

Synthesis and characterization of palm oleic acid based polyester for bioplastic applications

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Abstract

Oleic acid (OA) is a monounsaturated fatty acid and natural constituent of a number of foods, particularly plant oils. In this work, palm OA epoxidation was performed using formic acid and hydrogen peroxide. The epoxidation of OA showed that the relative conversion of oxirane oxygen (RCO) 97.4% with 85.3 % yield. The FTIR spectrum of epoxide oleic acid (EOA) clearly showed the signals at 1701 and 845 cm^{-1} attributed to C=O (carboxylic acid) and oxirane ring groups, respectively. The ^1H and ^{13}C NMR analysis showed the chemical shift of (-CH-O-CH-) group at 2.93 and the 54.30-57.40 ppm, respectively, for EOA. The bioplastic polyester was prepared from EOA as monomer through the polycondensation polymerization at 120 °C with different polymerization times (6, 12, 18, 24 and 30 hr). The synthesized bioplastic polyester showed about 97 % yield. The FTIR spectra showed the peaks of C=O and C-O of ester carbonyl group appeared at 1735 cm^{-1} and 1244 cm^{-1} respectively. The ^1H NMR showed the proton ester group -COO-CH- an appeared at 4.7 ppm while the ^{13}C NMR showed C=O ester appeared at 173.79 ppm. The molecular weights of bioplastic polyester were between 1963 g/mol to 5501 g/mol and having a glass transition of -19 °C. The thermal degradations of the bioplastic polyester occurred at temperatures higher than 328 °C. The synthesized bioplastic is plausible to be used as plastic wrapping material.

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1. Introduction

Oleic acid (*cis*-9-octadecenoic acid) is an omega-nine fatty acid, it is a prime example of a monounsaturated fatty acid (MUFA). OA is the most widely distributed of all the natural fatty acids and present in practically all lipids. It is the main fatty acid in olive oil pressed from the ripe fruit of the olive (*Olea europaea*). OA makes up 55-80% of olive oil, 15-20% of grape seed oil and sea buckthorn oil [1]. In general, edible oils such as soybean oil, palm oil and corn oil contain about 10-40% OA. Among them, olive oil contains 75% OA which is more than 5 times higher than safflower oil. OA is best obtained from a plant and a useful starting material especially. It is considered one of the healthier sources of fat in the diet and commonly used as a replacement for animal fat sources that are high in saturated fat [2]. OA is a major component of the Mediterranean diet, presents different properties that can be useful both in the immunomodulation, treatment and prevention of different types of disorders such as cardiovascular or autoimmune diseases, metabolic disturbances, skin injury and cancer, besides exerting prominent role in drug absorption [3]. Furthermore, OA is commonly made use of in several industrial applications that include oleate, lotions, a pharmaceutical solvent, cosmetic ointments, lubricating oils, and bioplastic [4]. The rapid industrial development witnessed over the years is largely dependent on the use of fossil materials, mainly coal and crude oil. This explains the extensive use of crude oil and coal in various areas of life, such as plastics, due to the relatively low prices. Plastics are used worldwide from drinking cups to various parts of automobiles and motorbikes. They are imperative to the trade market as well as the packaging of materials all over the world. However, they have been an environmental concern because of its prolonged rate of degradation. Furthermore, the crude oil and its derivatives are the most important raw materials for the oleochemical industry. Nevertheless, crude oil as a fossil source is depleting raw material. A few researches have introduced the use of animal fat and plant oils as feedstock for the synthesis of biodegradable polymers such as bioplastic in place of fossil source. Besides that, the produced polymer is a biodegradable, environmentally friendly, and substitute materials for polymers derived from petroleum resources [5]. According to the European Bioplastics Organization, bioplastics can be defined as biodegradable plastics or plastics produced from renewable feedstocks (biobased), such as starch, cellulose, plant oils and plant fats. They may or may not be biodegradable and some are only partially biobased that is they contain both renewable and fossil-fuel-based carbon. Both the amount of biobased constituents and the conditions under which these polymers biodegrade can vary widely. Depending upon the composition, degree of crystallinity, and environment, degradation times can range from several days to several years. Plant oils are renewable resources that can be chemically modified. They are cheap, and considered as a viable alternative to petroleum. Fatty acids (saturated and unsaturated) derived from plant oils are considered as raw materials for the production of biobased polymers [6]. Most plant oils are composed of a long fatty acid chain of 12-22 carbon atoms and up to three double bonds. These acids are considered as monomers for further polymerization via chemical modifications. Fatty acids are naturally occurring and can be obtained from plant oils and then chemically modified to be having readily hydrolysable bonds. Amongst the plant oils, crude palm oil (CPO) has been utilized for synthesis of diverse biodegradable polymers [7]. A substantial and near equal amount of saturated and unsaturated fatty acids at about 50% each in CPO, makes it unique amongst other plant oils. One of the most modern applications of CPO is the production of bioplastic, also referred to as polyhydroxyalkanoates (PHAs). PHAs are microbial storage of polyester, produced naturally with the use of various kinds of bacteria practices [7]. However, the production of bioplastic using chemical pathway and CPO as raw material has not reported comprehensively. The development of biodegradable bioplastics has gained a lot attention in recent years. Whether these new plastics will gain a significant market share will partly depend on how strongly society is committed to protect the environment, i.e. to reduce waste, and to conserve irreplaceable fossil fuels. Many obstacles such as high price and limited

production capacity have to be overcome before biobased and biodegradable polymers will gain a significant market share. The global market of biodegradable plastics is to reach ca. \$3.5 billion by 2022, growing at Compound Annual Growth Rate (CAGR) of approx. 11.5 % [8]. The main objective of this work was the preparation and characterization of oleic-acid-based bioplastic from Malaysian high free fatty acid crude palm oil (HFFA-CPO).

2. Materials and methods

2.1. Materials

Malaysian high-FFA crude palm oil was obtained from a local refinery, Sime Darby, Sdn. Bhd, Carey Island, Selangor. The entire chemicals and solvents used in this study such as hydrogen peroxide 30%, formic acid 85.5 %, ethyl acetate, anhydrous sodium sulphate 99 % and tetrahydrofuran 99.5 % were analytical reagents and were used without additional purification.

2.2. Instrumentation

Calorimetric measurements of palm oleic acid based polyesters (POABP) were conducted using a differential scanning calorimetry (DSC) thermal analysis system in the range of -50 to 500 °C at a heating rate of 20 °C/min. The glass transition temperature (T_g) and decomposition temperature (T_d) were determined from the DSC thermogram of the second scan. The nuclear magnetic resonance analysis (NMR) for proton ^1H and ^{13}C (NMR) was carried out according to Gunstone et al. (2007) [9]. The spectra were recorded on a Bruker AV400111 (USA) 400 MHz at 30 °C. Tetramethylsilane (TMS) was used as an internal chemical shift reference. About 25 mg of sample was dissolved in 1 mL of deuterated chloroform (CDCl_3) in all experiments. Fourier transforms infrared spectroscopy (FTIR) was carried out according to Sherazi et al. (2009) [10]. FTIR spectra of the products were recorded (Perkin Elmer Spectrum GX spectrophotometer) in the range of 400–4000 cm^{-1} . A very thin film of sample was covered on NaCl cells (25 mm.d \times 4 mm thickness) was used for the analysis.

2.3. Epoxidation of palm OA

The epoxidation of OA to produce EOA was performed based on the studies by Nicolau et al. (2010) [11] and Jalil et al. (2014) [12]. OA (10 g) was poured into the three-necked glass. Under constant agitation, the OA was acidified with formic acid and hydrogen peroxide subsequently added in a dropwise motion. The molar ratio of hydrogen peroxide/formic acid/OA was set at 20:2:1. The reactor temperature was slowly elevated to 80 °C in order to complete the reaction. After 2 hr, the organic layer (containing the epoxide) was separated and mixed with ethyl acetate. The solution was rinsed three times with water to eliminate residual H_2O_2 . The water content was removed with anhydrous sodium sulphate, while the ethyl acetate was evaporated in a vacuum rotary evaporator at 45 °C. The resulting precipitate was obtained and recrystallized from ethanol to produce EOA as a whitish powdery solid. The iodine value (IV) and oxygen oxirane content (OOC) were calculated according to the AOCS (Cd 1-25) and (Cd 9-57) standard methods [13], respectively.

2.4. Synthesis of palm oleic acid based polyester (POABP)

POABP was prepared by heating the EOA at 120 °C for 6, 12, 18, 24 and 30 hr with magnetic stirring at 300 rpm. The polymer product was then cooled to room temperature.

2.5. Molecular weight (MW) determination

The MW of the POABP was determined at 35 °C using a gel permeation chromatography (Agilent 1200 GPC) system equipped with a refractive index detector and SHODEX K-802 and K-806M columns. The sample was prepared by

dissolving the polyester oleic acid (POA) in tetrahydrofuran (THF) at a concentration of 1 mg/mL. THF was used as the eluent at a flow rate of 1 mL/min. The weight-average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined from the elution curves obtained from this method.

3. Results and discussion

3.1. Synthesis of EOA

Epoxidized oils which are produced through the epoxidation of renewable materials, such as plant oils and their unsaturated fatty plant oils has recently garnered interest as a way of resolving environmental and economic issues. Furthermore, epoxidation of unsaturated fatty acids such as OA ($C_{18:1}$) has advantages for industrial applications such as plasticizers and plastic stabilizers. More specifically, EOA has been employed to manufacture adhesives, polymers, lubricants and plastics such as polyesters [14, 15]. There are several methods to epoxidize the double bonds of unsaturated fatty acids, such as epoxidation by conventional method, epoxidation using acid ion exchange, epoxidation using enzymes and epoxidation using metal catalyst [16]. In the epoxidation reaction of OA, the temperature reaction has been slowly raising from 60 to 80 °C to complete the reaction with low agitation speed of 350 rpm for 2 hr. The molar ratio of hydrogen peroxide, formic acid and OA was 20:2:1 respectively. In this reaction, a peracid from a short chain fatty acid such as formic acid as oxygen carrier with concentrated hydrogen peroxide as oxygen donor used for epoxidation of OA. Formic acid is preferred to acetic acid as oxygen carrier because, owing to its high reactivity, no catalyst is required in the formation of performic acid [17, 18]. The final EOA product was a white powdery-solid material. This is consistent with the study by Kozhevnikov et al. (1998) [19], who also suggested optimum reaction temperature range of 60-80 °C for epoxidation of OA. The results indicated that moderate epoxidation condition supports the formation of oxirane ring from OA. Abdullah and Salimon (2010) [20] also noted that epoxidation reaction carried out at higher temperature resulted in unwanted increase in the degree of oxirane ring cleavage to glycol and hence reduces the yield. The stirring speed of 350 rpm was also found to be adequate to overcome mass transfer resistance under the studied temperature range, as suggested by earlier studies [21]. Table 1 shows that the yield of EOA was 85.3 %, while the relative percentage conversion to oxirane (RCO %) was 97.40 %. The calculated IV showed a significant decrease from 91.88 for OA to 2.284 for EOA. This proves that the epoxidation process was effective.

Table 1. Physicochemical properties of EOA

Parameter	Values
Yield of EOA	85.3 %
OOCTheo of EOA	5.4751 %
OOCExp of EOA	5.333 %
RCO %	97.40 %
IV of EOA	2.284 g I ₂ /100g
IV of OA	91.88 g I ₂ /100g

Notes: OOCTheo = Theoretical oxirane oxygen content, OOCExp = Experimental oxirane oxygen content,

RCO % = Relative percentage conversion to oxirane, IV = Iodine value

3.2. Characterization analysis OA and EOA

FTIR spectra was used to comparatively analyze OA and EOA structures, the oxirane ring signal can be detected at 845 cm^{-1} while carboxylic acid carbonyl functional groups ($\text{C}=\text{O}$) absorption bands of OA and EOA are denoted by peaks at 1708 and 1703 cm^{-1} , respectively. The stretching vibration peak of $\text{C}=\text{C}$ for OA can be detected at 3008 cm^{-1}

¹. Peaks at 2927-2856 cm^{-1} indicate the $-\text{CH}_2-$ and $-\text{CH}_3$ scissoring of OA and EOA, as shown in Figure 1, while the absorption bands at 726 cm^{-1} indicate C-H vibration.

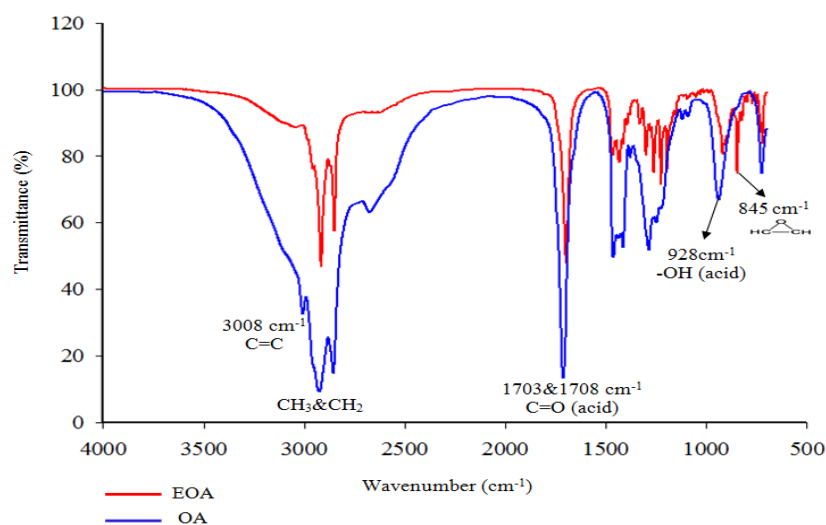


Figure 1. FTIR spectrum of OA and EOA

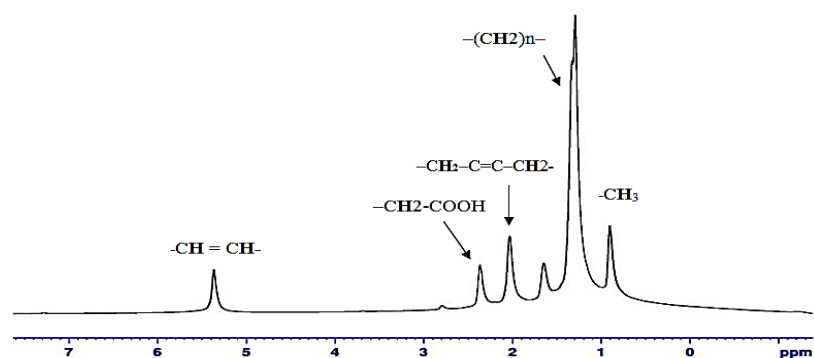


Figure 2. ^1H NMR spectrum of OA

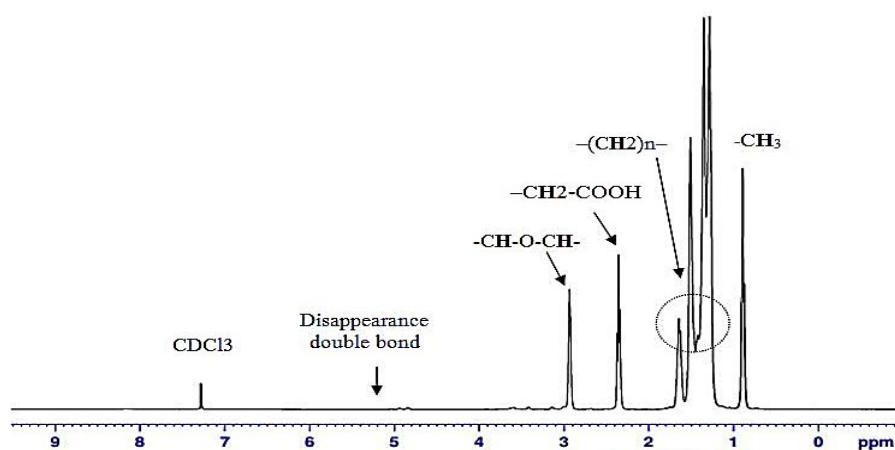


Figure 3. ^1H NMR spectrum of EOA

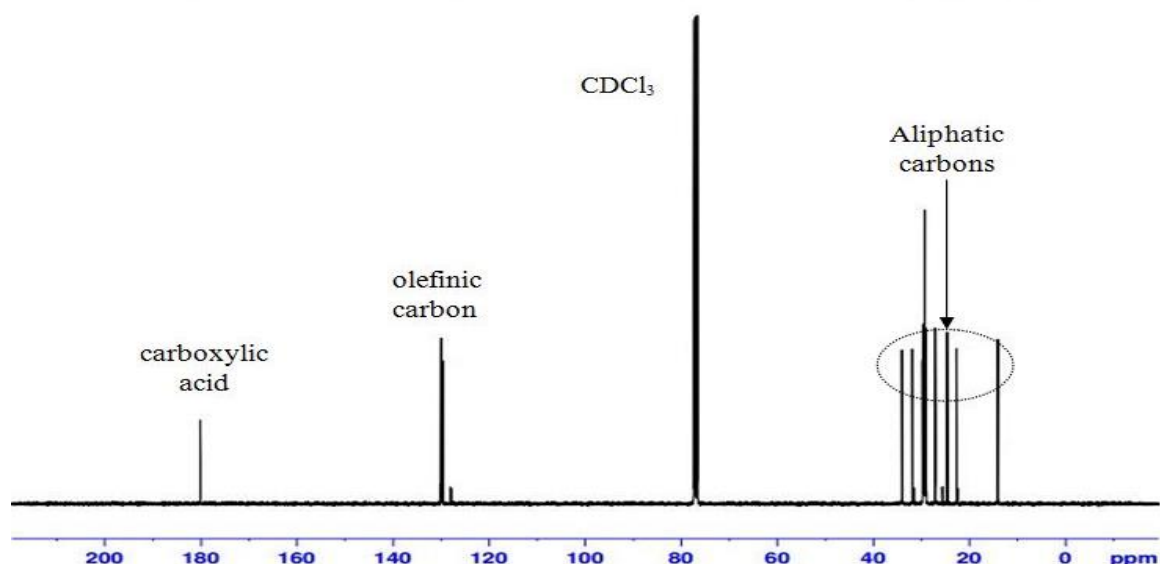


Figure 4. ^{13}C NMR spectrum of OA

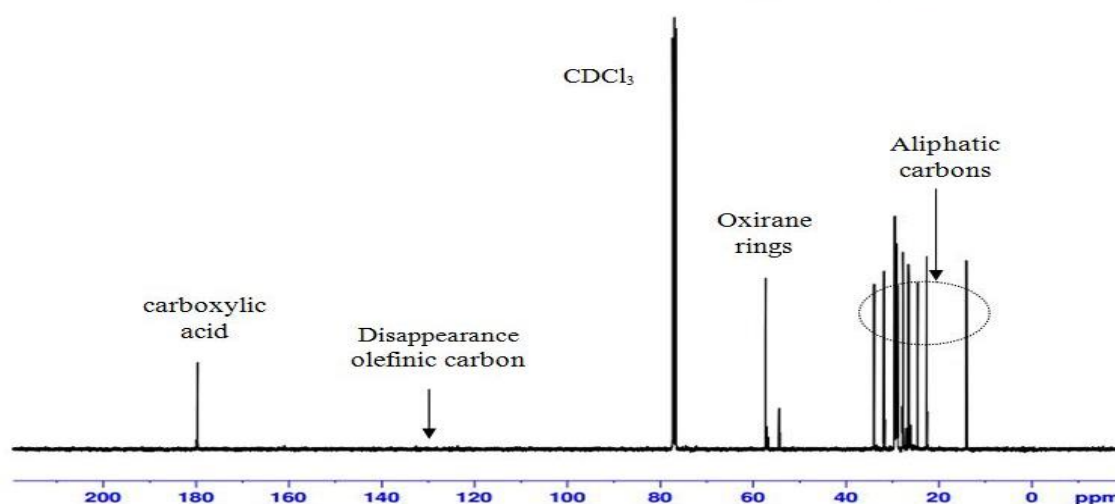


Figure 5. ^{13}C NMR spectrum of EOA

Typical ^1H NMR signals of OA and EOA appear in the region between 0.8 and 5.36 ppm as is shown in Figures 2 and 3, respectively. The ^1H NMR spectrum for the EOA show characteristic signal for $(-\text{CH}-\text{O}-\text{CH}-)$ group at 2.93 ppm. The signals at 0.9 ppm indicate terminal methyl group $(-\text{CH}_3)$ of OA, which also appear in EOA at 0.87- 0.88 ppm. However, the methylene proton signal $(-\text{CH}=\text{CH}-)$ were shifted at 5.36 ppm of OA, while they disappeared in EOA. The methylene groups were adjacent to one double bond $(-\text{CH}_2-\text{C}=\text{C}-)$ at 2.03 ppm of OA, while they also disappeared in EOA. The signal at 2.36 ppm of OA attribute to $-\text{CH}_2-\text{COOH}$ group, which also appear in EOA at 2.33-2.37 ppm. The signal at 7.28 ppm referred to CDCl_3 solvent. Furthermore, ^{13}C NMR spectra of OA and EOA are shown in Figures 4 and 5, respectively. The signal at 14.15 ppm indicates the carbon atom of terminal methyl group $(-\text{CH}_3)$ in OA, which also appears in EOA at 14.13 ppm. The carbon atoms of terminal methyl group $(-\text{CH}_2)$ identified by peaks at 22.6 - 34.07 ppm for OA, and 22.68-34.03 ppm of EOA, which are common for these kinds of compounds [11]. However, the signal at 180.20 ppm denote the carbon atom of carbonyl group $(\text{C}=\text{O})$ (carboxylic acid) of OA,

which also appears in the spectrum of EOA at 179.74 - 179.91 ppm. The other distinctive signal was at 129.75 - 130.24 ppm, which refers to the unsaturated carbon atoms (C=C) (olefinic carbon) in OA. On the other hand, the signal at 54.30 - 57.40 ppm confirm the presence of oxiran ring of EOA which indicates that the OA was converted to an EOA [22]. The signals at 76.72 - 77.36 ppm attribute to CDCl₃ solvent [11]

3.3. Synthesis of POABP

Polyesters comprise of a range of materials with different chemical structures and mechanical properties. Polyesters are extensively applied in laminates, industrial construction and installation, molding compounds, coatings, and adhesives [23]. There are several methods of synthesizing polyesters such as polycondensation of hydroxyl acids, diacid, and a diol, or by ring-opening polymerization of lactones [24]. This study synthesized POABP from the palm OA by heating the EOA monomer at 120 °C. The optimum reaction time was assessed by performing the synthesis in 6, 12, 18, 24 and 30 hr with magnetic stirring rate of 300 rpm. The synthesis process involves the reaction between the carboxyl and epoxy functional groups of the monomer. OA was first separated from high free fatty acids crude palm oil (CPO). The isolated OA was then reacted with hydrogen peroxide and formic acid via a process referred to as epoxidation to generate EOA, the temperature reaction has been slowly raising from 60 to 80 °C to complete the reaction with 350 rpm of agitation speed and in 2 hrs. The molar ratio of hydrogen peroxide: formic acid: OA was 20:2:1, respectively. Figure 6 shows the chemical formation pathway of POABP from EOA. A minimum of 97 % yield of synthesized POABP was achieved, as clearly shown in Table 2. In general it appears that polymerization from 6 to 12 hr, produced a viscous liquid of POABP, while longer polymerization duration produced an extremely solid POABP. In all five polymerization times selected in this study, it can be deduced that POABP will only solidify when the polymerization is performed for 18, 24 and 30 hr, as shown in Figure 7.

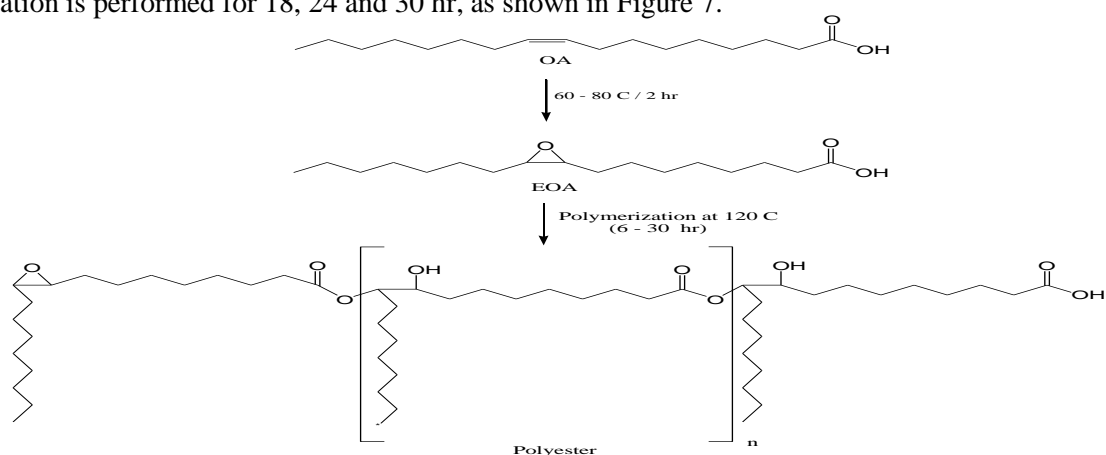


Figure 6. Synthesis reaction of POABP from palm OA



Figure 7. Final POABP synthesized products

3.4. Characterization analysis of POABP

The data from ¹H, ¹³C NMR and FTIR analysis offers insights on the chemical structure of the synthesized POABP. The thermal strength of POABP from palm OA was evaluated using differential scanning calorimetry (DSC). Evidently, each POABP produced from the five different polymerization times occupies different M_n. The molecular weight and polydispersity index values determined via gel permeation chromatography (GPC) are recorded in Tab 2.

3.4.1. Molecular weights determination

From the results of GPC, the polyester displayed the M_n values between 1810-2684 g/mol and M_w between 1963-5501 g/mol at 120 °C in 24 hr and 300 rpm for polyester. The polyester provided a range of 6–9 monomeric units, with maximum units observed at 18 and 24 hr. The M_w/M_n of the polyester ranged between 1.1 and 2.1. Table II shows calculation of number of monomeric units for polyester. The calculation number of monomeric units (M_n/M_0) was done through dividing M_n was done through dividing number average molecular weight (M_n) by the molecular weight of the monomer unit (M_0). The mass of the polyester monomer (EOA $C_{18}H_{34}O_3$) is first calculated: (18 carbon atoms \times 12 g/mol) + (34 hydrogen atoms \times 1 g/mol) + (3 oxygen atoms \times 16 g/mol) = 298 g/mol and M_n for polyester from GPC are shown in Table 2. Based on the data presented in Table 2, it can be inferred that the formation of high polyester M_n value is related to the duration of polymerization. Given the same reaction temperature of 120 °C, POABP required at least 18 hr to solidify. The highest polymerization time (18 hr) resulted in the highest M_n (2684 g/mol) with M_w/M_n (1.4). However, the solid polyester was insoluble in common organic solvents such as THF and chloroform because each EOA molecule contains only one carboxylic acid group, although, an oligomer chain of the epoxide has several existing hydroxyl side groups for the formation of branched polymers. Thus, the solidified product could be a mixture of linear and branched high molecular weight polyester.

3.4.2. Thermal properties analysis

Thermal behavior of the POABP was evaluated in the range of -50 to 500 °C using DSC in order to take advantage of possible emergence of transition peaks indicative of glass transition temperature and decomposition temperature simultaneously. The glass transition temperature (T_g) value of all samples were detected in the range of -19 to -20 °C, as shown in Figure 8. The decomposition temperature of POABA started between 328 and 343 °C, which was denoted as the degradation peak range of the polymers or the onset temperature, thereby termed decomposition temperature (T_d).

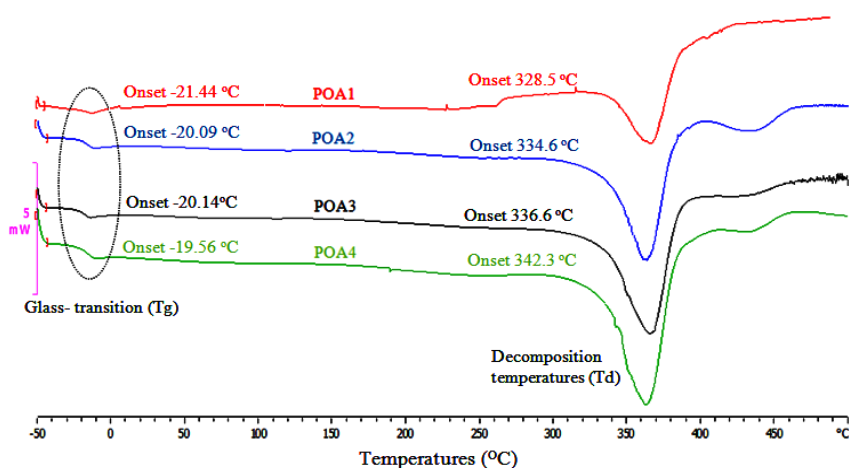


Figure 8. DSC Thermogram of the synthesized POAB

Table 2. Molecular weights and thermal properties of POABP

Polyester	Polymerization conditions			Thermal properties		M _w (g/mol)			NMUPs (M _n /M ₀)	PDI (M _w /M _n)	Yield (%)
	Time (hr)	Temp. (°C)	Stirring (rpm)	T _g	T _d	M _n	M _w	M ₀			
POABP 1	6	120	300	-21.44	328.5	1810	1963	298	6	1.1	98.46
POABP 2	12	120	300	-20.09	334.6	2309	2682	298	8	1.2	98.30
POABP 3	18	120	300	-20.14	336.6	2684	3637	298	9	1.4	97.95
POABP 4	24	120	300	-19.56	342.3	2591	5501	298	9	2.1	97.86
POABP 5	30	120	300	-	-	-	-	298	-	-	97.80

Notes: T_g = Glass transition temp; T_d = Decomposition temp; M_n = Number average molecular weight; M_w: Weight average molecular weight; M₀ = Molecular weight of the monomer unit of (EOA); NMUPs = Number of monomeric units for polyesters; PDI: Polydispersity index (M_w/M_n)

3.4.3. FTIR, ¹H and ¹³C NMR analysis

The highly predicted outcome of this study is the formation of ester group in the POABP, the presence of ester was validated using FTIR analysis. According to Pavia et al. (2010) [25], characteristic peak of stretching vibration of the carbonyl group for aliphatic esters may be present in the range of 1732 to 1736 cm⁻¹, while the C-O esters are denoted by characteristic peak of stretching vibration of carboxylic acids in the range of 1690 to 1718 cm⁻¹.

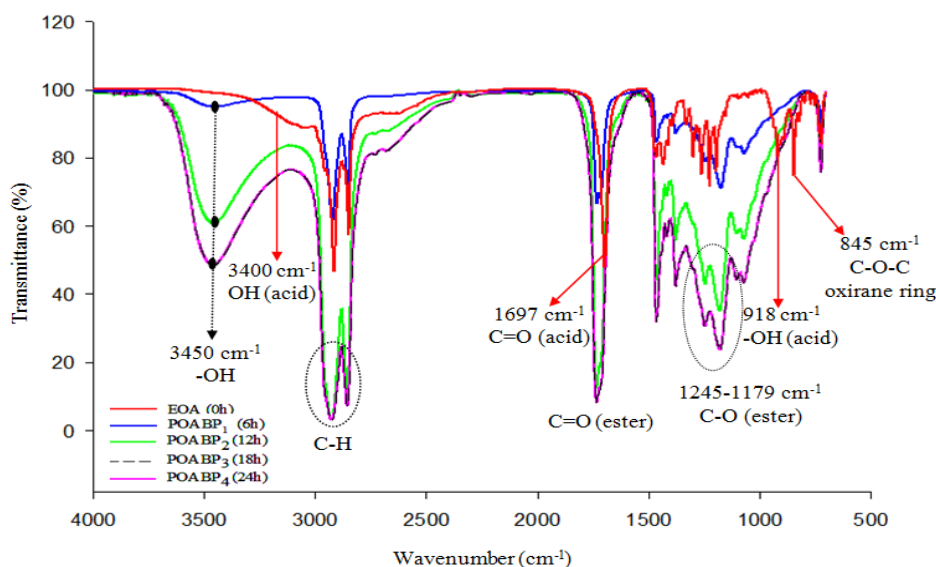


Figure 9: FTIR spectra for all the POABP synthesized at 6, 12, 18 and 24 hr

The functional groups and their positions for all the POABP synthesized at 6, 12, 18 and 24 hr were extracted from the FTIR spectra and compiled in Fig. 9. It is rather interesting to detect the peak of carboxyl group (C=O) at 1697 cm⁻¹. Meanwhile, the new peaks observed at 1732 and 3450 cm⁻¹ suggest the formation of ester group (-COOR) and hydroxyl group (-OH), respectively. The peaks of carboxyl

group at 1713 and 1717 cm^{-1} appeared to be larger for polymers synthesized for 6 and 12 hr compared to those synthesized for 18 and 24 hr, indicating higher conversion yields at longer synthesis duration, given the constant polymerization temperature (120 $^{\circ}\text{C}$) for each set. The bands observed at 1245 and 1173 cm^{-1} in all synthesized POABP indicate the presence of C–O ester linkage. ^1H and ^{13}C NMR analysis are possibly the most valuable techniques for analyzing the chemical structure. The ^1H NMR spectrum of POABP is exhibited in Figure 10. As anticipated, the epoxide group (proton signal shown at 2.9 ppm) disappeared after polymerization. The chemical shift at 4.8 ppm indicates the presence of ester group RCOO-CH_2 (i). The chemical shifts at 2.34, 3.4, and 3.6 ppm are assigned to -aliphatic $-\text{CH}_2\text{-COOR}$ (f), HO-CH- branch (g), and H-C-OH (h), respectively. The $-\text{CH}_2-$ (d & e) chemical shift was detected at 1.53 and 1.62 ppm, while the signal at 0.87 ppm is assigned to the methyl group ($-\text{CH}_3$ (a)). Finally, the chemical shift at 1.25–1.30 ppm is assigned to terminal methyl $-\text{CH}_2-$ (b). Furthermore, as shown in Figure 11, the ^{13}C NMR chemical shifts at 173.79 and 72.5 ppm indicate the presence of (C=O) (ester group in POABP structure) and C atom adjacent to oxygen (O-CH_2) (i), respectively. The signals at 34.48 and 33.86 ppm indicate the presence of C atom adjacent to carbonyl ($\text{CH}_2\text{C=O}$) (f), and 24.7 ppm for $-\text{CH}_2-$ (d). The chemical shifts at 31.88, 31.86, 30.59, 29.72, 29.53, 29.09, 25.08 and 22.68 ppm are assigned to $-\text{CH}_2-$ (b), while that of 14.14 ppm denotes terminal methyl $-\text{CH}_3$.

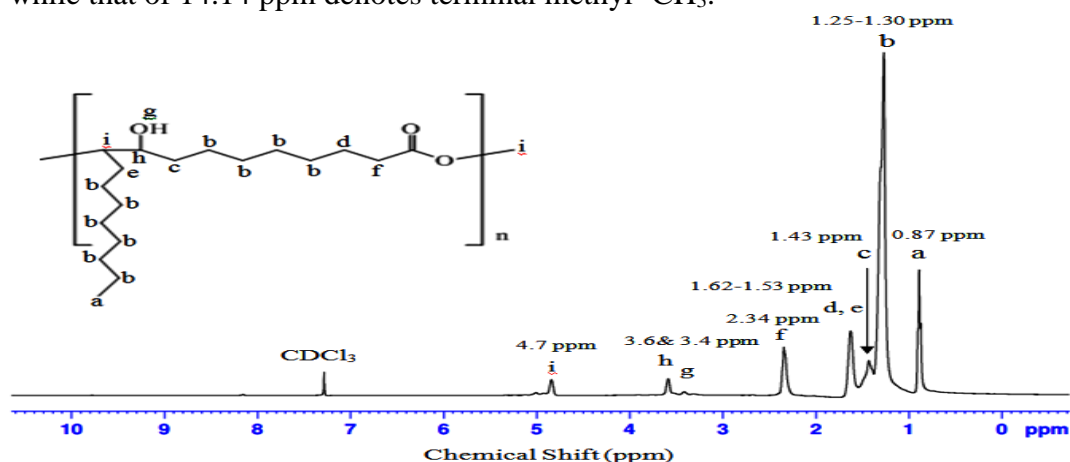


Figure 10. ^1H NMR spectrum of the synthesized POABP



Figure 11. ^{13}C NMR spectrum of the synthesized POABP

4. Conclusion

OA is a key component of unsaturated fatty acids (USFAs) in CPO, and is used in several industrial applications such as bioplastic, biolubricant, biodiesel and mineral processing. This study involves the successful preparation of EOA from OA originating from CPO, which was subsequently heated at 120°C to synthesize a polyester polymer. The chemical structure and formation of internal ester groups of the polyester were determined by ¹H, ¹³C NMR and FTIR analysis. The polyester polymer oleic acid products exhibited glass transition temperature at -19 °C and thermal degradation after 328 °C.

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