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CHEMICAL MODIFICATION OF EPOXIDIZED PALM OIL FOR BIOLUBRICANT APPLICATION

(Pengubahsuaian Kimia Minyak Sawit Terepoksida Untuk Aplikasi Biopelincir)

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Abstract

Refined, bleached and deodorized (RBD) palm oil is one of the interesting renewable resources in biolubricant application. It is due to some advantages such as biodegradable, non-toxic, excellent lubricity and high viscosity index properties. However, direct application of RBD palm oil as biolubricant is restricted due to its poor low temperature property, which limits its use at low operating temperature. This drawback can be overcome by molecule structural redesign through chemical modification process. To produce palm oil based biolubricant with good pour point, epoxidized palm oil (EPO) was chemically modified via ring opening process. EPO was reacted with oleic acid in the presence of *p*-toluenesulfonic acid (PTSA) as catalyst. The molecular structure confirmation of ring opening product which is palm oil hydroxy oleate (POHO) was proven through the oxirane oxygen content (OOC) value, iodin value, hydroxyl value, Fourier transformation infra-red (FTIR), proton and carbon nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectroscopy analysis. The physicochemical properties of POHO were determined through its pour point and flash point values. The results showed that the ring opening process for putting bending and branching molecule structures of the oil have improved the pour point (-8.5 °C) and increased the flash point of the biolubricant (255 °C).

Keywords: epoxidized palm oil, oleic acid, ring opening, pour point

Abstrak

Minyak sawit tertapis, terluntur dan terbau (RBD) merupakan salah satu sumber boleh diperbaharui yang menarik dalam penghasilan biopelincir. Ini adalah disebabkan oleh kelebihannya seperti boleh dibiodegradasikan, tidak bersifat toksik, mempunyai kebolehpelinciran yang cemerlang dan indeks kelikatan yang tinggi. Walau bagaimanapun, penggunaan secara terus mintak masa RBD sebagai biopelincir adalah terhad disebabkan oleh sifat suhu rendah yang lemah, yang telah mengehadkan penggunaannya dalam operasi bersuhu rendah. Kelemahan ini boleh diatasi dengan melakukan ubahsuai struktur molekul melalui pengubahsuaian kimia. Dalam usaha untuk menghasilkan biopelincir berasaskan minyak sawit dengan nilai takat tuang yang baik, minyak sawit terepoksida telah diubahsuai secara kimia melalui proses pembukaan gelang epoksida. Minyak sawit terepoksida ditindakbalaskan dengan asid oleik dengan kehadiran asid *p*-toluenasulfonik (PTSA) sebagai mangkin. Pengecaman struktur molekul hasil pembukaan gelang epoksida iaitu hidroksi oleate minyak sawit (POHO) dibuktikan melalui nilai kandungan oksigen oksiran, nilai iodin, nilai hidroksil, spektroskopi Infra merah transformasi Fourier (FTIR), proton dan karbon resonans magnetik nuklear (^{1}H-NMR dan ^{13}C-NMR). Sifat fiziko-kimia POHO ditentukan melalui nilai takat tuang dan takat kilat. Hasil kajian menunjukkan proses pembukaan gelang epoksida dengan penambahan struktur molekul bercabang dan bengkok minyak telah memperbaiki nilai takat tuang (-8.5 °C) dan meningkatkan nilai takat kilat biopelincir (255 °C).

Kata kunci: minyak sawit terepoksida, asid oleik, pembukaan gelang, takat tuang

Introduction

Nowadays, plant oil become one of the interesting renewable resources in biolubricant production in order to replace mineral oil. It is due to some advantages such as biodegradable, non-toxic, excellent lubricity and high viscosity index property [1 – 4]. However, plant oil has some drawback such as poor low temperature properties and it need to be resolved [1]. Poor low-temperature properties include cloudiness, precipitation, poor flowability and solidification at relatively high temperatures [1, 2]. Its poor cold flow property will also limit its use at low operating temperature [5]. The possible way to improve this low temperature properties is molecule structural redesign through chemical modification process. Chemical modifications of the vegetable oils to give more complex structures should improve the low-temperature properties [1]. In general, one of the important modification in plant oils is epoxidation. Refined, bleached and deodorized (RBD) palm oil become one of the potential plant oil for epoxidation to produce biolubricant. RBD palm oil contain high percentage of unsaturated fatty acid (49.4%) which makes it as good starting material for the epoxidation process [6].

The most important modification that can be used to improve poor low temperature properties of plant oil is ring opening reaction. The oxirane ring opening by acidic or alkaline catalyzed reaction with suitable reagent provides interesting polyfunctional compounds [2, 7] whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve the low-temperature performance [2, 8]. The branching group which resulted from ring opening reaction will interfere the formation of macro-crystalline structures during low-temperature applications and provide enhanced fluidity to plant oils [9]. These modified plant oils with chain branching were reported to have superior performance of the physicochemical properties and are promising as biolubricant [9]. Products obtained from ring opening can be used as low-temperature lubricants [10].

Epoxidized RBD palm oil become a promising reactive intermediate, since the epoxy group can be converted to other functional groups through ring-opening reaction due to high reactivity of the oxirane ring [11]. The oxirane ring opening reaction can be carried out through epoxy moiety and takes place through cleavage the carbon oxygen bonds which can be initiated by either electrophiles or nucleophiles, or catalyzed by either acids or bases [12]. The epoxide can react with different nucleophiles to produce alcohols, diols, alkoxyalcohols, hydroxy esters, N-hydroxyalkylamides, mercaptoalcohols, aminoalcohols and so forth [12, 13]. Amongst these classes of products, hydroxy esters find application as biolubricants, polyurethane foams, or casting resins [12]. The physicochemical properties of biolubricants derived from hydroxy esters can be modified using different carboxylic acids [12, 14].

In this paper, we reported the modification of epoxidized palm oil (EPO) molecule structure via ring opening process to produce a base stock oil for lubricant application. Epoxidized palm oil (EPO) was reacted with oleic acid in the presence of *p*-toluenesulfonic acid (PTSA) as catalyst to enhance the lubrication properties. The product of ring opening process which is palm oil hydroxy oleate, (POHO) was screened for low-temperature property through determination of pour point. The pour point of a biolubricant is a good indicator of its low-temperature fluidity. The product also monitored by oxirane oxygen content (OOC) value, iodin value (IV) and hydroxyl value (HV) tests. The physicochemical properties analysis was performed according to the standard methods for pour point and flash point.

Materials and Methods

Materials

RBD palm oil was obtained from Sime Darby Jomalina, Teluk Panglima Garang, Selangor, Malaysia. Formic acid (88%) was obtained from Fisher Scientific and hydrogen peroxide 30% from Merck, Germany. Sodium hydrogen carbonate, sodium sulphate, sodium chloride, potassium iodide, Wijs solution, ethyl acetate and *p*-toluenesulfonic acid (PTSA) were purchased from Systerm. Hydrogen bromide 33 wt.% in acetic acid, glacial acetic acid and oleic acid (90%) were obtained from Sigma Aldrich.

Epoxidation of RBD palm oil

In epoxidation reaction, the mole ratio of RBDPO, formic acid and hydrogen peroxide is 1:5:3. The epoxidation process began by adding RBDPO with formic acid into 250 mL three necks round bottom flask equipped with mechanical stirrer, thermometer and reflux condenser. The mixture of RBDPO and formic acid were heated and continuously stirred (900 rpm). Hydrogen peroxide was added slowly drop wise. The reaction was carried out for 2.5 hours at 45 ^{o}C. At the end of reaction, heating was stopped, and product was neutralized with sodium hydrogen carbonate solution (5%), sodium chloride solution (5%) and distilled water. The product which is epoxidized palm oil was kept for overnight by adding anhydrous sodium sulphate to remove water. Then, product was filtered using Whatmann No. 1 filter paper.

Ring opening of epoxidized palm oil

In ring opening reaction, the mole ratio of epoxidized palm oil (EPO) and oleic acid is 1: 3. EPO and oleic acid were weighed into a 250 mL three-neck round bottom flask and heated at 70 ^{o}C to 80 ^{o}C for 15 minutes. Then, 1% of *p*-toluenesulfonic acid (PTSA) was added to the mixture. The reaction was carried out for 5 hours at 110 ^{o}C with continuous stirring of 900 rpm using a magnetic stirrer. At the end of reaction, the heating was stopped. The product was neutralized with sodium hydrogen carbonate solution, sodium chloride solution and ethyl acetate. The product which is palm oil hydroxy oleate (POHO) was kept for overnight by adding anhydrous sodium sulphate. The product was filtered by Whatmann No 1 filter paper and the solvent used was isolated by rotary evaporator at 70 ^{o}C.

Characterizations

The formation of palm oil hydroxy oleate (POHO) was confirmed using Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. FTIR spectra was recorded on a Perkin Elmer Infrared Spectrophotometer in the range 500 – 4000cm^{-1}. NMR spectroscopy was carried out to confirm the molecular structure of the product. ^{1}H and ^{13}C NMR were recorded on JEOL-ECP 400 spectrometer (400 MHz ^{1}H/100.61 MHz^{13}C) using $CDCl_3$ as a solvent.

Determination of oxirane oxygen content

Oxirane oxygen content (OOC) determines the quantity of oxygen of epoxy groups in percent of mass. Oxygen is directly titrated with hydrobromic acid in acetic acid under defined conditions according to the AOCS Analysis Method Cd 9-57[15]. OOC percentage can be calculated using the following equation 1:

$$\text{Oxirane oxygen content (\%)} = \frac{\text{Volume of hydrobromic acid solution (mL) x N x 1.60}}{\text{Weight of sample (g)}} \tag{1}$$

whereas N is normality of hydrobromic acid solution

Determination of iodine value

Iodine value (IV) is a parameter that determines the degree of unsaturation in oils and fats, which are associated with the double bond or triple bond. IV shows the value in grams of iodine absorbed by 100g of fat or oil in the condition specified. Determination of IV generally practiced by Wijs method according to Ainie et al. [16]. IV can be determined by following equation 2:

$$\text{Iodin value (IV)} = \frac{12.69 \text{ x N x } (V_2\text{-}V_1)}{W} \tag{2}$$

whereas N is normality of sodium thiosulphate solution, V_2 is volume of sodium thiosulphate solution (mL), required for titration of sample, V_1 is volume of sodium thiosulphate solution (mL), required for titration of blank and W is weight of sample (g).

Determination of hydroxyl value

The hydroxyl value (HV) is the weight of potassium hydroxide in milligrams (mg) balanced with hydroxyl content of one gram of sample. HV is applied in the determination of oil or its derivatives that have the oxirane ring structure. HV was performed according to the method AOCS Analysis Method Tx 1a-66 [15]. HV can be determined using this following equation 3:

$$\text{Hydroxyl value (HV)} = \frac{B + (WA/C) - S \times N \times 56.1}{W} \tag{3}$$

whereas A is volume of potassium hydroxide solution (mL), required for titration for acidity value and B is volume of potassium hydroxide solution (mL) required for titration of blank test. C is weight of sample (g) used in acid titration, S is volume of potassium hydroxide solution (mL), required for titration in samples that have undergone acetylation process, W is weight of sample (g) used in acetylation and N is normality of potassium hydroxide solution.

Datermination of flash point value

Flash point is the lowest temperature at which the vapor sample burns or ignite at a pressure of 101.3 kPa (760 mmHg). Determination of the flash point was carried out by Cleveland open cup method according ASTM D92-05a [17] with modifications.

Determination of pour point value

Pour point is the lowest temperature at which the sample begins to flow. Pour point is a good indicator for low temperature fluidity determination. Determination of pour point was conducted according to ASTM D97-98 [17] method with modifications.

Results and Discussion

Many nucleophilic reagents are known to add to an oxirane ring, resulting in ring opening [13]. The ester branching groups produced from oxirane ring opening based esterification reactions are effective for attaining the desired molecular spacing [13]. Most of the oxirane ring groups were opened and converted into ester bonds in the molecule with hydroxyl group [13]. The modified plant oils with chain branching are reported to have superior performance properties and are promising as biodegradable lubricant [13, 18].

This study reports the oxirane ring opening reaction of epoxidized palm oil (EPO) by the nucleophilic addition of oleic acid (OA) in the presence of homogenous acid catalysts which is *p*-toluenesulfonic acid (PTSA). PTSA was preferred to use in the reactions due to the maximum yield of epoxy ring opening and no evidence of any side reaction occurs during the reaction [9]. The nucleophilic attack by fatty acid molecule which is oleic acid on the oxirane ring of epoxidized palm oil (EPO) in the presence of PTSA as catalyst resulted in the ring opened product which is palm oil hydroxy oleate (POHO).

The results for the ring opening process are shown in Table 1. The average percentage yield of ring opening is 82% (by weight). The ring opening process can be monitored through the OOC value which the value should be as smaller as possible after ring opening process. There is a significant different was observed between the OOC values before and after ring opening process. The initial OOC value of epoxidized palm oil (EPO) before ring opening process is 3.42%. The value of OOC obtained for POHO after ring opening process was significantly low approaching zero (0.04%) with 98% conversion. The reduction of OOC value is proportional to significant number of epoxide ring opening and it prove that the entire epoxide ring was successfully opened during the ring opening reaction with the oleic acid to produce POHO.

The entire epoxide ring has been successfully converted to hydroxyl oleate ester functional groups during the ring opening reaction with oleic acid. This can be evidenced by the increasing of iodine value and hydroxyl value of the product. The addition of the olefin which exist from oleate acyl group has increased the iodine value from initial iodine value of epoxidized palm oil (EPO) which is 0.45 mg/g to 59.9 mg/g after ring opening process.

There is also increasing of hydroxyl value which is from 25 mg/g to 124.8 mg/g after ring opening process. Figure 1 shows the schematic reactions for the modification of RBD palm oil via the epoxidation and ring opening reactions represented by the structure of 1,3-dipalmitoyl-2-oleoyl-gliserol (POP) as the dominant triacylglycerol in RBD palm oil.

Table 1. Analysis tests for ring opening process of epoxidized palm oil

Compound	**EPO**	**POHO**
Yield (%)	85	82
OOC value (%)	3.42	0.04
Conversion (%)	98	98
Iodine value (mg/g)	0.45	59.9
Hydroxyl value (mg/g)	25	124.8

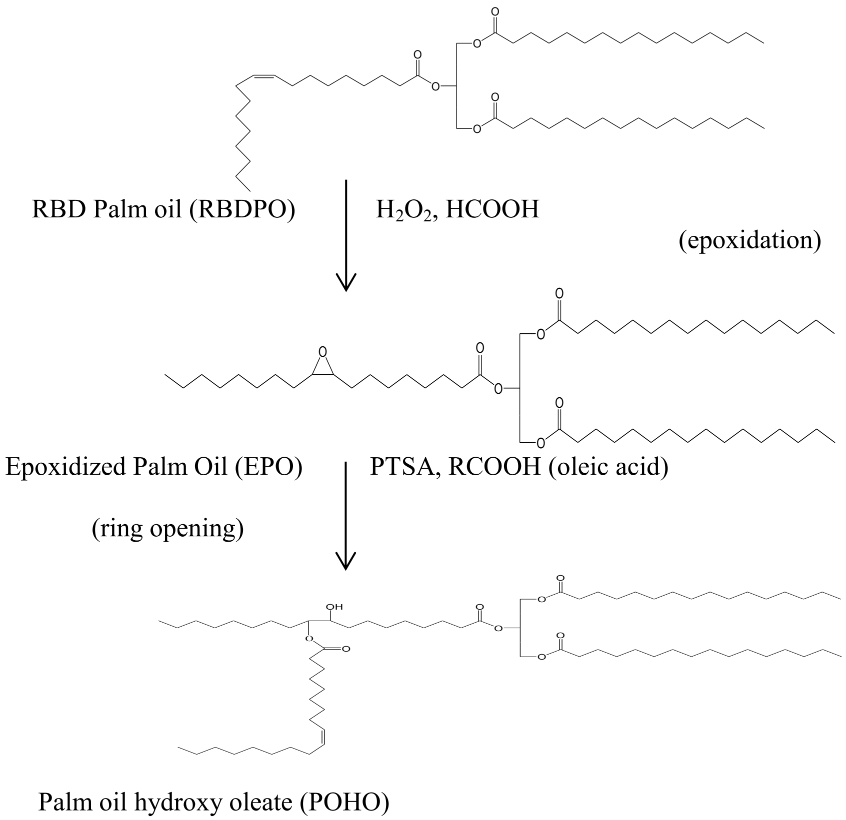

Figure 1. The schematic reactions for the modification of RBD palm oil via epoxidation and ring opening reactions

FTIR spectra

The presence of functional groups in the POHO produced were identified by using FTIR spectroscopy. Figure 2 shows comparison of FTIR spectra between RBDPO, EPO and POHO. The disappearance of double bond functional group peak at 3007 cm^{-1} which initially present in RBDPO spectra indicates the conversion of double bond to epoxy group. It can be proved by presence of C-O-C epoxide peak at 826 cm^{-1} in EPO spectra.

The disappearance of the epoxide peak showed that the entire oxirane ring has been successfully converted to hydroxyl oleate ester functional groups in POHO during the ring opening reaction with oleic acid. This is evidenced by the increasing of peaks intensity of the hydroxyl (OH) functional group at 3470 cm^{-1} and C=O stretching at 1741 cm^{-1} in POHO spectra. A significant change in the ring opening process is also can be evidenced by existence of C=C olefin peak of oleate acyl group at 3005 cm^{-1} in POHO spectra.

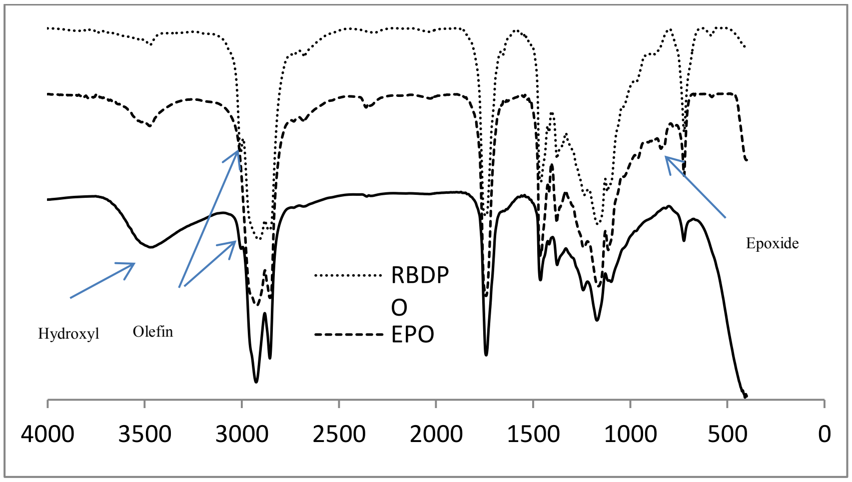

Figure 2. FTIR spectra of RBDPO, EPO and POHO

NMR spectroscopy

Table 2 shows the chemical shifts of ^{1}H NMR and Table 3 shows chemical shifts of ^{13}C NMR spectra for RBDPO, EPO and POHO. In Figure 3(a), the signal at 5.3 ppm is corresponding to vinyl proton (-CH=CH-), while the signal at 2.1 - 2.0 ppm indicate the presence of allylic proton (C=C-C-H), both represent double bond peaks in RBDPO.

Table 2. Chemical shifts of ^{1}H NMR spectra for RBDPO, EPO and POHO

Compound	**Chemical shift, ppm**	**Chemical shift, ppm (Theoretical[19])**	**Remarks**
RBDPO	2.1 - 2.0	1.6-2.6	C=C-C-H
	5.3	4.5-6.5	C=C-H
EPO	1.4-1.5	1.4-1.5	CH_2-CHOCH-CH_2 CHOCH
	2.8	2.5-3.5	
POHO	2.0-1.9	1.6-2.6	C=C-C-H
	4.9	0.5-5.0	C-O-H
	5.3	4.5-6.5	C=C-H

Table 3. Chemical shifts of ^{13}C NMR spectra for RBDPO, EPO and POHO

Compound	**Chemical shift, ppm**	**Chemical shift, ppm (Theoretical[19])**	**Remarks**
RBDPO	130.1- 129.6, 128.0-127.8	100-150	C=C
EPO	57.2-56.6, 54.3-54.1	40-80	C-O-C
POHO	73.5	40-80	HC-OH
	130.2- 129.7	100-150	C=C

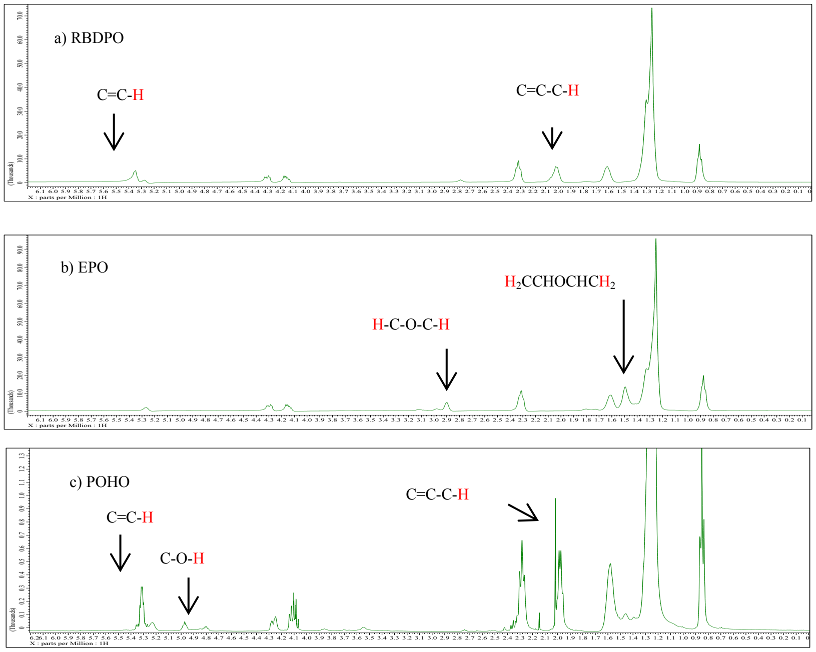

Figure 3. ^{1}H NMR spectra for a) RBDPO, b) EPO and c) POHO

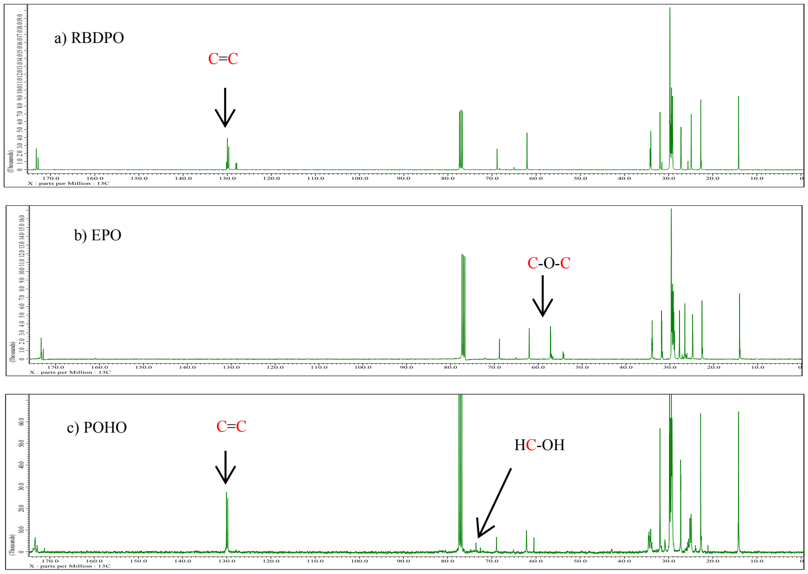

Figure 4. ^{13}C NMR spectra for a) RBDPO, b) EPO and c) POHO

Physicochemical properties of palm oil hydroxyl oleate (POHO)

The physicochemical properties results obtained are shown in Table 4. The ability of a substance to remain liquid at low temperatures is an important attribute for many industrial application materials, such as biolubricants, surfactants and fuels [1, 5]. The cold flow property of plant oils is extremely poor, and this limits their use at low operating temperature especially as automotive and industrial fluids [5]. Plant oils tend to form macrocrystalline structures at low temperatures through uniform stacking of the ‘bend’ triacylglycerol (TAG) backbone [5]. Such macrocrystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking [2, 5, 20]. The low temperature properties can be screened by determination of pour point. The pour point of a biolubricant is a good indicator of its low-temperature fluidity. In this study, pour point of RBDPO, EPO and POHO were -3.8 °C, 0.1 °C and -8.5 °C, respectively. After ring opening process, POHO shows a lowest pour point which is -8.5 °C, due to the branching in carbon chain and bent structure. It makes more restrict to self-stacking and more hollows in structure, thus easier to flow which contributed to the lowest pour point. In general, the presence of branching group in the molecule will disrupt this stacking process and create a steric barrier around the individual molecules and inhibits crystallization [11]. This will result in the formation of microcrystalline structures rather than macro structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another resulting in better fluidity of the total matrix [5], resulting in lower pour point.

Table 4. The physicochemical properties of RBDPO, EPO and POHO

Compound	RBDPO	EPO	POHO
Pour point (°C)	-3.8	0.1	-8.5
Flash point (°C)	240	245	255

Another important factor that determine the efficiency of oil as biolubricant is flash point. The flash point is often used as a descriptive characteristic of fuel oil and it is also used to describe oils that are not used as fuels such as lubricant [5]. Flash point refers to both flammable oils and combustible oils [5]. The oils with a flash point less than 43 ^{o}C are flammable, while those having a flash point above this temperature are combustible [5]. High flash point is important to ensure that the lubricant is not burned in the engine during its operation. Biolubricant which has a low flash point value is considered to have been contaminated by volatile and usually requires precautions special care when handling this biolubricant [2]. In this study, flash point of RBDPO, EPO and POHO were 240 °C, 245 °C and 255 °C, respectively. After ring opening process, POHO shows the highest flash point which is 255 °C. This is due to an increase in carbon number causes an increasing molecular weight that gives a higher flash point. In addition, POHO also have branched carbon chain molecular structure. The big branched-chain structure requires more energy to burn. This will increase the flash point of POHO.

Conclusion

The chemically modified epoxidized palm oil (EPO) has improvement in pour point and flash point. The ring opening product which is palm oil hydroxy oleate (POHO) has lowest pour point due to the greater ability of the branching chain esters to disrupt crystalline formation. A bent and branching structure make the molecule less compact, thus improve the lubricity of lubricant. This shows that the cold flow property of biolubricant has improved by reducing the pour point value.

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