Preparation of Epoxidized Palm Oil by using Performic Acid

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The epoxidation process of palm oil was carried out using *in situ*-generated performic acid. Formic acid acts as an oxygen carrier and hydrogen peroxide acts as an oxygen donor in the reaction system. The epoxidation process was performed using a molecular ratio of 5.91 moles of formic acid to 3.60 moles of hydrogen peroxide, reaction temperature of 40°C and reaction time of 2.55 hours. The validation of the epoxidized palm oil (EPO) molecular structure was confirmed by Fourier Transformation Infra-Red (FTIR) and proton and carbon Nuclear Magnetic Resonance (¹H-NMR and ¹³C-NMR) spectroscopy. High conversion (99.43%) of oxirane ring was obtained with 86% (w/w) yield of EPO. The existence of epoxy group was evidenced by FTIR at 843 cm⁻¹, ¹H-NMR chemical shift at 2.89 ppm and ¹³C-NMR at 54.19-57.22 ppm. The physicochemical properties results show that EPO has higher oxidative stability (190°C), flash point (255°C) and viscosity index (133), which make EPO plausible to be used as an industrial fluid.

Key words: Epoxidation, epoxidized palm oil, oxygen oxirane content, performic acid

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In recent years, renewable materials have been increasingly used in various industries to replace mineral oils due to increasing costs of mineral oils and rising concerns about environmental pollution [1]. Renewable sources such as plant oils and animal fats are used after appropriate chemical modification [2]. Among the chemical modifications of polyolefin, epoxidation is a simple and effective method of converting double bonds to form new and reactive functional compounds [3].

Epoxidation can be carried out from olefinic molecules through four methods: (a) epoxidation with percarboxylic acid [4], which is the most widely used in industry and can be catalyzed by acids or enzymes [5,6]; (b) epoxidation with organic and inorganic peroxide including alkaline and nitrile hydrogen peroxide epoxidation as well as transition metalcatalyzed epoxidation [7]; (c) epoxidation with halohydrins using hypohalous acids and their salts as reagents for the epoxidation of olefins with electron deficient double bonds [4]; and (d) epoxidation with molecular oxygen [4]. The most widely used process is the epoxidation of unsaturated compounds with either pre- or in-situ-formed organic per acids [8]. The epoxidation process is one of the most important functional reactions of the double bond to other stable functional groups to enhance the oxidative stability of plant oils [9,10]. It is also industry's most widely used process towards highly unsaturated plant oils to increase their industrial use [8].

Epoxidized oils have a wide range of industrial and commercial uses because of the richly varied chemical reactivity due to the high strain energy of the

three-membered oxirane rings [11, 12]. Due to the high reactivity of the oxirane rings in epoxidized oils, epoxidized oils are used as renewable raw materials to produce intermediate products such as alcohols, alcoxyalcohols, glycols, hydroxyesters, Nhydroxyalkylamides, mercaptoalcohols, hydroxynitriles, alkanolamines and carbonyl compounds [13, 14]. They are also widely used in lubricants, stabilizers and plasticizers detergents, in polyvinylchloride (PVC). Plant oils with high content of unsaturated fatty acids are used to produce high quality epoxy functional materials [15]. Epoxidized plant oil products from the epoxidation process can be used as high-temperature lubricants [16, 17], plasticizers [18] and high temperature coating materials [19].

Epoxidation of plant oils such as mahua oil [13], Jatropha curcas oil [11, 15, 20], soybean oil [15, 21, 22], rubber seed oil [23], canola oil [12], rapeseed oil [24], jojoba oil and castor oil [8] have been investigated. Recently, palm oil has become one of the potential plant oils to produce renewable materials [25, 26, 27]. Palm oil, which is abundantly available all over Malaysia contains a high percentage of unsaturated fatty acids (49.4%) [28], which serves as a good starting material for the epoxidation process. The epoxidation of palm oil was studied by Hoang and Kim [29]. This study focused on the effect of reaction time on palm oil epoxidation process. The conversion of double bond to oxirane group in palm oil was investigated in four different reaction times (120 min, 150 min, 180 min and 210 min). The mole ratio of unsaturated, formic acid and hydrogen peroxide was set at 1: 5: 4 and the reaction temperature was 50°C.

The optimized epoxidation time was obtained at 180 minutes with 98.9% double bond conversion to oxirane ring and 70% yield. In 2010, Derawi and Salimon [30] discussed the synthesis of epoxidized palm olein (POo) using performic acid and its characterization. Effects of formic acid (HCOOH) and hydrogen peroxide (H₂O₂) concentration, temperature, stirring effect and reaction time were studied. The optimum reaction conditions were 5 moles of HCOOH, 2 moles of H₂O₂, 45°C, 150 min and 350 rpm of stirring speed. At this optimum conditions, the reaction yield was 91.3% with 96.5% of oxirane conversion. Table 1 shows a summary of the research findings on epoxidation of palm oil and palm olein using performic acid.

The objective of this study is to produce epoxidized palm oil (EPO) through epoxidation of palm oil. Lower reaction temperature was used to produce higher percentage of epoxide yield and higher oxirane conversion. Epoxidized palm oil (EPO) was characterized using Fourier Transformation Infra-red (FTIR) and proton and carbon Nuclear Magnetic Resonance (¹H-NMR and ¹³C-NMR), and the physicochemical properties were examined using several tests such as oxidative stability, pour point, flash point and viscosity index. Figure 1 shows the proposed schematic reaction for the epoxidation of palm oil represented by the 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) structure as the dominant triacylglycerol content (30.2%) in palm oil.

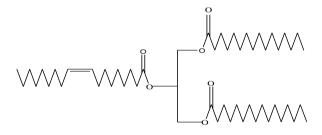
MATERIALS AND METHODS

Materials

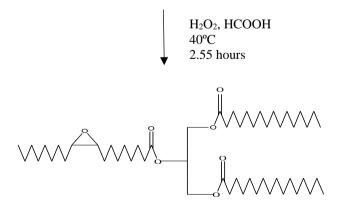
Palm oil was obtained from Jomalina Refinery, Teluk Panglima Garang, Selangor, Malaysia. Formic acid (88%) was obtained from Fisher Scientific and hydrogen peroxide (30%) from Merck. Sodium hydrogen carbonate and sodium chloride were purchased from Systerm.

Table1. Summary of the research findings on epoxidation.

Study	Hoang and Kim ^[29]	Derawi and Salimon ^[30]
Yield (%)	70	91.3
Oxirane conversion (%)	98.9	96.5



1,3-dipalmitoyl-2-oleoyl-glycerol (POP)



Epoxidized 1,3-dipalmitoyl-2-oleoyl-glycerol (POP)

Figure 1. The schematic reaction of epoxidation of palm oil.

Epoxidation of Palm Oil

Epoxidation of palm oil was carried out at optimum conditions of: 5.91 moles of formic acid to 3.60 moles of hydrogen peroxide, reaction temperature of 40°C and reaction time of 2.55 hours, as reported by Nurazira et al. [26]. Epoxidation process began by adding palm oil with formic acid into a 250 mL threeneck round bottom flask equipped with mechanical stirrer, thermometer and reflux condenser. The mixture of palm oil and formic acid was heated and stirred continuously (900 rpm) using a magnetic stirrer. Hydrogen peroxide was slowly added. At the end of the reaction, the heating was stopped and the product was neutralized with sodium hydrogen carbonate solution (5%) and added with sodium chloride solution (5%) and distilled water. The product was kept overnight with the addition anhydrous sodium sulphate to remove water. Then, the product was filtered using Whatmann No. 1 filter paper.

Characterization of Palm Oil and Epoxidized Palm Oil

The unsaturation of PO was determined by iodin value (IV) test using Wijs method according to Kuntom et al. [31]. Oxirane oxygen content (OOC) was determined according to the AOCS Analysis Method Cd 9-57 [32]. Fatty acid and triacylglycerol compositions in PO were analyzed by Gas Chromatography equipped with a Flame Ionization Detector (GC-FID- Shimadzu 17A) and High Performance Liquid Chromatography (HPLC- Waters 1515). The PO and EPO structures were validated using Fourier Transformation Infra-red (FTIR) and

proton and carbon Nuclear Magnetic Resonance (¹H-NMR and ¹³C-NMR). FTIR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer in the range of 400-4000 cm⁻¹. ¹H and ¹³C-NMR spectra were recorded on a JEOL-ECP 400 spectrometer (400 MHz ¹H/100.61 MHz ¹³C), using CDCl₃ as solvent. All physicochemical properties analyses were performed according to standard methods for pour point, flash point, oxidative stability and viscosity index.

RESULTS AND DISCUSSION

Palm oil (PO) is golden yellow and exists in semi-solid form at room temperature. The liquid fraction contains unsaturated triacylglycerol (TAG), whereas the solid fraction contains more saturated TAG. The epoxidation process is more likely to occur in unsaturated TAG.

TAG and fatty acid composition analyses were performed to determine their main compositions in PO. Table 2 shows that the main TAG in PO are POP (39.89%), followed by POO (26.69%), PLP (7.43%), PLO (7.34%) and other TAGs. POP and POO show higher percentages because palmitic acid and oleic acid are the main fatty acids in PO. It is evidenced by the fatty acid composition shown in Table 3. The main fatty acid compositions of PO are oleic acid with 44.8%, followed by palmitic acid (41.9%), linoleic acid (9.1%), stearic acid (3.6%) and myristic acid (0.6%). The composition of fatty acids in PO is close to the value of PO fatty acid composition reported by Chowdhury et al. [33]. PO contains a high percentage of unsaturated fatty acids (53.9%), which serves as a good starting material for the epoxidation process.

Triacylglycerol Percentage (%) Free fatty acid 7.03 Monoacylglycerol + Diacylglycerol 2.88 1-oleoyl-2,3-dilinoleoyl-glycerol (OLL) 0.04 1-palmitoyl-2,3-dilinoleoyl-glycerol (PLL) 0.68 1-miristoyl-2-linoleoyl-3-palmitoyl-glycerol (MLP) 0.07 1,3-dioleoyl-2-linoleoyl-glycerol (OLO) 0.45 1-palmitoyl-2-linoleoyl-3-oleoyl-glycerol (PLO) 7.34 1,3-dipalmitoyl-2-linoleoyl-glycerol (PLP) 7.43 1,2,3-tri-oleoyl-glycerol (OOO) 1.55 1-palmitoyl-2,3-dioleoyl-glycerol (POO) 26.69 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) 39.89 1,2,3-tri-palmitoyl-glycerol (PPP) 3.11 1-sterioyl-2,3-dioleoyl-glycerol (SOO) 0.61 1-palmitoyl-2-oleoyl-3-sterioyl-glycerol (POS) 1.99 1,2-dipalmitoyl-3-sterioyl-glycerol (PPS) 0.24

Table 2. Triacylgycerol composition (percentage) of palm oil.

Fatty acid	Percentage (%)
Myristic acid (C14)	0.6
Palmitic acid (C16)	41.9
Stearic acid (C18)	3.6
Oleic acid (C18:1)	44.8
Linoleic acid (C18:2)	9.1
∑Saturated fatty acid	46.1
\sum Unsaturated fatty acid	53.9

Table 3. Fatty acid composition (percentage) of palm oil.

$HCOOH + H_2O_2 \longrightarrow HCOOOH + H_2O$

Figure 2. The performic acid generation reaction.

In epoxidation reaction, hydrogen peroxide acts as an oxygen donor, while formic acid acts as an oxygen carrier and regenerates once epoxidation reaction has occurred [12]. Formic acid also participates in the overall reaction as a catalyst in the formation of oxirane ring and as a reactant in the hydrolysis of the oxirane ring. To achieve maximum oxirane oxygen content, formic acid level should be such that both effects are balanced [13,20]. Epoxidation of palm oil is performed using *in situ*generated performic acid (HCOOOH), which is produced by mixing formic acid (HCOOH) and hydrogen peroxide (H₂O₂). The performic acid generation reaction is given in Figure 2.

The epoxidation process involving the mechanism of electrophilic addition is shown in Figure 3. Peroxyacid transfers an oxygen atom to the alkene with syn stereochemistry - both C-O bonds form on the same face of double bond through a one-step mechanism without intermediates. The farthest oxygen atom from the carbonyl group is the one transferred. Peroxyacid is commonly used as epoxidizing agent. It has an extra oxygen atom between the carbonyl group and its acidic hydrogen, and is electrophilic at oxygen. Attack at this position by a nucleophile displaces carboxylate, which is a good leaving group. The mechanism is essentially an

electrophilic attack, with a proton being transferred from the epoxide oxygen to the carboxylic acid byproduct. Firstly, the nucleophilic π bond donates its electrons to the oxygen, breaking the O-O bond to form a new carbonyl bond. The electrons from the old O-H bond form a new C-O bond and the original carbonyl group uses its electrons to pick up the proton. The transition state of the reaction makes the bond formation and bond breaking processes much clearer [34].

The results of the epoxidation of palm oil are shown in Table 4. The average percentage yield of epoxidation is 86% (w/w). The epoxidation process can be monitored through IV and OOC values. IV should be as small as possible after epoxidation while OOC should be as large as possible. There is a difference between IV before and after epoxidation. The initial IV of palm oil before epoxidation was 57.8 m/g while the IV for EPO after epoxidation was low, approaching zero (0.09 mg/g). EPO showed a high OOC value (3.46%) with 99.43% of relative conversion oxirane (RCO). The theoretical value of OOC is 3.48% as reported by Nurazira [35]. This means that almost all unsaturated fatty acids in PO were epoxidized and converted to oxirane rings to produce EPO.

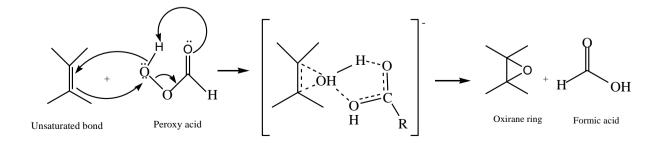


Figure 3. The mechanism of epoxidation reaction.

Compound	PO	EPO
Yield (%)	0	86
Iodin value (mg/g)	57.8	0.09
OOC value (%)	0	3.46
RCO (%)	0	99.43

Table 4. Analysis results for epoxidation of PO.

Epoxide Identification and Characterization

FTIR spectroscopy was performed to identify and validate the presence of oxirane ring in EPO. Figure 4 shows the comparison between FTIR spectra of PO and EPO. The disappearance of double bond functional group (C=C) peak at 3005 cm⁻¹ and weak peak (HC=CH) at 1500-1750 cm⁻¹, which initially present in PO spectrum indicates the conversion of double bond to epoxy group. This can be proven by the presence of C-O-C oxirane peak at 843 cm⁻¹ in EPO spectrum. Pavia et al. [36] reported that the presence of epoxy group can be monitored at wavenumber range of 815-950 cm⁻¹ that corresponds well to this study.

The comparison of ¹H and ¹³C-NMR spectra between PO and EPO is shown in Figure 5 and 6. In Figure 5(a), the signal at 5.34 ppm corresponds to the vinyl proton (-CH=CH-), while the signal at 2.00 -2.05 ppm indicates the presence of allylic proton (C=C-C-H), both represent the peak of the double bond in PO. In EPO spectrum (Figure 5(b)), it can be seen clearly that there is a disappearance of both peaks (double bond), while new peaks appear at 2.89 ppm, that corresponds to the CH protons attached to the oxygen atom (-CHOCH-) and at 1.49 ppm, that corresponds to the epoxy protons (-CH₂-CHOCH- CH_2). The results indicate that the double bond in PO was converted to the epoxy group during the epoxidation reaction. Analysis of ¹³C-NMR (Figure 6(a)) showed that the peaks at 127.85-130.17 ppm represent double bond (C=C). The conversion of double bond to oxirane ring can be evidenced by the disappearance of double bond peaks and the presence of epoxy carbon peaks (C-O) at 54.19-57.22 ppm (Figure 6(b)).

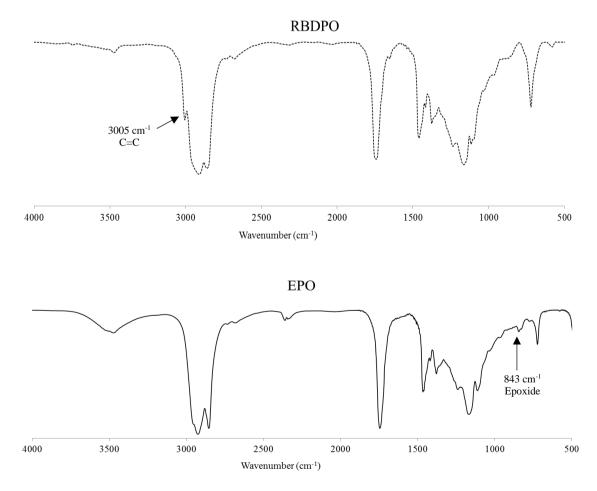


Figure 4. FTIR spectra of PO and EPO.

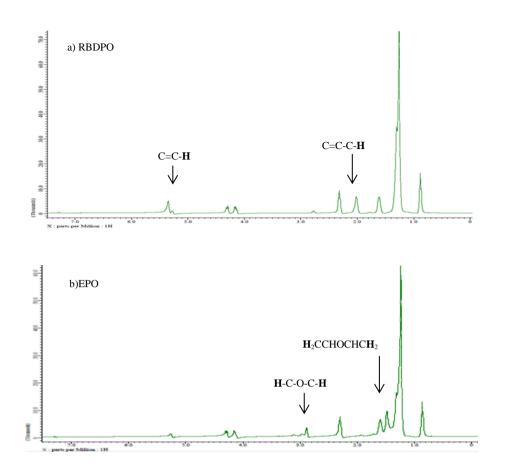


Figure 5. ¹H-NMR spectra for (a) PO; and (b) EPO.

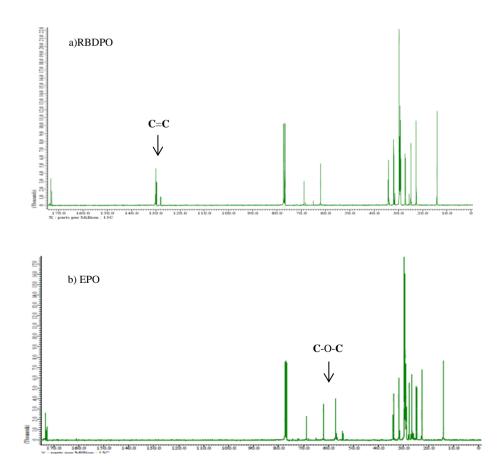


Figure 6. ¹³C-NMR spectra for (a) PO; and (b) EPO.

Physicochemical Properties of Epoxidized Palm Oil

There were several tests that have been conducted to determine the physicochemical properties of PO and EPO. The results are summarized in Table 5. The ability of a substance to withstand oxidative degradation is an important property of industrial fluid. Oxidative stability is determined by onset temperature (OT) using Differential Scanning Calorimetry (DSC). OT is the temperature at which a rapid increase in the rate of oxidation is observed at a constant, high pressure (200 psi). A high OT would suggest high oxidation stability of the material [37]. In this study, there was an increase in oxidative stability of EPO (190°C) compared to PO (181°C). This is due to the conversion of double bond to epoxy which reduces the amount of unsaturated fatty acids. The removal of hydrogen atoms from the methyl group adjacent to the double bond will form free radicals. These free radicals can easily react with oxygen to form peroxy radicals. Peroxy radicals attack other fat molecules to remove one of their hydrogen atoms and form other hydroperoxides and free radicals. This condition will double the oxidation process [38]. The rate of oxidation process can be attributed to the amount of unsaturated fatty acids in its composition [39]. Therefore, reduction of the double bond content via epoxidation will enhance the oxidative stability of the oil.

Pour point is one of the important quality parameters to determine cold flow properties of the fluid. EPO showed higher pour point $(18^{\circ}C)$ compared to PO (7°C) due to the reduction of double bond in oil structure. The result shows that unsaturated carbons play an important role in decreasing pour point. Another important factor in assessing the performance of industrial fluids is flash point [37, 40]. Flash point refers to both flammable oils and combustible oils. Fluids with a flash point less than $43^{\circ}C$ are flammable, while those with a flash point above this temperature are combustible [37]. Both PO and EPO have high flash point is very important to ensure fluid is not burned in the engine during operation.

Viscosity is also an important factor influencing fluid efficiency in reducing friction and wear [37]. In this study, the viscosity of PO is lower than EPO due to the existence of double bonds which give liquid lubrication properties by a degree of unsaturation. The viscosity of EPO is in the middle range. Generally, the least viscous fluid that still forces both moving surfaces is required [37]. If the fluid is too thin, the surfaces will rub and friction will increase, while if the fluid is too viscous, the surfaces will need a large amount of energy to move [37]. Increasing the temperature will reduce the viscosity. It can be observed when temperature rose from 40°C to 100°C for both fluids. Viscosity index shows the change of viscosity with temperature variation. The best fluid is a fluid that has a high viscosity index and does not change in viscosity over the temperature range and therefore works well [37]. EPO showed a high viscosity index. This shows that the viscosity of EPO is less affected by temperature change and does not drastically change as temperature changes. This is a good indicator and is suitable for use in large temperature ranges.

CONCLUSION

Epoxidized palm oil (EPO) was successfully synthesized with high yield (86%) and high oxirane conversion (99.43%). The OOC value (3.46%) is close to the theoretical value (3.48%). There is an increase in the oxidative stability, flash point and viscosity index of EPO which makes EPO plausible to be used as industrial fluid.

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Fluid	РО	EPO
Oxidative stability (°C)	181	190 °C
Pour point (°C)	7	18
Kinematic viscosity at 40°C (cSt)	56.97	97.72
Kinematic viscosity at 100°C (cSt)	9.24	14.56
Viscosity index (VI)	130	133
Flash point (°C)	240°C	255°C

Table 5. Physicochemical properties of PO and EPO.

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