

PALM OLEIN BASED BIOLUBRICANT BASESTOCKS: SYNTHESIS, CHARACTERISATION, TRIBOLOGICAL AND RHEOLOGICAL ANALYSIS

(Stok Asas Biolubrikan Berasaskan Minyak Sawit Olein: Sintesis, Pencirian, Analisis Tribologi dan Reologi)

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Abstract

Palm olein (PO_o) was modified through chemical reaction to produce biolubricant basestock (di-oleate- PO_o and oleate-ether- PO_o). PO_o was epoxidised to produce epoxidised palm olein (EPO_o), then ring opening process were performed by hydrolysis and alcoholysis to produce di-hydroxy- PO_o and hydroxy-ether- PO_o . Both intermediate products were esterified with oleic acid to produce di-oleate- PO_o and oleate-ether- PO_o . Detection analyses were done by using fourier transformation infra-red (FTIR), proton and carbon nuclear magnetic resonance (1H -NMR and 1S C-NMR). Di-oleate- PO_o recorded of its oxidative stability (140 $^{\circ}$ C), pour point (-5 $^{\circ}$ C), flash and fire point (215 $^{\circ}$ C and 245 $^{\circ}$ C), kinematic viscosity about 417.5 cSt (40 $^{\circ}$ C) and 45.4 cSt (100 $^{\circ}$ C) with the viscosity index of 166. While, oleate-ether- PO_o recorded of its oxidative stability (178 $^{\circ}$ C), pour point (1 $^{\circ}$ C), flash and fire point (190 $^{\circ}$ C dan 210 $^{\circ}$ C), kinematic viscosity about 113.7 cSt (40 $^{\circ}$ C) and 21.5 cSt (100 $^{\circ}$ C) with the viscosity index of 217. The biolubricant basestocks grade of ISO VG 460 (di-oleate- PO_o) and ISO VG 100 (oleate-ether- PO_o) were successfully produced. Di-oleate- PO_o and oleate-ether- PO_o were Newtonian and non-Newtonian fluid. Both products were hydrodynamic lubricant with low friction coefficients at 40 $^{\circ}$ C and 100 $^{\circ}$ C.

Keywords: Biolubricant Basestock, Palm Olein, Tribology, Rheology

Abstrak

Minyak sawit olein (PO_o) dimodifikasi melalui tindak balas kimia untuk menghasilkan stok asas biolubrikan (di-oleate-PO_o dan oleate-eter-PO_o). PO_o diepoksidakan untuk menghasilkan minyak sawit olein terepoksida (EPO_o), kemudian dijalankan proses pembukaan gelang secara hidrolisis dan alkoholisis untuk menghasilkan di-hidroksi-PO_o dan hidroksi-eter-PO_o. Kedua-dua produk pertengahan tersebut dijalankan pengesteran dengan asid oleik untuk menghasilkan di-oleate-PO_o dan oleate-eter-PO_o. Analisis pengecaman menggunakan transformasi fourier infra-merah (FTIR), resonans magnetik nukleus proton dan karbon (¹H-NMR and ¹³C-NMR) telah dilakukan. Di-oleate-PO_o mencatatkan kestabilan oksidatif (140 °C), takat tuang (-5 °C), takat kilat dan api (215 °C dan 245 °C), kelikatan kinematik sebanyak 417.5 cSt (40 °C) dan 45.4 cSt (100 °C) dengan indeks kelikatan 166. Oleate-eter-PO_o mencatatkan kestabilan oksidatif (178 °C), takat tuang (1 °C), takat kilat dan api (190 °C dan 210 °C), kelikatan kinematik sebanyak 113.7 cSt (40 °C) dan 21.5 cSt (100 °C) dengan indeks kelikatan 217. Stok asas biolubrikan bergred ISO VG 460 (di-oleate-PO_o) dan ISO VG 100 (oleate-eter-PO_o) telah berjaya dihasilkan. Di-oleate-PO_o dan oleate-eter-PO_o adalah bendalir Newtonian dan bukan Newtonian. Kedua-dua produk merupakan lubrikan hidrodinamik dengan pekali geseran yang rendah pada suhu 40 °C and 100 °C.

Kata kunci: Stok Asas Biolubrikan, Minyak Sawit Olein, Tribologi, Reologi

Introduction

Since industrial revolution, lubricants are widely used in all sectors of industry for lubricating their machines and materials. Reports indicate that nearly 38 million metric tons of lubricants were used globally in 2005, with a projected increase of 1.2% over the next decade [1]. Approximately 85% of lubricants being used around the world

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are petroleum based oils [2]. Generally, lubricants are made by combining basestock oil with suitable additives that enhance oil inherent characteristics or to impart new performance properties to the blend. The basestock oil is the main constituent and has traditionally been of mineral or synthetic nature [3]. These petroleum based basestocks present a potential danger when they are not readily biodegradable and thus tend to persist in the environment, having, a negative impact on the ecosystem [4,5]. The major negative effect is particularly linked to their inappropriate use, which results in surface water and groundwater contamination, air pollution, soil contamination, and consequently, agricultural product and food contamination [6]. In this sense, environmental concerns have risen considerably worldwide during the last 25 years and, consequently, there is growing interest in the use of environmentally friendly products such as biolubricants.

For these reasons, the uses of vegetable oils as basestock oils represent an important alternative in environmentally sensitive applications. These vegetable oils can be considered as a source of biolubricant. Vegetable oils are triesters of straight-chained, mostly unsaturated fatty acids with glycerol and have higher levels of biodegradability and lower toxicity than conventional mineral or synthetic oils [7]. In addition, vegetable oils have others advantages such as very low volatility, good high lubricity and high viscosity index, as well as lower cost than synthetic oils [8, 9, 10]. Unfortunately they have low thermal and oxidative stabilities, narrow viscosity range and higher pour points than both mineral or synthetic oil-based lubricants, so their use in industry is not yet extensive [11, 12, 13].

In Malaysia, palm oil as a major crop product has the possibility to be used as industrial lubricating oil. Palm oil is a vegetable oil, which is biodegradable, and also has a high production rate, which could fulfill the demand for vegetable-based lubricating oil in the future. One hectare of palm trees can produce almost 10 times as much oil compared to other sources of vegetable oil [14]. Therefore, palm oil has the potential to fulfill the supply volume in the demand for vegetable-based lubricants. One of refined products by palm oil is palm olein (PO₀). PO₀ contains higher unsaturated triacylglycerol (TAG) compared to the saturated TAG [15]. These unsaturated TAGs chains give a large potential in chemical modification to produce biolubricants.

Previously, some of researchers in Malaysia carried out research on the palm oil based lubricant products. A palm based hydraulic fluid was produced with the lubricant grade of ISO VG 46 [16]. Food grade palm oil based lubricants also produced as spindle oil (ISO VG 15 and ISO VG 22), hydraulic fluid (ISO VG 32, ISO VG 46 and ISO VG 68) and circulating oil (ISO VG 100) [17]. But mostly, PO_o was not used as raw materials in chemical modification because of its usage in food industries as cooking oils.

In this paper, palm olein used as a raw material to produce biolubricant basestocks (di-oleate- PO_o and oleate-ether- PO_o) via chemical modifications. Detection analyses were done by using Fourier Transformation Infra-red (FTIR), proton and carbon nuclear magnetic resonance (1 H, 13 C-NMR). Then, both biolubricant basestocks were characterized and analysed their tribological and rheological properties.

Materials and Methods

Raw materials

Palm olein (PO_o) (Seri Murni Brand, FFM Marketing Sdn. Bhd.) was purchased directly from market. 1-Decanol was supplied by Emery Oleochemicals (M) Sdn. Bhd, Teluk Panglima Garang, Selangor. Oleic acid (90 % of purity) was obtained from Sigma Aldrich.

Chemical reactions

The first reaction is epoxidation of PO_o to produce epoxidised palm olein (EPO_o) by using generated *in situ* performic acid with mol ratio of PO_o:HCOOH:H₂O₂ (1:5:2) [18]. Then, EPO_o was performed ring opening reaction by two approaches which that by water hydrolysis and alcoholysis with 1-decanol to produce di-hydroxy-PO_o and hydroxy-ether-PO_o. Both intermediate products were performed esterification process by using oleic acid to produce biolubricant basestocks (di-oleate-PO_o and oleate-ether-PO_o). Each level of products were detected and compared by using FTIR, ¹H-NMR and ¹³C-NMR. Then, the biolubricant basestocks were characterised and analysed on their tribology and rheology properties.

Detection tests

FTIR spectrometer (GX model) was used to detect the differences of functional groups by using the NaCl salt window method. The wavenumber of vibrations absorption was ranged between 4000 – 700 cm⁻¹. Proton and carbon analysis was performed by using FT-NMR spectrometer 600 MHz Cryo-Probe (Advance 111 600MHz model). Sample was prepared by using chloroform (CDCl₃) as a solvent [18].

Characterisation tests

Di-oleate-PO_o and oleate-ether-PO_o characterised of their moisture contents (A.O.C.S. Tb 2-64), pour point (ASTM D 97-66) [19], oxidative stability [20], flash and fire point, kinematic viscosity at 40 °C and 100 °C (ASTM D 445-79) [19], viscosity index (ASTM D2270) [21], then their lubricant grade were determined [22].

Tribology and rhelogy analysis

Tribological properties of di-oleate- PO_o and oleate-ether- PO_o were determined by using Anton Paar rheometer (Physica MCR 301 model) with one ball geometry. The sliding speed was manipulated between $10^{-1} - 10^3$ mm/s at temperature 40 °C and 100 °C [23]. The tribological properties were discussed based on their Stribeck curves at 40 °C and 100 °C (Figure 1).

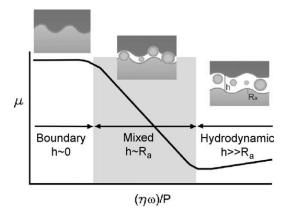


Figure 1. Sketch of a Stribeck curve relating friction coefficient; h: fluid film thickness, R_a : average surface roughness

Rheological properties of di-oleate- PO_0 and oleate-ether- PO_0 were observed by the same rheometer with cone and plate geometry [24]. The cone spindle used was CP 25-2 with diameter 0.051 mm. The shear rate was manipulated between $0 - 100 \text{ s}^{-1}$ at temperature 25 °C. A plot of shear rate vs. shear stress shown as Figure 2.

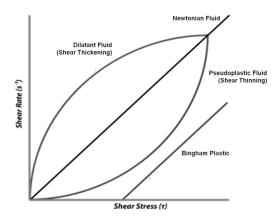


Figure 2. Shear rate vs. shear stress plots of Newtonian and non-Newtonian fluid

Results and Discussion

Figure 3 shows the overall chemical modification processes that were involved to produce biolubricant basestocks. By using chemical modifications, the unsaturated bond of palm olein (PO_o) was converted to a new functional group that can be further the modification process to produce biolubricant basestocks (di-oleate- PO_o) and oleate-ether- PO_o). At the epoxidation process, double bonds of PO_o were converted to oxirane ring to produce epoxidised palm olein (EPO_o) . Then, oxirane ring cleavage done to produce hydroxyl and ether groups. At the end of modification, both ring opening products (di-hydroxy- PO_o and hydroxy-ether- PO_o) undergo esterification with oleic acid to produce ester group of di-oleate- PO_o and oleate-ether- PO_o .

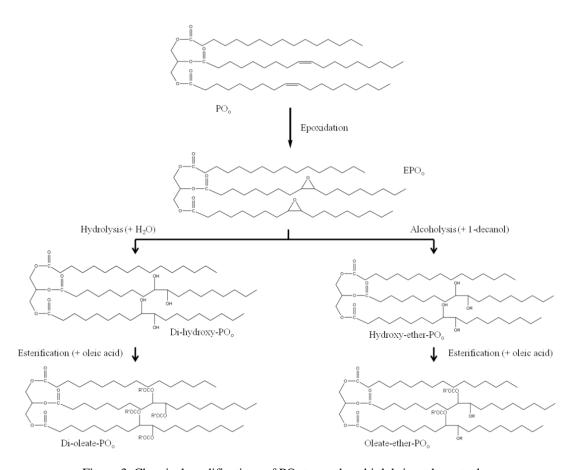


Figure 3. Chemical modifications of PO₀ to produce biolubricant basestocks

Epoxidation of palm olein (PO_0) was carried out by using generated *in situ* performic acid (HCOOH). HCOOOH was a peroxy acid which prepared by mixing of formic acid (HCOOH) as oxygen carrier and hydrogen peroxide (H_2O_2) as oxygen donor. Preparation HCOOOH as epoxidation agent was carried out as *in situ* since the reaction condition is highly exothermic and not stable [18, 25]. The epoxidation process involved of electrophilic addition mechanism as Figure 4. Unsaturated bond at triacylglycerol (TAG) PO_0 was converted to oxirane ring to produce epoxidised palm olein (PO_0).

Figure 4. Electrophilic addition mechanisms on unsaturated bond to give oxirane ring

First ring opening process involved water hydrolysis by using perchloric acid as catalyst [26]. EPO₀ was converted to di-hydroxy-PO₀. At the first step, oxirane ring was protonised to produce a strong electrophile. Then, back-side electrophilic attack happened to make oxirane cleavage. Finally, de-protonisation occurred to produce diol. Figure 5 shows the mechanisms of water hydrolysis.

Step 1: Oxirane ring was protonised to produce a strong electrophile

Step 2: Back-side electrophilic attack to make ring opening

Step 3: De-protonisation to produce diol

Figure 5. Ring opening mechanisms through water hydrolysis

Second ring opening process via alcoholysis with 1-decanol. 1-decanol is a medium chain fatty alcohol with ten carbon chains. EPO_o was converted to hydroxy-ether-PO_o. This reaction used sulphuric acid as catalyst. At the first step, oxirane ring was protonised to produce a strong electrophile. Then, electrophilic attack happened to make ring opening and produce hydroxyl group. Finally, de-protonisation occurred to produce ether group. Figure 6 shows the mechanisms of alcoholysis process to produce hydroxy-ether compound.

Step 1: Oxirane ring was protonised to produce a strong electrophile

Step 2: Electrophilic attack to make ring opening

Step 3: De-protonisation to produce ether group

Figure 6. Ring opening mechanisms through alcoholysis

Both ring opening products reacted with oleic acid through esterification process. This process used a mineral acid such as sulphuric acid or hydrochloric acid. An oxygen atom at carbonyl group of carboxylic acid was protonised by mineral acid to give positive charge on the carboxylic acid in order to make it more reactive. Then, the reactive carboxylic acid was attacked by alcohol to release water and forming ester compound [26]. Figure 7 shows the mechanisms of esterification.

Figure 7. Mechanisms of esterification process

FTIR Analyses

The comparison data of FTIR analyses shown at Table 1. PO_0 contains of unsaturated functional group where the chemical reactions can be occurred. The peak of sp^2 C-H (=C-H) and double bond were appeared at wavenumber 3003 cm⁻¹ and 1600 cm⁻¹. For EPO_0 , oxirane ring peaks presence at wavenumber 844 cm⁻¹ and the double bond peaks were disappeared. All of the double bonds were totally converted to oxirane ring [27]. While, both ring opening products (di-hydroxy-PO₀ and hydroxy-ether-PO₀) showed the presence of stretching vibration peaks of hydroxyl group and hydrogen bonded of hydroxyl group at wavenumber 3650-3600 cm⁻¹ and 3400-3300 cm⁻¹. The stretching vibration of C-O (ether) hydroxy-ether-PO₀ supposes to be appeared at wavenumber 1260-1000 cm⁻¹ but due to the highly intensity of -CH₂- and -CH₃ bending of TAGs chains, the peaks were overlapped with each other. Di-oleate-PO₀ and oleate-ether-PO₀ showed the presence of unsaturated stretching region of sp^2 =C-H, HC=CH and =C-H (oop) at wavenumber 3003, 1600 and 960 cm⁻¹ [28]. So, all of the hydroxyl group were converted to ester group and the presence of oleic acid chain in the biolubricant basestocks were confirmed.

	Compound	Wavenumber (cm ⁻¹)	Wavenumber, Ref. (cm ⁻¹) ^[28]	Conclusion
	PO_{o}	3003	> 3000	sp ² C-H (=C-H)
		1600	1600	HC=CH
	EPO_o	844 (sharp)	950 – 815	-C-O-C- (oxirane ring)
	Di-hydroxy-PO _o	3650-3600 (sharp)	3650 - 3600	stretch. vib. (O-H)
		3400-3300 (broad)	3400 - 3300	stretch. vib. H-bonded (O-
H)				
	Hydroxy-ether-PO _o	3650-3600 (sharp)	3650 - 3600	stretch. vib. (O-H)
		3400-3300 (broad)	3400 - 3300	stretch. vib. H bond (O-H)
	Di-oleate-PO _o	3003 (small)	> 3000	$sp^2 = CH$
		1600 (sharp)	1600	HC=CH
		960	900 - 690	=C-H (oop)
	Oleate-ether-PO _o	1600 (sharp)	1600	HC=CH
	-	960	900 - 690	=C-H (oop)

Table 1. Comparison Data of FTIR analyses

¹H-NMR and ¹³C-NMR analyses

The comparison data of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ shown at Table 2 and 3. Proton analysis of PO $_0$ showed that the presence of proton attached to the carbon double bond (δ 5.3 ppm) and proton attached to the carbon that attached to carbon double bond (2.0 ppm). While, proton attached to carbon (oxirane ring) appeared at δ 2.9 ppm for the EPO $_0$. So, the double bond of PO $_0$ was totally converted to oxirane ring to produce EPO $_0$ [18]. Di-hydroxy-PO $_0$ and hydroxy-ether-PO $_0$ recorded the presence of proton peaks that attached to the carbon next to the hydroxyl group at δ 3.4 and 3.6 ppm. The presence of proton peaks of hydroxyl group was at δ 4.6 and 4.8 ppm. For hydroxy-ether-PO $_0$, the peaks attached to carbon (ether) showed at δ 3.5 and 3.2 ppm. Both of the biolubricant basestock products showed the presence of proton peaks attached to carbon double bond (δ 5.3, 5.4 ppm) and peaks attached to carbon next to the carbon double bond (δ 2.0 ppm) [28].

Carbon analysis of PO_o showed that the presence of carbon double bond peaks at δ 130 ppm. While the carbon peaks of oxirane ring of EPO_o appeared at δ 57 and 54 ppm [18]. For both ring opening products, there was carbon peaks attached to hydroxyl group at δ 75 ppm. For carbon (ether) peaks of hydroxy-ether- PO_o appeared at δ 71 and 82 ppm. Di-oleate- PO_o and oleate-ether- PO_o were recorded the presence of carbon double bond peaks at δ 130 ppm [28]. These proved that the oleic acid chains are presence in the biolubricant basestock products.

Characterisation, tribological and rheological properties

Comparison of characterisation between PO_o , di-oleate- PO_o and oleate-ether- PO_o shown at Table 4. Oxidative stability of di-oleate- PO_o lower than oleate-ether- PO_o . This is due to the higher number of double bond at its structure. Both biolubricant products showed lower temperature properties of their flash and fire points compared to the PO_o . The pour point of di-oleate- PO_o and oleate-ether- PO_o were improved compared to the PO_o . Both of

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products recorded of high kinematic viscosity (40 $^{\circ}$ C and 100 $^{\circ}$ C) and good viscosity index. Based on their kinematic viscosity at 40 $^{\circ}$ C, di-oleate-PO $_{o}$ and oleate-ether-PO $_{o}$ can be considered as ISO VG 460 and ISO VG 100.

Table 2. Comparison Data of ¹H-NMR analyses

Compound	Chemical Shift, δ (ppm)	Chemical Shift, δ Ref. $(ppm)^{[28]}$	Conclusion
PO_0	2.0	1.6 - 2.6	C=C-C-H
	5.3	4.5 - 6.5	C=C- H
EPO_0	2.9	2.5 - 3.5	H -C-O-C- H (oxirane ring)
Di-hydroxy-PO _o	3.4	3.2 - 3.8	H -C-OH
	4.6	0.5 - 5.0	C-O- H
Hydroxy-ether-POo	3.5, 3.2	3.2 - 3.8	R-O-C- H
	3.6	3.2 - 3.8	H-C-OH
	4.8	0.5 - 5.0	C-O- H
Di-oleate-PO _o	2.0	1.6 - 2.6	C=C-C- H
	5.3	4.5 - 6.5	C=C- H
Oleate-ether-PO _o	2.0	1.6 - 2.6	C=C-C- H
	3.5, 3.2	3.2 - 3.8	R-O-C- H
	5.4	4.5 - 6.5	C=C- H

Table 3. Comparison Data of ¹³C-NMR analyses

Compound	Chemical Shift (ppm)	Chemical Shift, Ref. (ppm) ^[28]	Conclusion
POo	130	100 – 150	C=C
EPO _o	57, 54	40 - 80	C-O-C (oxirane ring)
Di-hydroxy-PO _o	75	40 - 80	н-С-ОН
Hydroxy-ether-PO _o	72	40 - 80	RH ₂ -C-O-C
	75	40 - 80	н-С-ОН
	82	40 - 80	R_2H -C-O-C
Di-oleate-PO _o	130	100 - 150	$\mathbf{C} = \mathbf{C}$
Oleate-ether-PO ₀	71	40 - 80	RH ₂ -C-O-C
-	82	40 - 80	R_2H -C-O-C
	130	100 - 150	C=C

Table 4. Characterisation of POo, di-oleate-POo and oleate-ether-POo

Parameter	Unit	PO_{o}	Di-oleate-POo	Oleate-ether-POo
Moisture content	%	0.22	0.46	0.45
Oxidative stability	°C	179.7	155.8	178.3
Flash point	°C	> 320	215	190
Fire point	°C	> 320	245	210
Pour point	°C (± 2 °C)	5	-5	1
Pour point (+additive)	°C	-	-10	-13
Kinematic viscosity (40 °C)	$cSt (\pm 5 ^{\circ}C)$	45.9	417.5	113.7
Kinematic viscosity (100 °C)	$cSt (\pm 5 ^{\circ}C)$	9.4	45.4	21.5
Viscosity index	-	195	166	217
Lubricant grade (ISO VG)	-	46	460	100

Comparison of tribological properties between PO_o, di-oleate-PO_o and oleate-ether-PO_o shown at Figure 8. By referring to Figure 1, the Stribeck curve has three types of lubricant conditions which are boundary, mixed and hydrodynamic lubricant. In the middle between mixed and hydrodynamic lubricant condition, there was a elastohydrodynamic lubricant which is the friction coefficient decreasing during the increasing of parameter [29]. All of the samples showed low friction coefficient at 40 °C. But PO_o recorded a higher friction coefficient than dioleate-PO_o and oleate-ether-PO_o at 100 °C. The friction coefficient of di-oleate-PO_o and oleate-ether-PO_o still below than 0.5. This showed that both biolubricant basestock products had a better quality of their tribological properties even the temperature was increased compared to the PO_o.

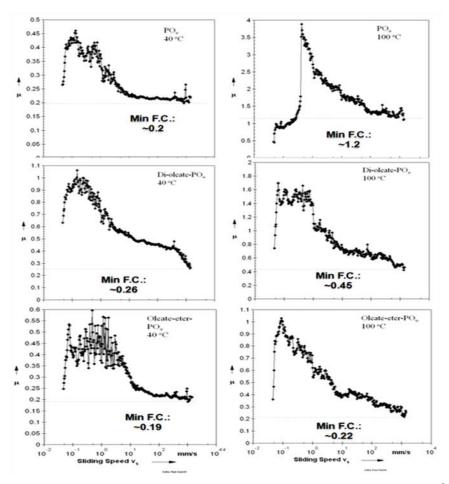


Figure 8. Comparison of Stribeck curves between PO₀, di-oleate-PO₀ and oleate-ether-PO₀ (40 °C and 100 °C)

Rheology analysis of samples produced shear stress vs. shear rate plot (Figure 9). From this plot, a fluid can be decided as Newtonian or non-Newtonian fluid. Newtonian fluid was classified as a fluid that has a constant viscosity by increasing shear rate and *vice versa* for non-Newtonian fluid [30]. Based on figure given, PO_0 and oleate-ether- PO_0 are non-Newtonian fluids. While di-oleate- PO_0 is a Newtonian fluid.

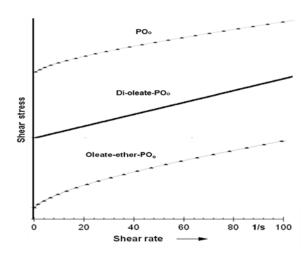


Figure 9. Shear stress vs. shear rate plots of PO₀, di-oleate-PO₀ and oleate-ether-PO₀ (25 °C)

Conclusion

Biolubricant basestocks grade ISO VG 460 (di-oleate-PO_o) and ISO VG 100 (oleate-ether-PO_o) were successfully synthesized from palm olein and characterized their lubrication, tribological and rheological properties. These products are having potential to be used as a lubricant basestock in the industrial field at moderate operation temperature in tropical countries.

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References

- 1. Kline & Company Inc. 2006. Competitive intelligence for the global lubricants industry 2004–2014, Kline & Company, Inc.
- 2. Loredana P., Cosmina P., Geza B., Gabriela V., Remus N. 2008. Basestock oils for lubricants from mixtures of corn oil and synthetic diesters. *J Am Oil Chem Soc.* 85: 71–6.
- 3. Erhan, S.Z., Adhvaryu, A. 2002. Vegetable-based base stocks. In: Erhan, S.Z., Perez, J.M. (Eds.), Bio-Based Industrial Fluids and Lubricants. Champaign, USA, AOCS Press.
- 4. Lawate, S. 2006. Environmentally friendly hydraulic fluids. In: Rudnick, L.R. (Ed.), Synthetics, Mineral Oils, and Bio-Based Lubricants. Chemistry and Technology, Taylor & Francis, CRC Press, PA, USA.
- 5. Sharma, B.K., Adhvaryu, A., Liu, Z., Erhan, S.Z. 2006. Chemical modification of vegetable oils for lubricant applications, *JAOCS*, 83: 129–136.
- 6. Birova A, Pavloviova A, Cvengro J. 2002. Lubricating oils based on chemically modified vegetable oils, *J Synth Lubr*. 18: 291.
- 7. Adhvaryu, A., Erhan, S.Z. 2002. Epoxidized soybean oil as a potential source of high temperature lubricants, *Ind. Crop Prod.* 15: 247–254.
- 8. Erhan, S.Z., Asadaukas, S. 2000. Lubricants base stocks from vegetable oils, *Ind. Crop Prod.* 11: 277–282.
- 9. Erhan, S.Z., Adhvaryu, A., Sharma, B.K. 2006. Chemically functionalized vegetable oils. In: Rudnick, L.R. (Ed.), Synthetics, Mineral Oils, and Bio-Based Lubricants. Chemistry and Technology, Taylor & Francis, CRC Press, PA, USA.
- 10. Campanella, A., Rustoy, E., Baldessari, A., Baltanas, M.A. 2010. Lubricants from chemically modified vegetable oils. *Bioresour. Technol.* 101: 245–254.
- 11. Erhan, S.Z., Asadaukas, S. 2000. Lubricants base stocks from vegetable oils, *Ind. Crop Prod.* 11: 277–282.

- 12. Sharma, B.K., Stipanovic, A.J. 2003. Development of a new oxidation stability test method for lubricating oils using high-pressure differential scanning calorimetry, *Thermochim. Acta* 402: 1–18.
- 13. Duangkaewmanee, S., Petsom, A. 2011. Synergistic and antagonistic effects on oxidation stability of antioxidants in a synthetic ester based oil *Tribol. Int.* 44: 266–271.
- 14. Ming KK, Chandramohan D. 2002. Palm oil industry at crossroad and its future direction, *Oil Palm Industry Economic Journal* 2: 10–5.
- 15. Ramli, M. R., Siew, W. L., Cheah, K. Y., 2009. Production of high oleic palm oils on a pilot scale, *J. Am. Oil. Chem. Soc.* 86: 587-594.
- 16. Yeong, S. K., Ooi, T. L., Salmiah, A., 2005. Palm-Based Hydraulic Fluid, MPOB, KL.
- 17. Loh, S. K., Choo, Y. M., 2006. Food-Grade Palm-Based Industrial Lubricants, MPOB, KL.
- 18. Derawi, D., Salimon, J., 2010. Optimization on epoxidation of palm olein by using performic acid, *E-J.Chem.* 7(4): 1440-1448.
- 19. Emery, 1983. Emery Analytical Testing Procedures, Emery Industries, USA.
- 20. Fox, N.J., Stachowiak, G.W. 2007. Vegetable oil-based lubricants—A review of oxidation, *Tribology International* 40: 1035–1046.
- 21. Stachowiak, G. W., Batchelor, A. W. 2005. Engineering Tribology, Elsevier Inc., UK.
- 22. ISO 3448, 1975. International Standard, Industrial Liquid Lubricants, ISO Viscosity Classification.
- 23. Kalin, M., Velkavrh, I., Vizintin, J. 2009. The Stribeck curve and lubrication design for non-fully wetted surfaces, Wear 267: 1232-1240.
- 24. Coussot, P., Tocquer, L., Lanos, C., Ovarlez, G., 2009. Macroscopic vs local rheology of yield stress fluids. J. Non-Newtonian Fluid Mech., 158: 85-90.
- 25. Gunstone, F.D. 2004. The Chemistry of Oils and Fats: Sources, Composition, Properties and Uses, Blackwell Publishing Ltd., U.K.
- 26. Wade, L. G., 2006. Organic Chemistry, 6th ed., Pearson Prentice Hall, United States.
- 27. Derawi, D., Salimon, J. 2011. Effect of Performic Acid Concentration on Epoxidation of Palm Olein, *Sains Malaysiana* 40(9): 1023-1027
- 28. Pavia, D. L., Lampman, G. M., Kriz, G. S. 2001. Introduction to spectroscopy, Thomson Learning, Inc., USA.
- 29. Hironaka, S., 1984. Boundary Lubrication and Lubricants., Three Bond Co. Ltd., Japan.
- 30. Batchelor, G. 2000. An Introduction to Fluid Mechanics, Cambridge University Press, UK.