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PREPARATION OF EPOXIDIZED PALM OLEIN AS RENEWABLE MATERIAL BY USING PEROXY ACIDS

(Penyediaan Minyak Sawit Olein Terepoksida Sebagai Bahan Keterbaharuan Menggunakan Asid Peroksi)

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Abstract

Epoxidized palm olein (EPO_o) was prepared through generated *in situ* of performic acid (HCOOOH), and peracetic acid (CH_3COOOH) as epoxidation agent with the presence of sulphuric acid (H_2SO_4) 3 % v/wt as catalyst. Formic acid (HCOOH) or acetic acid (CH_3COOH) as oxygen carrier and hydrogen peroxide (H_2O_2) as oxygen donor in the reaction system. Highly conversion (95.5 %) of oxirane ringwas obtained by usingperformicacid as epoxidation agent at 150 minutes of reaction time. The reaction yield was 90 % by weight. EPO_o has showed good physicochemical properties as renewable material for industrial applications. Carbon (^{13}C-NMR) and proton (^{1}H-NMR) spectra showed the present of epoxy profile at 54 ppm and 2.9 ppm. Epoxy group was detected on 844 cm^{-1} byfourier transformation infra-red (FTIR) spectra.

Keywords: epoxidation, palm olein, *in-situ*, peroxy acid, renewable material

Abstrak

Minyak sawit olein terepoksida (EPO_o) disediakan melalui proses pengepoksidaan secara *in situ* menggunakan asid performik (HCOOOH), asid perasetik (CH_3COOOH) sebagai agen pengepoksidaan dengan kehadiran mangkin asid sulfurik (H_2SO_4) 3 % v/wt. Asid formik (HCOOH) atau asid asetik (CH_3COOH) sebagai pembawa oksigen dan hydrogen peroksida (H_2O_2) sebagai penderma oksigen dalam sistem tindak balas. Peratus penukaran gelang oksirana yang tinggi (95.5 %) diperolehi dengan menggunakan asid performik pada 150 minit tindak balas. Peratus hasil tindak balas adalah sebanyak 90 % berdasarkan berat. EPO_o telah menunjukan sifat fiziko kimia yang baik sebagai bahan keterbaharuan untuk aplikasi industri. Spektrum karbon (^{13}C-NMR) dan proton (^{1}H-NMR) menunjukan kehadiran profil epoksi pada 54 ppm dan 2.9 ppm. Kumpulan epoksi dikesan pada nombor gelombang 844 cm^{-1} dengan merujuk spektrum transformasi fourier inframerah (FTIR).

Kata kunci: pengepoksidaan, minyak sawit olein, *in-situ*, asid peroksi, bahan keterbaharuan

Introduction

Over the last decade, world concern about utilizing of renewable sources in product synthesis. Fats and oils are renewable resources that can be chemically or enzymatically treated to produce materials that can often act as a replacement for materials derived from petroleum [1]. Among of chemical modifications of polyolefins, epoxidation is a simple and efficient method for introducing a new reactive group and useful properties and wide use in a variety of applications [2]. Epoxidized oils have a high commercial importance and are widely utilized in plastics manufacture, lubricants, detergents, and as intermediates in chemical reactions [1 - 6]. Epoxidized oil has been used widely as stabilizer and plasticizer in polyvinylchloride (PVC). Epoxidized ester can be used as solvent to replace the volatile organic solvent in paints. It also has been studied actively for lubricant production through the reaction of the epoxy group with linear or branching chain [7]. Epoxidized oil with higher oxirane oxygen value and lower iodine value is considered to be of better quality [8, 9]. There are four known technologies to produce epoxides from olefinic type of molecules[1]: (a) epoxidation with per carboxylic acids [10], the most widely used in industry, can be catalyzed by acids or by enzymes [11,12]; (b) epoxidation with organic and inorganic peroxides which includes alkaline and nitrile hydrogen peroxides epoxidation as well as transition metal catalysedepoxidation [13]; (c) epoxidation with halohydrins using hypochalous acids (HOX) and their salts as reagents for the epoxidation of olefins with electron deficient double bonds [10]; and (d) epoxidation with molecular oxygen [10]. Epoxidation methods vary from case to case depending on the nature of reactants and catalyst used for epoxidation[14].

Palm olein (PO_o) is a vegetable oil and liquid fraction of palm oil (the largest renewable resources in Malaysia), consists of mainly mono-unsaturated triacylglycerol (TAG), POP (42.8 %) and di-unsaturated TAG, POO (35.7 %). The iodine value of PO_o is about 51.0 – 61.0 [15]. The present of 40.0 % oleic acid in the PO_o [16] is widely open for further reaction such as epoxidation process. Despite the development of many new oxidation procedures, the use of peroxy acids still constitutes a useful synthetic procedure for the epoxidation of alkenes on a laboratory scale. In the laboratory, epoxides are prepared by treatment of an alkene with a peroxy acid (RCO_3H). Commonly epoxidation reactions are carried out using a peroxy acid such as performic and peracetic, either preformed or formed *in situ*, by reacting a carboxylic acid as oxygen carrier with concentrated hydrogen peroxide (H_2O_2) as oxygen donor. Formic acid is preferred than acetic acid as oxygen carrier since, owing to its high reactivity, no catalyst is required in the formation of performic acid, but the production costs increase because formic acid's price is frequently higher than acetic acid's price [17].

Comparison between performic and peracetic acid as epoxidation agent on PO_o are not yet been studied. Kinetic study on the epoxidation and oxirane cleavage of methyl ester palm olein (MEPO) by using performic acid generated *in situ* as catalyst has been reported [5]. Performic acid has been used in the epoxidation process on fatty acid methyl ester (FAME) of soybean [18]. High epoxidation yield was obtained at 40 ^oC with using high concentration of hydrogen peroxide (60 wt. %). A study on partial and fully epoxidation of plant oils with perhydrolysis lipase as catalyst has been reported [19]. Epoxidation of unsaturated plant oils conducted in industrial process by Prileshajev-epoxidation using short chain peroxy acid generated *in situ*. Novozym ® 435 and hydrogen peroxide have been used to epoxidize the unsaturated plant oils and over than 90 % of conversion was obtained [19].

In this paper, we discuss the preparation of epoxidized palm olein (EPO_o) by using three different approaches and the physicochemical properties of the product.

Materials and Methods

Raw Materials

Palm olein (Seri Murni brand, FFM Marketing Sdn. Bhd.) was used as raw material. Formic acid (HCOOH) (99 %) and glacial acetic acid (CH_3COOH) (100 %)were purchased from Univar and Bendosen. While, hydrogen peroxide (H_2O_2) (30 %) from J. T. Baker.

Production of Epoxidized Palm Olein

Epoxidized Palm Olein (EPO_o) was produced by using generated *in situ* peroxy acid with a constant molar ratioof PO_o:HCOOH/CH_3COOH:H_2O_2 (1:5:4 mole/mole) under continuous magnetic stirring at constant temperature (45 ^oC) [20].The reaction was carried out in a three necked glass (250 ml capacity) flask equipped with thermometer and reflux condenser. Generated *in* situ peroxy acid is produced by mixing formic acid (HCOOH) or acetic acid (CH_3COOH) with H_2O_2 simultaneously. Hydrogen peroxide was slowly added drop wise into the acidic media. Fast introduction to this reagent will cause an excessive development of oxygen due to the decomposition of H_2O_2 at high temperature and is not recommended [2]. After the reaction finished, samples of reaction mixture were taken out and thoroughly washed with sodium bicarbonate (5 wt%), distilled water and sodium chloride (5 wt%) to separate the organic layer from the mixture. The sample was then analyzed for oxirane oxygen content (OOC) value and the percentage of oxirane conversion was calculated.

Determination of oxirane oxygen content

Oxirane oxygen content (OOC) value was determined by direct method using hydrobromic acid solution in glacialaceic acid (AOCS Cd 9-57) [21,22]. The percentage of conversion can be calculated based on the theoretical

OOC value of PO_o [1,16]. From the oxirane content values, the relative percentage conversion to oxirane was calculated using the Equation 1:

$$\text{Relative percentage conversion to oxirane} = (OOC_{exp} / OOC_{the}) \text{ x } 100 \qquad \text{(Eq .1)}$$

where OOC_{exp} (g/100 g sample) is the experimentally obtained oxirane oxygen and OO_{the} is the theoretically obtainable maximum oxirane oxygen, which was determined from the Eq. 2:

$$OO_t = \{(IV_0/A_i) / [100 + (IV_0/2A_i)\, A0]\} \text{ x } A_0 \text{ x } 100 \qquad \text{(Eq. 2)}$$

where A_i (126.9) and A_o (16.0) are the atomic weights of iodineand oxygen respectively and IV_0 is the initial iodine value of oil sample.

Detection tests

FTIR spectrometer (GX model) was used to detect the present of epoxide group by using the NaCl salt window method. Epoxide group can be detected at wavenumber 750 - 880 cm^{-1} and 815 - 950 cm^{-1} [23]. 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 ($CDCl_3$) as a solvent [11].

Characterisation tests

Physicochemical tests were carried out to analyze the iodine value, oxidative stability [4], flash and fire point, pour point (ASTM D 97-66) [15], kinematic viscosity at 40 ^oC and 100 ^oC (ASTM D 445- 79) [15] and viscosity index (ASTM D2270) [13].

Results and Discussion

Epoxidation of palm olein (PO_o) was carried out by using generated *in situ* performic acid (HCOOOH) and a peracetic acid (CH_3COOOH). They prepared by mixing of formic acid (HCOOH) and acetic acid as oxygen carrier and hydrogen peroxide (H_2O_2) as oxygen donor [24]. Generation reaction of peracid are given in Figure 1.

$$HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O$$

$$CH_3COOH + H_2O_2 \rightleftharpoons CH_3COOOH + H_2O$$

Figure 1. Generation reaction of performic acid (HCOOOH) and a peracetic acid (CH_3COOOH)

Preparation HCOOOH and CH_3COOOH as epoxidation agents were carried out as *in situ* since the reaction condition is highly exothermic and not stable. The epoxidation process involved of electrophilic addition mechanism as Figure 2. Unsaturated bond at triacylglycerol (TAG) PO_o was converted to oxirane ring to produce epoxidized palm olein (EPO_o) [24]. Peroxy-acids are commonly used epoxidizing agents. They have an extra oxygen atom between the carbonyl group and their acidic hydrogen, and are electrophilic at oxygen. Attack at this position by a nucleophile displaces carboxylate, which is a good leaving group. An example of one such reaction is shown below involving ethylene and peroxyformic acid. The mechanism is essentially an electrophilic attack, with a proton being transferred from the epoxide oxygen to the carboxylic acid by-product. Firstly the nucleophilic π bond donates its electrons to the oxygen, breaking the O-O bond to form the new carbonyl bond. The electrons from the old O-H bond make up the second new C-O bond, and the original carbonyl group uses its electrons to pick up the proton. The transition state for the reaction makes the bond-forming and bond-breaking processes much clearer.

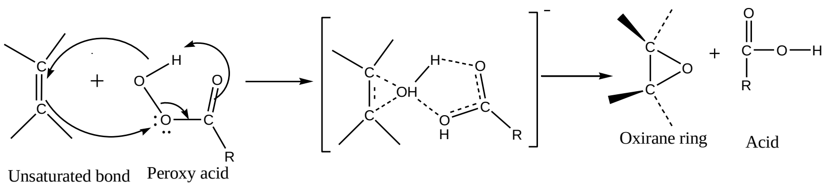

Figure 2. Mechanism for oxirane formation

Based on Figure 3, by introducing acid catalyst in the epoxidation system, it seems to give a high OOC value in a short period (30 minutes) but at the same time, the oxirane cleavage rapidly occur, then, the OOC value will decrease along with the reaction time. The epoxidation process was exothermic and high concentration of peroxy acid must be avoided [7]. Besides, the epoxidation process by using peracetic acid just only gave OOC value below 1.00 %. CH_3COOOH is not an effective epoxidation agent compared to the HCOOOH. HCOOH is better than CH_3COOH for this work because, when reacted with H_2O_2, HCOOOH forms at a much faster rate than CH_3COOOH [25,26,4]. The optimum oxirane oxygen content (OOC) value obtained was 3.57 % (± 2.8) compared to the theoretical OOC value was 3.74 % [13]. The optimum oxirane conversion was 95.5 % with 90.0 % yield. Table 1 shows the physicochemical properties of EPO_o. It has good properties on oxidative stability (193.9 ^oC), flash and fire points (> 320 ^oC), and kinematic viscosity.

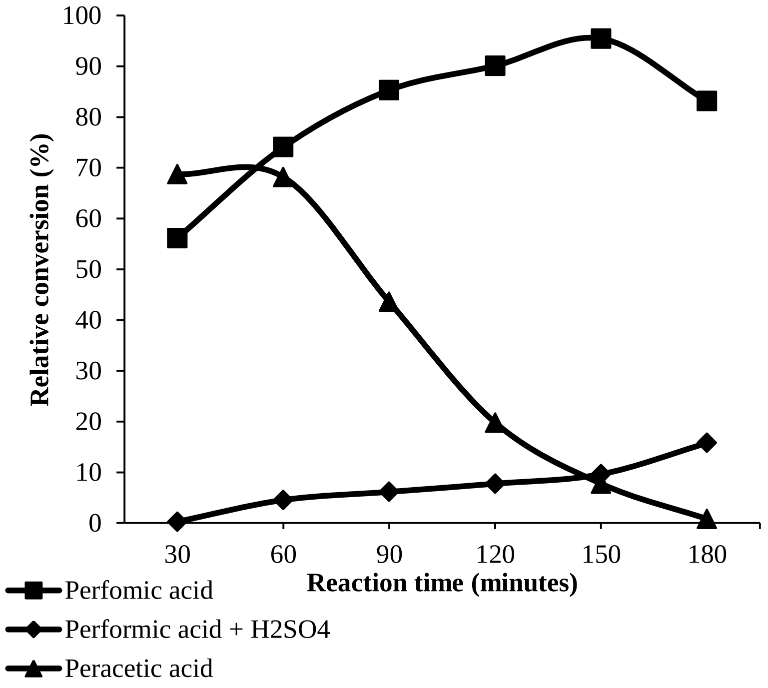

Figure 3. Relative conversion of EPO_o

Table 1. Physicochemical properties of EPO_o

Characterization	**Unit**	**EPO_o**
Oxidative stability	^oC	193.9
Flash point	^oC	> 320
Fire point	^oC	> 320
Pour point	^oC	16
Kinematic viscosity, 40 ^oC	cSt	158.6
Kinematic viscosity, 100 ^oC	cSt	19.8
Viscosity index	-	144
Physical state (Room temperature)	-	Semi solid
Percentage of conversion	%	95.5
Yield	%	90

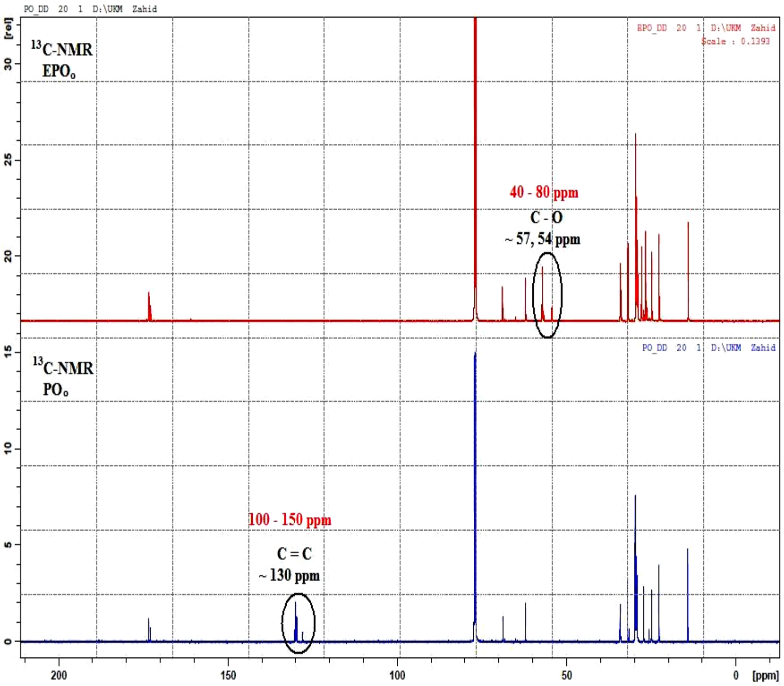

Figure 4. Comparison ^{13}C-NMR spectra between PO_o and EPO_o

The present of oxirane ring of EPO_o proved by ^{13}C-NMR and ^{1}H-NMR spectra. Based on Figures 4 and 5, the presents of oxirane ring can be confirmed with the theoretical ^{13}C and ^{1}H chemical shift ranges (ppm). ^{13}C chemical shift ranges for unsaturated bond was 100 - 150 ppm while for C - O was 40 - 80 ppm. ^{1}H chemical shift ranges for vinyl hydrogen (C=C–H) was 4.5 - 6.5 ppm and for allyic hydrogen (C=C–C–H) was 1.6 - 2.6 ppm while for epoxide ring appeared in the range 2.5 - 3.5 ppm [23]. Based on comparison between PO_o and EPO_o FTIR (Figure 6), the spectrum of PO_o showed an overtone streching vibration peak of C=O for ester at wavenumber 3473 cm^{-1}, streching vibration peak of =CH (3003 cm^{-1}) and unsaturation peak of HC=CH (cis) at wavenumber 1651 cm^{-1}. While, for the FTIR spectrum of EPO_o, the unsaturation peak and streching vibration peak of =CH for PO_o have been disappeared. But the presents of oxirane ring peak was detected at wavenumber 844 cm^{-1}. Theoretical [27] explained that oxirane ring can be detected at wavenumber 750 – 880 cm^{-1} and 815 – 950 cm^{-1}, while overtone streching vibration peak of C=O for ester at wavenumber ~3450 cm^{-1}, streching vibration peak of =CH can be detected at wavenumber 3050 – 3000 cm^{-1} and bonding peak of HC=CH (cis) at wavenumber 1650 – 1600 cm^{-1}. Based on Figure6, FTIR spectrum of PO$_o$ showed an overtone streching vibration peak of C=O for ester at wavenumber 3473 cm^{-1}, streching vibration peak of =CH (3003 cm^{-1}) and unsaturation peak of HC=CH (cis) at wavenumber 1651 cm^{-1}. While, for the FTIR spectrum of EPO$_o$, the unsaturation peak and streching vibration peak of =CH for PO$_o$ have been disappeared. But the presents of oxirane ring peak was detected at wavenumber 844 cm^{-1}.

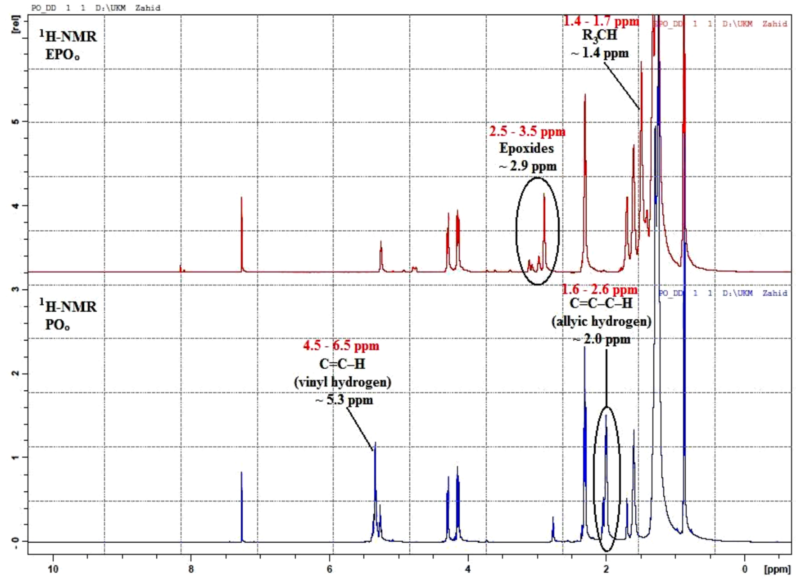

Figure 5. Comparison ^{1}H-NMR spectra between PO$_o$ and EPO$_o$

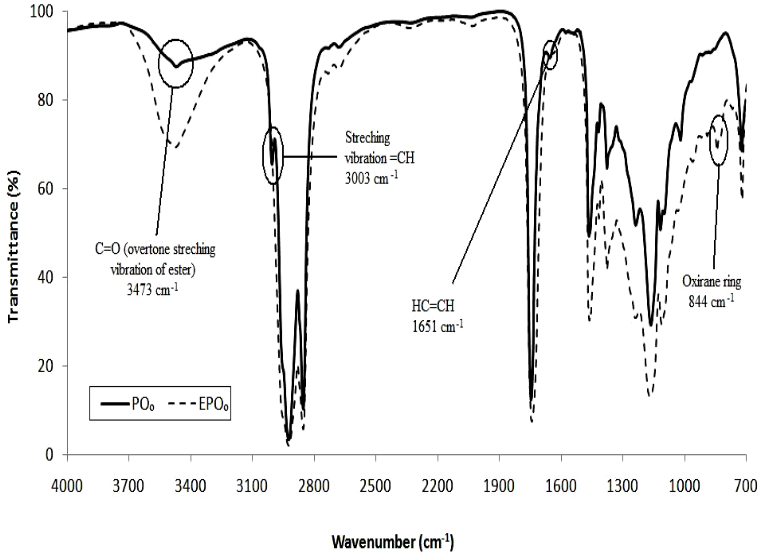

Figure 6. Comparison FTIR spectra between PO$_o$ and EPO$_o$

Conclusion

Epoxidized palm olein is successfully produced by using peroxy acids. Performic acid is the best epoxidation agent for epoxidation process on palm olein. The presence of epoxide was proved by ^{13}C, ^{1}H-NMR and FTIR spectra. EPO$_o$ is potentially to be used as renewable material in synthesis process, coating, biolubricant, plasticizer and polymer industry.

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