in mild conditions with higher reaction rate which saves more energy and costs (Maleki et al., 2022). For instance, boron trifluoride etherate is a Lewis acid categorized as an alkaline homogeneous catalyst. Its benefits are easy accessibility and high reaction rate that 4000 times faster than the acidic catalysts to give greater amounts of

reaction products. But, it has disadvantages of making the reaction irreversible and more effluent is yielded from the purification process (Hájek et al., 2021).

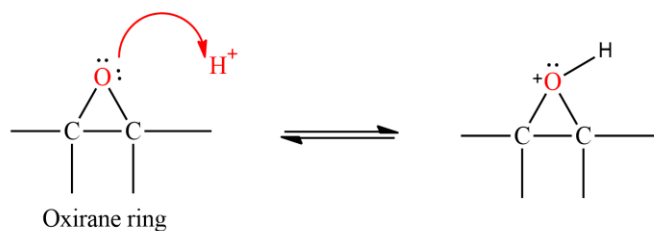
The chemical composition and the hydroxyl contents of the ring-opening intermediate is decided by the types of alcohols used in the ring-opening reaction. Alcohols with more hydroxyl groups such as diols are preferred than mono-alcohols to yield the polyols. The polyols from the diols behave better hydroxyl functionality with higher reactivity (Paraskar et al., 2021). Using higher epoxy values of oils, the polyols are synthesized with higher hydroxyl values, average molecular weight, dispersity, and water content (Polaczek et al., 2021). This is compatible with the study that the maximum hydroxyl values by the high epoxy of linseed and sunflower oils have reached 306 and 237 mg/g KOH respectively (Gomez et al., 2020). The research by Samavi and Rakshit (2020) have produced a bio-polyol with 299.53 mg KOH/g of hydroxyl group after the epoxidation and ring opening reaction. Apart from that, long-chain of alcohols with branched alkyl chains tend to improve the thermal property of oils while the short-chain alcohols enhance the hydrolytic stability of product (Sousa et al., 2023). The existence of branching in the alcohols are used to improve the pour point temperature so the secondary alcohols present better low-temperature property than the straight-chain alcohols (Gotovuša et al., 2022). The branched structure can form steric hindrance to inhibit the formation of macro-crystalline molecules so the low-temperature flow characteristics are slightly improved. The macro-crystals should be avoided to enhance the fluidity of plant oils. The viscosity of the polyols increases when the reagent with higher molecular weight is used to ring-open the epoxidized vegetable oils. After the chemical modification, the existence of hydroxyl groups in the vegetable oil promote the intermolecular interactions of particles which enhanced the viscosity and the

oxidative stability (Sundang et al., 2022). The bio-based polyols also more sustainable than the petrochemical polyols (Fridrihsone et al., 2020).

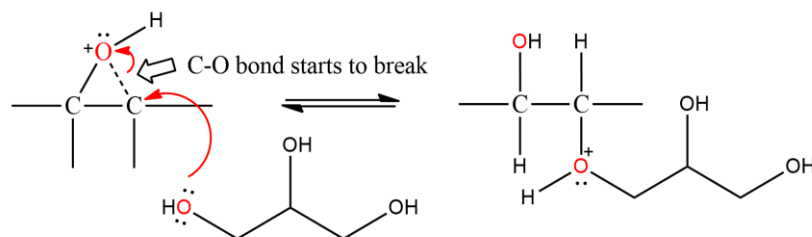
The epoxide ring-opening reaction via alcoholysis demonstrates the S_N1 reaction mechanism (Kamairudin et al., 2021). This is principally happening at the water-oil interface (Santacesaria et al., 2020). The protonation is introduced on the oxygen atom of the oxirane ring by a Lewis acid catalyst of boron trifluoride diethyl ether complex to form a leaving group which is a strong electrophile. Then, the carbon-oxygen bond is broken with the positive charge constructing on the more substituted carbon. The nucleophile of glycerol begins the electrophilic attack to open the oxirane ring together with the attachment of hydroxyl group. Then, the deprotonation generates the ether group. As a result, the process is completed with an anti-orientation typed ring-opening intermediate containing hydroxyl and ether groups.

The mechanism of alcoholysis reaction is discussed in Scheme 2.3 (Kamairudin et al., 2021). It is validated by the structural elucidation via the FTIR and NMR spectroscopies. In the first step, it is started with the Lewis acid of a homogeneous catalyst ($BF_3 \cdot Et_2O$) protonate the oxygen atom on the oxirane rings of the EPO_o to form an electrophile which is a good leaving group. In step 2, the primary terminal hydroxyl group in the glycerol backbone begins the electrophilic attack to break the carbon-oxygen (C-O) bond and form a positive charge on the more substituted carbon. The last step is the nucleophile attack of the glycerol to the electrophile carbon followed by the deprotonation of oxygen atom to form the ether group. As seen from the schematic outline, there is a substitution of the hydroxyl and ether groups into the oil.

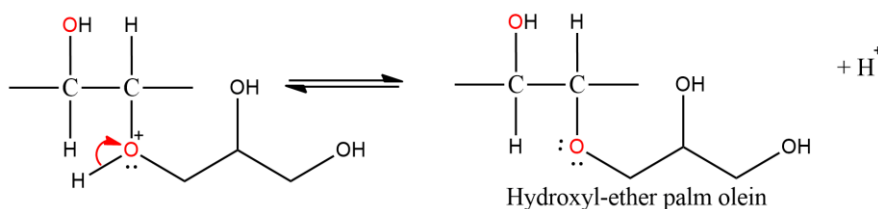
Step 1: Protonation on oxirane ring to produce electrophile



Step 2: Electrophilic attack to open the oxirane ring



Step 3: Deprotonation to produce ether group



Scheme 2.3: The alcoholysis reaction mechanism (Kamairudin et al., 2021)

2.4 Esterification

At first, the epoxidation followed by ring-opening reaction could enhance the damaging characteristics resulting from the double bonds of the plant oils but the defect of poor cold flow behaviour still remains. In response to this, the Fischer esterification reaction is utilized after the epoxidation and alcoholysis to craft a good cold flow performance of bio-lubricant with the ester groups. The ester yield is significantly impacted by different interaction factors of variables such as the reaction temperature, reaction time, types of catalysts and solvents. The esterification reaction is carried out by reacting the bio-polyols with the renewable reagents of organic fatty acids under the optimal reaction conditions. The aim of esterification reaction is to include the ester moiety into the oil's structure. It is investigated that the esterification reaction without the organic solvent medium requires

longer reaction time for in-depth mixing to ensure a sufficient contact between the reactants and catalysts (Sulihatimarsyila et al., 2022). With the use of solvent, the study has reported that the acetonitrile is the best polar organic reagent solvents among others because it produces the highest yield of 93.10% compared to DMSO (18.47%), 1,4-dioxane (19.22%), acetone (26.68%), tetrahydrofuran (17.33%), tert-butanol (45.65%), tert-amyl alcohol (54.04%), and 1,2-dichloroethane (16.34%). This is because the acetonitrile has a low $\log P$ values of -0.33 with a high dielectric constant of 37.5 so the conversion rate of the reagents become faster in this hydrophobic acetonitrile solvent (Lee et al., 2022). Besides that, the hydrophobic solvent of toluene has volatile organic compounds (Lapa et al., 2020) that can penetrate into the water layer to interact with the functional groups to give higher ester conversion of 93.18%. The toluene also promote the solubility and mixing of the fatty acids and alcohols in the reactor (Sangsiri et al., 2022). The hydrophilic solvents are not preferred in the esterification process because they tend to dissolve the water layer at the active sites which affect the rate of reaction (Shin et al., 2020).

Esterification is an equilibrium-limited reaction which removes the water molecule as the main side product (Sripada & Kastner, 2024). It is widely acknowledged that the esterification reaction is typically reversible. Hence, the reaction is generally triggered by the catalytic action. The homogeneous acid catalysts display highly catalytic activity such as H_2SO_4 shifts the esterification reaction equilibrium towards the forward direction via carbocation activation to produce more esters. In the esterification, the acid catalysts are more preferred than alkaline catalysts because this can prevent the formation of soaps that usually happen on the alkaline catalysts (Monteiro et al., 2024). Specifically, the strong acid catalyst is less sensitive to impact the free fatty acids and it has a good solubility in the hydrophobic solvents like non-polar toluene (Pedersen et al., 2020). However, homogeneous

acid catalysts are non-renewable and highly acidic to cause the corrosive on the instruments so the neutralization process should be applied after the reaction to remove the contaminants (Ahmed et al., 2023). The concentration of catalysts should be monitored at optimum as higher amount of catalyst could complex the neutralization reaction which raise the purification cost (Margarida et al., 2021). Meanwhile, the heterogenous catalyst carries less environmental damage but it also develops more complicated systems. This is due to the reaction takes place in different phases which the system is created in three phases namely a solid phase of catalyst and another two immiscible liquid phases with the fatty acids and alcohols (Zhang et al., 2020). The researchers have explored that the homogeneous catalyst of H_2SO_4 could develop higher ester yields (98.0%) than the blank esterification reaction without the catalyst (33.4%). The catalytic activity is enhanced by the H_2SO_4 because it consists of double acid sites (Yu et al., 2022). The protonation of carbonyl oxygen by an acid catalyst makes the carbonyl carbon to become a better electrophile.

Oleic acid (9-octadecenoic acid) features the monounsaturated fatty acid chain with the only double bond located between the specific carbon 9 and carbon 10 among its long carbon chains of 18 carbon atoms. Oleic acid is an oily, pale yellow, and viscous liquid at the room temperature. It is insoluble in water with low melting point of 15.3°C and high boiling point of 360°C (Manurung et al., 2023). The yield of esterification reaction is determined by the molar ratio of the reactants that the excess amounts of reactants can generate more products (Aziz et al., 2020). According to the prior research, the highest ester yield of 95.68% is obtained using 3.9 moles of oleic acid and 1 mole of alcohol at 70°C (Sulihatimarsyila et al., 2021). The ester yield is raised by high moles of oleic acid because there is more molecular interactions between the catalysts and the reactants that the thermodynamic equilibrium shifts in a favourable direction (Lee et al., 2022). In the similar

way, there is less ester yield from esterification if the mole of oleic acid below the optimal amount because of reduced mass transfer which reverse the reaction. Besides, the result is significantly different using fixed mole of oleic acid but with different moles of alcohols. The researches have indicated that the increasing moles of alcohol from 9 to 15 increase the ester content from 83.36% to 93.37% as well as another research using moles of 15 to give 96.76% of ester yield (Ahmed et al., 2023; Zhang et al., 2020). Excess amounts of alcohols favour the esterification reaction but not necessary because it needs more energy consumption and operating costs due to more catalysts needed to function (Razali et al., 2020). This is confirmed by Hamerski and her research partners in 2020 that the increasing moles of alcohol from 2 to 3 has obtained the exact same results of 65.9% and 66.1% after a long reaction time of 8 h.

In spite of oleic acid, the esterification reaction has conducted using the linoleic acid as the reagent with 2 wt.% H_2SO_4 at 80 °C in 6 h which introduce 92.5% of conversion rate and also 73.2% yield of ester products that characterized higher kinematic viscosity, higher fluid's viscosity index, and lower pour point value than the mineral based lubricants (Xu et al., 2021). Linoleic acid exhibits greater experimental effect than the oleic acid in the improvement of oil's cooling performance. The saturated fatty acid with numerous carbon numbers can improve the adsorption capacity and strengthen the adsorption films to enhance the lubricating and cooling effects (Dong et al., 2021). The only disadvantage of linoleic acid is the characteristic of being thermally unstable due to the presence of unsaturated double bonds in the long alkyl chains of linoleic acid.

With the use of catalyst, the ester yield of 87.6% is explored with 100% diester selectivity using the molar ratio of fatty acid: neopentyl glycol at 2.26: 1 in the presence of 1.12% H_2SO_4 catalyst at 138°C in 4.79 h (Nurazira et al., 2022). This is consistent to another

study using the molar ratio at 2:1 with 1% H₂SO₄ catalyst at 145°C in 4.56 h to get 90% of ester and 100% of diester composition (Nurazira & Salimon, 2022). Moreover, a high molar ratio of fatty acid to trimethylolpropane at 3.05 to 1 with 1.01% catalyst at 150°C in 6 h have provided 87.77% of tri-ester yield and 99.15% of selectivity (Bahadi et al., 2022). This is nearly similar to another study using 4.5 moles of fatty acid with 1 mole of pentaerythritol under 1% H₂SO₄ catalyst at 165°C in 7.2 h that result in 85% of yield and 97.4% tetra-ester conversion (Nurazira & Salimon, 2023). This proposed that the optimal catalyst concentration is covered between 1.0 wt.% and 2 wt.%.

Esterification is a high energy-demanding endothermic reaction so a typical high temperature is required to increase the rate of reaction. With the increase in temperature, the solvent's viscosity decreases so the mass transfer between the catalysts and the reagents can occur easier. This is affirmed by the study that higher selectivity of ester is observed when the reaction temperature is raised from 100°C to 150°C (Bahadi et al., 2021). In the study, the optimal reaction temperature for esterification is between 105°C and 120°C. This is due to the temperature beyond 150°C stimulates the reactions of oxidation and dehydration to darken the colour of products (Kopchev & Bayryamov, 2022). Higher temperature enhances the homogeneity of mixture but also produces higher reactor pressure to cause a backward reaction that make the loss of reactants through evaporation. By using extremely high temperature of 200°C, only 78.1% of yield with 80% selectivity is reached under the molar ratio of alcohol to oleic acid of 3:1, with a 0.2% catalyst (Neji et al., 2023). This experiment has modelled the industrial esterification reaction condition that normally above 150°C. Some investigators have suggested the chemical process of esterification to be conducted at milder reaction temperature below 80°C to avoid thermal degradation that may form side products and also low-quality compounds. The by-product of water molecule has higher

affinity than the reagent to attach with the active acid sites as it forms a competitive adsorption that disrupt the esterification reaction yield. To address this issue, it is solved by the high reaction temperature that can evaporate the water layer and at the same time to reduce the adsorption interactions of the water on the active acid sites to make the ester conversions become higher (Hamerski et al., 2020).

Salicylic acid is an organic compound with disubstituted benzene ring (Thomas et al., 2021). One research project has performed the esterification reaction between the salicylic acid and methanol at the molar ratio of 1:10 with a 1.5% of catalyst at 65°C for 150 mins which lead to 82% of ester conversion. From that study, increasing the catalyst concentration from 0.5% to 1.5% enlarges the ester conversion from 50% to 82% (Farouq & Selim, 2023) and also improve the oxidative stability index of the oils. Esterification is a nucleophilic substitution reaction which is slow at room temperature so it must cooperate with the intense heat and catalyst to enhance the performance. This is caused by the structure of ester bound with the weak intermolecular forces that is difficult to form hydrogen bonds in the mixture. The reaction mechanism starts from the salicylic acid that absorbed on the acid sites of the functionalized catalyst surface by its carbonyl oxygen. Then, the alcohol attacks the unstable cationic intermediate. After the electron transfer, it forms the final ester product.

In short, esterification reaction is less expensive compared to other methods. The esterification reaction is able to solve the problem of unstable hydrogen atom in the beta position by introducing the alkyl side chains into the oil's molecular structure to increase the chain length and minimize the structural uniformity (Murru et al., 2021). This improves the oil's temperature flow behaviour and make the structure becomes 10 times better than the raw sample oils to resist the oxidation (Owuna et al., 2020). The amphiphilic behaviour of

the ester brings about the lubricity property due to their polar ends which perform the adsorption of close-packed monolayers as well as their hydrocarbon chains which covalently bonded to the surface (Sharma et al., 2023). The ester has low polarity that form weak intermolecular interactions of van der Waals forces in the absence of positively charged hydrogen dipoles that increases the adhesion, flow behaviour, and biodegradability (Soodoo et al., 2023). Hence, esterification reaction can form a green lubricant with higher thermo-oxidative resistance, lower pour point value, and better lubricity (Almasi et al., 2021).

2.5 Nanoadditive

Additive is a microchemical compound whether macro-sized or nano-sized structure can be used to mix with the lubricating oils for the purpose of parameter upgrade. The additives are categorized into types of chemically active and chemically inert substances. Chemically active additives involve the friction modifier, anti-wear, oxidation, and corrosion inhibitors yet the chemically inert additives include the pour point depressants and oil viscosity modifier that both enhance the physical features of the lubricants (Chowdary et al., 2021). For lubricity, nano-sized additives with the diameter that less than 100 nm is recommended to reduce the energy loss of machine, engine wear, friction, and corrosion. That is the reason why the nano-lubricants with excellent features are implemented by the industries to protect the engine parts and also to save the maintenance costs of the systems (Kashefi et al., 2022).

To make the nano-lubricants, only a small amount of nanoparticle is needed to disperse with the lubricating oils via the ultrasonic and mechanical agitation methods (Karmakar et al., 2020). The function of ultrasonic homogenizer is to maintain the homogeneity of the composition in the meaning of well-suspension of nanoparticles in the lubricating oils. Based on the literature, the synthesis of nano-lubricants by the sonication

process and magnetic stirring is considered as cost effective so it is applied by most of the industries for a large production scale (Suhaimi et al., 2022). The longer the time of mixing, the lower the chance of aggregation so the optimal dispersion duration is monitored between 30 minutes and 1 h (Jason et al., 2020).

There are two different categories of lubrication mechanisms which are direct and indirect mechanisms. The examples of direct lubrication mechanism are ball bearing and the formation of protective films on the rough sliding friction surfaces. While, the indirect lubrication mechanisms have two effects of mending and polishing. The mending is to gather the nanoparticles on the contact surfaces to reduce the abrasion. The polishing effect by the nanoparticles can smooth the contacting surfaces simultaneously fill in the micro or nano-sized gaps (Fahad & Abdulmajeed, 2021). In consequence, a tribo-layer appears on the top of the worn surfaces to minimize the direct contact between the two rubbing surfaces so the coefficient of friction becomes lower (Sabri et al., 2023).

Nano-additive of titanium dioxide (TiO_2) has low toxicity, anti-oxidant, and non-volatility characteristics so it is considered environmentally sustainable. TiO_2 is a natural mineral that exist in the crystalline forms such as the phases of rutile and anatase. It has a general particle size of around 18 nm. The study (Roselina et al., 2020) has reported that the titanium dioxide at the concentration of 1.0 % (w/w) improved the oil's viscosity index by 4.1%. From the study, the lubricants with high viscosity is able to endure intense heat above 250°C because it has a more stable molecular structure than the raw plant oils. Nevertheless, the dispersion and long-term stability of the nanoparticles in the lubricating fluids still become the top concern for every investigator. Higher concentration of nanoparticle causes the agglomeration, sedimentation, and aggregation on the surfaces due to their high surface energy and attractive forces within the particles that increase the molecular collisions with

strong Van der Waals forces (Mousavi et al., 2020). The aggregation and sedimentation of nanofluids are happened when the Brownian motions and attractive Van der Waals interaction forces within the nanoparticles are larger than the repulsive forces (Sofiah et al., 2021). In agglomerated situation, the large particles with irregular shapes increase the interparticle interactions to form the particle clusters within the mixture that affects the flowability (Uppar et al., 2024).

To enhance the dispersion stability effect of the nanoparticles, a suitable surfactant is selected to form an efficient repulsive force within the nanoparticles to prevent the agglomeration (Banavathu et al., 2023). This method is considered easy and low-cost. Surfactant is able to modify the physical property of nanoparticles to improve the electrostatic and steric characteristic of insulating oils which prevent the nanoparticles from clumping together. As mentioned by Roselina et al. at 2020, they have used the surfactant of ethylene glycol in the dispersion of TiO_2 with the palm oil because the non-volatile and odorless ethylene glycol has altered the TiO_2 nano-additive's surface to create more flow resistance that increases the viscosity of the products. As illustrated in the study, the optimal concentration of ethylene glycol surfactant is ranged at 0.5 to 1 millimeter (Farouq & Selim, 2023).

The addition of TiO_2 do not damage the molecular structure of lubricant but improve its chemo-physical property to maximize the lubricating performance. It is nano-sized with a large surface area to volume ratio that brings the repairing effect by filling into the rough rubbing surfaces and form a thin physical protective film. After the incorporation of TiO_2 , the lubricant is thermally stable with a good dispersion stability that the oil remains fluid at room temperature and even elevated temperature for a long period of time (Popoola & Ikpambese, 2021). This is due to Brownian motions and the inter-particle forces that enhance

the heat transfer and avoid the sedimentation of particles so a stable colloidal nanoparticle solution is created. The friction coefficient decreases when the sliding friction is replaced by the rolling friction so the nanoparticles in the lubricant flow into the friction zone to improve the lubricating, anti-friction, and anti-wear capabilities (Piri et al., 2024). The protective film is formed by the deposition of nanoparticles on the interacting surfaces (Figure 2.1). TiO₂ nanoparticles significantly enhance the performance of vegetable oil-based lubricants by acting as spacers due to their nanoscale size and interlayer interactions with natural oils, which further contribute to superior antifriction characteristics under extreme pressure and temperature conditions (Karmakar et al., 2020).

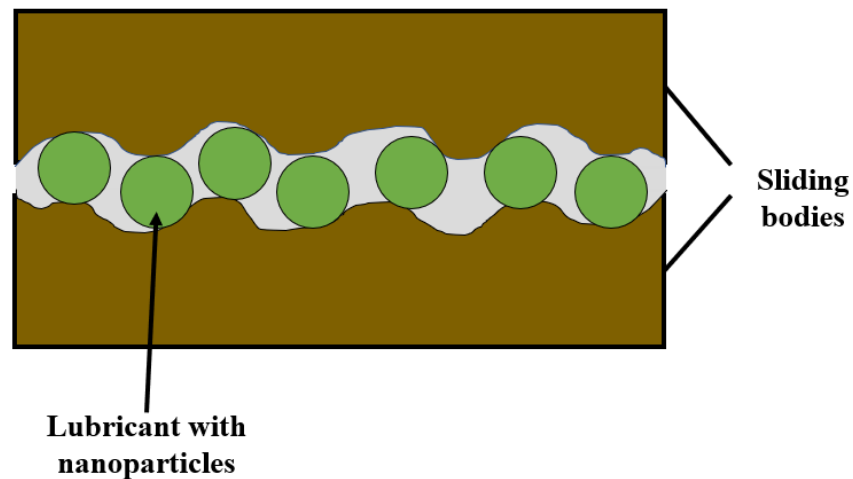


Figure 2.1: Nano-lubricant working principle (Karmakar et al., 2020).

For example, the study has detailed that 1.0 % (w/w) of TiO₂ decreases the volumetric wear by 70.1% and surface roughness by 78.0% (Cortes et al., 2020). TiO₂ is a popular additive used in the liquid-based lubricant to demonstrate ideal tribological performance. Regardless of TiO₂ nano-powder, the research has revealed that two different additives of 0.5 vol% copper (II) oxide and the copper-silver alloy nanoparticles improve the coefficient of lubricant efficiency by 14.55% and 20.88% respectively (Yilmaz, 2020). Table 2.1 presents a summary of various additives used in lubricating oils as pour point improvers.

Table 2.1: Summary of different additives used in lubricating oils as pour point improvers

Year	Oil Type	Additive Type	Wt. (%)	Pour point (°C)	Reference
2020	SAE 40 base oil	MoS ₂	0.70	From -17.8 to -18.7°C (Positive effect)	(Mousavi et al., 2020)
2020	SAE 40 base oil	ZnO	0.70	From -17.8 to -20.5°C (Positive effect)	(Mousavi et al., 2020)
2021	SAE 5w-30 base oil	Multiwalled carbon nanotubes	0.10	From -40 to -12°C (Negative effect)	(Kamel et al., 2021)
2021	Sandbox seed oil	TiO ₂	1.50	From -3 to -4°C (Positive effect)	(Popoola & Ikpambese, 2021)
2021	Base oil (60-stock)	TiO ₂ -CuO	0.80	From -6 to -12°C (Positive effect)	(Fahad & Abdulmajeed, 2021)
2021	SAE 20 W40	TiO ₂	0.10	From -10 to -11°C (Positive effect)	(Deepak & Ram, 2021)
2021	Coconut oil	TiO ₂	0.10	From -17.5 to -27°C (Positive effect)	(Deepak & Ram, 2021)
2022	SAE 40 base oil	SiO ₂	0.10	Remain -6 °C (No change)	(Kashefi et al., 2022).
2022	SAE 5w-30 base oil	Graphene	0.15	From -37 to -15°C (Negative effect)	(Alqahtani et al., 2022)

2.6 Cold Flow

Pour point (PP) lists as the lowest temperature that the fractions can flow after the cooling. It determines the particular point that the lubricating oils become too thick, viscous and stop to flow (Kamel et al., 2021). PP is one of the critical properties used to examine the lubricating oils' performance and suitability to be used in cold conditions. In the cold weather, the engine oils should have low PP value to ensure its cold flow efficiency and effectiveness, without any solidification. The oil with excellent cold flow characteristic is allowed to flow freely without stirring under the standard test conditions (Alqahtani et al., 2022). The drawback of using vegetable oil as the bio-lubricant is it tends to solidify at the

cold temperature below -10°C which may block the oil pipelines. This is due to the presence of saturated fatty acids (Fathurrahman et al., 2021).

PP is affected by the degree of unsaturation and the length of carbon chain. The higher the unsaturation and the shorter the carbon chain of the oil, the lower the PP value (Wahyudi et al., 2020). Highly unsaturated oils are generally achieving better results of cold stability and lower melting point because the bend and kinks of double bonds restrict the molecules to pack closely and form crystals (Khairin et al., 2021). In the cool situation, the crystallization is caused by the regular stacking of the bent shaped triglyceride backbone of oils which can be solved by attaching the ester side chains via the esterification chemical modification process on the fatty acid chains to replace the original hydroxyl group. A steric hindrance is created by the large branching ester groups at the middle position of the fatty acid chains which slow the solidification process (Samidin et al., 2021). The incorporation of branching groups also destruct the molecular spatial symmetry of the oil's composition and interfere with the shaping of macro-crystalline structures (Chin et al., 2021). This can be seen from the esterification reaction using the linoleic acid as the reagent has improved the oil's mobility under the low-temperature conditions due to the presence of *cis* double bonds in the fatty acid chains. This is related to the statement that PP value is controlled mainly by the relative molecular mass and the degree of branching. The researchers also have discovered that the fatty acid chains with excessive levels of branch chain numbers would increase the molecular weight to form an active van der Waals force between the molecules that raise the PP values so the oils crystallize or immobile faster (Zhang et al., 2020).

In the oil, there exists large quantities of highly saturated long-chain palmitic acid methyl ester and methyl palmitate that cause the freezing of oils during the low-temperature

applications consequently lead to machine start-up and operation troubles (Çamur & Alassi, 2021). The uniform linear shape of the fatty acid chain promotes the molecules to undergo self-stacking. The molecules bind themselves into the macro-crystals after the loss of kinetic energy (Nurazira & Salimon, 2022). The undesirable crystals formed in the oils contain a lot of tightly packed compounds which cannot move in the cool environment. To form a good lubricant, it should be in a liquid form with the individual molecules that stay farther apart from one another to allow more freedom of movement (Nie et al., 2020).

In response to the poor cold flow property of the lubricant, the topic of nano-additive is largely explored nowadays to tackle the problem. For instance, the enrichment of TiO₂ nanoparticles in the bio-lubricants successfully enhance the PP value of the oils from -3°C to -4°C due to the functions of nano-additive together with the presence of ester groups and the absence of beta-hydrogen in the glycerol configuration (Popoola & Ikpambese, 2021). This finding is consistent to another study which stated the use of nano-lubricant with 0.1 wt.% of TiO₂ shows a significant decrease of 1.2°C in the pour point temperature (Pourpasha et al., 2021). A strong non-polar covalent bond is formed between the nano-additive and the lubricating oil. At low temperature, nano-molecules inhibit the development of large three-dimensional wax crystals on the polymer by adsorbing itself onto the surface of the crystal lattice. The nanoparticles change the morphological structure of the lattice to form fine scattered crystals. Microcrystalline configurations possess better fluidity in the system because the molecules are easier to slide over one another. Nano-additive decreases the cohesion and the size of the crystals so the cold flow behaviour of lubricant is improved (Kamal et al., 2021).

Other than that, the cloud point is the temperature at which wax crystals or clouds begin to form in the lubricant under controlled conditions. It is identified by the initial

appearance of haze, indicating the onset of phase separation in the mixture. These wax crystals increase the lubricant's viscosity and deposit on the equipment to block the narrow passages. Therefore, the operating temperature should be maintained above the cloud point to ensure a smooth flow and system efficiency. The composition with a high content of long-chain saturated methyl esters raised the cloud point (Fathurrahman et al., 2021). Lubricants with a high cloud point are more easily to become cloudy and undergo solidification, which negatively affects their lubricating performance in cold temperatures (Zhang et al., 2020). Table 2.2 presents the cloud points of various vegetable oils (Masripan et al., 2020).

Table 2.2: The cloud point of vegetable oils (Masripan et al., 2020)

Vegetable oils	Cloud point (°C)
Coconut	0.0
Linseed	-3.8
Olive	-
Soybean	1.0
Sunflower	-3.4
Palm	13.0
Peanut	5.0
Rapseed	-3.3
Ricebran	0.3
Castor	-13.4
Jatropha	2.7
Karanja	9.0
Mahua	-
Neem	14.4

Furthermore, the pour point of the bio-lubricant is influenced by its viscosity index. High viscosity results in thicker lubricant film while low viscosity corresponds to a thinner film (Nurazira & Salimon, 2023). A lubricant with higher viscosity index is less affected by the temperature change. Additionally, a molecular structure with increased branching tends to lower the viscosity index, whereas an increased carbon chain length generally raises the

viscosity (Cecilia et al., 2020). Improved cold flow is achieved by using fatty acids with higher degree of branching and shorter chain lengths. In addition, the incorporation of additives has been shown to reduce the oil viscosity, as reported by Jurid and other research partners (2020), indicating that the oils without any additives are more prone to degradation.

According to Nurazira and Salimon (2022), the chemical modification processes of epoxidation and ring opening reactions increase the viscosity of the oil due to the decrease in the degrees of unsaturation, as well as the formation of intermolecular hydrogen bonding from hydroxyl groups. The higher polarity of hydroxyl group makes the oil more viscous. However, the subsequent esterification reaction reduces the lubricant's viscosity due to the elimination of hydroxyl group. The researchers found that structural modifications using diesters of fatty acids showed better pour points, ranging from -70 to -40°C along with the polyol ester also exhibited lower pour points between -60 and -15°C (Salih & Salimon, 2021). In their study, Salih and Salimon (2021) summarized the viscosity index and pour point of the raw plant oils and their respective synthetic ester bio-lubricants, as shown in Table 2.3. In comparison with mineral oil-based lubricants, bio-lubricants exhibit a better viscosity index enabling them to remain stable and withstand a broader temperature range (Khan et al., 2023). Overall, low pour point, viscosity, and cloud point are critical for improving the cold flow properties of bio-lubricants.

Table 2.3: The physicochemical properties of plant oils and their respective synthetic ester bio-lubricants (Salih & Salimon, 2021) and mineral oils (Cecilia et al., 2020)

Lubricants	Viscosity index	Pour point (°C)
Plant oils		
Castor	220	-27
Castor/TMP	127	-
Castor (Modified)	240	-53
<i>Jatropha curcas</i>	205	-6
<i>Jatropha</i> /TMP	180	-30
Palm	186	-5
Palm/TMP	176	-2
Palm Oil/TMP	158	8
Olive	190	-3
Olive/PE	190	-24
Rapeseed	180	-12
Rapeseed/alcohols	205 to 224	-31.3 to -18
Rubber	271	-30
Rubber/TMP	283	-40
Soybean	246	-9
Soybean/alcohols	45 to 195	-
Sunflower	206	-12
Sunflower/octanol	226	-3
Mineral oils		
ISO VG32	>90	-6
ISO VG46	>90	-6
ISO VG68	>198	-6
ISO VG100	>216	-6
Paraffin VG45	102	-
Paraffin VG460	97	-
R150	-	-
SAE20W40	132	-21
AG100	103	-18
75W-90	140	-48
75W-140	174	-54
80W-140	139	-36

2.7 Chapter Summary

To summarize from the literatures, palm olein is selected in this study instead of regular palm oil for chemical modification into green lubricant via epoxidation, alcoholysis, and esterification reactions. This choice is based on previous studies showing PO_o contains higher levels of oleic acid (43%) and linoleic acid (13%) (Jadhav et al., 2021) compared to

the conventional palm oil, which contains 39% oleic acid and 9% linoleic acid (Padial-Jaudenes et al., 2020; Wang et al., 2020). The higher degree of unsaturation is favourable for further functionalization. Moreover, PO_o is more affordable than other plant oils (Yang et al., 2022) and is abundantly available in Malaysia (Ayompe et al., 2021).

There are still very limiting studies on the use of TiO₂ nanoadditive as the pour point improver in bio-lubricants synthesized from palm olein. To synthesize nano-lubricants, only a small amount of nanoparticle is needed, which can easily dispersed into the lubricating oils using the simple way of ultrasonic and mechanical agitation methods (Karmakar et al., 2020). The addition of TiO₂ does not damage the molecular structure of the lubricant but improve its chemo-physical property to enhance lubricating performance. Its nano-scale size and large surface area-to-volume ratio provides the repairing effect by filling into the rough rubbing surfaces and form a thin physical protective film to reduce the energy loss of machine, engine wear, friction, and corrosion (Popoola & Ikpambese, 2021).

For cold flow improvement, TiO₂ acts as a physical barrier that delays and disrupts wax crystal formation at low temperatures. This results in the formation of smaller wax crystals instead of big size which allows the lubricant to remain fluid under cold conditions. TiO₂ has high surface energy that can interact with the polar functional groups of bio-lubricants to enhance the molecular mobility and reduce the formation of rigid structures when applied to equipment at low temperatures. Therefore, the incorporation of TiO₂ offers a promising and effective approach to enhance the cold flow properties of bio-lubricants. Table 2.4 provides an overview of synthetic methods reported in previous studies.

Table 2.4: Overview of synthetic methods from previous studies

Synthetic Method	Materials (Molar ratio)	Reaction conditions	Key Findings	Limitations	References
Epoxidation, Ring opening, Esterification	Epoxidation: Palm oil + Formic acid+ Hydrogen peroxide (1: 5.91 :3.6) Ring opening: Epoxidized palm oil + Oleic acid (1:3) + <i>p</i> -Toluenesulfonic acid (1.02%) Esterification: Ring opening product + Oleic acid (1:3) + Sulphuric acid (1.86%)	Epoxidation: 40°C, 2.55 h Ring opening: 119°C, 4.73h Esterification: 135°C, 4.96h	Epoxidation: Yield was 86%. Pour point was 18°C. Ring opening: Yield was 84%. Pour point was -8°C. Esterification: Yield was 80%. Pour point was -10°C.	The controls, which were the commercial lubricants of 100A and 100 B, performed better pour points of -19°C and -27°C, respectively.	(Nurazira and Salimon, 2022)
Epoxidation	Palm oil + Formic acid + Hydrogen peroxide (1: 1: 1.5) + Sulphuric acid (0.5g)	75°C, 20 min	Yield was 85.6%.	The use of high temperature and a catalyst created an explosive mixture, as the reaction was exothermic.	(Jalil et al., 2021)
Epoxidation	Palm olein + Acetic acid + Hydrogen peroxide (1: 1: 9)	70°C, 1h	The highest average oxirane number achieved was 0.99.	The resulting epoxidized palm olein had a pale-yellow colour. It addressed the problem of handling waste by-products and was recommended to use with pour point depressants and antioxidants to enhance its physical properties.	(Hambali and Puspita, 2021)
Epoxidation	Palm olein + Formic acid + Hydrogen peroxide (1: 1: 6)	45°C, 6h	The FTIR spectrum exhibited the peak of oxirane ring.	No calculation of oxirane oxygen content was performed.	(Sayuti et al., 2021)

Table 2.4: continued

Synthetic Method	Materials (Molar ratio)	Reaction conditions	Key Findings	Limitations	References
Ring opening reaction	Epoxidized palm olein + Iso-butanol (1:10) + Catalyst of Boron trifluoride diethyl ether complex (1.0%)	60°C, 1h	The presence of a homogeneous catalyst showed a high reduction in oxirane oxygen content of 98%. Its hydroxyl value was 95.5 mg KOH/g, and its iodine value was 4.7 g I ₂ 100 g ⁻¹ .	The epoxide ring-opening via alcoholysis reaction was a very slow reaction that required the addition of a catalyst to accelerate the reaction rate. The functionality of palm olein-based polyol ranged from 2.26 to 3.42, and the high average molecular weight was due to high degree of undesirable oligomerisation during ring-opening reaction.	(Norhayati et al., 2021)
Ring opening reaction	Epoxidized palm oil (20 mL) + Ethylene glycol (30 mL) + Catalyst of Sulphuric acid (1.0%)	50°C, 3h	The hydroxyl value of polyol was 118.14 mg KOH/g.	A polyol of lower hydroxyl value was synthesized beyond the optimum time of 3h. Prolonged reaction time degraded the polyols with darker colour and also increased its molecular weight and viscosity.	(Neswati et al., 2021)
Esterification	Palm oil-polyols + Trimethylolpropane (3.45:1) + Lipozyme 435 (3% w/w)	Room temperature, 48h	The highest yield of tri-ester was 82%, achieved without an additional purification step. Its pour point was -37°C.	The enzymatic esterification reaction was time-consuming as long as 2 days.	(Sulihatimarsyila et al., 2022)

Table 2.4: continued

Synthetic Method	Materials (Molar ratio)	Reaction conditions	Key Findings	Limitations	References
Esterification	Crude palm oil fatty acid + Neopentyl glycol (2.26:1) + Sulphuric acid (1.12%)	138°C, 4.79h	The yield was 87.6% with 100% diester selectivity. The pour point was 10°C.	It has good lubrication properties but poor cold flow characteristic.	(Nurazira et al., 2022)
Esterification	Palm oil fatty acids + Pentaerythritol (4.5:1) + Sulphuric acid (1.0%)	165°C, 7.2h	The yield was 85% with 97.4% tetra-ester selectivity. The pour point was 17°C.	It has good lubrication properties but poor cold flow characteristic.	(Nurazira and Salimon, 2023)
Incorporation of nano-additives	Palm olein based bio-lubricant + Zinc oxide (0.05 wt.%)	Room temperature, 30min	It improved the pour point from 9°C to 6°C, enhanced the load-carrying capacity by up to 60%, and reduced friction from 0.1 to 0.07.	The pour point remained at 6°C for zinc oxide concentration from 0.05 to 0.5 wt.%. No improvement in cold flow property was observed when using graphene oxide nano-additives from 0.5 to 2 wt.%.	(Nassef et al., 2024)
Incorporation of nano-additives	Palm oil lubricant + Titanium dioxide (1.0 wt.%)	Room temperature, 30min	The viscosity index of the lubricant increased by 4.1%.	Titanium dioxide was studied exclusively as a viscosity modifier, with insufficient information available on its potential to improve the cold flow property.	(Roselina et al., 2020)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The vegetable oil of palm olein (PO_o) (Buruh brand, Lam Soon Edible Oils Sdn. Bhd.) was used as raw material and purchased from local market. Formic acid (90% HCOOH), hydrogen peroxide (50% H₂O₂), glycerol (99.8%), hydrochloric acid (37% HCl), and paraffin liquid were purchased in brand of R&M Chemicals. Chemicals of boron trifluoride diethyl ether complex (50% BF₃·Et₂O), oleic acid (99%), linoleic acid (99%), titanium dioxide (99.5% TiO₂), and ethylene glycol (99.8%) were obtained from Sigma-Aldrich chemical company. Salicylic acid (99.5%), ethyl acetate (99.95%), and sodium bicarbonate (99.5% NaHCO₃) were supplied by Bendosen laboratory chemicals while the anhydrous magnesium sulphate (98% MgSO₄) and potassium hydroxide pellets Grade AR (85%) were purchased from QREC Sdn. Bhd. Malaysia. Sulphuric acid (95% H₂SO₄), ethanol (99.5%), and toluene (99.5%) were obtained in brands of EMSURE, System, and HmbG chemicals respectively. Sodium chloride (99.8% NaCl) and anhydrous calcium chloride (96% CaCl₂) were purchased from Uni-Chem. Deuterated chloroform (99.75% CDCl₃) and acetonitrile (99.9%) were purchased from Acros Organics and J.T. Baker chemicals company, respectively.

3.2 Epoxidation

Preparation of epoxides was carried out based on the method developed by Nurazira and Salimon (2022). Epoxidation was conducted by mixing PO_o (50.0 g, 58.5 mmol, 0.0585 equiv) with HCOOH (17.691 g, 384.4 mmol, 0.384 equiv) in a 250 ml single-necked round bottom flask connected with a reflux condenser. H₂O₂ (14.334 g, 421.9 mmol, 0.844 equiv)

was added dropwise into the mixture with a flow rate of 2 ml min^{-1} under continuous magnetic stirring (900 rpm). The reaction was exothermic so it was monitored regularly in the ice bath (4°C). The molar ratio of PO_o : HCOOH : H_2O_2 was controlled as constant variable which was adjusted at optimum of 1: 5.91: 3.60 (Nurazira & Salimon, 2022). The conversion of PO_o into EPO_o was optimized by two variables parameters which were reaction temperature and reaction time. During the epoxidation reaction, the reaction temperatures were operated between 30 to 60°C meanwhile the reaction time was controlled at ranged between 30 to 153 minutes. The development of epoxidation reaction was observed based on the oxirane oxygen content (OOC) until the percentage had exceeded 90% of the theoretical value. When the reaction was completed, it was set aside for cool down until it reached the room temperature. Then, the mixture was neutralized with 5% NaHCO_3 solution (100 ml), 5% NaCl solution (100 ml), and extracted into 5% ethyl acetate (100 ml) until the pH reached between 6 and 7 . The organic layer was separated from an aqueous layer by separating funnel, dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo* to give the crude product EPO_o (47.874 g , 90.65%) as yellowish-white oil.

3.3 Ring Opening Reaction via Alcoholysis

Starting the alcoholysis, a mixture of EPO_o (50.0 g , 55.4 mmol , 0.0554 equiv) and the glycerol (51.132 g , 555.6 mmol , 0.556 equiv) was added into a 250 ml of single-necked round bottom flask equipped with a reflux condenser. The mixture was stirred and preheated to a temperature of 120°C . The catalyst of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (7.864 g , 55.4 mmol , 0.166 equiv) was then added dropwise into the mixture. The molar ratio of EPO_o : glycerol: $\text{BF}_3\cdot\text{Et}_2\text{O}$ remained constant at $1: 10: 1$ (Kamairudin et al., 2021). The reaction was optimized at different reaction time ranged between 1 to 6 h and the reaction temperature of $90 - 120^{\circ}\text{C}$, respectively. The OOC analysis was performed for every 60 minutes to monitor the progress

of reaction until the percentage of OOC was less than 0.1%. The product was subsequently neutralized with 100 ml of 5% NaCl solution followed by 100 ml of 5% NaHCO₃ solution, and diluted with 100 ml of 5% ethyl acetate until the pH of the product was adjusted to pH 5 to 6. The organic layer was separated from an aqueous layer by separating funnel, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give polyols as yellow-orange oil (56.389 g, 85.93%).

3.4 Esterification

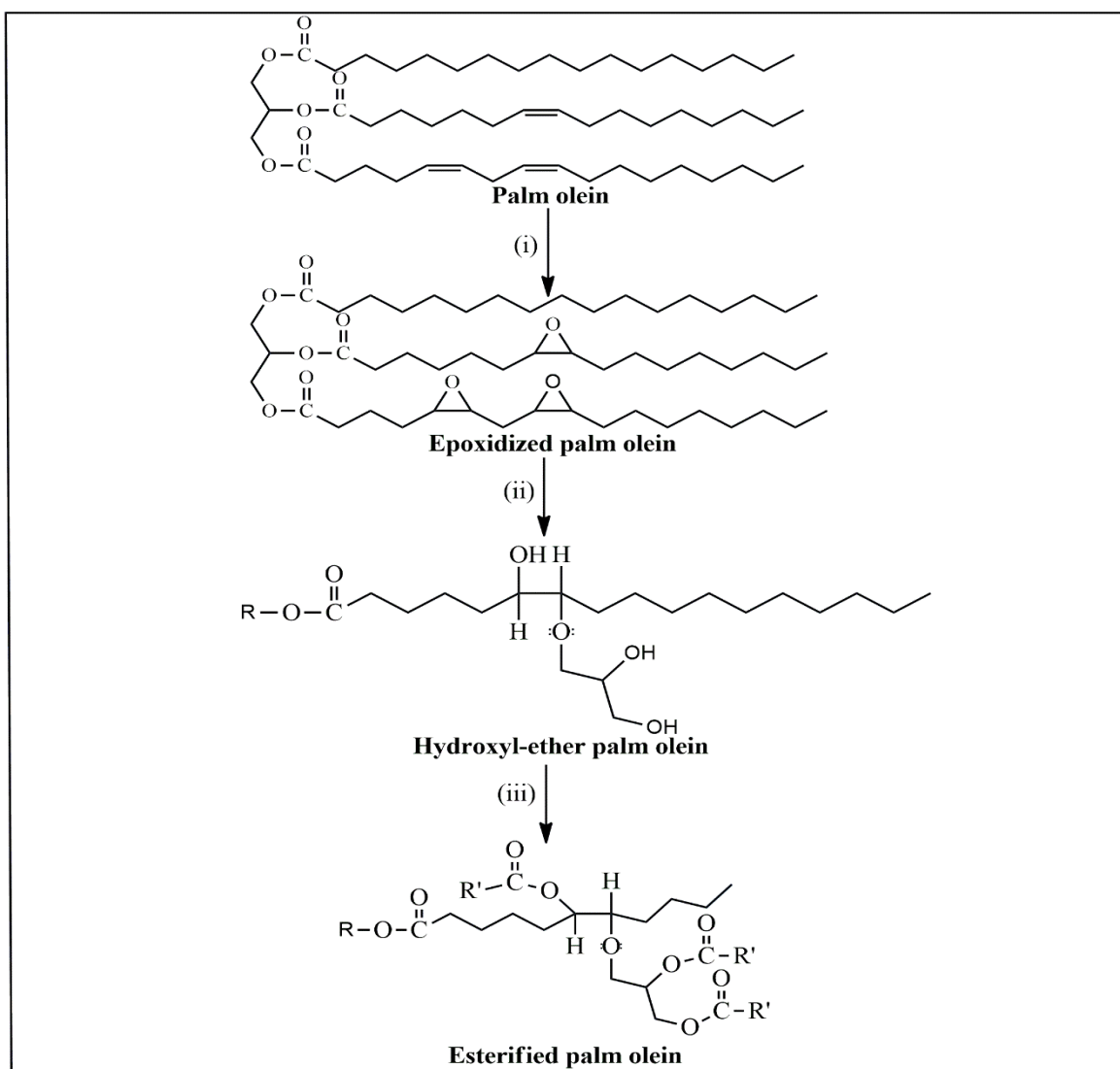
Esterification reaction was carried out using three different starting materials including salicylic acid, oleic acid, and linoleic acid according to the method developed by Nurazira and Salimon (2023) with slight modification. In this method, 0.237 ml of 95% H₂SO₄ (0.436 g, 4.44 mmol, 0.009 equiv) was added as a catalyst to a solution of salicylic acid (0.586 g, 4.25 mmol, 0.004 equiv) in toluene (100 ml) at room temperature and the mixture allowed to stir continuously (200 rpm) for 1 h to ensure complete protonation. The mixture was then poured into the round bottom flask containing polyols (5.0 g, 4.23 mmol, 0.004 equiv). The resulting mixture was refluxed at temperature between 80 - 140°C for 2 - 6 h for optimization. The molar ratio of polyols: salicylic acid: sulphuric acid was fixed at 1:4:1. Upon cooling to the room temperature, the product was neutralized with 100 ml of 5% NaCl solution followed by 100 ml of 5% NaHCO₃ solution, and diluted with 100 ml of 5% ethyl acetate until the pH was adjusted to pH 6 to 7. The organic layer was separated from an aqueous layer, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to obtain desired ester as dark oil (9.497 g, 99.29%).

The similar procedure was repeated using oleic acid (1.205 g, 4.26 mmol, 0.004 equiv) and linoleic acid (1.196 g, 4.26 mmol, 0.004 equiv) as starting material to react with polyols (5.0 g, 4.23 mmol, 0.004 equiv) to give both esters as dark oil (14.667 g, 97.46%)

and (14.402 g, 96.19%), respectively. To evaluate the effectiveness of various solvents and catalysts, several experiments were repeated using two different solvents of toluene and acetonitrile under varying catalysts of H_2SO_4 and HCl .

3.5 Method flow chart

The proposed synthetic scheme of esterified palm olein was summarized in Scheme 3.1 as well as the summary of synthetic method flow in Table 3.1.



Scheme 3.1: Proposed synthetic scheme of esterified palm olein (i) formic acid, hydrogen peroxide, 40°C , 2.55 h (Nurazira & Salimon, 2022), (ii) glycerol, 120°C , 4 h (Kamairudin et al., 2021), and (iii) R' (linoleic acid, oleic acid, and salicylic acid), 140°C , 4 h (Nurazira & Salimon, 2023)

Table 3.1: Summary of synthetic method flow

Synthesis step	1	2	3
Synthesis method	Epoxidation	Alcoholysis	Esterification
Starting material	Palm Olein	Epoxidized palm olein	Hydroxyl-ether palm olein
Reagents	Formic acid, Hydrogen peroxide	Glycerol, Boron trifluoride diethyl ether complex	Carboxylic acid (Salicylic acid, Oleic acid, Linoleic acid), Sulphuric acid
Molar ratio of reagents	Palm olein: Formic acid: Hydrogen peroxide (1: 5.91:3.60)	Epoxidized palm olein: Glycerol: Boron trifluoride diethyl ether complex (1:10:1)	Hydroxyl-ether palm olein: Carboxylic acid: Sulphuric acid (1:4:1)
Reaction temperature	30 – 60 °C	90 – 120 °C	80 – 140 °C
Reaction time	30 – 153 minutes	1 – 6 hours	2 – 6 hours
Synthesis outcome	Epoxidized palm olein	Hydroxyl-ether palm olein	Esterified palm olein

3.6 FTIR Analysis on Oxirane Oxygen Content (OOC) and Iodine Value (IV)

For the analysis of OOC and IV, the samples (0.5 ml) were taken regularly during the epoxidation and alcoholysis reactions to get their ATR-FTIR spectra. The ATR-FTIR spectra were documented using smart iTR diamond ATR in the wavenumber range between 400 and 4000 cm^{-1} . For the OOC, the oxirane band area of epoxy functional group absorption was calculated based on FTIR spectrum region from 1432.0 to 1497.3 cm^{-1} relative to the baselines between 762.2 and 862.3 cm^{-1} . For IV, the double bond absorption was appeared at the region areas of 3004.2 to 3017.5 cm^{-1} relative to the baseline points lined at 2500.4 to 3035.2 cm^{-1} . Then, the measured FTIR peak areas were converted into OOC and IV values. To compute the maximum percentage of OOC (% OOC_{calculated max}) that all the double bonds of the PO_o had converted into the oxirane rings of EPO_o, the following equation was given (Afifah et al., 2021):

$$\% \text{ OOC}_{\text{calculated max}} = \left[\frac{(IV_i/2A_i)}{100+(IV_i/2A_i)A_o} \right] \times A_o \times 100 \quad \text{Equation 3.1}$$

where the atomic weight of oxygen, A_o (16.0 g/mol), atomic weight of iodine, A_i (126.9 g/mol) and the IV_i was the initial iodine value of PO_o as 62 (Jurid et al., 2020).

The loss of double bonds during the epoxidation reaction was calculated by equation 3.2:

$$\% \text{ Loss of IV (conversion)} = (\text{FTIR } \Delta IV / IV_i) \times 100 \quad \text{Equation 3.2}$$

where FTIR ΔIV was the FTIR measured iodine value.

Furthermore, the yield of epoxide by the epoxidation reaction was measured by equation 3.3:

$$\% \text{ Yield} = (\text{FTIR OOC}_{(1432-1497)} / \% \text{ OOC}_{\text{calculated max}}) \times 100 \quad \text{Equation 3.3}$$

where the FTIR OOC was measured at the FTIR bands from 1432 to 1497 cm^{-1} .

During epoxidation, there was a small change in the iodine value, ΔIV due to the increase of oil total mass. The incorporation of oxygen on the oxirane rings increased the weight of the oil. Thus, this mass increase should be calculated to correct the ΔIV to ensure more accurate iodine value calculation ($\Delta IV_{\text{corrected}}$) by the equations as below (Tavassoli-Kafrani et al., 2017; Wai et al., 2019):

$$\% \text{ Mass increase} = \left[\frac{100}{(100 - \text{FTIR OOC}\%) - 1} \right] \times 100 \quad \text{Equation 3.4}$$

$$\Delta IV_{\text{Corrected}} = IV_i - \{[(IV_i - \Delta IV) \times \% \text{ mass increase}]/100\} \quad \text{Equation 3.5}$$

where IV_i was the initial iodine value and the ΔIV was the FTIR measured iodine value.

3.7 Characterization Analysis by FTIR and NMR

The raw sample, epoxides, polyols, and the ester products from each chemical modification processes were contacted with NaCl plate and examined on the Perkin-Elmer Spectrum One FTIR Spectrometer by infrared light in the wavenumber range between 400 and 4000 cm^{-1} . The OMNIC spectroscopy software provided the absorption spectrum to identify the chemical composition of the structures. On the other hand, the NMR characterization analysis was carried out by proton (^1H) and carbon (^{13}C) Nuclear Magnetic Resonance (NMR). The sample was diluted with 600 μL of CDCl_3 in the NMR tube and then sited between the magnet poles probe and radiated with the energy to get their NMR spectra. The spectra were recorded on JEOL JNM-ECP 400 spectrometer by 400.13 MHz for ^1H -NMR and 100.77 MHz for ^{13}C -NMR.

3.8 Acid Value (AV) Measurement

The AV test was conducted based on ISO 660:1996 to determine the content of free fatty acids present in 1 g of fat. The sample (2.0 g) was mixed with the ethanol (50 ml) in the Erlenmeyer flask and boiled (75-80°C) on the heating plate for about 1 h to complete the

mixing. Then, the mixture was added with two drops of phenolphthalein solution. It was titrated with 0.1 N KOH solution and agitated vigorously until the end point of pale pink colour was appeared for at least 15 seconds. The AV test was repeated in triplicates and calculated using the following equation (Nduka et al., 2021):

$$AV = \frac{T \times N \times 56.1}{W} \quad \text{Equation 3.6}$$

where T was the volume of titrant KOH (ml) required for sample, N was the normality of standard KOH solution, and W was the weight of sample (g).

3.9 Saponification Value (SV) Measurement

According to ASTM D464, the oil sample (2.0 g) was dissolved thoroughly with 0.5 N ethanolic KOH (25 ml) in the Erlenmeyer flask and heated on the hot plate at about 70°C for an hour. The hot mixture was added with 2 drops of 1% phenolphthalein solution to get a pale pink colour then it was titrated immediately with 0.5 N H₂SO₄ until a colourless solution was formed. To prevent highly variable test results, the samples were titrated immediately when it was still warm at 60 to 70°C. SV analysis was repeated for three times for the blank and the samples. The equation for this potentiometric method was calculated using the equation displayed as below (Nduka et al., 2021):

$$SV = \frac{(A-B) \times N \times 56.1}{W} \quad \text{Equation 3.7}$$

where A was H₂SO₄ (ml) needed for titration of the blank, B was H₂SO₄ (ml) required for titration of the samples, W was the weight of sample (g), N was the normality of H₂SO₄. The data of SV was reported to the nearest whole number.

3.10 Ester Value (EV) Measurement

The EV was measured from the amount of KOH (mg) needed to react with the ester content of sample (1.0 g) after the saponification reaction. Thus, EV was the difference between the SV and AV (Tajau et al., 2020):

$$EV = SV - AV \quad \text{Equation 3.8}$$

where SV was the saponification value and AV was the acid value of sample.

3.11 Ester Value (EV) Percentage

The ester percentage (%) was determined by equation (Tajau et al., 2020):

$$\% \text{ Ester} = (EV \times \text{MW ester}) / (10 \times 56.1) \quad \text{Equation 3.9}$$

where MW ester was the molecular weight of ester which was 126.11 g/mol.

3.12 Preparation of Lubricant Formulation

The lubricant formulation was prepared in different concentration of 0 weight by weight concentration percentage % (w/w), 0.1 %, 0.2 %, 0.3 %, 0.4 %, and 0.5 %. For 0.1 % (w/w), TiO₂ nanoparticle powder (0.002 g) was added into the esterified palm olein (2.0 g) with the surfactant of ethylene glycol (0.018 g). The function of surfactant was to reduce the agglomeration or sedimentation of TiO₂ nano-powders. The mixture was stirred for 30 minutes using the magnetic stirring bar in the beaker and then it was heated at 40°C for another 30 minutes together with the ultrasonication method to disperse the nanoparticles well in the lubricating oils (Roselina et al., 2020).

3.13 Pour Point (PP) Value Determination

The pour point of sample was determined according to the standard procedure of American Society for testing Materials (ASTM D 97-05) with some modifications (Samidin

et al., 2021). The apparatus was set up as shown in Figure 3.1 with dimensions in millimetres. The sample was filled into the test jar until the level mark of 5.4 cm height and dipped into different cooling baths for several temperature. Three cooling baths used for analysis were 100 g crushed ice with 100 g water (0°C); 100 g crushed ice with 33 g NaCl crystals (-12°C), and 100 g crushed ice with 41 g calcium chloride crystals (-27°C). The temperature drop was observed in every 3°C using the thermometer. The temperature was recorded once the sample stopped to flow after tilted in a horizontal position for 5 seconds. The readings were recorded in triplicates and the average temperature was added with 3°C as the final temperature of PP value (Yeong et al., 2022).

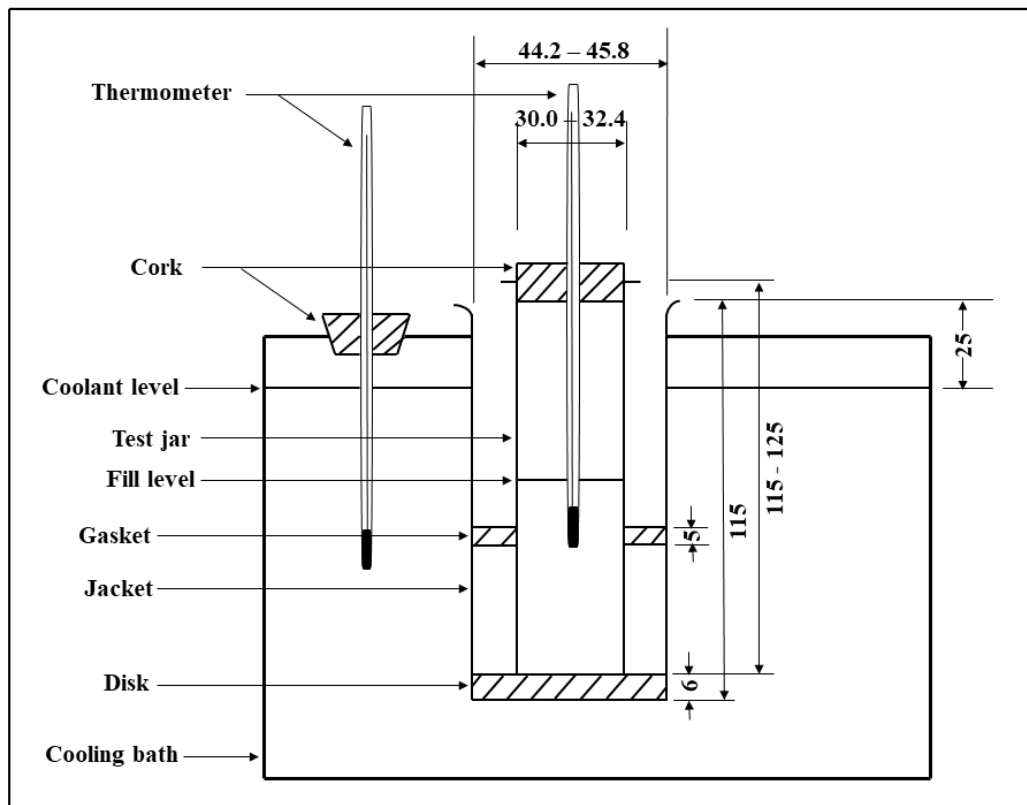


Figure 3.1: Apparatus of pour point test (Samidin et al., 2021)

3.14 Scanning Electron Microscopy (SEM) Analysis

A small amount of sample was prepared and coated with a thin layer of conducting material usually the carbon then fitted into the SEM chamber. The data were collected over

the selected surface areas of samples from 1 to 10 microns using the magnification ranging from 1000 X to approximately 50,000 X. The SEM images indicated the surface morphology and the nanoscale characteristics of the TiO₂ nanoparticles as well as the esterified palm olein enriched with the nano-additive of LA-EPO-TiO₂ and SA-EPO-TiO₂.

3.15 Statistical Analysis

The experimental results data were recorded at three repeated tests. The statistically significant differences between the group means were determined by the one-way Analysis of Variance (ANOVA) using the Microsoft Excel statistical software. The p-values less than 0.05 were regarded as significant.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Epoxidation and Analysis of OOC and IV value

Chemical modification process was started with the epoxidation reaction by converting unsaturated double bonds (C=C) of the palm olein (PO_o) into a new functional group, epoxy (C-O-C) to give epoxidized palm olein (EPO_o). In this methodology, performic acid was prepared *in situ* by addition of hydrogen peroxide (H₂O₂) into formic acid (HCOOH) (Scheme 2.1). This reaction was highly exothermic and unstable so the temperature was controlled regularly in the ice bath condition when H₂O₂ was added dropwise at the rate of 2 ml min⁻¹. In this reaction, HCOOH functioned as an oxygen carrier while the H₂O₂ acted as an oxygen donor.

The epoxidation progress was tracked continuously and monitored by the OOC and IV via the simple and rapid ATR-FTIR method. The parameters of OOC and IV represent the formation of oxirane groups and the loss of double bonds. IV indicated the number of double bonds while the OOC displayed the percentage of epoxy content. The maximum calculated percentage of oxirane oxygen content (%OOC_{calculated max}) for all the double bonds in the PO_o to be converted into the oxirane ring was 3.76% which calculated from the equation provided in Chapter 3.5. In order to have a good quality of EPO_o, the OOC% should be as high as possible, while the IV should be very low after the epoxidation. The initial IV of PO_o was 62 mg/g. During the epoxidation, the IV of the sample was decreasing over the time due to the loss of double bonds until the lowest of 9.5 mg/g was analysed from the small peak area at frequency 3009.86 cm⁻¹ of 0.08 in absorbance (a.u.) unit in the FTIR spectrum. This indicated the great loss of double bonds at 84.68% in which almost all of the double

bonds in the PO_o were converted into the epoxy groups leaving only minor percentage remained in EPO_o. This was also explained by Polaczek et al. (2021) that there were remaining double bonds in the oil's structure if the IV was greater than 0.

During the epoxidation reaction, the molar ratio of PO_o: HCOOH: H₂O₂ was controlled at a constant variable in optimum value of 1: 5.91: 3.60 for every use. The manipulated variables of the epoxidation were the reaction temperature and the reaction time which were selected differently at 30°C, 35°C, 40°C, 45°C, 50°C, 55°C, and 60°C within 2.55 h. The response variable was the OOC% related to the epoxy conversion. The sample was taken every 30 minutes (min) during the epoxidation reaction to study their OOC%. Based on analysis from Figure 4.1, the highest OOC content was achieved at 3.69%, the closest to the %OOC_{calculated max} of 3.76%, which was obtained during reaction at 40°C for 153 min. At this temperature, the OOC values increased significantly during the first 90 min (3.44%), and continued to rise gradually to the maximum of 3.69%. The OOC percentage increased over the reaction time due to the increasing content of epoxy (oxirane) moieties that formed during epoxidation process. There was a slow increase of OOC trend by conducting the reaction at low temperature (30°C) by contributing only a low OOC% of 2.62% which was 69.68% of epoxy conversion. This slow epoxidation rate resulted most probably due to limited activation energy that required more reaction time to increase the epoxy conversion (Neswati & Nazir, 2021). The longer the reaction time, the higher the epoxidation rate due to the fact that more reactant molecules collide with each other to form the epoxy groups. Similarly, the OOC content for both reactions carried out at 35°C and 40°C grew strikingly in the beginning of reaction, but after 90 min, the trend at 35°C climbing more slowly to 3.55% in which lower than 40°C.

On the contrary, the reaction conducted at slightly higher temperature (45°C, 50°C, 55°C, and 60°C) resulted in smaller OOC% of 3.53%, 3.14%, 3.10%, and 2.89% respectively, for duration up to 153 minutes. The trends showed a rapid rise at the beginning of the epoxidation reaction until they reached their maximum point then followed by a sharp downturn began after 60 min (55°C, 60°C) and 120 min (45°C, 50°C). Since the reaction temperature was conducted above 40°C, higher temperature beyond the optimum also resulted in greater possibilities for the degradation of oxidant. In this study, the highest temperature was 60°C which it reached its maximum experimental OOC% of 3.42% at 60 min then dropped obviously to 2.89% at 153 min. This seems to suggest that after 60 min, the temperature had surpassed its equilibrium limit since the epoxidation was a reversible reaction (Ho et al., 2022). In addition, the high temperature resulted in less epoxy content due to oxirane cleavage as it expected to undergo partially hydrolysis causing some of the epoxy groups to degrade. This finding was consistent to the study of Arbain et al., (2022) who had revealed that the drop of OOC% was began in the elevated reaction temperature over 50°C due to epoxy ring opening and hydrolysis. In another study, the researchers interpreted that the oxirane formation was still exist but may slower than or equal to the rate of oxirane cleavage so the OOC% declined significantly along the reaction time after their upper limit (Alsofiany & Resul, 2021). These side reactions gave the adverse effects to reduce the epoxy content present in the sample which resulted in lower yield of oxirane ring. The epoxidation reaction followed the Le Chatelier's principle that the increasing temperature over the optimum will shift the equilibrium of the performic acid to the undesirable direction with less oxirane conversion (Zin et al., 2020). It was investigated that the side reactions not only occurred at the high temperature but also at the low temperature. The effect of side reaction was not significant at low temperature because it was slower than

the epoxidation rate so the OOC% still be seen in increasing amounts across the reaction time (Sawitri et al., 2020). In addition, the side reaction caused by the excess water molecules released from the degradation of H_2O_2 was reported able to destruct the oxirane rings to form diol or glycol as the by-products (Pongmuksuwan et al., 2023). Thus, this side reaction could explain on slightly lower value of OOC obtained for every sample taken during the epoxidation than the theoretical value of OOC calculated.

In optimization, the temperature of 40°C was the best experimental value for the epoxidation reaction because it demonstrated a steady rise in the OOC% to produce more stable oxirane rings and it also achieved the highest oxirane conversion of 98.14%. At the end of the epoxidation for 2.55 h, the reaction temperature of 30°C displayed the poorest OOC% of 2.62% followed by the reaction at 60°C with the OOC% of 2.89%. The difference in the OOC% has revealed the importance of reaction temperature and time for the epoxidation.

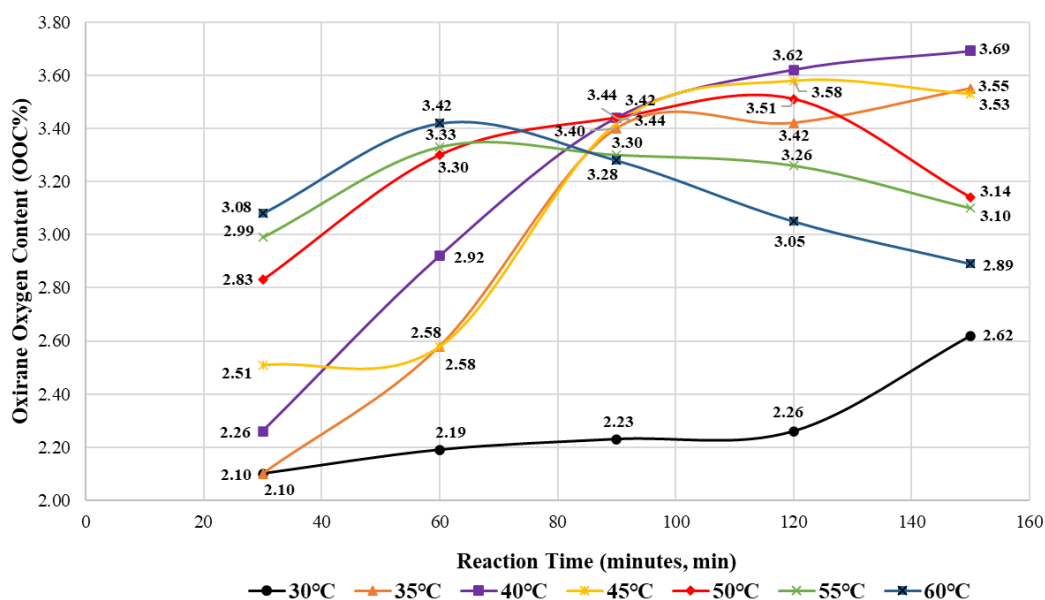


Figure 4.1: Percentage of OOC (%) during epoxidation of palm olein versus reaction time and temperature

Other than IV and OOC, the epoxy yield was also one of the important parameters to be highlighted in this experiment as illustrated in Figure 4.2. The yield of epoxidation

reaction versus the reaction time and temperature was investigated particularly at 60 min, 120 min, and 153 min. In this study, the highest epoxide yield obtained was 90.65% by carrying the reaction at 40°C for 2.55 h in which considered as most productive compared to other temperature conducting at 30°C, 35°C, 45°C, 50°C, 55°C, and 60°C that resulted in epoxy yields of 62.03%, 82.40%, 87.13%, 71.37%, 67.82%, and 60.51% respectively. This outcome was consistent to Nurazira and Salimon (2022) who produced the epoxidized palm oils with a high relative oxirane conversion of 99.43% and percentage yield of 86% under the optimal reaction temperature of 40°C for 2.55 h. As illustrated in Figure 4.2, the epoxy yield at low temperatures of 30°C, 35°C, and 40 °C increased gradually with time till their maximum values at 153 min. Both reactions at 45°C and 50°C showed the increasing trends up to 120 min with the epoxy yield of 89.46% and 74.82% then declined gradually to 87.13% and 71.37% respectively at 153 min. Treatment at higher temperatures of 55°C and 60°C produced the most oxirane rings at shorter time of 60 min with the epoxy yield of 77.79% and 73.74% respectively but their trends began to drop to 67.82% and 60.51% at longer reaction time of 153 min due to the depletion of oxirane rings.

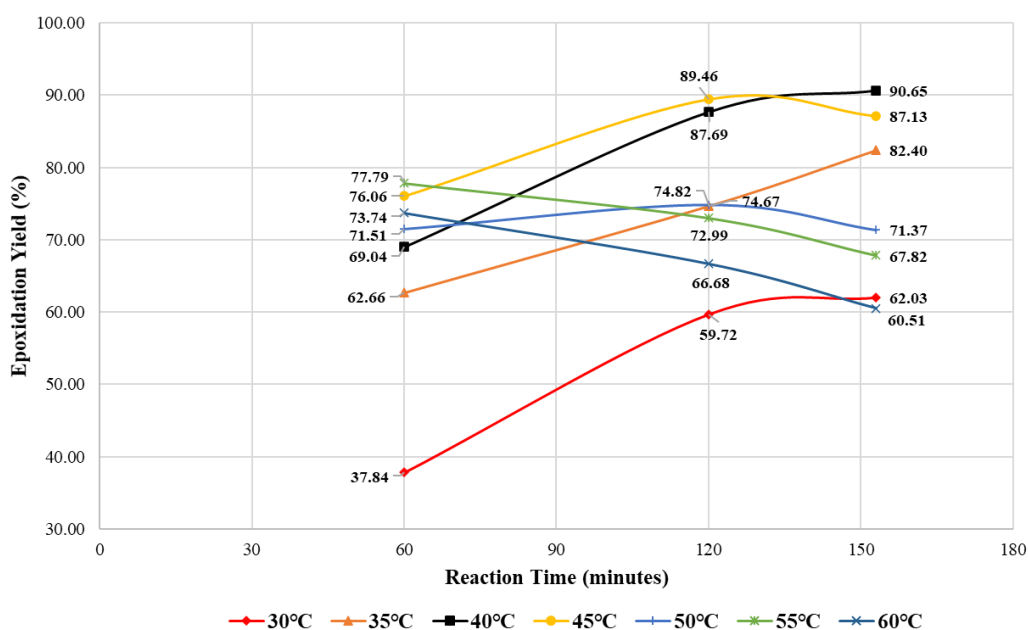


Figure 4.2: Epoxidation yield versus reaction time and temperature

The directions of arrows in Figure 4.3 summarised the increasing and decreasing trends of FTIR absorbance during epoxidation of palm olein. It was clearly seen when the epoxidation proceeded with time, there was a continual reduction in the peak area of the strong double bond (H-C=) stretching at around 3004.2 cm^{-1} to 3017.5 cm^{-1} as well as its weaker double bond absorption at 1655.88 cm^{-1} indicating successful conversion to epoxide. At the same time, the formation of epoxide also supported by the appearance of C-O-C oxirane peak regions that became larger as shown by stronger absorption bands from 762.2 cm^{-1} to 862.3 cm^{-1} as well as its weaker absorption peak for epoxide group over the regions from 1432.0 cm^{-1} to 1497.3 cm^{-1} . As described, OOC was calculated from the changes in the oxirane absorption bands that can be observed from increasing intensity pattern over the time until it reached its maximum value. Overall, based on the Figure 4.1 and 4.2, it can be concluded that the optimal reaction temperature and time for the epoxidation process was at 40°C for 2.55 h.

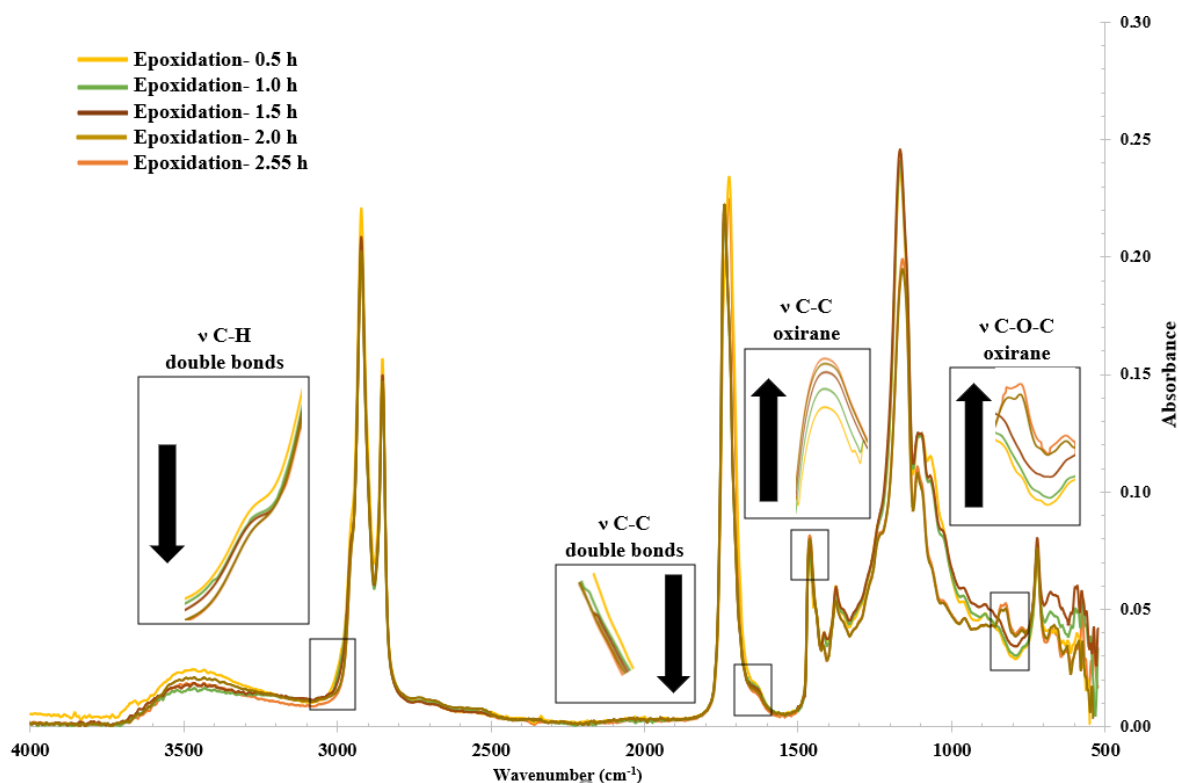


Figure 4.3: Comparison of ATR-FTIR epoxidation spectra on IV and OOC over the reaction time

4.1.1 Characterization Analysis of PO₀ and EPO₀ by FTIR and NMR

FTIR analysis was performed to examine the chemical bonds in the sample composition as the profiles of natural PO₀ and EPO₀ were compared in Figure 4.4. As illustrated, there were some changes in the absorption bands between the two characteristic profiles which scanned at the ranges from 500 to 4000 cm⁻¹. For the raw sample of PO₀, there were two small peaks observed at the wavenumber of about 3009.86 cm⁻¹ and 1655.88 cm⁻¹ which were the unsaturated double bonds in the fatty acid composition. In contrast, the FTIR spectrum of EPO₀ showed a different characteristic pattern compared to PO₀ by appearance of a new peak at 836.94 cm⁻¹ indicating the presence of epoxide group (C-O-C). At the same time, the small peaks for unsaturated double bonds at 3009.86 cm⁻¹ and 1655.88 cm⁻¹ had disappeared. This confirmed that the transformation of double bonds into the oxirane rings had occurred during the epoxidation modification process. This result was consistent to the study of Salih and Salimon (2023) confirming the epoxide group was observed in the frequency range of 823 cm⁻¹ to 843 cm⁻¹. Both FTIR spectra also consist of stretching peaks at approximately 2852 cm⁻¹ and 2921 cm⁻¹ which were the methylene CH₂ and methyl CH₃ stretching vibration as well as the bending vibration of CH₂ at 1462 cm⁻¹. Meanwhile, the aliphatic chain with CH₂ oscillatory vibration was located at 721 cm⁻¹.

Apart from FTIR analysis, proton NMR (¹H-NMR) and carbon NMR (¹³C-NMR) spectra were used to support the formation of epoxide during epoxidation reaction. To carry out the NMR analysis, the sample was dissolved in deuterated chloroform (CDCl₃). The ¹H-NMR spectra of PO₀ and EPO₀ were shown in Figure 4.5 and 4.6, respectively. The solvent peak appeared at the chemical shift of 7.25 ppm (¹H-NMR spectrum) and between 76-77 ppm (¹³C-NMR spectrum). The presence of unsaturated double bonds (HC=CH) of natural PO₀ can be seen at 5.30 ppm. The appearance of a new signal peak at 2.85 ppm in the EPO₀

spectrum indicated the successful formation of epoxide groups (H-C-O-C-H) in which corroborated by earlier finding of Kamairudin et al. (2021) revealing the epoxide ring were seen at 2.88 ppm. After the epoxidation, both of the peaks of olefin proton (C=C-H) at 5.30 ppm and its allylic proton (C=C-C-H) at 2.01 ppm in the PO_o had disappeared and replaced by the oxirane ring peak signal (H-C-O-C-H) at 2.85 ppm and the epoxy proton (CH₂-CHOCH-CH₂) at 1.44 ppm. In other words, the disappearance of the peak area for the double bonds with 13.336 arbitrary unit (a.u.) but the presence of oxirane ring with 11.359 a.u (Figure 4.6) had evidenced the successful of epoxidation reaction. Furthermore, the signals of long aliphatic chain (CH₂) and the terminal CH₃ were shown in the both spectra at 1.22 ppm (peak 2) and 0.84 ppm (peak 1) respectively.

Figure 4.7 and 4.8 displayed the ¹³C-NMR analysis of PO_o and EPO_o, respectively. In PO_o spectrum, the peaks of unsaturated double bonds (C=C) were shown at the chemical shift from 127 to 130 ppm. The conversion of double bonds into the oxirane rings during the epoxidation process was supported by the appearance of new peaks at 54 to 57 ppm in which represented the oxirane ring (C-O-C). Both spectra showed a sharp peak at 14 ppm which was R-CH₃ followed by the peaks from 14 to 34 ppm which generated from the aliphatic chains of carbon, R-(CH₂)₅-CH₂-CH₃. Lastly, the peaks that ranged at 172 to 173 pm were considered as the carbonyl ester (C=O) of the sample. This characterization was consistent to the findings by Nurazira and Salimon (2022). The proton and carbon peaks in the EPO_o were summarized in Table 4.1 and 4.2. As a result, both FTIR and NMR analysis had proved the successful attempt of epoxidation process to yield the EPO_o at 90.65%.

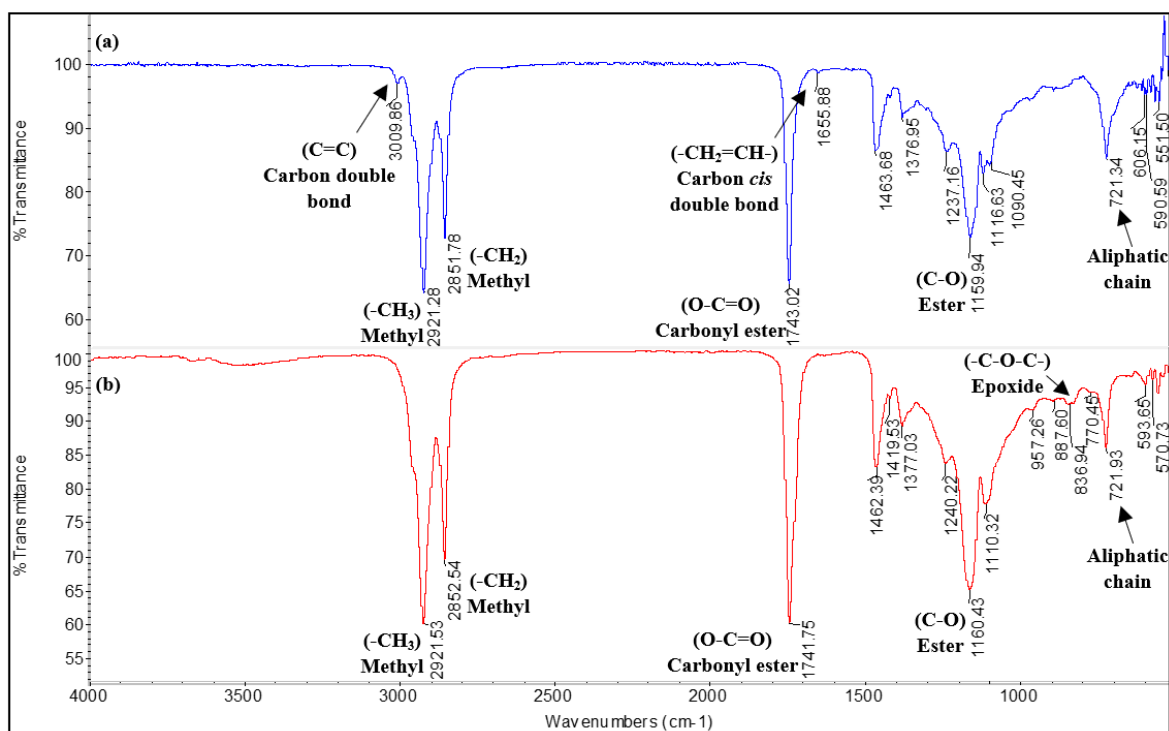


Figure 4.4: FTIR spectra of PO_o (a) and EPO_o (b)

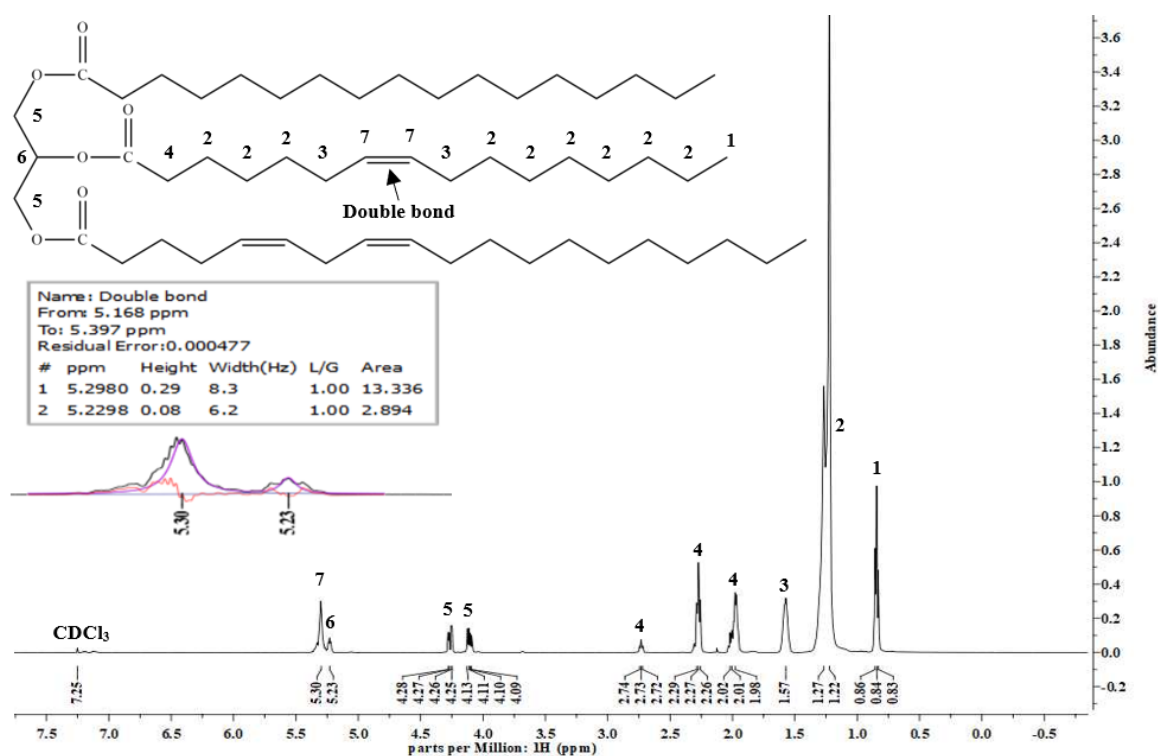


Figure 4.5: ¹H-NMR spectrum of PO_o

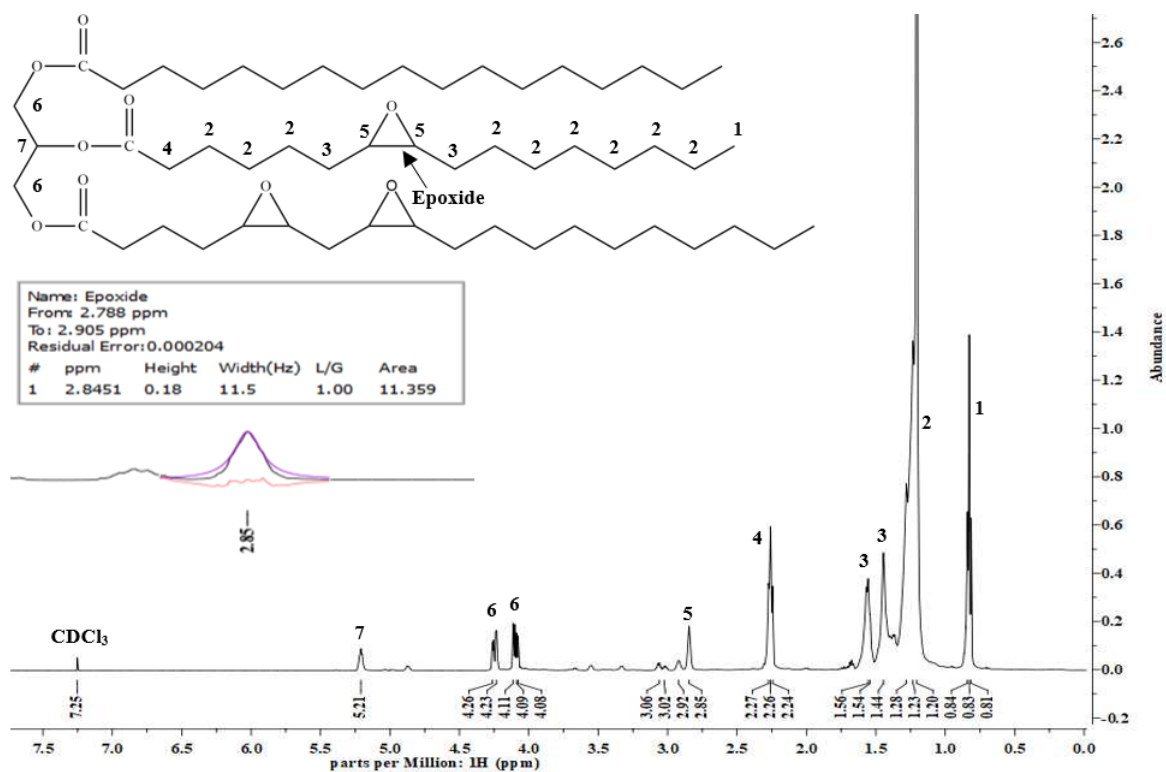


Figure 4.6: ^1H -NMR spectrum of EPO.

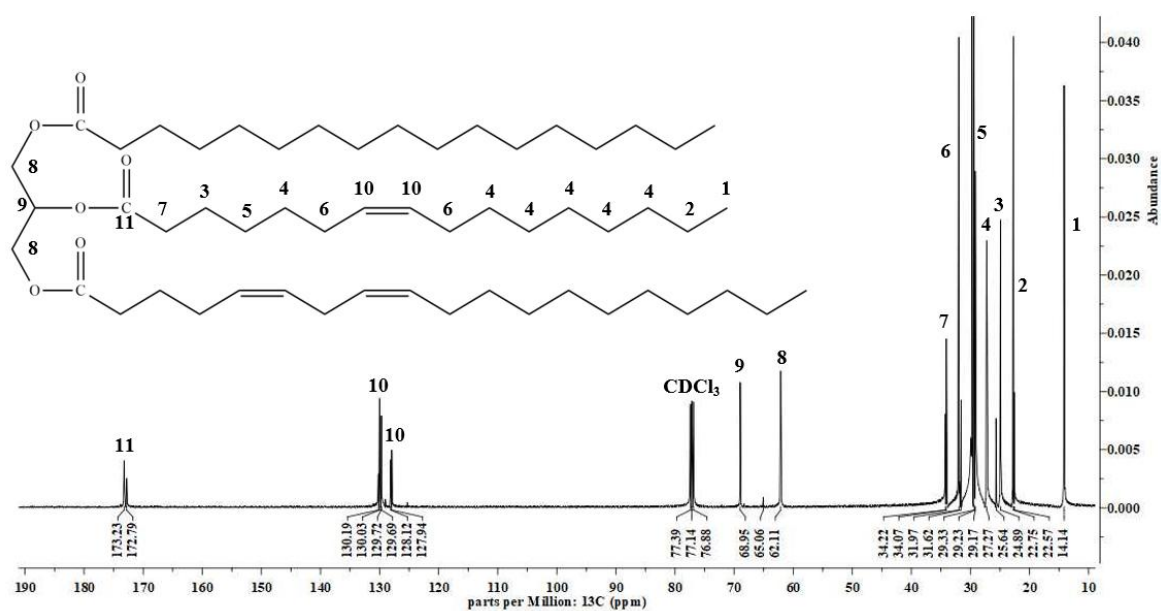


Figure 4.7: ^{13}C -NMR spectrum of PO.

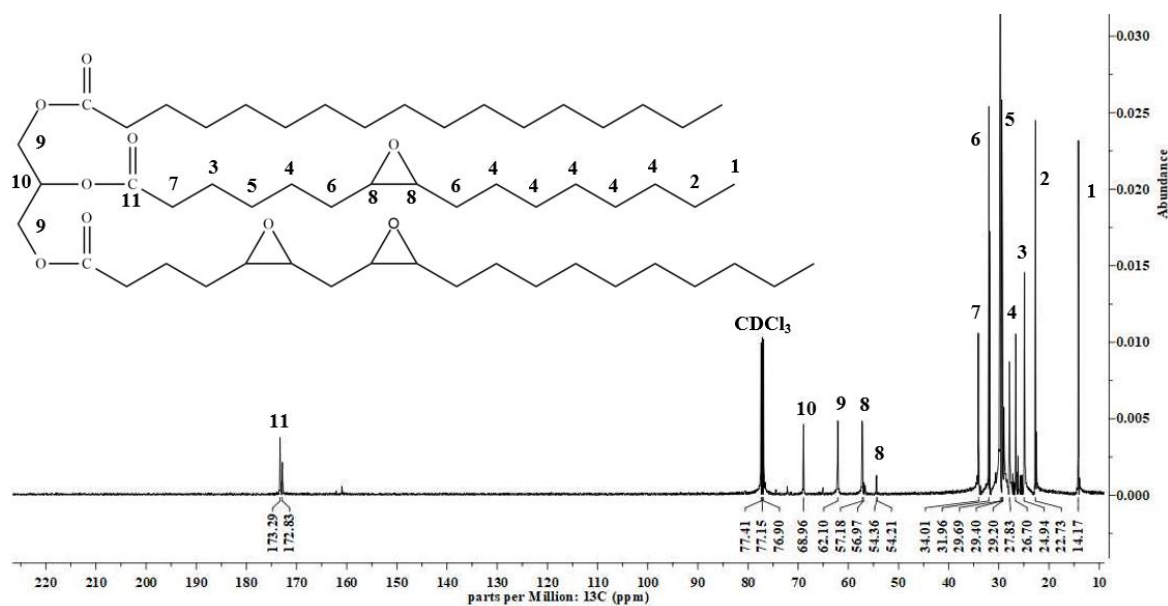


Figure 4.8: ^{13}C -NMR spectrum of EPO.

Table 4.1: ^1H NMR and ^{13}C NMR analysis of EPO.

Position	^1H (δ , ppm)	^{13}C (δ , ppm)
1	CH_2CH_3 (0.81 - 0.84)	CH_2CH_3 (14.17)
2	$\text{CH}_2\text{CH}_2\text{CH}_2$ (1.20 - 1.28)	CH_2CH_3 (22.73)
3	$\text{CHOCH}_2\text{CH}_2$ (1.44 - 1.56)	$\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ (24.94)
4	$\text{O}=\text{CCH}_2\text{CH}_2$ (2.24 - 2.27)	$\text{CH}_2\text{CH}_2\text{CH}_2$ (26.70 - 27.83)
5	$\text{CH}_2\text{CHOCHCH}_2$ (2.85)	$\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ (29.20 – 29.40)
6	OCH_2CHO (4.08 - 4.26)	$\text{CH}_2\text{CHOCHCH}_2$ (31.96)
7	$\text{CH}_2\text{CHOCH}_2$ (5.21)	$\text{O}=\text{CCH}_2\text{CH}_2$ (34.01)
8		$\text{CH}_2\text{CHOCHCH}_2$ (54.21 – 57.18)
9		OCH_2CHO (62.10)
10		$\text{CH}_2\text{CHOCH}_2$ (68.96)
11		$\text{CHOC}=\text{OCH}_2$ (172.83 – 173.29)

4.2 Ring Opening Reaction and an Analysis of OOC and OH value

The second step of chemical modification of palm olein was alcoholysis reaction. This reaction was carried out to prepare polyols intermediate using glycerol reagent with the aim to introduce three hydroxyl groups during ring opening of each epoxide (EPO_o). By installing more hydroxyl groups in the structure of palm olein is hoped to increase the esterification value and broaden the mid-chain length between fatty acids. This reaction was conducted at the water-oil interface in the aqueous phase as the epoxide rings were dissolved in the oil phase (Santacesaria et al., 2020). The alcoholysis was a slow and reversible reaction so the rate of reaction was accelerated by the catalyst of boron trifluoride diethyl ether complex (BF₃·Et₂O).

FTIR analysis on OOC was used to confirm the successful synthesis of polyols during alcoholysis reaction. Figure 4.9 illustrates the changes of OOC percentage versus reaction temperature and time. In this experiment, the parameter of the mole ratio of EPO_o: glycerol: BF₃·Et₂O was fixed at 1: 10: 1. The mole ratio of nucleophilic glycerol was used as high as 10 because the ring opening process favoured a high amount of alcohol reagent but a low amount of catalyst in order to increase the hydroxyl values of the polyols (Kamairudin et al., 2021). Also, the selection of the ring opening agent should be suitable and appropriate as it may affect the quality of the polyols. In this view, the naturally occurring alcohol of glycerol which consisted of three hydroxyl (OH) groups on its carbon backbone was selected and expected could improve the ring opening reaction. In addition, the existing of primary OH groups of glycerol which were more reactive than the secondary OH groups will increase the chances to form the bio-polyols.

After running numerous times of ring-opening reaction, the results were summarised in Figure 4.9. From the analysis, it can be seen that the reaction temperature and time showed

a great influence on the rate of ring-opening reaction. This study suggested the best reaction temperature for the alcoholysis reaction was discovered at 120°C for the duration of 4 h. Under this condition, the lowest OOC% of 0.28% with a high conversion to polyols of 92.45% was obtained. At 120°C, the OOC% was decreasing from 2.34% to 0.28% from 1 h to 4 h then it developed again and stayed the constant value of 1.35% after 4 h. This indicated that it had reached its equilibrium at 4 h but it became reversible beyond the 4 h due to the limiting amounts of the reactants. Thus, an extended reaction time to 6 h at 120°C was not applicable because it did not show any remarkable result. This result was agreed with Kamairudin et al. (2021) with their best OOC of 0.05% for alcoholysis reaction conducting at 120°C and the molar ratio of EPO_o to the glycerol of 1 to 10. Additionally, it was investigated that the increasing temperature up to 120°C demonstrated better conversion because the catalyst of BF₃·Et₂O tends to be limited and deactivated above 120°C. Furthermore, its boiling point was 130°C so the evaporation, decomposition, and the loss of catalytic activity may occur. Thus, the reaction temperature higher than 120°C was not designed in this experiment setup following suggestion from another study stating high temperature is used to form the crosslinked polymer (Ulanova et al., 2022).

However, treatment at low temperature of 90°C showed the poorest ring-opening performance. Its OOC value was decreasing slowly each hour beginning with the highest OOC% of 3.34% during the first hour and slowly decrease to 3.12% (2 h), 3.05% (3 h), 3.05% (4 h), 2.63% (5 h), and 1.92% (6 h). At the end of the ring-opening reaction, the OOC values for the temperature of 90°C, 100°C, and 110°C were 1.92%, 1.28%, and 0.78% respectively after 6 h. This result indicated that there were still remaining oxirane rings in the EPO_o at the reaction temperature below 120°C requiring further improvement. To achieve higher hydroxyl values, it was recommended to reduce the OOC values to the lowest

until it stayed constant to confirm the completion of ring-opening reaction. At the temperature below 120°C, the OOC% continued to drop and failed to reach its constant value even by conducting the reaction for 6 h suggesting that longer reaction time may require. In general, the lower the OOC%, the lower the oxirane ring concentration. The higher the loss of oxirane rings, the higher the rate of ring-opening reaction with more introduction of hydroxyl and ether groups into the desired intermediate. The relationship between the reaction temperature and time towards the percentages of yield of polyols was summarised in Figure 4.10. Based on the analysis, there were a continual rise in the yield of products at reaction temperature of 90°C, 100°C, and 110°C from 1 h to 6 h which reached at 58.95%, 66.02%, and 70.43% respectively. Overall, the optimum operating condition for ring-opening reaction was at 120°C for 4 h. This treatment promoted the ring-opening reaction to reach its maximum of OOC reduction corresponding with the highest reaction yield of 85.93% for 4 h.

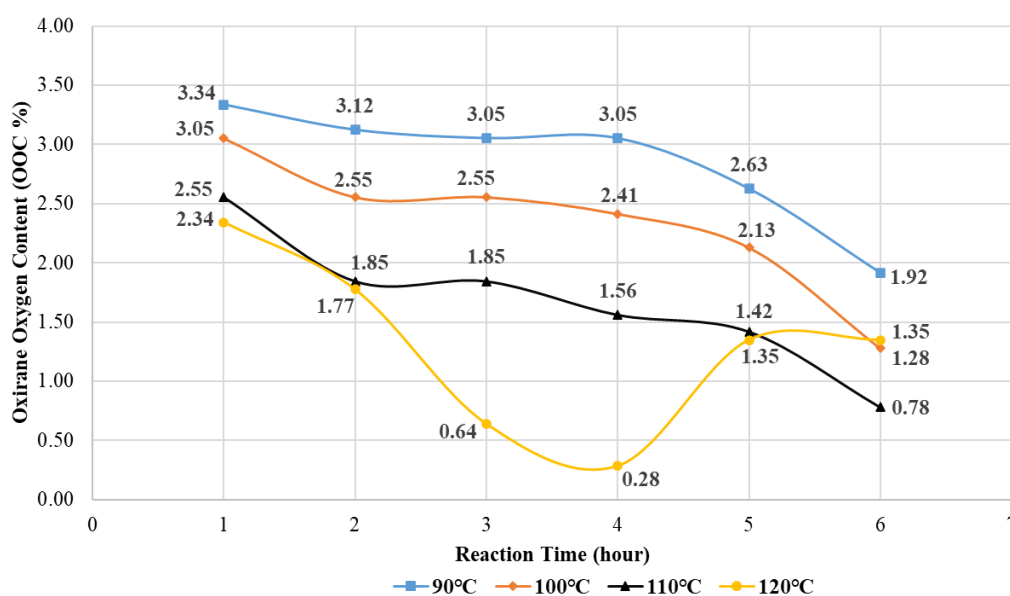


Figure 4.9: Percentage of OOC (%) during alcoholysis of EPO₀ versus reaction time and temperature

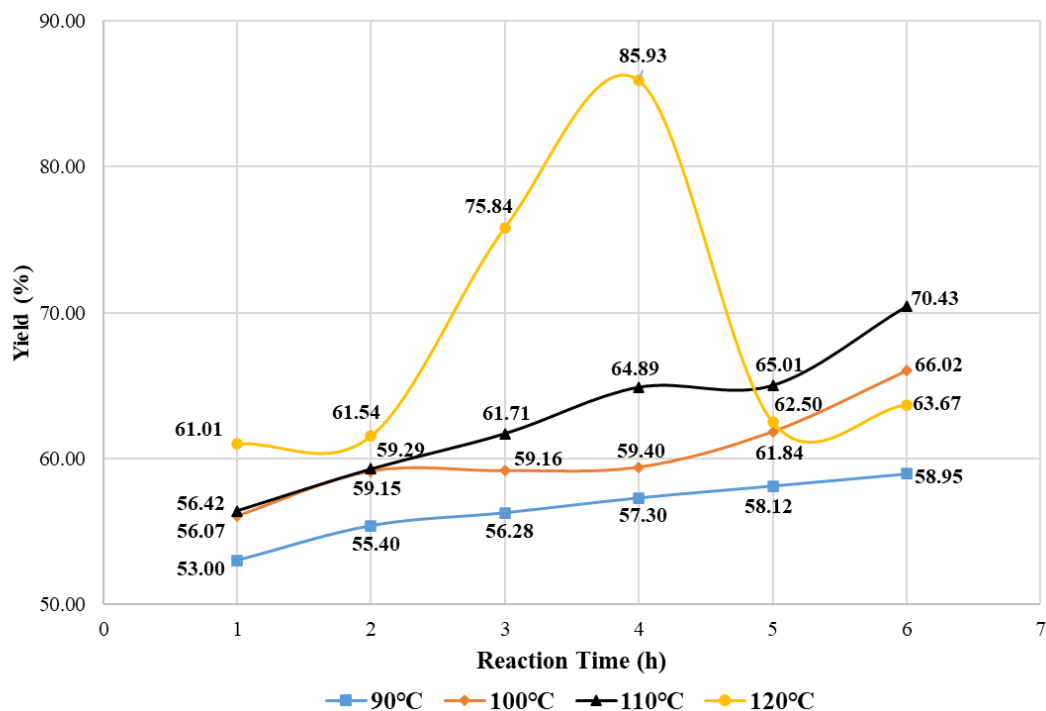


Figure 4.10: Percentage yield of polyols (%) versus reaction time and temperature

As an alternative to the traditional methods, the progress of ring-opening reaction was monitored and determined according to the simple FTIR method via the FTIR peak areas of the reactive hydroxyl (OH) group according to method developed by Dai et al. (2023). The amount of hydroxyl groups present in the samples was allied with the peak areas measured at frequency between 3300 to 3650 cm^{-1} (Figure 4.11). The higher the hydroxyl values of the ring-opening intermediate, the larger the FTIR peak area between 3200 and 3550 cm^{-1} . In this method, the temperature of 90°C, 100°C, and 110°C were prescribed an increasing tendency throughout the experiments until their highest peak areas (a.u.) of 447.77, 614.02, and 680.26 respectively. Their maximum values were relatively lower than at 120°C. This can be inspected clearly in the FTIR spectra prepared in Figures 4.12 and 4.13 which express the changes in the peak areas specifically on the OH groups for every hour up to 6 h at 120°C. The peak area (a.u.) of OH groups synthesized in the first hour was 437.28 continued to expand by the following second hours (466.23), third hours (698.81), and the highest at the fourth hours (766.99). Then, it started to diminish in the reaction time

of five hours (543.16) and six hours (523.30). In view of this, the ring-opening reaction was greatly influenced by both of the reaction temperature and reaction time. From the findings, the optimal experimental conditions of the ring opening reaction using glycerol was 4 hours at reaction temperature of 120°C.

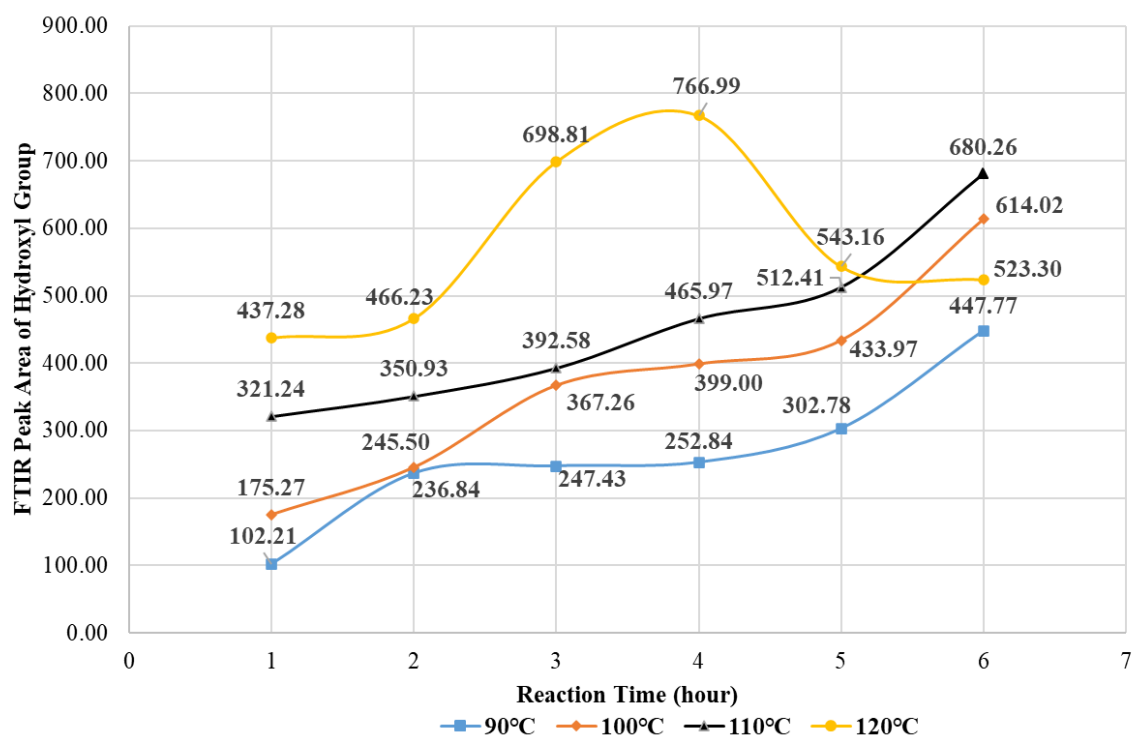


Figure 4.11: FTIR peak area of OH group versus reaction time and temperature

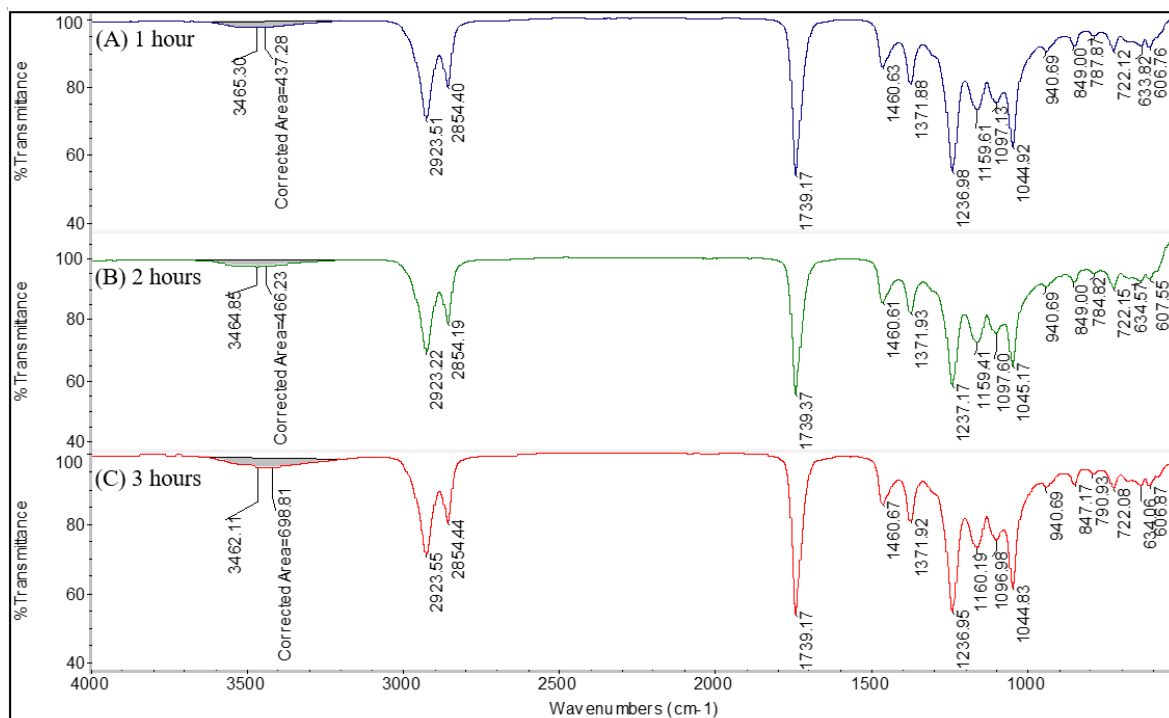


Figure 4.12: FTIR spectra of peak areas between 3300 to 3650 cm^{-1} for polyols within 1 h (A), 2 h (B), and 3 h (C) of reaction at 120°C

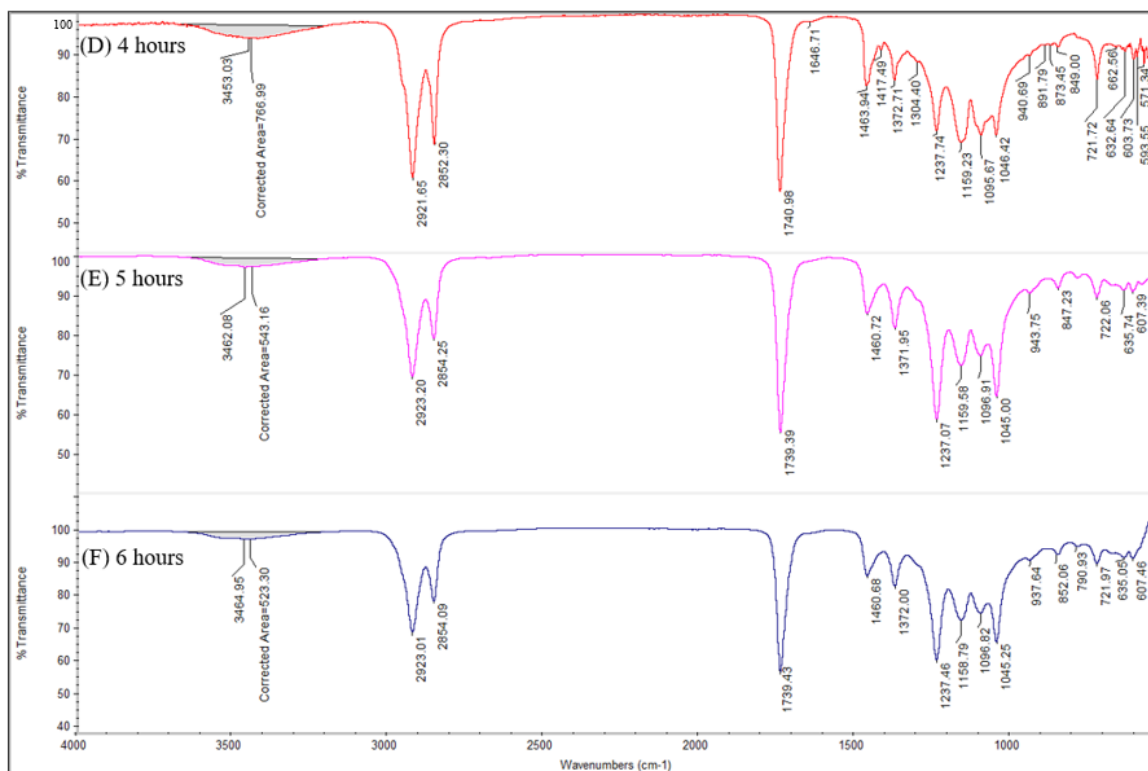


Figure 4.13: FTIR spectra of peak areas between 3300 to 3650 cm^{-1} for polyols within 4 h (D), 5 h (E), and 6 h (F) of reaction at 120°C

4.2.1 Characterization Analysis by FTIR and NMR

Once the ring opening process was completed, the product of hydroxyl-ether-PO_o was characterized using FTIR spectroscopy to obtain FTIR spectrum as shown in Figure 4.14. This spectrum provides evidence that the ring opening process had occurred successfully using glycerol. The appearance of a new broad band in the FTIR spectrum between 3200 to 3550 cm⁻¹ represented the stretching vibrations of hydroxyl (O-H) groups. This indicated that the EPO_o ring was successfully opened by glycerol with incorporation of hydroxyl functional groups into the structure. This finding was consistent with a report from Ghodke et al. (2021). Two peaks at 1096.91 cm⁻¹ and 1237.07 cm⁻¹ represented the C-C-O and C-O-C stretching of the ether groups respectively. The composition of the hydroxyl-ether-PO_o was manifested by the FTIR spectrum including the CH₂ stretching at 2854.25 cm⁻¹, CH₃ stretching at 2923.20 cm⁻¹, aliphatic chains with the bends of CH₂ and CH₃ at 1371.95 to 1460.72 cm⁻¹, C=O ester stretching at 1739.39 cm⁻¹ as well as the C-O stretching of ester at 1159.58 cm⁻¹. These characteristic peaks that appeared in the FTIR spectrum was similar to the previous study (Norhayati et al., 2022). This confirmed the successful in the synthesis of the large branched palm olein-based polyols by incorporating hydroxyl and ether groups into the fatty acid chains. The absence of epoxy group peak at 836.94 cm⁻¹ provides more support on the conversion of EPO_o to polyols.

The intermediate of hydroxyl-ether-PO_o was also characterized by proton and carbon NMR analysis. The solvent peak of deuterated chloroform was observed at 7.25 ppm (¹H-NMR spectrum) and between 76.85 ppm - 77.36 ppm (¹³C-NMR spectrum). Figure 4.15 shows the proton NMR spectrum of polyol. The spectrum confirmed the disappearance of the epoxy group in the structure due to the absence of peak at 2.85 ppm indicating the oxirane ring has been opened successfully from alcoholysis reaction. This finding was consistent to

Kamairudin et al. (2021). The appearance of a new signal peak at 2.66 ppm in the spectrum indicated the successful formation of OH groups.

Based on carbon NMR analysis, two missing peaks observed at 54 to 57 ppm for the epoxy groups explained the successful conversion to polyols (Figure 4.16). This was supported by the appearance of the new peaks at 70.18 to 74.38 ppm for OH group and at 68.96 ppm for the ether group. The result of carbon NMR analysis was in agreement with the data from proton NMR and FTIR spectra analysis. The proton and carbon peaks of polyols were summarized in Table 4.2. From these experiments, hydroxyl-ether-PO_o (polyols) was successfully prepared via alcoholysis reaction using glycerol at 85.93% yield which allowed more incorporation of the hydroxyl groups into the structure prior to esterification reaction.

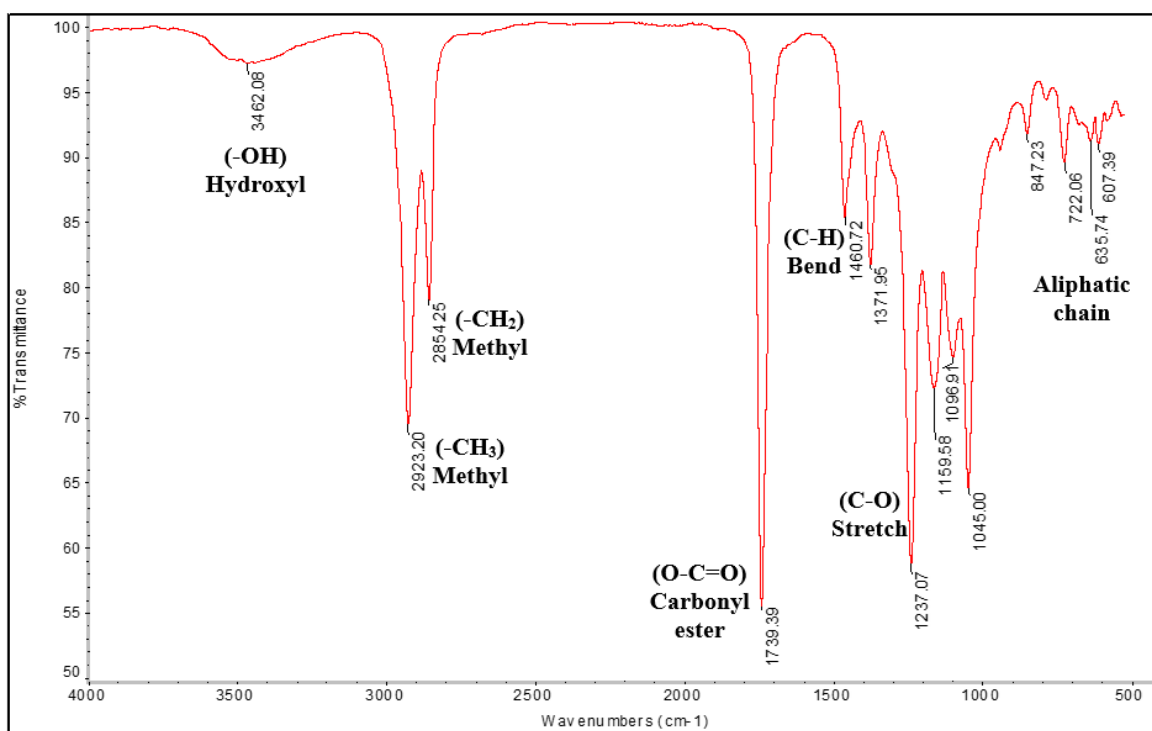


Figure 4.14: FTIR spectrum of hydroxyl-ether-PO_o at 120°C for 4 h

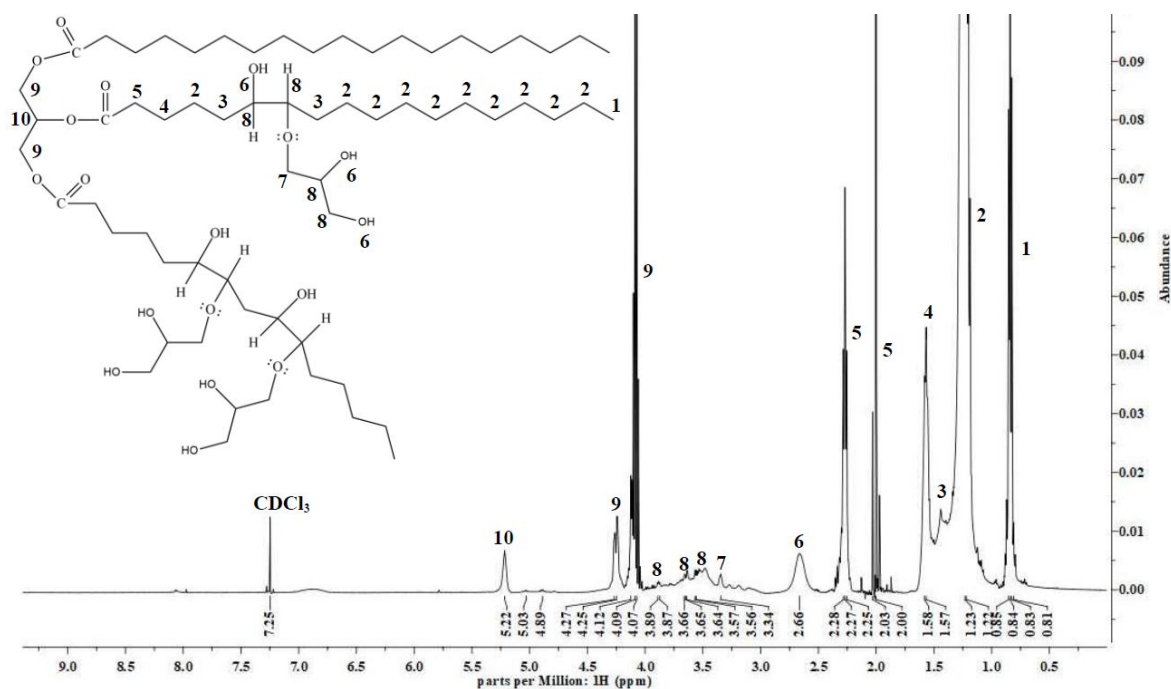


Figure 4.15: ^1H -NMR spectrum of hydroxyl-ether- PO_0

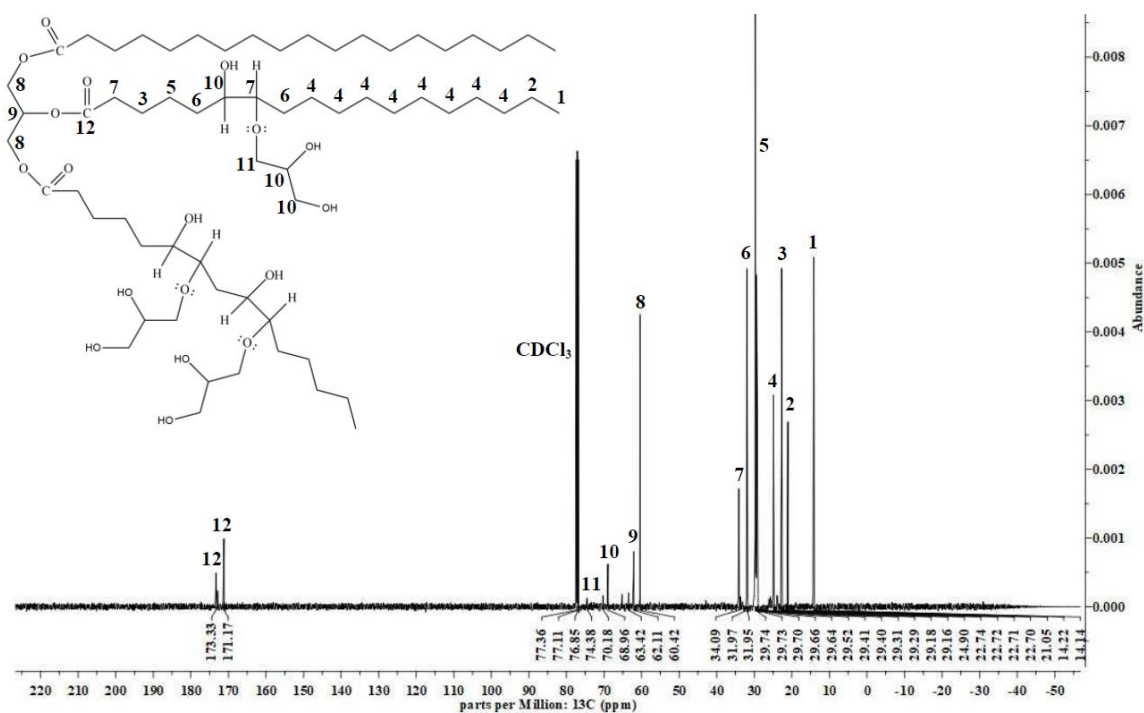


Figure 4.16: ^{13}C -NMR spectrum of hydroxyl-ether- PO_0

Table 4.2: ^1H NMR and ^{13}C NMR analysis of polyol

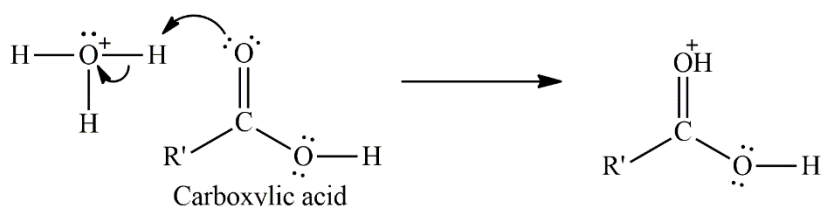
Position	^1H (δ , ppm)	^{13}C (δ , ppm)
1	CH_2CH_3 (0.81 - 0.85)	CH_2CH_3 (14.14 - 14.22)
2	$\text{CH}_2\text{CH}_2\text{CH}_2$ (1.22)	CH_2CH_3 (21.05 - 22.74)
3	$\text{CHOCH}_2\text{CH}_2$ (1.23)	$\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ (24.90)
4	$\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ (1.57 - 1.58)	$\text{CH}_2\text{CH}_2\text{CH}_2$ (29.16 - 29.74)
5	$\text{O}=\text{CCH}_2\text{CH}_2$ (2.00 - 2.28)	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH}$ (31.95)
6	CHOH (2.66)	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH}$ (31.97)
7	$\text{CHOCH}_2\text{CHOH}$ (3.34)	$\text{O}=\text{CCH}_2\text{CH}_2$ (34.09) CHOHCHOCH_2 (34.09)
8	$\text{CH}_2\text{CHOHCHO}$ (3.56 - 3.57) CHOHCH_2OH (3.64 - 3.66) $\text{CH}_2\text{OCHOHCH}_2\text{OH}$ (3.87 - 3.89)	CHOCH_2O (60.42)
9	CHOCH_2O (4.07 - 4.27)	$\text{CH}_2\text{CHOCH}_2$ (62.11)
10	$\text{CH}_2\text{CHOCH}_2$ (5.22)	$\text{CH}_2\text{OCHOHCH}_2\text{OH}$ (63.42) CHOHCH_2OH (68.96) $\text{CH}_2\text{CHOHCHO}$ (70.18)
11		$\text{CHOCH}_2\text{CHOH}$ (74.38)
12		$\text{CHOC}=\text{O}$ (171.17 - 173.33)

4.3 Esterification

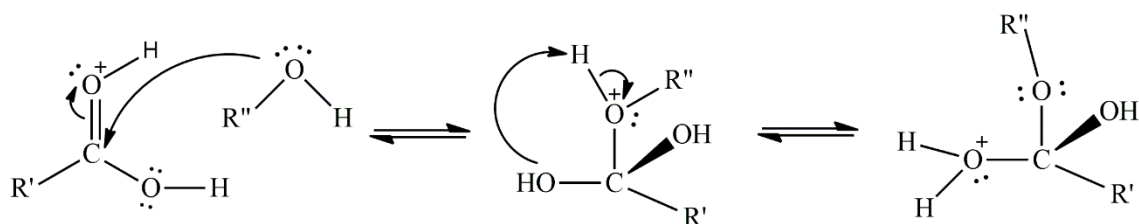
4.3.1 Reaction Mechanism of Esterification

Esterification is a condensation reaction that generates the product of ester along with by-product of water molecules by using fatty acid and alcohol as starting material. The reaction mechanism between polyols intermediate and different type of acids including oleic acid, linoleic acid and salicylic acid via Fischer esterification is proposed as illustrated in Scheme 4.1. In this reaction, the OH groups of polyols convert into ester (C=O) groups which will further broaden the mid-chain length between triglycerides of palm olein. The initial step involves the protonation of carboxylic acid when carboxyl oxygen accepting a proton from the strong acid catalyst of H_2SO_4 to form an oxonium ion. The carbonyl's carbon atom becomes more electrophilic because there is a partial positive charge on the electronegative oxygen atom. The second step involves the attack of the nucleophile from hydroxyl-ether- PO_6 on the carbonyl group to give a tetrahedral intermediate. One of the hydroxyl groups receives the proton to form a good leaving group ($^+\text{OH}_2$). This step forms an unstable tetrahedral intermediate which needs a further rearrangement. Hence, in a step 3, the loss of water molecule occurs to give a protonated ester. It is then followed by a proton transfer to Lewis base from protonated ester that will lead to a desired product of an ester. In the reaction, the catalyst is regenerated and its surface is available for the next catalytic cycle. This mechanism is consistent to Ahmed et al. (2023) stressing that the nucleophilic substitution step of the esterification reaction is slow since the pi-bond is difficult to break although the rate of proton donating step is rapid (Step 1).

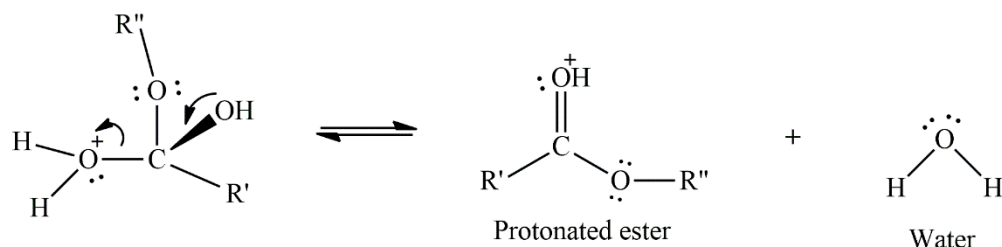
Step 1: Protonation of carbonyl group of carboxylic acid by strong acid catalyst



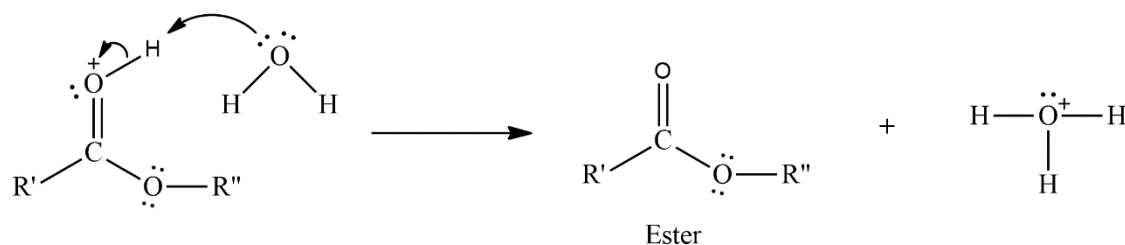
Step 2: Nucleophilic attack on carbonyl group by alcohol to give a tetrahedral intermediate then rearrange after proton transfer



Step 3: Elimination of a water molecule to give a protonated ester



Step 4: Transfer of a proton to a base to form ester



Scheme 4.1: A proposed mechanism of Fischer esterification reaction between polyols intermediate and different types of acids including oleic acid, linoleic acid, and salicylic acid (Solomons et al., 2014)

4.3.2 Optimization of Esterification Reaction

To improve the limitations of the natural palm olein at low temperature, the esterification reaction was optimised in order to lower down the pour point even more than existing study. In this study, the esterification was carried out by reacting the ring opening intermediate (polyols) with three different reactants which were linoleic acid, oleic acid, and salicylic acid separately from 80°C to 140°C. Two types of catalysts were selected in this

experimental design which were sulphuric acid and hydrochloric acid. Meanwhile, two organic solvents of toluene and acetonitrile were chosen as the medium for the esterification reaction. In this study, the variables used to optimize the esterification reaction were based on five parameters which were reaction temperatures, reaction time, types of solvents, types of reactants, and different catalysts. To produce an ester, the molar ratio of hydroxyl-ether-PO₆: reactant: catalyst was set as constant at the ratio of 1:4:1. As described, an excess reactant (4 moles) was supplied in the esterification process to ensure the limiting reactant of hydroxyl-ether-PO₆ to be completely used up during the reaction.

Figure 4.17 showed the relationship between the esterification reaction over the time at different temperatures. In this study, it was found that by carrying the reaction at temperature of 80°C, 100°C, and 120°C with longer duration demonstrated notable increasing trends in the ester yield (%). By using oleic acid, it was discovered that the highest yield of 97.46% was achieved at the operating temperature of 140°C for 4 h of reaction. The reflux temperature of 140°C gained its maximum value at 4 h followed by the drop of the reaction yield to 70.86% at even longer duration of 6 h. The decrease in the reaction yield was noticed in a longer reaction time which was caused by the dilution effect from the by-product of water molecules that accumulated at the active sites of the protonated catalysts (Hamerski et al., 2020; Sripada & Kastner, 2024). This phenomenon may inhibit the activity of acidic protonation at the active sites of the catalyst which led to less amount of desired product. As a result, it was observed that the reaction rate and the conversion yield increased rapidly during the first 4 h at 140°C from 48.73% to 97.46%. It was known that the esterification reaction was generally reversible, so more activation energy from the heat could improve the esterification reaction rate to attain the equilibrium state so that the molecules become easier to enter the inner pore of the catalyst (Neji et al., 2023). However,

at 140°C, the ester yield resulted at 4 h was better than 6 h because at this time the equilibrium state has been achieved. By extending the reaction time to 6 h had slightly inhibited the function of catalyst to have lower rate of esterification. According to Nurazira and Salimon (2022), the use of 1:3 molar ratio of the polyols: oleic acid with 1.86% of H₂SO₄ at 135°C for 4.96 h contributed 80% of the ester yield. This was supported by Almasi et al. (2021) stressing that the esterification reaction conducted by using oleic acid at high temperature has successfully improved the quality of oil apart of more economical than other methods. From this finding, the use of high temperature was highly recommended in carrying out the esterification process. However, increasing the temperature to 150 °C is not recommended because it would not only fasten the reaction rate but also lead to even higher risk of undesirable side reactions like oxidation reaction (Kopchev & Bayryamov, 2022). By considering this suggestion, therefore, the reaction temperature above 140°C was not demonstrated in this study. This also was demonstrated when the esterification reaction was conducted at higher temperature of 180-200°C for 4 h, it could only afford 71.8-79.78% of ester yield (Fawaz et al., 2020; Neji et al., 2023). Similarly, treating at lower temperature of 65-80°C but longer time of 2.5-6 h contributing to lower ester yield as well (73.2-82%) (Farouq & Selim, 2023; Xu et al., 2021).

Esterification reaction is not recommended to be carried out at low temperature or room temperature because it's taking longer time for a nucleophilic substitution to occur which is not economical and practical. This can be seen from Figure 4.17 that the temperature of 80°C resulted in the lowest conversion efficiency which only reached at 27.28% of ester yield at 6 h. At 80°C, there was no major significant change in the ester conversion during the first 2 h that only attained 18.56% followed by a slightly increased to 25.73% and 27.28% for 4 h and 6 h, respectively. This poor performance in the formation of

the ester could be due to the presence of weak intermolecular forces in the structure of ester that was hardly to form the hydrogen bonds in the mixture as well as they faced the problem of insufficient heat to carry out the activity in the system (Bahadi et al., 2021; Hamerski et al., 2020). In contrast, the application of higher temperature of 100°C and 120°C facilitated the ester conversion with more ester yield of 66.17% and 81.59% respectively after 6 h of reaction. Thus, from this study, it can be concluded that the reaction temperature was one of important parameters that could control the reaction time during esterification reaction as high optimum temperature was proven could reduce the amount of time to produce a better yield of ester. In this study, the optimal esterification reaction condition was discovered at 140°C for 4 h with the highest reaction yield of 97.46%.

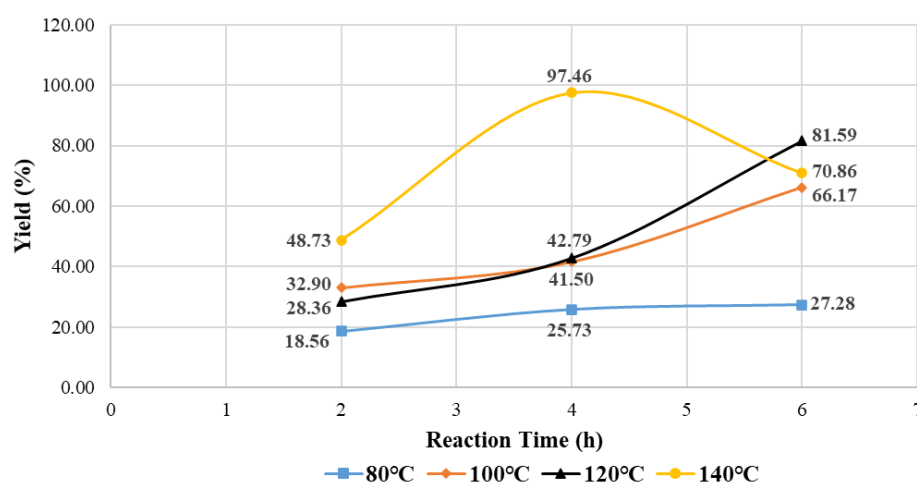


Figure 4.17: The percentage yield of ester (%) using oleic acid during esterification versus reaction time and temperature

The esterification reaction was also carried out using different type of acid as starting material which was salicylic acid to react with the hydroxyl-ether-PO_o in the presence of different catalyst and solvent to produce the salicylic acid-esterified PO_o. From Table 4.3, it can be seen that the best reaction yield was 99.29% with the ester value of 93.61% pointing the reaction catalysing by H₂SO₄ in the organic solvent of toluene at 140°C. Using the solvent of acetonitrile in the presence of H₂SO₄, the highest ester value was achieved at

97.04 % with the ester yield of 98.71%. Based on this study, it was observed that the reaction temperature played a key role in the ester conversion. At low temperature, the salicylic acid attributed a low conversion which was similar to the reagent of oleic acid. The ester yield produced by using salicylic acid was significantly improved from 40.20% to 99.29% when the temperature increased from 90°C to 140°C due to an increase in the collisions between the molecules that promoted the reaction rate. In this transformation, the esterification equilibrium was promoted by the solvents due to the liquid-phase reaction environment that could speed up the catalyst utilization and contributed to a greater solubility of samples (Pedersen et al., 2020). More solutes were able to dissolve absolutely in the solution at the elevated temperature due to higher reaction kinetics and catalytic activity. The analysts also emphasized that the toluene was the common organic solvent which used to boost the catalysis in the food industries. In the meantime, the catalyst of H₂SO₄ was more preferred than HCl because H₂SO₄ behaved higher boiling point than HCl just as the esterification reaction required higher temperature prior to 140°C. The abundant acidic concentrations of the catalysts also enhanced the rate of esterification reaction. In spite of better reaction yield, the catalysts of H₂SO₄ and HCl existed a major challenge of catalyst separation and the recyclability as the homogeneous catalyst was difficult to be isolated from the final products which restricted the reuse of catalyst. Based on this issue, the dosage of homogeneous catalyst utilized in the esterification reaction should be controlled at optimum so there was only one mole of catalyst was used in this experiment.

From these promising results, the parameters of reaction temperature at 140 °C, reaction time of 4 h, the hydrophobic solvent of toluene, and the catalyst of H₂SO₄ were chosen as the optimal esterification reaction conditions in the synthesis of esterified palm olein. On top of that, the oleic acid-esterified palm olein (OA-EPO) gave the highest ester

values of 96.79% followed by the salicylic acid-esterified palm olein (SA-EPO) with 93.61% and the linoleic acid-esterified palm olein (LA-EPO) of 92.86%. Apart from the ester values, the ester products which gained the best reaction yield was the SA-EPO with 99.29% which was higher than OA-EPO of 97.46% and LA-EPO of 96.19%. Overall, oleic acid, salicylic acid and linoleic acid gave excellent ester value (92.86-96.79%) and percentage yield (96.19-99.29%) during esterification reaction. Only a slightly lower difference of ester value and yield were observed from linoleic acid. This might be due to the minor effect coming from its length of fatty acid chain which was longer with more double bonds that caused itself to be more difficult to react with others so the ester conversion was reduced. Therefore, the salicylic acid was more preferable in the esterification reaction likewise it was also less expensive compared to oleic acid and linoleic acid. In short, the esterification reaction was listed as an efficient chemical process to convert a large number of OH groups in the bio-polyols into the large-branched esterified palm olein.

Table 4.3: Optimization of esterification reaction by using salicylic acid

No	Temperature (°C)	Solvent	Catalyst	Yield (%)	Ester value (%)
1	90	Toluene	H ₂ SO ₄	40.20	74.22
2	90	Acetonitrile	H ₂ SO ₄	42.93	61.47
3	90	Toluene	HCl	41.73	72.51
4	90	Acetonitrile	HCl	31.82	63.17
5	120	Toluene	H ₂ SO ₄	71.58	63.19
6	120	Acetonitrile	H ₂ SO ₄	72.07	64.47
7	120	Toluene	HCl	75.12	78.25
8	120	Acetonitrile	HCl	77.78	84.37
9	140	Toluene	H ₂ SO ₄	99.29	93.61
10	140	Acetonitrile	H ₂ SO ₄	98.71	97.04
11	140	Toluene	HCl	80.42	92.17
12	140	Acetonitrile	HCl	82.80	87.57

4.3.3 Characterization Analysis by FTIR and NMR

After the esterification reaction, FTIR analysis was carried out to identify and characterised the functional groups presence in the esterified palm olein. The FTIR spectra of LA-EPO, OA-EPO, and SA-EPO were illustrated in Figure 4.18. Both FTIR spectra of LA-EPO and OA-EPO shared a common point when the broad OH absorption bands that ranged between 3200 to 3650 cm^{-1} had disappeared indicating the successful conversion of OH groups to esters. These conversions were supported by the appearance of intense peaks of C=O esters at 1739.65 cm^{-1} (LA-EPO) and 1740.64 cm^{-1} (OA-EPO) concurrently with the C-O ester stretching peak at around 1162.41 cm^{-1} (LA-EPO) and 1160.27 cm^{-1} (OA-EPO). The small peak observed at 1672.82 cm^{-1} (LA-EPO) and 1628.50 cm^{-1} (OA-EPO) were contributed from the unsaturated double bonds in the fatty acid composition of the linoleic and oleic acid. This characterization was consistent to Nurazira et al. (2023) for C=O ester peak (1740 cm^{-1}) and C-O esters (1000 to 1300 cm^{-1}) (Bahadi et al., 2022; Esmaeili et al., 2022).

As observed in the FTIR spectrum of SA-EPO (Figure 4.18), it also displayed the C-O ester peaks from 1156.04 to 1240.34 cm^{-1} , unsaturated α , β C=O ester compounds at 1678.39 to 1710.82 cm^{-1} , and the carbonyl stretching C=O ester peak at 1737.60 cm^{-1} . According to the structure of the chemical compound, salicylic acid consisted of a hydroxyl group that adjacent to the carboxyl group by attaching on the benzene ring. That was why the FTIR spectrum detected the O-H stretching vibration at 3455.41 cm^{-1} . The appearance of aromatic C-C stretching peaks in the benzene rings at 1485.01 cm^{-1} and 1613.34 cm^{-1} as well as C-H aromatic stretching peaks at 3021.64 revealed the successful conversion to esters. From the FTIR analysis, the ester functionalities had been observed in all the esterified palm olein of LA-EPO, OA-EPO, and SA-EPO.

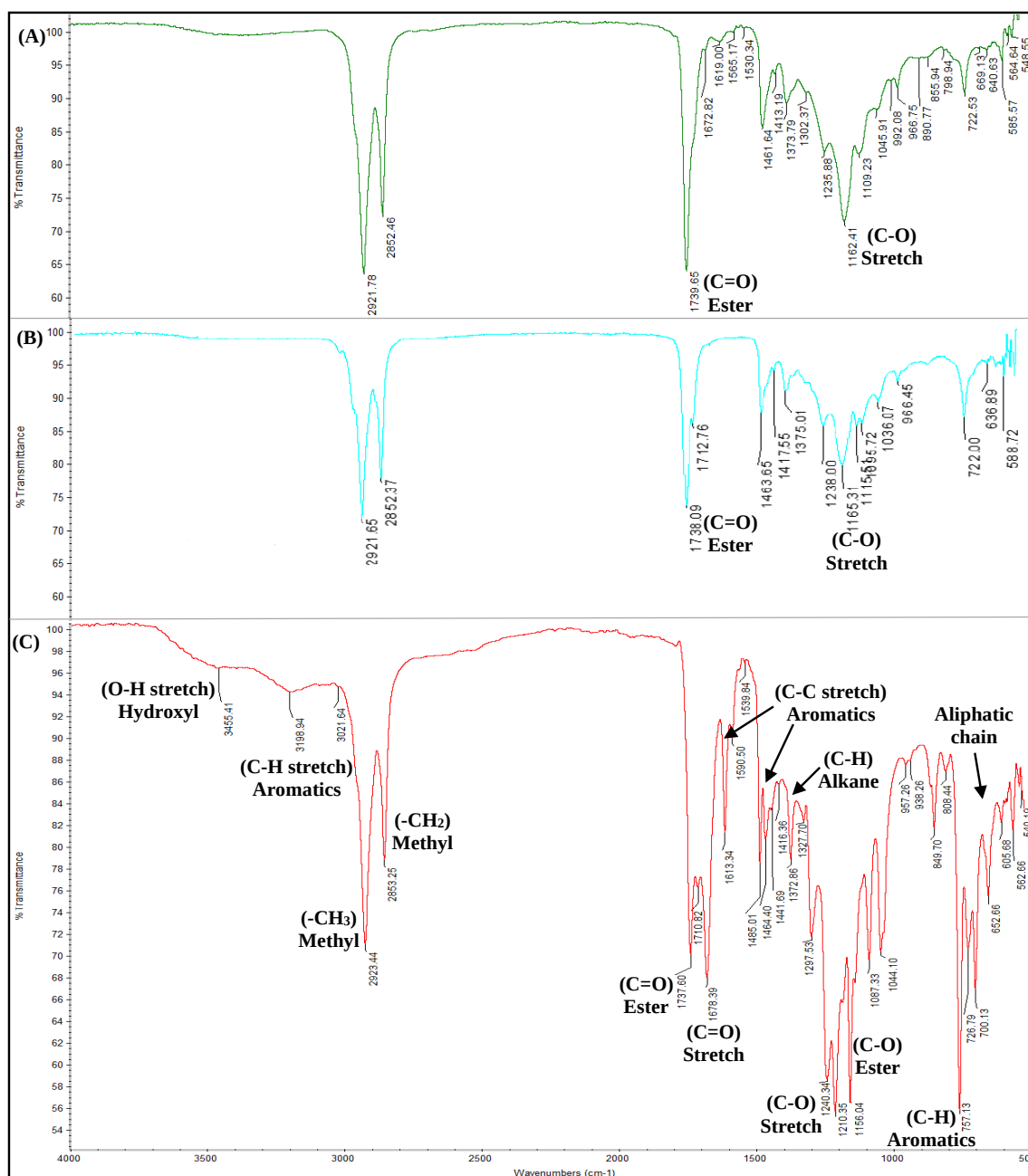


Figure 4.18: FTIR spectra of LA-EPO (A), OA-EPO (B), and SA-EPO (C)

The NMR analysis was conducted to provide more support on the characterization of ester during esterification reaction. The ^1H -NMR spectra of LA-EPO (Figure 4.19), OA-EPO (Figure 4.20), and SA-EPO (Figure 4.21) as well as the ^{13}C -NMR spectra of LA-EPO (Figure 4.22), OA-EPO (Figure 4.23), and SA-EPO (Figure 4.24) were given below. Typically, ^1H -NMR of LA-EPO, OA-EPO, and SA-EPO all demonstrated the structure of ester (RCOO-CH) with the peaks between 4.06 ppm and 4.50 ppm along with the protons

associated to the ester group ($\text{H}_2\text{C-COOR}$) from 2.00 to 2.37 ppm, and the ether group (HC-OR) at 3.93 ppm. These characterizations were consistent to Nor et al. (2023) for ester protons ($\text{CH}_2\text{-O}$) (4.05 to 4.11 ppm) and the protons of $\text{CH}_2\text{C=O}$ (2.29 to 2.33 ppm). Fundamentally, the ester formation was accompanied with the disappearance of hydroxyl groups at 2.66 to 3.89 ppm in the proton NMR spectrum because the OH groups had been converted to ester groups during the esterification reaction. Based on previous studies, peaks of alkene groups from the unsaturated fatty acids were still be observed for protons of double bonds (-C=C-H) at the chemical shift between 5.33 ppm to 5.39 ppm as well as the proton of -C=C-C-H between 2.02 to 2.29 ppm. This was exactly similar to the spectra of LA-EPO and OA-EPO in the of Figure 4.19 and 4.20. The proton peaks of unsaturation (-C=C-H) from the reactants of linoleic and oleic acid were observed at 5.31 to 5.36 ppm and also the proton of -C=C-C-H from 2.01 to 2.28 ppm. It can be observed that both proton NMR spectra of LA-EPO and OA-EPO have shown almost the same figures because both of them used their carbonyl oxygen positions to react with the ring-opening intermediates to form the final ester. The only difference was the structure of linoleic acid carried more double bonds than the oleic acid. For SA-EPO, the protons attached to the hydroxyl's oxygen atom of aromatic rings had revealed at 5.38 ppm while the protons directly attached to the benzene rings were appeared in the regions from 6.83 to 7.76 ppm. Additionally, the proton of ether was distinguished at 3.29 ppm. From the structure of SA-EPO, it can be confirmed that the salicylic acid had combined completely with the ring-opening intermediates to form the large-branched esters throughout the esterification reaction (Figure 4.21).

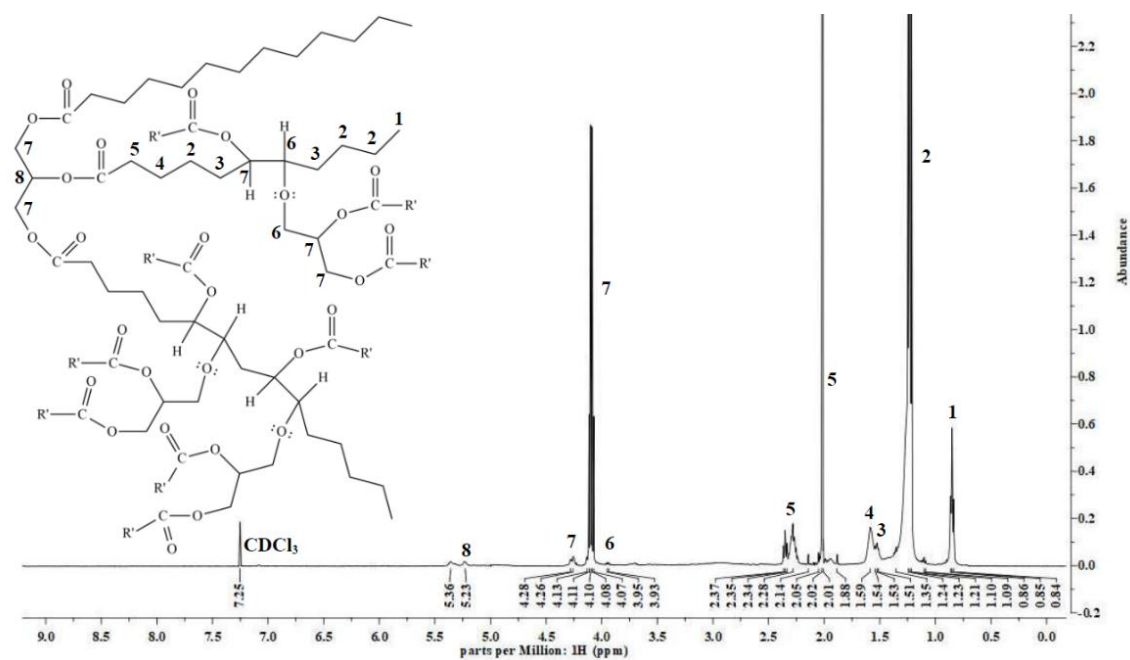


Figure 4.19: ^1H -NMR spectrum of LA-EPO

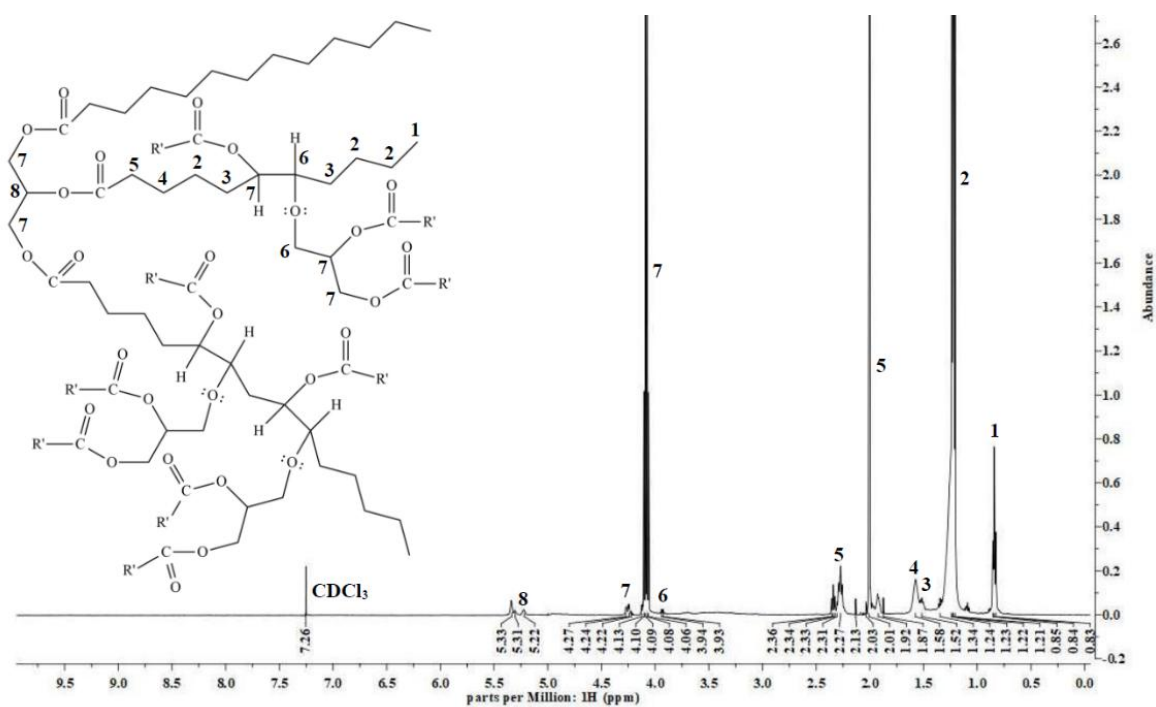


Figure 4.20: ^1H -NMR spectrum of OA-EPO

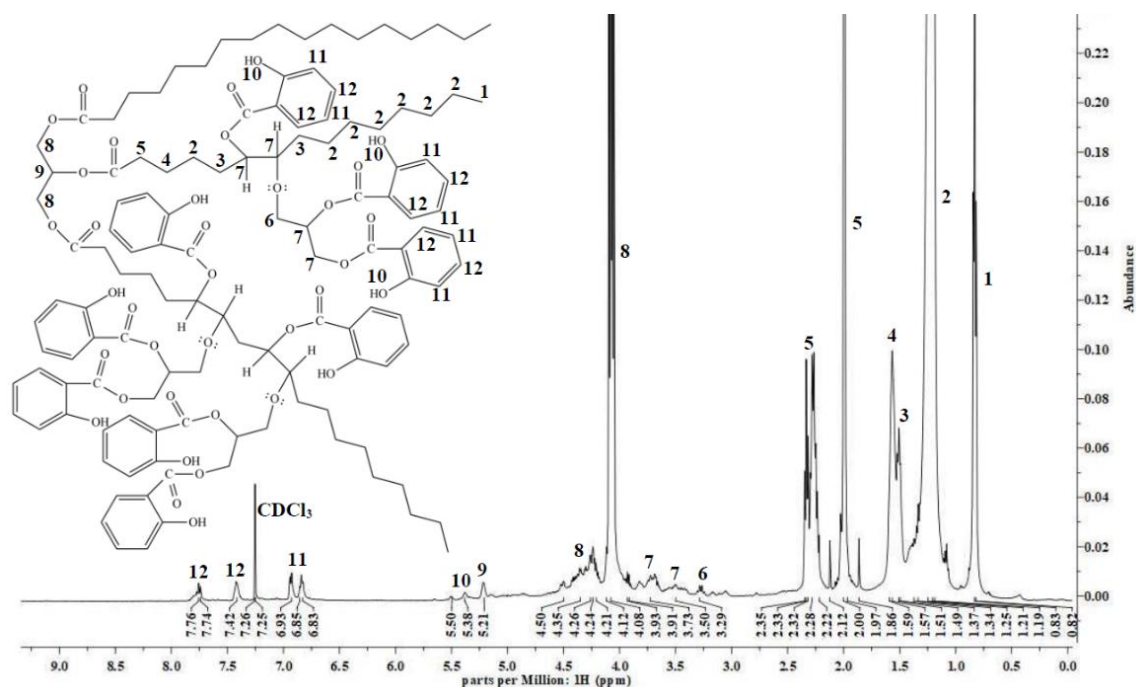


Figure 4.21: ^1H -NMR spectrum of SA-EPO

Based on carbon NMR analysis (Figure 4.22 and 4.23), the appearance of new peaks at 171.57 ppm and 171.17 ppm for LA-EPO and OA-EPO, respectively indicated the successful conversion of polyols (OH groups) to ester ($\text{C}=\text{O}$) groups corroborating the findings by Bahadi et al. (2022). The ether peak ($\text{C}-\text{O}-\text{C}$) was observed at 66.10 ppm in LA-EPO and 68.86 ppm in OA-EPO in which agreeable to the literature (40-80 ppm) (Kamairudin et al., 2021; Nurazira & Salimon, 2022). For LA-EPO, the carbon next to the ester ($\text{R}-\text{CH}_2-\text{C}=\text{O}$) was figured at the chemical shift of 34.10 to 34.50 ppm followed by the aliphatic chains of carbon, $\text{R}-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_3$ at 20.92 to 31.96 ppm and also the $\text{R}-\text{CH}_3$ carbon fall between 14.14 and 14.30 ppm. This result was comparable to the figure of OA-EPO. There were obviously sharp peaks ranged at 61.08 to 63.63 ppm in LA-EPO as well as 60.35 to 60.42 ppm in OA-EPO which were owned by the carbons associated to the carbonyl oxygen from the linoleic and oleic acid. These values were aligned with the reference that the signal of $\text{C}-\text{O}$ was appeared at 62.07 to 64.96 ppm (Bahadi et al., 2021). In other words, the ester was the most important functional group that should be present in

the chemical synthesis of the lubricant. LA-EPO indicated strong signal peaks at 127.94 to 130.31 ppm which was the presence of double bonds in the linoleic acid. In ^{13}C -NMR spectrum of OA-EPO, there was no apparent peak that signified the double bonds present in the oleic acid but it can be seen from ^1H -NMR spectrum considering the oleic acid was structured by a small amount of double bond. Other than these, the structure of SA-EPO was provided in Figure 4.24 which revealed the aromatic carbons of the benzene rings from 111.91 to 169.94 ppm. Overall, the esterification reaction was successful by using linoleic acid, oleic acid, and salicylic acid for the conversion of hydroxyl-ether- PO_6 to ester with an excellent yield and ester value aiming in installing large-branched structure between triglycerides backbones.

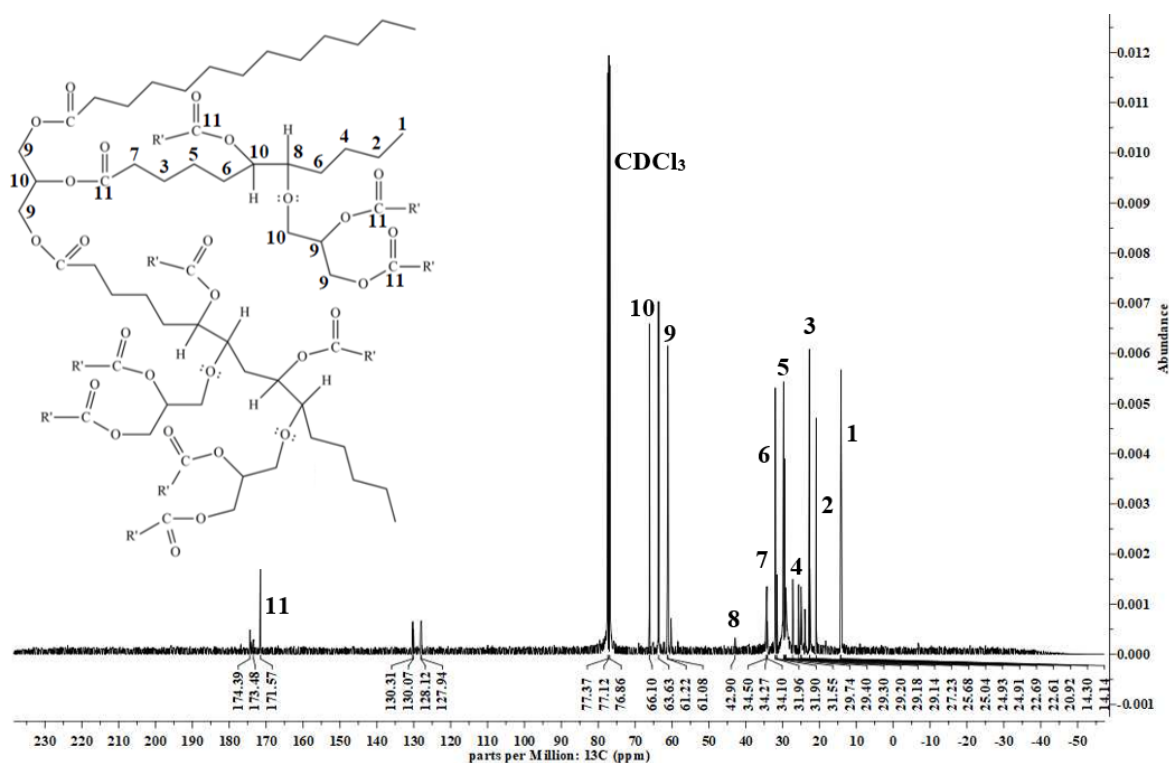


Figure 4.22: ^{13}C -NMR spectrum of LA-EPO

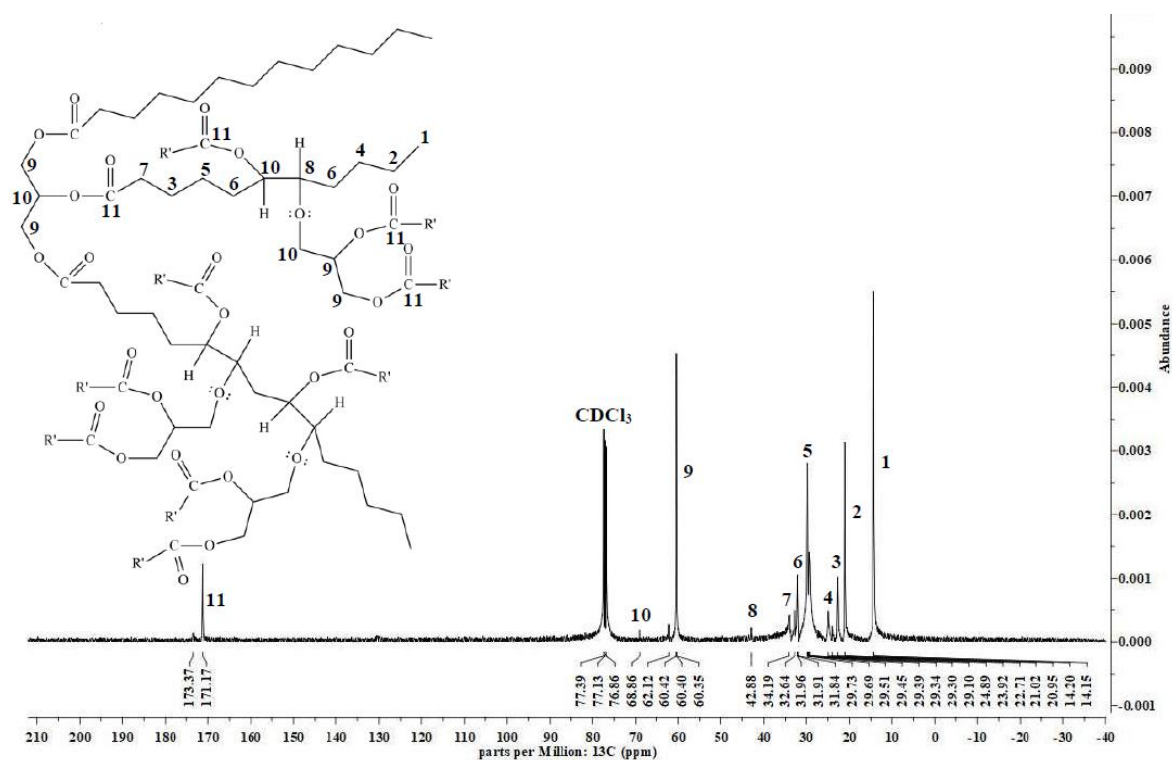


Figure 4.23: ^{13}C -NMR spectrum of OA-EPO

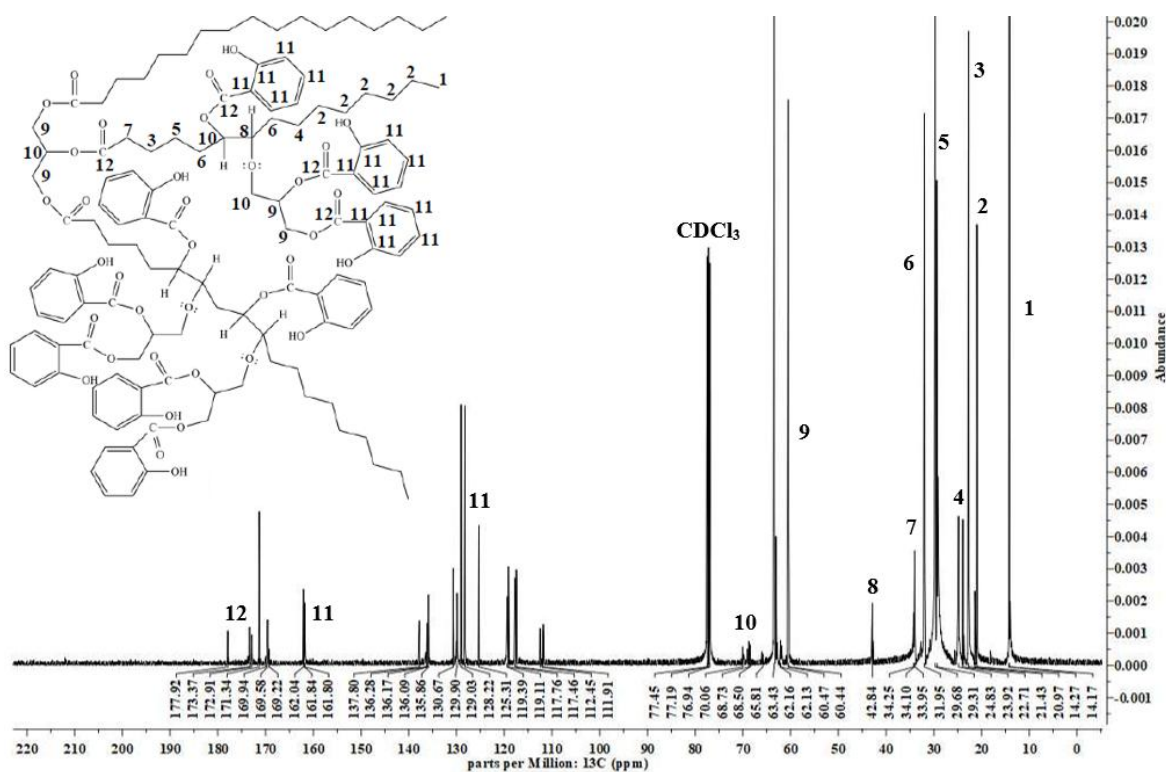


Figure 4.24: ^{13}C -NMR spectrum of SA-EPO

4.4 Physicochemical Properties

4.4.1 Pour Point Test

Pour point (PP) is an essential performance indicator in petroleum products at which the movement of specimen at the lowest temperature is observed (Kamel et al., 2021). Low temperature can restrict the mobility of the molecules into the multiple states such as viscous liquid, crystals, and the solids. Furthermore, the PP could be affected by the degree of the unsaturation and the length of the carbon chain. The higher the unsaturation, the shorter the carbon chain, the lower the PP value (Wahyudi et al., 2020). The drawback of natural PO_o is the tendency to solidify at low temperature due to high PP value of 6°C which may limit its application as lubricant in many industries including food industry by blocking the pipelines of industrial machines operated at low temperatures (Fathurrahman et al., 2021). When the temperature dropped, the oil is easily crystallized that will hinder the engine operability. The solidification might be triggered by the structure of PO_o that can align uniformly by stacking of triglyceride backbone of saturated fatty acids (Samidin et al., 2021). This cause the drawback of poor cold flow behaviour of PO_o and restrict its direct application as lubricating oil. With its abundance and potential, in this study, we have aimed to chemically redesign the molecular structure of PO_o through epoxidation, ring-opening reaction via the alcoholysis followed by the esterification reaction in order to improve its cold flow property. A good quality of bio-lubricant should be more resistant to the temperature fluctuation and able to remain fluid at the freezing condition.

The PP values of EPO_o, polyols, and esterified palm oleins were given in Table 4.4. All the analyses were run in triplicates. Based on the results, the PP value of the PO_o was improved from 6°C to -1°C after the epoxidation reaction but increased to 5°C after the ring-opening reaction. At warmer condition ($T > -1^{\circ}\text{C}$), the EPO_o remained fluid state but some

cloudiness was observed. The poor cold flow property of the ring opening intermediate might be attributed by the increasing number of branched chains with the presence of hydroxyl groups. The issue of poor cold flow has still existed after the epoxidation and oxirane ring opening reaction which requiring another step of esterification to be proceeded for further improvement. The OH group was the crucial functional group to engage in the esterification reaction. The chemical modification was mainly happened on the mid-point of the fatty acid chains by attaching a large branching group to disrupt the symmetry of molecular spatial arrangement that create a steric hindrance which could delay the crystallization process (Zhang et al., 2020). The participation of the ester moiety also strengthened the molecular attraction with stronger van der Waals forces.

Based on the findings, esterified palm olein of SA-EPO showed the best low-temperature characteristic with the lowest PP value of -12°C compared to OA-EPO (-7°C) and LA-EPO (-11°C) (Table 4.4). The esterified palm olein of LA-EPO also demonstrated a better low-temperature behaviour than OA-EPO because it was affected by the number of unsaturation in the fatty acid chains as it contained more *cis* double bonds. Both oleic and linoleic acid shared the similarity of a long fatty acid chain with 18 carbon atoms highlighting the only difference between them of double bond's number that affecting the PP value. This was also explained by other researchers that the mobility of the linoleic acid was more flexible and desirable under the cold condition (Nie et al., 2020). This finding was agreeable to Wahyudi et al. (2020) stating that the increase of unsaturation degree in the fatty acid chains could lower the PP value of oil and reduce the speed of solidification at the low temperature. The bio-lubricant can remain in the liquid state because of the availability of *cis* carbon-carbon double bonds with the fatty acid tails in the bent or kink to constrain the fatty acids from packing closely (Khairin et al., 2021). Instead of the unsaturation and the

chain length, the salicylic acid is not a fatty acid but it structured with an aromatic benzene ring attached to carboxyl and hydroxyl group also able to decelerate the crystallization of oil when exposed to a cold environment. The salicylic acid was described as a weak acid which was highly soluble in the oil due to the presence of phenolic hydroxyl group (Anicescu et al., 2022; Nepomuceno et al., 2023; Wiśniewska et al., 2023). The cost of salicylic acid also much lower than the linoleic and oleic acid. The use of low concentration of salicylic acid in the synthesis of bio-lubricant not only could improve the cold flow property but also considered safe for the environment because it has a high biodegradation rate (Arif et al., 2020; Song et al., 2022). Generally, the salicylic acid was commonly used in the skin care products and the medicines so this approach is new application for salicylic acid.

The statistical analysis was conducted on the pour point values between raw sample, intermediates and esterified palm oleins using one-way ANOVA tool. From the analysis, there was a significant difference between the means of the pour point values of the intermediates and the esterified products from the raw sample. The result showed significant cold flow improvement ($P < 0.05$) of all large-branched esterified palm olein in a range of -12 to -7 °C relative to natural PO_o at which the cold flow at 6 °C (Appendices, Table 4.6 and 4.7). Overall, esterified palm olein of SA-EPO and LA-EPO that demonstrating the lowest PP value of -12°C and -11°C, respectively, were proposed as potential bio-lubricants candidates to be used at low operating temperatures which may require other additional tests for further development. This signified that the large-branched ester installed between triglycerides of natural palm olein was able to address the major drawback of natural palm olein by preventing self-stacking to form macrocrystalline structures to at least -12°C.

Table 4.4: Pour point values of EPO_o, polyols, and esterified products

Compound	PP (°C)
EPO _o	-1 ± 0.00
Hydroxyl-ether-PO _o	5 ± 0.58
OA-EPO	-7 ± 0.88
LA-EPO	-11 ± 0.33
SA-EPO	-12 ± 0.33

4.4.2 Acid Value (AV), Saponification Value (SV), and Ester Value (EV)

To further explore the properties of esterified palm olein, the acid-base titration was carried out to determine the acid value (AV), saponification value (SV), and ester value (EV) of raw sample, intermediates, and final products. From AV and SV, the ester value (EV) can be calculated by formula specified in Chapter 3 (3.9 and 3.10). The AV measures the quantity of carboxylic acid groups present in the sample. The AV is expressed in the unit by the mass of alkaline potassium hydroxide (KOH) required in the milligrams to neutralize the acidic element in one gram of the sample. AV also determines the rancidity of the oil as the increasing AV promotes the oxidation to break down the triglyceride which release the free fatty acids (Omowonuola et al., 2023). The initial AV of PO_o was 10 mg KOH/g which was closer to 8.32 mg KOH/g that reported by Hartawan et al. (2022) for the crude palm oil. The AV had increased to 32 mg KOH/g after the epoxidation reaction because it was induced by the water molecules released from the reaction mixture that triggered the hydrolysis of esters. The AV of EPO_o was the highest of 32 mg KOH/g because it contained the most amounts of fatty acids. Then, the acid number started to decrease significantly after the ring-opening and esterification reactions due to the removal of prevalent free fatty acids by the chemical modification process (Agu et al., 2022). Based on the AV values, the quality of esterified palm oleins of LA-EPO and SA-EPO are better than OA-EPO due to lower acid values, 3 mg KOH/g and 8 mg KOH/g, respectively (Table 4.5) (Trilaksani et al., 2023). According

to Trilaksani et al (2023), the lower the acid number (AV value), the higher the quality of the oil.

Saponification number is also an essential parameter to review the quality of oil. SV is practiced by saponify the sample using the back titration of excess alkali with strong acid. SV reflects the chemical composition of the fat or oil on its molecular weight, length of the fatty acid chains, and the presence of ester linkages. Based on previous study, the sample containing a long chain of fatty acid on the glycerol backbone gave a small saponification number, meanwhile, the shorter fatty acid chain delivers a high saponification number (Ivanova et al., 2022). From Table 4.5, it was investigated that the SV of natural PO_o was 154 mg KOH/g which considered almost equivalent to EPO_o of 153 mg KOH/g and hydroxyl-ether-PO_o of 159 mg KOH/g. These similar findings might be attributed by the same ester linkages at the backbone of the long chain triglyceride fatty acids in their molecular structures (Tajau et al., 2020). In short, SV was influenced by the content of the fatty acids so the esterified palm olein of OA-EPO, LA-EPO, and SA-EPO with higher SV of 443 mg KOH/g, 416 mg KOH/g, and 424 mg KOH/g respectively manifested that their triglycerides were composed of great number of fatty acids in smaller molecular weight and size so more alkali was required to break the structures down during the SV analysis (Nduka et al., 2021).

Ester value (EV) quantifies the amount of KOH required (mg) to react with the ester portion of one gram of fat through saponification (Tajau et al., 2020). Based on the analysis, the EV of OA-EPO, LA-EPO, and SA-EPO after esterification reaction were significantly higher than the natural PO_o (32.38%) with the EV of 96.79%, 92.86%, and 93.61%, respectively (Table 4.5). A high EV indicated that the fatty acids are predominantly in ester form and present relatively low molecular weight (Azmi et al., 2022; Cecilia et al., 2020).

According to Cecilia et al. (2020), a high content of esterified fatty acids in the bio-lubricant enhanced the thermo-oxidative stability and low temperature properties of the oil.

Table 4.5: The AV, SV and EV values of raw sample, intermediates, and esterified products

	PO_o	EPO_o	Hydroxyl- ether-PO_o	OA-EPO	LA- EPO	SA-EPO
Yield (%)	-	90.65 ± 0.00	85.93 ± 0.00	97.46 ± 0.00	96.19 ± 0.00	99.29 ± 0.00
OOO value (%)	0	3.69 ± 0.00	0.28 ± 0.00	-	-	-
Conversion (%)	-	98.14 ± 0.00	92.45 ± 0.00	-	-	-
Iodine value (mg/g)	62 ± 0.00	9.5 ± 0.01	-	-	-	-
Acid value (mg KOH/g)	10 ± 0.94	32 ± 0.94	13 ± 2.47	12 ± 1.00	3 ± 0.77	8 ± 1.48
Saponification value (mg KOH/g)	154 ± 3.28	153 ± 1.53	159 ± 2.22	443 ± 20.68	416 ± 1.17	424 ± 21.90
Ester value (mg KOH/g)	144 ± 4.06	121 ± 2.52	146 ± 4.41	431 ± 21.28	413 ± 1.45	416 ± 20.76
Ester value (%)	32.38 ± 0.91	27.25 ± 0.57	32.90 ± 0.99	96.79 ± 4.78	92.86 ± 0.33	93.61 ± 4.67

4.5 Addition of Nanoadditive

4.5.1 Optimization of Nanoadditive Concentration

Metal oxide nanoparticle is one of the lubricant additives with a tiny size which allow itself to enter the contact regions of the lubricating oils to enhance its properties particularly the lubricating performance. In general, titanium dioxide (TiO₂) is an odourless white nanoparticle with three-dimensional structure (Popoola & Ikpambese, 2021). In this experiment, the primary particle sizes of TiO₂ nano-powders used were approximately 21 nm with more than 99.5% of trace metals basis. It was known that TiO₂ nanoparticle was normally used as the booster in the oil's tribology performance but there was lack of study focusing its effect on the pour point of esterified palm olein. The aim of this present study

was to observe whether the prepared esterified palm oleins could remain flowable at cold temperatures after addition of TiO_2 nanoparticle. In this research work, TiO_2 was added into the esterified palm olein of LA-EPO and SA-EPO at different ranges from 0 to 0.5 % (w/w) according to the method developed by Roselina et al. (2020). TiO_2 nanoparticles tend to easily aggregate into larger particle size by the chemical bonds (Mousavi et al., 2020). Thus, a surfactant of ethylene glycol was blended into the liquid lubricant and stabilized under the ultrasonication method with the mechanical stirring to avoid the precipitation. From Figure 4.25, it was noticed that the addition of TiO_2 was not effective for esterified palm olein of SA-EPO as the PP values became worst and higher than -12°C . High PP values caused the lubricant to be less resistant to the crystallization at low temperature. At low temperatures, the macrocrystalline polymer in the lubricant was susceptible to freeze with other waxy carbohydrates to form the crystal lattice that halted the flowability of oil (Kamal et al., 2021). The dispersion of the metal oxide into the SA-EPO caused the emergence of solidification and inhomogeneity which affected the pour point value. This noted that the TiO_2 nanoparticle was not suitable for SA-EPO as the PP improver. In contrast, TiO_2 was desirable for the esterified palm olein of LA-EPO specifically at 0.1 % (w/w) which slightly improved the PP value from -11°C to -12°C . In this sample, the TiO_2 nanoparticle was able to create stronger non-polar covalent bonds in the oil molecules so that it can remain in the liquid state for a longer time at low temperature which lead to a better PP result (Kamel et al., 2021). Similarly, the increase of TiO_2 concentration starting from 0.2 to 0.5 % (w/w) degraded the cold flow property of the LA-EPO because the oil had saturated with the nanoparticles. The high surface areas of nano-additive resulted in higher chances of agglomeration and sedimentation. The present study showed the low-temperature property of the tested esterified palm oleins favoured small concentration of nano-additive. According to Sofiah et

al. (2020), the aggregation of nano-additive was attributed by the greater Brownian motion and van der Waals attractive forces than the repulsive forces. Other than the concentration of nano-additive, the observation of sedimentation was also essential to ensure the quality of the nano-lubricant (Sofiah et al., 2021). It was observed that the LA-EPO enriched with 0.1 % (w/w) TiO_2 nanoparticles still remain fluid in 21 days with no sediment was discovered at the bottom of the glass vial (Appendices, Figure 4.36). However, a slight precipitation can be seen after 28 days as the nanoparticles initiated to segregate from the lubricating oil and settled. In response to the long-term industrial applications, a good suspension stability was important to extend its shelf life. As a result, the composition of 0.1 % (w/w) was recognized as the optimal concentration of TiO_2 for the esterified palm olein of LA-EPO to show the lowest PP value of -12°C . This was comparable to the SA-EPO in the absence of nanoparticle that also demonstrated the best PP value of -12°C .

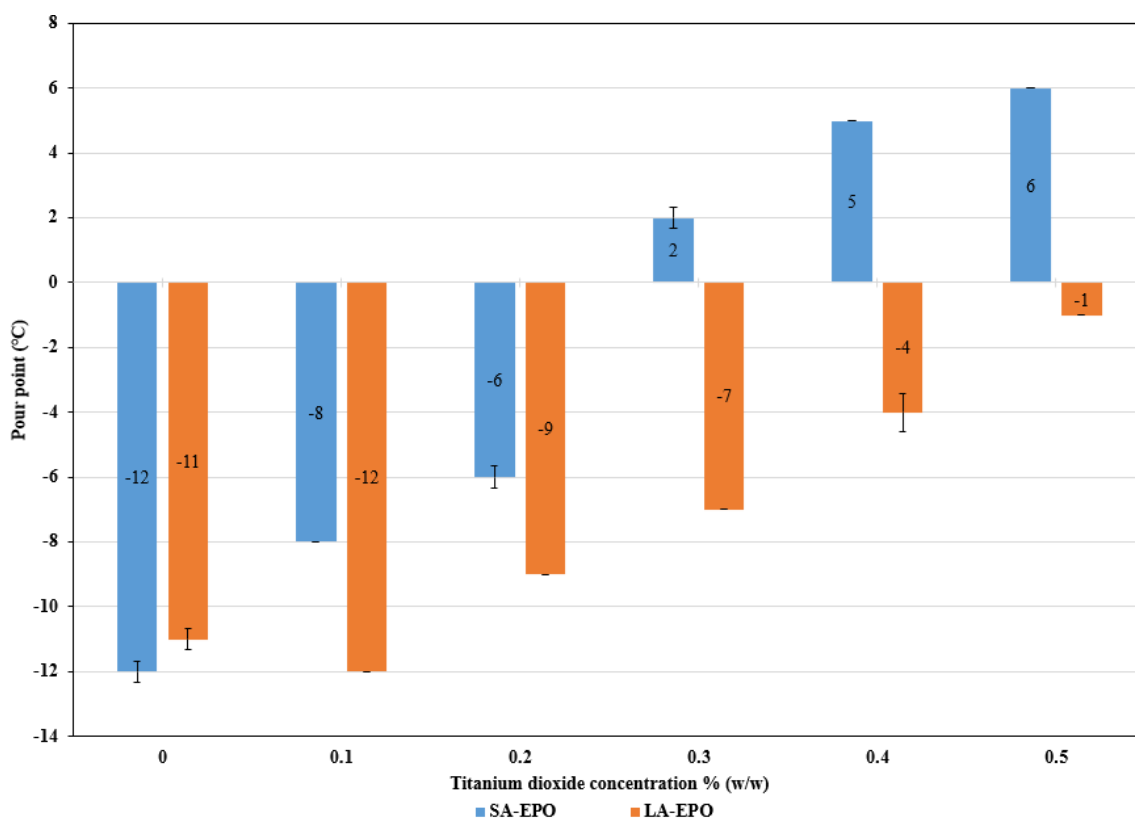


Figure 4.25: Effect of nano-additive concentration on the pour point values of esterified palm oleins

The statistical analysis was conducted on the effect of TiO₂ concentration in the range of 0 to 0.5 % (w/w) on the PP values of SA-EPO and LA-EPO using one-way ANOVA tool. The model was regulated with a 95% confidence level. Based on the statistical analysis, the p-value of both lubricating oils were approximately zero which was lesser than the significance level of 0.05 so the parameter was significant and there was a noteworthy variation between the means of groups. There was at least one group of the mean scores was distinct from the others.

4.5.2 Characterization Analysis by FTIR and NMR

The FTIR spectra of esterified palm oleins with TiO₂ nanoadditive (SA-EPO-TiO₂ and LA-EPO-TiO₂) were provided in Figures 4.26 and 4.27, respectively. FTIR analysis of TiO₂ nanoparticle was also conducted to serve as a standard for comparison as given in Figure 4.28. Peak at 1637.99 cm⁻¹ and 664.22 cm⁻¹ showed stretching vibrations of Ti-O-Ti (Figure 4.28). After addition of TiO₂ nanoparticles, the FTIR spectra of LA-EPO-TiO₂ and SA-EPO-TiO₂ were almost similar to LA-EPO and SA-EPO (Figure 4.18). There was only a small contrast in the vibration bands shifting and the intensities which considered as negligible. The only variation in the FTIR spectrum was the appearance of a broad band at the wavenumber of 3500 cm⁻¹ which corresponding to the hydroxyl group (O-H) stretching vibrations that emitted by the surfactant of ethylene glycol. Additional peaks at 1606.33 cm⁻¹ and 694.42 cm⁻¹ (LA-EPO-TiO₂) and at 1679.29 cm⁻¹ and 659.63 cm⁻¹ (SA-EPO-TiO₂) were attributed by the Ti-O-Ti stretching vibration. These values were consistent to the standard spectrum of TiO₂ nanoparticles (Figure 4.28) and FTIR results reported by Popoola and Ikpambese (2021) in the synthesis of bio-lubricants from the sandbox seed oil. From Figure 4.27 of LA-EPO-TiO₂, it can be observed that there were the existence of carbonyl (C=O) ester of triglycerides at 1740.27 cm⁻¹, weak unsaturation stretching peak from the

carbon-carbon double bonds at 3008.97 cm^{-1} also the stretching vibration of the C-O at 1163.92 cm^{-1} with its shoulders at 1087.37 cm^{-1} and 1237.95 cm^{-1} . Next, SA-EPO-TiO₂ also displayed with a strong stretching vibration of methylene (-CH₂) group at 2852.85 cm^{-1} followed by strong peak of CH₃ methyl group and weak C-H stretching at 2922.62 cm^{-1} . The ester carbonyl (C=O) functional group can be seen clearly at 1738.62 cm^{-1} and the C-O absorption at 1157.25 cm^{-1} . Apart from that, there were peaks of asymmetrical CH₂ bend at 1462.01 cm^{-1} , aromatic C-C stretching vibrations at 757.34 cm^{-1} , 1485.41 cm^{-1} , and 1614.28 cm^{-1} as well as the aliphatic long chain compounds at the range of 602.64 to 722.96 cm^{-1} . These values were consistent to the study by Sofiah et al. (2020).

Hence, from the FTIR analysis, it was observed that the incorporation of metal oxide nano-additive into the esterified palm olein remained its chemical molecular structure without any destruction. In other words, the TiO₂ nano-additives only physically interacted with the tested esterified palm oleins without further change the functional group in the structure. There was no undesirable side reaction between nano-additive and the esterified palm olein. In addition, Figure 4.29 and 4.30 showed ¹H-NMR spectra of esterified palm oleins with TiO₂ nano-additives of SA-EPO-TiO₂ and LA-EPO-TiO₂ together with their ¹³C-NMR spectra in Figure 4.31 and 4.32, respectively. Both proton and carbon NMR spectra exhibited identical signal peaks relative to esterified palm olein of SA-EPO and LA-EPO (Figure 4.19-4.24).

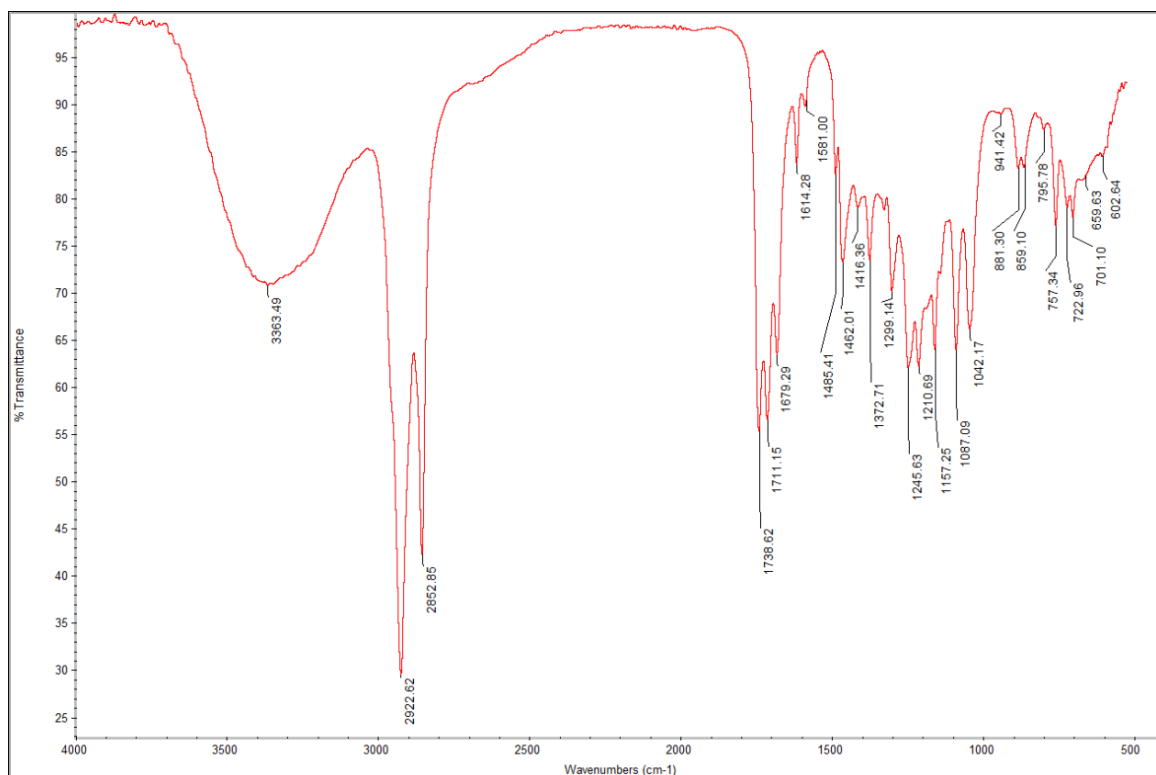


Figure 4.26: FTIR spectrum of SA-EPO-TiO₂

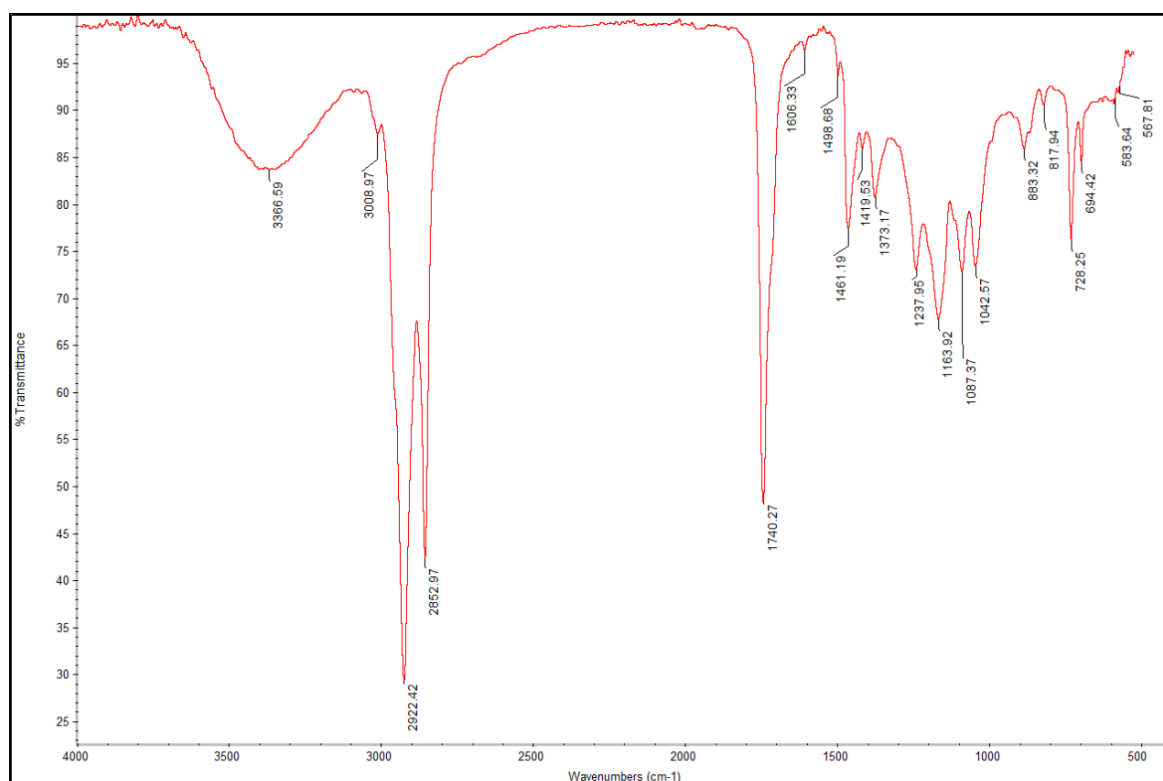


Figure 4.27: FTIR spectrum of LA-EPO-TiO₂

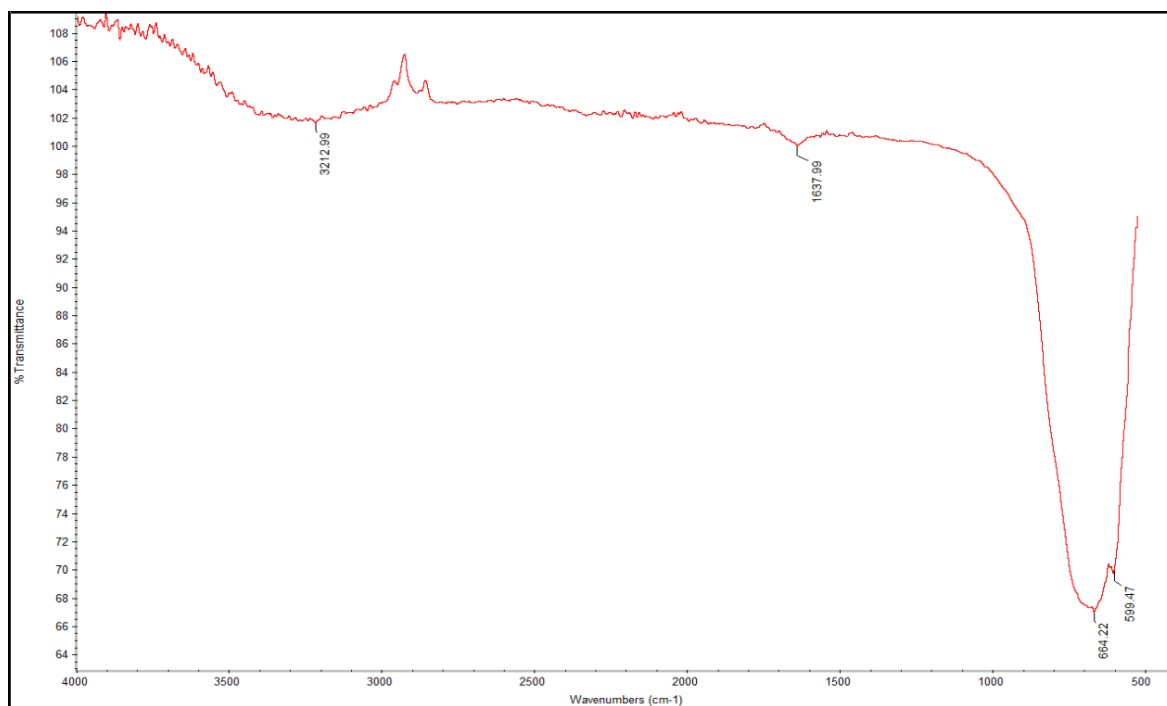


Figure 4.28: FTIR spectrum of TiO₂

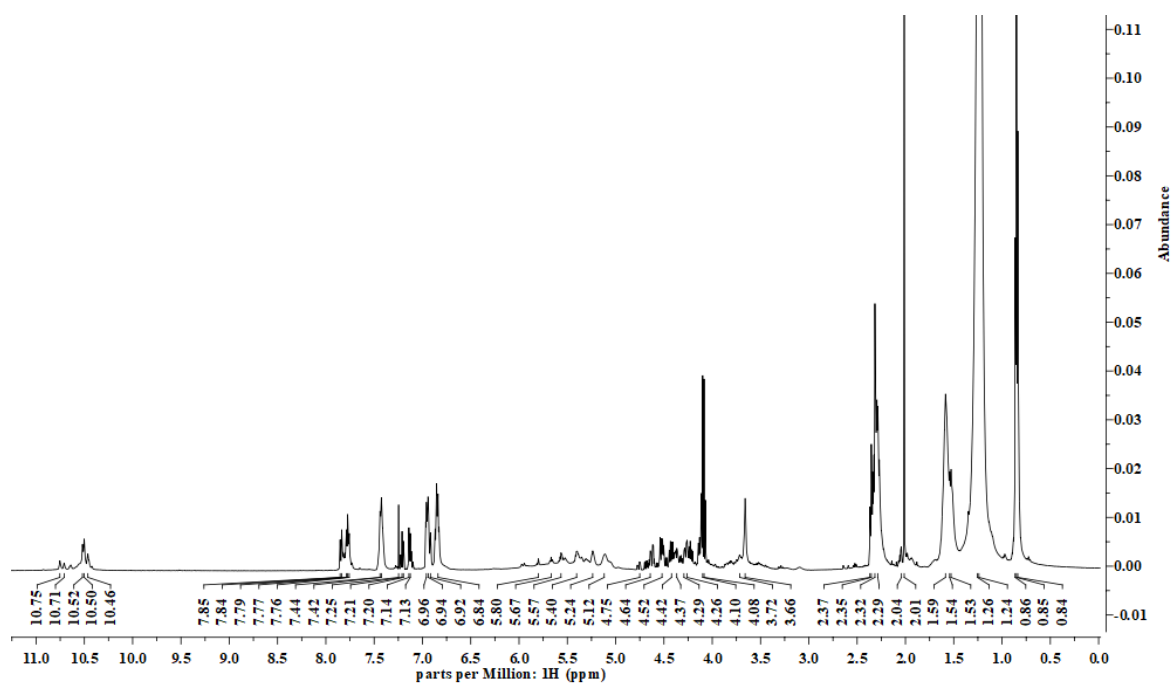


Figure 4.29: ¹H-NMR spectrum of SA-EPO-TiO₂

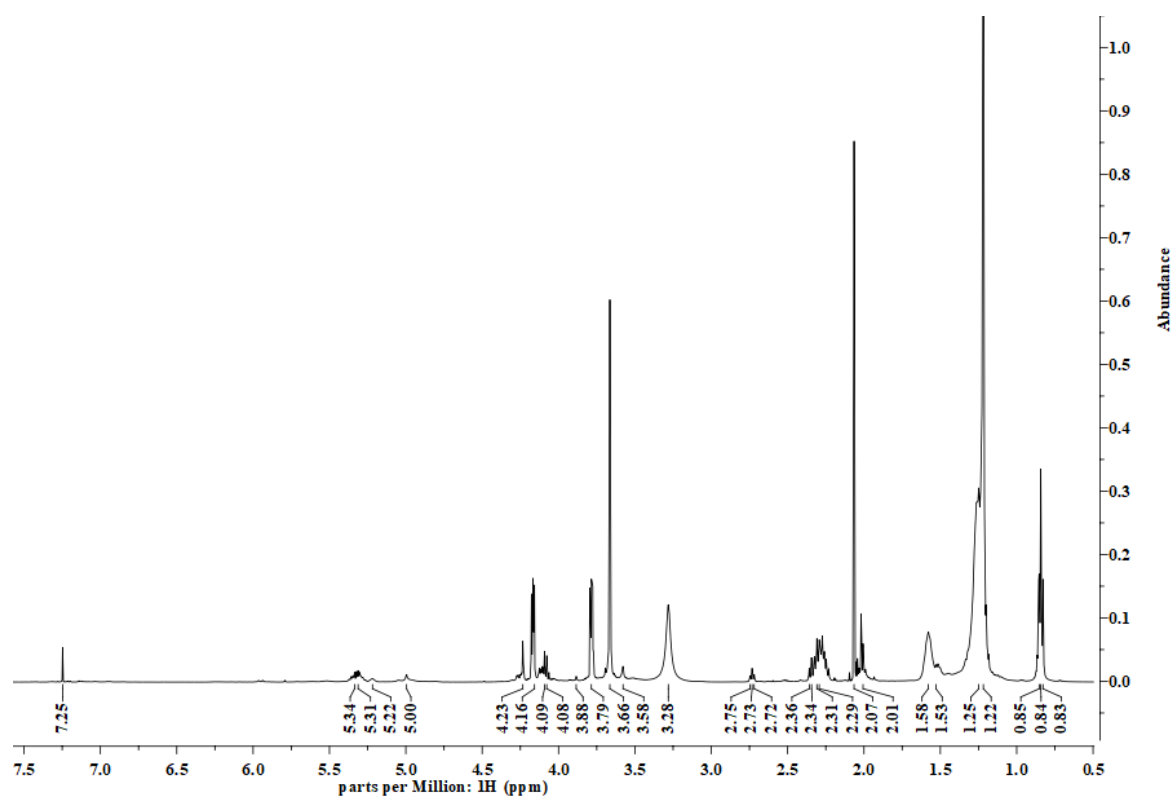


Figure 4.30: ^1H -NMR spectrum of LA-EPO-TiO₂

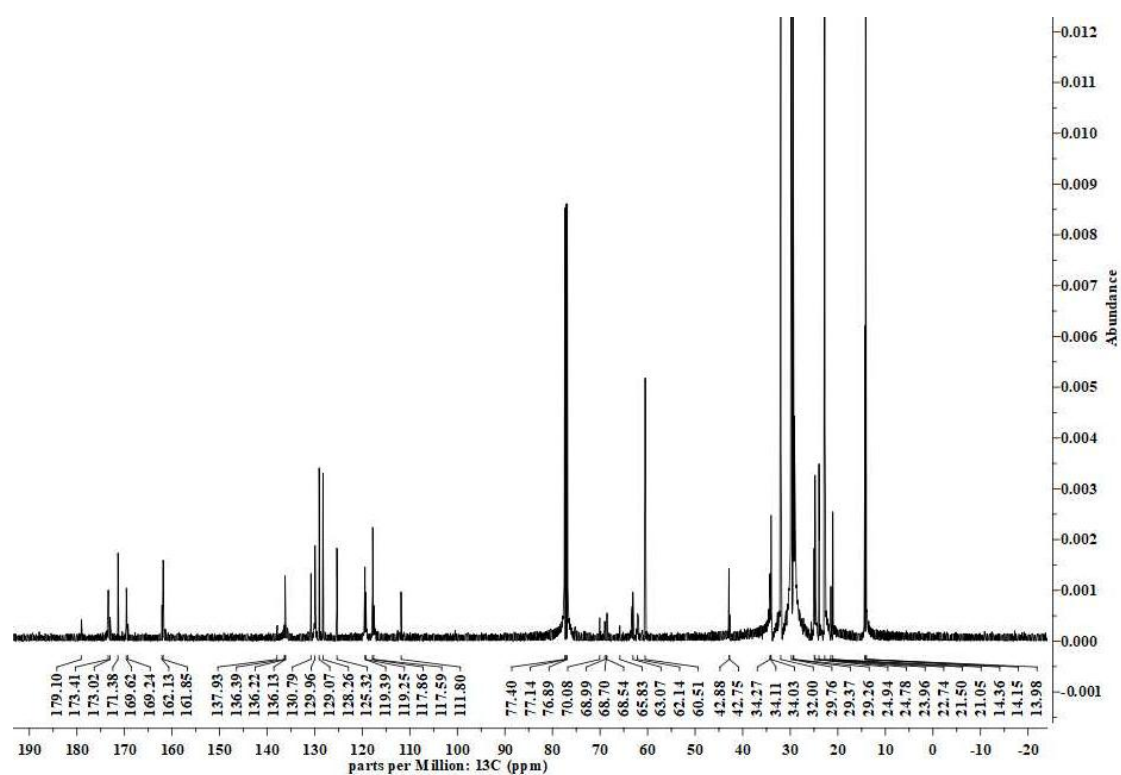


Figure 4.31: ^{13}C -NMR spectrum of SA-EPO-TiO₂

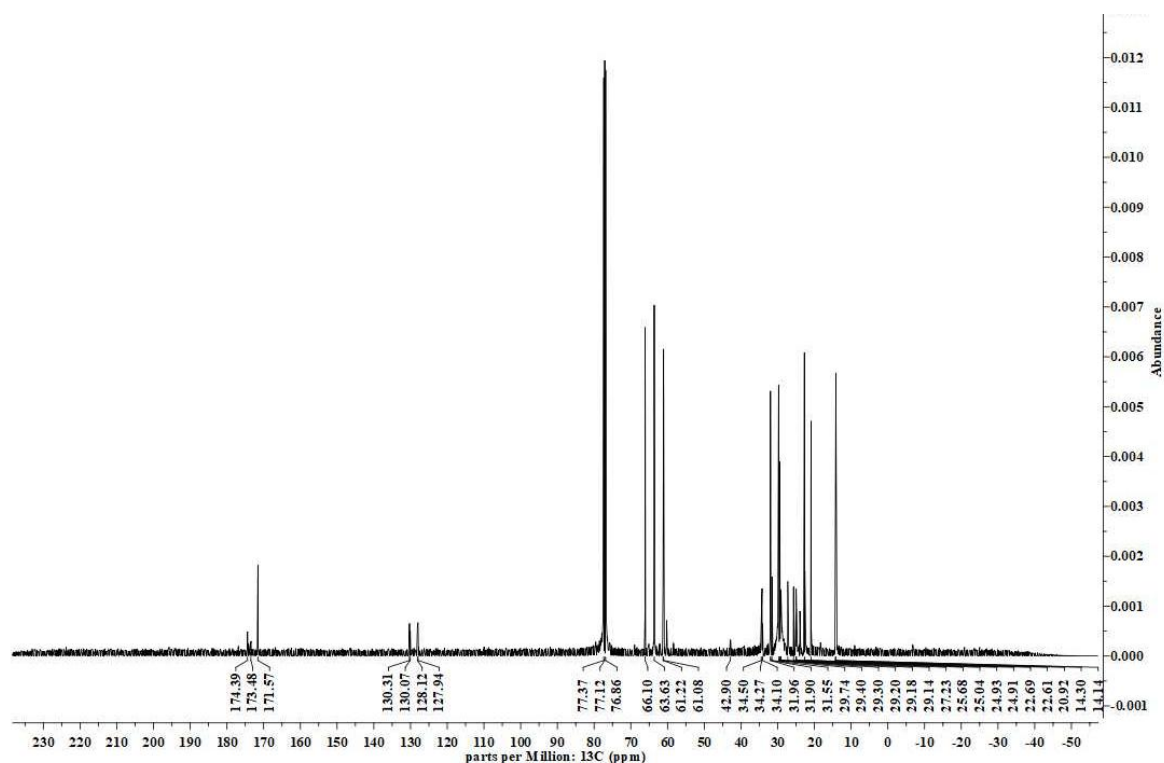


Figure 4.32: ^{13}C -NMR spectrum of LA-EPO- TiO_2

4.5.3 SEM Analysis

SEM analysis was carried out to observe the surface morphology of the samples with nanoadditives in two-dimensional. The presence of TiO_2 nanoparticles was clearly seen and distributed in a spherical shape in the SEM images (Figure 4.33). The SEM image figured that the TiO_2 nanoadditives were aggregated in the cluster due to some agglomerations had occurred between the nanoparticles by the intermolecular forces. This was driven by the high surface activities of the nanoparticles that easily attracted to each other to form the bunch arrangement into a large proportion. Due to its small particle size of 21 nm, a very low concentration of TiO_2 nanoparticles tend to have a very high surface-to-volume aspect ratio (Alqahtani et al., 2022). In Figure 4.34, the agglomerations also made the particle sizes to be seen larger than 21 nm. According to Zhao et al. (2020), nanoparticles with the spherical shape demonstrated a better dispersion stability. Figure 4.35 and 4.36 illustrated the SEM

images of SA-EPO-TiO₂ as well as Figures 4.37 and 4.38 for LA-EPO-TiO₂. It can be observed that the nanoparticles were deposited along the side of esterified oils which could improve the tribological performance as reported by previous literature (Cortes et al., 2020; Jason et al., 2020). This affirmed that the nanoparticles did not dissolve in the oil but suspended or dispersed within them so the liquid structure of lubricant was retained (Popoola & Ikpambese, 2021).

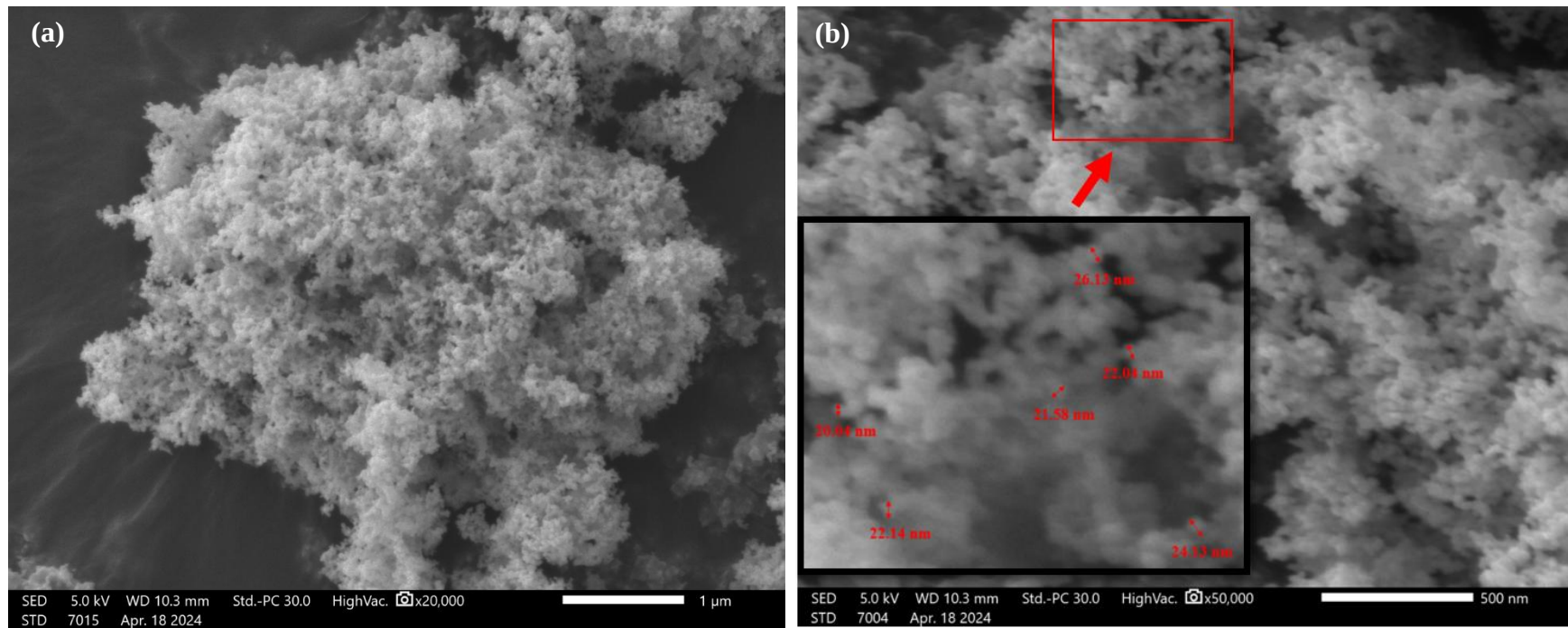


Figure 4.33: SEM image of TiO₂ nano-additive (a) with measurement (b)

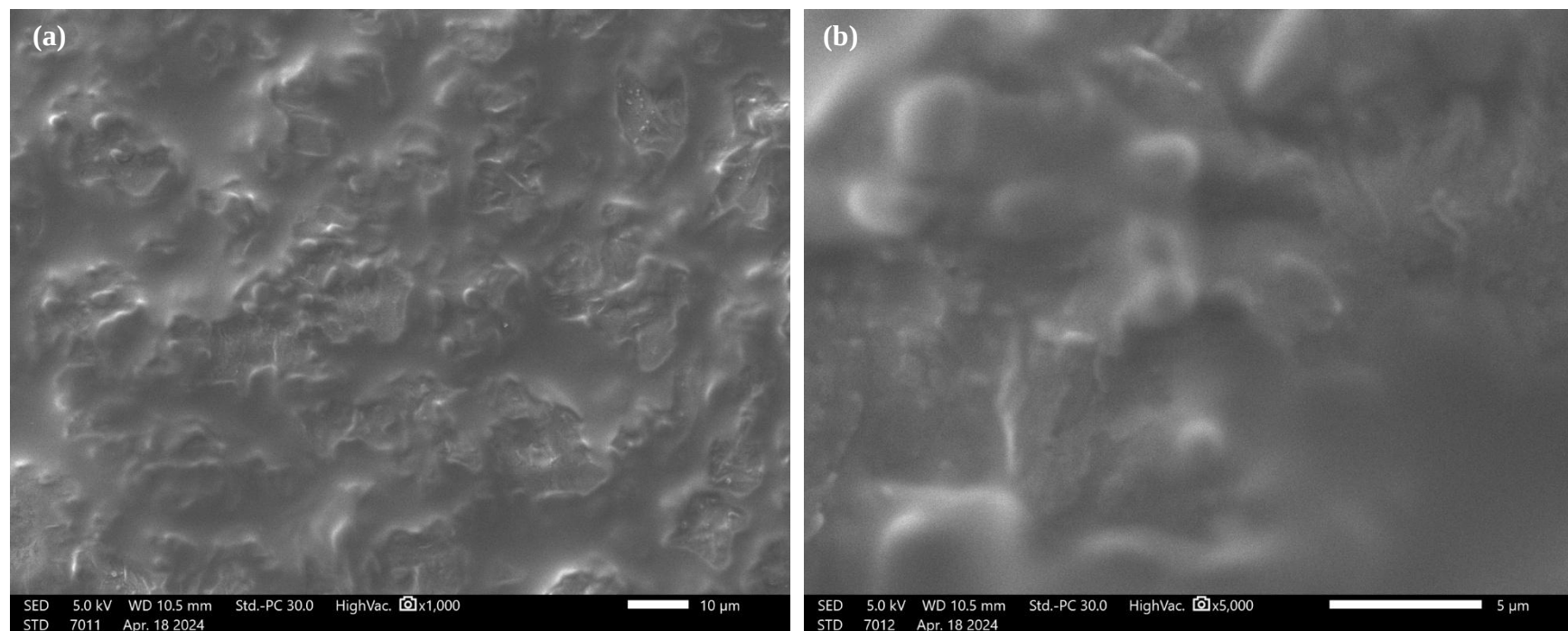


Figure 4.34: SEM image of SA-EPO-TiO₂ at 1000 X magnification (a) and 5000 X magnification (b)

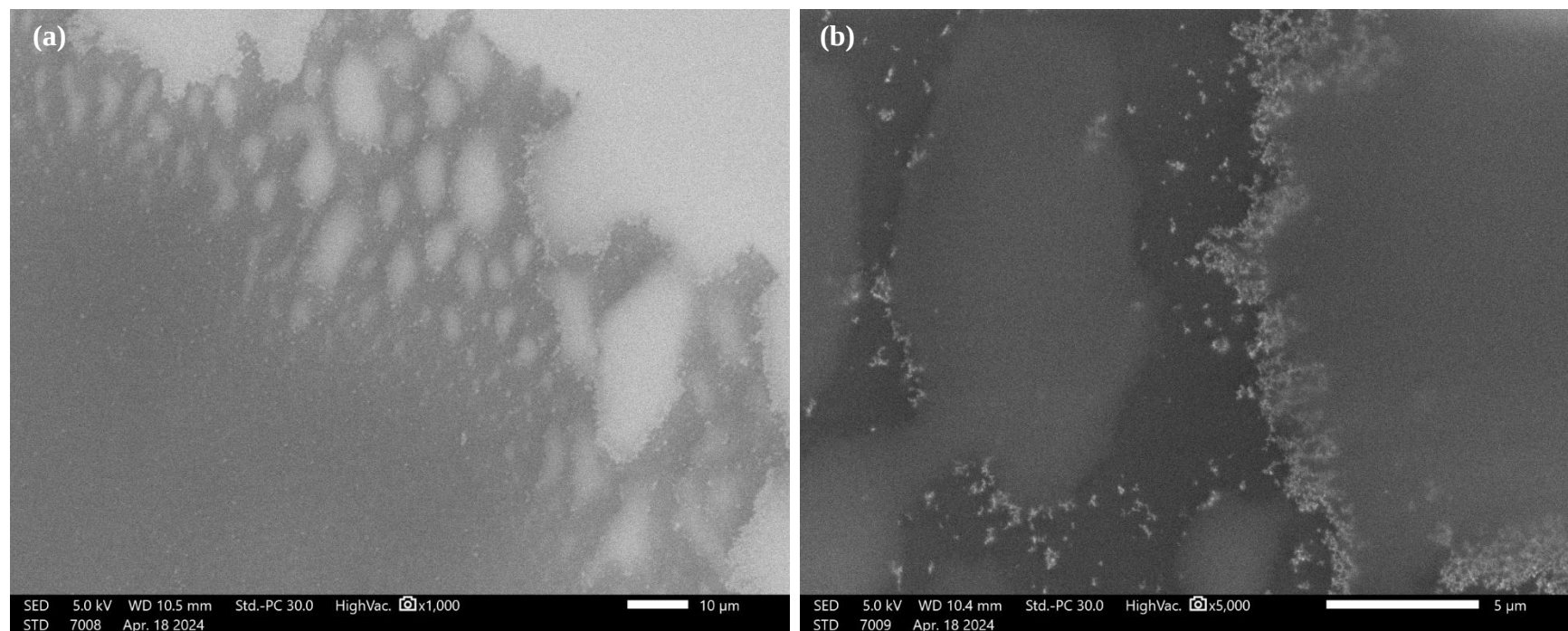


Figure 4.35: SEM image of LA-EPO-TiO₂ at 1000 X magnification (a) and 5000 X magnification (b)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research study focused on the synthesis of green lubricant by chemically modifying the structure of selected vegetable oil of palm olein via three main processes which were the epoxidation, alcoholysis, and the esterification reactions. The biodegradable palm olein consisted of a high level of unsaturation is a promising source for the chemical modification process as the key conversion starts from alkene. The esterification reactions allowed the incorporation of the ester moiety into the oil structure which increased the mid-chain length between the fatty acid backbones. It was followed by the addition of TiO₂ nano-additive into the esterified palm olein formula and its effect on the pour point was investigated.

In this study, the epoxidation had been carried out to convert the double bonds of the palm olein into epoxides. The results indicated that the best reaction temperature and duration was treatment at 40°C for 2.55 h under the constant molar ratio of PO_o: HCOOH: H₂O₂ at 1: 5.91: 3.60. The epoxide yield was achieved at 90.65% with a high oxirane conversion of 98.14%. The experimental OOC% was 3.69% relative to the theoretical OOC value of 3.76%. This can be seen from the iodine value of palm olein that reduce from 62 mg/g to 9.5 mg/g in the epoxidized palm olein due to the loss of double bond. The pour point value of the natural palm olein was improved by the epoxidation from 6°C to -1°C but some cloudiness was observed in the epoxidized palm olein after a period of time.

Then, the oxirane ring opening was completed by alcoholysis reaction using glycerol to form ring-opening intermediate at 85.93% of yield. The OOC% of this intermediate was

as low as 0.28% with a high conversion of 92.45% indicating most of the oxirane rings had transformed into the hydroxyl and ether groups. It was performed at the optimum reaction conditions of 120°C and 4 h with the fixed molar ratio of epoxidized palm olein: glycerol: $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 1: 10: 1. The use of glycerol in the epoxide ring opening allowed the three incorporation of hydroxyl groups into the structure letting for the installation of large branched esters. The pour point value of the ring-opening intermediate was 5°C. The OH group in this intermediate was the vital functional groups for the following esterification reaction.

To synthesize the ester groups, the esterification reaction was conducted using three different reagents of oleic acid, linoleic acid, and salicylic acid to react with the ring-opening intermediates in the presence of sulphuric acid as the catalyst and also the solvents of toluene and acetonitrile. The ideal reaction temperature and time was achieved at 140°C for the duration of 4 h to form the esterified palm olein of OA-EPO, LA-EPO, and SA-EPO at 97.46%, 96.19%, and 99.29% of yield, respectively. The molar ratio of ring-opening intermediate: reactants: catalyst was fixed at a constant ratio of 1: 4: 1. The salicylic acid was found to be the most favorable reagent due to its high reaction yield of 99.29% and the ester value of 93.61%.

For the characterization purposes, FTIR and NMR analysis were utilized to determine the molecular structures of the raw sample, epoxides, ring-opening intermediates, and the esters. The specific signal peaks shown in the spectra confirmed that the olefinic structure of the palm olein had been successfully converted to ester moiety. In the pour point test, all the large-branched esterified palm olein showed significant cold flow improvement particularly esterified palm olein of SA-EPO and LA-EPO with the PP value of -12°C and -

11°C, respectively which was better than the OA-EPO (-7°C) relative to the natural palm olein with a poor cold flow behavior of 6°C.

After the addition of 0.1 % (w/w) of TiO₂ nanoparticles, the pour point value of LA-EPO-TiO₂ was slightly improved from -11°C to -12°C. However, the addition of TiO₂ nanoparticles did not show any improvement for the SA-EPO. This summarized that only a small amount of TiO₂ nano-additive was required for esterified palm olein of LA-EPO to improve its low-temperature flowability. The suspension of LA-EPO-TiO₂ also showed a good dispersion stability up to 21 days. The presence of TiO₂ nanoparticles was observed along the side of esterified oil in a spherical shape from the SEM analysis in which led it to become a perfect feeder for the sliding interface corroborating many previous literatures suggesting it as one of excellent anti-wear lubricant additives. TiO₂-based bio-lubricants are ideal for the use in modern industries, industrial systems or fluids, and eco-sensitive applications where cold flow performance is critical.

Overall, the findings from this study suggested large-branched esterified palm oleins prepared by extending the gap between triglycerides molecules were able to reduce the pour point values up to -12°C highlighting their potentials as source of green lubricant candidates by addressing the major drawback of natural palm olein. However, a slight improve on the pour points after incorporation of TiO₂ nano-additive might need more further studies related to nanoadditives to explore their potential by using ecofriendly materials.

5.2 Recommendations

For further study, a continuous research and development on esterified palm oleins of SA-EPO and LA-EPO in the field of green chemistry is strongly recommended in order to produce local value-added green lubricating products. The esterified palm olein

comprising large-branched structure prepared in this study have great potential as an alternative to mineral oil-based lubricants and also convenient for large scale production. The use of TiO_2 nano-additive or other eco-friendly materials should be explored more as the pour point improver in the refrigerant and the system's performance due to a limited number of research paper was available to date.

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APPENDICES

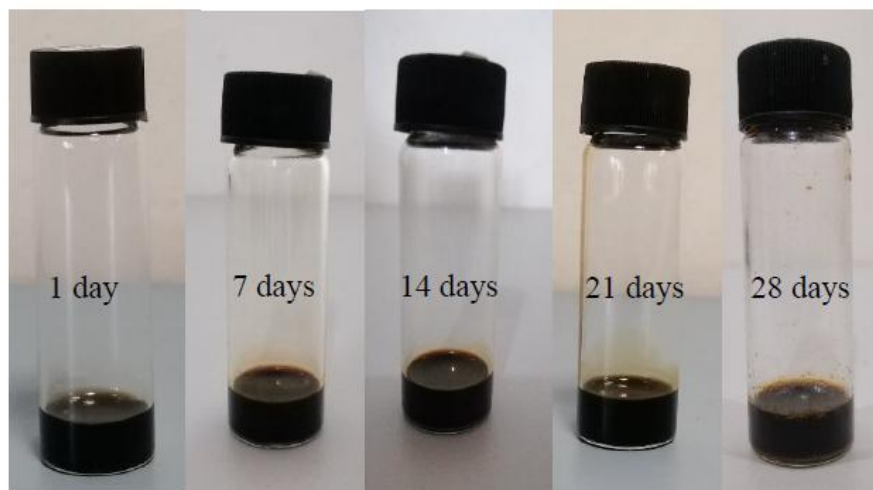


Figure 4.36: The condition of LA-EPO-TiO₂ nano-lubricant with 0.1 % (w/w) of TiO₂ nano-additive

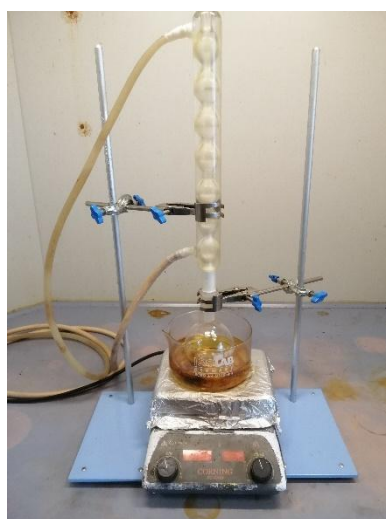


Figure 4.37: The experimental setup for epoxidation, alcoholysis, and esterification reactions



Figure 4.38: The raw sample of palm olein

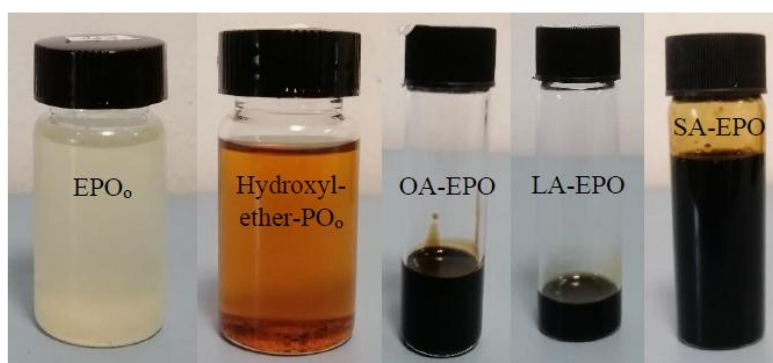


Figure 4.39: The appearance of EPO_o, hydroxyl-ether-PO_o, OA-EPO, LA-EPO, and SA-EPO

Table 4.6: ANOVA results for the pour point of esterified palm oleins

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	379.56	2	189.78	213.50	2.66E-06	5.14
Within Groups	5.33	6	0.89			
Total	384.89	8				

Table 4.7: ANOVA results for the pour point of raw sample, intermediates, and esterified products

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	769.78	5	153.96	197.94	4.27E-11	3.11
Within Groups	9.33	12	0.78			
Total	779.11	17				

Table 4.8: ANOVA results for the pour point of SA-EPO-TiO₂ with 0 to 0.5 % (w/w) nanoadditive

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	824.00	5	164.80	988.80	2.95E-15	3.11
Within Groups	2.00	12	0.17			
Total	826.00	17				

Table 4.9: ANOVA results for the pour point of LA-EPO-TiO₂ with 0 to 0.5 % (w/w) nanoadditive

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	275.61	5	55.12	248.05	1.12E-11	3.11
Within Groups	2.67	12	0.22			
Total	278.28	17				