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MICROSCOPIC, SPECTROSCOPIC AND THERMOANALYTICAL CHARACTERIZATIONS OF MODIFIED PALM OIL AND RICE BRAN OIL INTO BIOPOLYMERS

(Ciri-Ciri Mikroskopi, Spekroskopi dan Termoanalitik Minyak Kelapa Sawit Dan Minyak Dedak Padi yang Diubahsuai Menjadi Biopolimer)

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Abstract

This study reported an approach of producing biopolymer material from epoxidation of vegetable oils such as palm oil and rice bran oil. The epoxidation of vegetable oils converts from carbon double bonds into oxirane group and achieves by using the conventional method of *in situ* generated formic acid for 6 hours followed by further treatment with citric acid. The presence of oxirane group was proven by Spectroscopy (FTIR) analysis, and shown at the wavenumber of 773 cm^{-1}. Through direct titration, oxirane oxygen content (OOC) for epoxidized palm oil (EPO) and epoxidized rice bran oil (ERBO) were both determined as 2.89% and 3.05% respectively. Surface morphological studies were carried out for both EPO and ERBO bioplastic films by using Scanning Electron Microscopy (SEM). Further analysis with Energy Dispersive X-ray (EDX) spectroscopy showed 68.93% and 78.80% of carbon mass percentages for EPO and ERBO films, respectively. Whilst oxygen mass percentages were exhibited in EPO and ERBO as 31.07% and 21.20%. EPO film is degraded to approximate 50% at 223 °C whereas ERBO at 225 °C from thermogravimetric analysis (TGA). This green initiative of creating bioplastic film is desired to be a substitution for current plastic product which is mostly non-degradable. In long term prospect, it is also hoped to answer to the global plastic issues such as land dumping site and ocean plastic pollution that brings adverse effect to the marine organisms.

Keywords: bioplastic, Malaysian crops, edible oil, plastic pollution

Abstrak

Kajian ini melaporkan pendekatan untuk menghasilkan bahan biopolimer daripada proses pengepoksidaan minyak sayuran seperti minyak kelapa sawit dan minyak dedak padi. Pengepoksidaan minyak sayuran menukarkan daripada ikatan berganda karbon kepada kumpulan oksirana dan dicapai dengan menggunakan kaedah konvensional asid formik secara *in situ* selama 6 jam diikuti dengan rawatan lanjut dengan asid sitrik. Kehadiran kumpulan oxirane telah dibuktikan oleh Spektroskopi (FTIR) analisis, dan ditunjukkan pada nombor gelombang 773 cm^{-1}. Melalui pentitratan terus, kandungan oksigen oksiran (OOC) untuk minyak kelapa sawit terepoksida (EPO) dan minyak dedak padi terepoksida (ERBO) kedua-duanya ditentukan sebagai 2.89% dan 3.05%. Kajian morfologi permukaan telah dijalankan untuk kedua-dua filem bioplastik EPO dan ERBO dengan menggunakan Mikroskopi Pengimbas Elektron (SEM). Analisis lanjut menggunakan spektroskopi X-ray Penyebaran Tenaga (EDX) masing-masing menunjukkan 68.93% dan 78.80% peratusan jisim karbon untuk filem EPO dan ERBO. Sementara itu, peratusan jisim oksigen dipamerkan dalam EPO dan ERBO sebagai 31.07% dan 21.20%. Filem EPO terdegradasi dianggarkan 50% pada 223 °C manakala ERBO pada 225 °C daripada analisis termogravimetrik (TGA). Inisiatif untuk mencipta filem bioplastik ini diingini untuk menjadi pengganti kepada produk plastik semasa yang kebanyakannya tidak terdegradasi. Dalam prospek jangka panjang, ia juga diharap dapat menjawab isu plastik global seperti tapak pelupusan tanah dan pencemaran plastik lautan yang membawa kesan buruk kepada organisma marin.

Kata kunci: bioplastik, tanaman Malaysia, minyak makan, pencemaran plastik

Introduction

The production of plastic globally was recorded more that 280 million tonnes in 2012, and increase to more than 335 million tones 4 years later [1]. These numbers are expected to grow exponentially over the next 20 years. Part of these plastics can be recycled; however, it was reported that only 21% is recovered over 91% plastic waste, where no less than 8 million tons of plastic as of now winds up in the sea consistently [2]. In Malaysia, the generation of plastic wastes has consistently increased 5% of every 5-years since 1995, where it was reported to produced 0.94 million tonnes in the year of 2018 [3], and projected to exceed 1 million tonnes in 2022. In environment, mismanaged plastic that underwent weathering or degradation process can broke down into smaller pieces to form secondary microplastics, which leads to many questions on the environmental, ecological and human health risks posed by them [4-5]. Therefore, the production of bio-based polymers (bioplastics) has gain interest from the world, as part of mitigation of this issue. With the price of petroleum is continually increase and the problem arise from environmental issues become the factors to utilize biodegradable products, for instance from vegetable oil. Bioplastic is considered to be a great alternative of petroleum free plastic in the industry. To maximize the value of bioplastic, its production should be done by using more environmentally friendly or greener method and resource. It could be seen that fast-growing trend on bioplastic is replacement for the petroleum in polymer industry as it is helpful in reducing a huge tons of carbon dioxide and the usage of petroleum [6].

The term of “bio” in bioplastic is defined as biological based derived plastic or polymer product such as vegetable oil, cellulose, and starch products that undergo chemical reaction to change into associated form, which later can degrade easily or able to be decomposed by microorganisms, therefore it is more sustainable and eco-friendlier [7]. For instance, vegetable oil-derived bioplastic is a type of vegetable oil-based cross-linking polymer plastics that has many repeating units. While fatty acid profiles of commodities such as soy bean and canola oils are major lipid of interest in the world in producing lipid biopolymer, local commodities Malaysia such as palm oil and rice bran oil were given consideration in this proposed study. Malaysia has ranked the top world largest exporter for palm oil production and second largest for palm oil production just a place right after Indonesia [8]. This oil can be obtained from harvesting the cluster or a bunch of palm oil fruit (*Elaeis guineensis*) at about forty to fifty kilograms. Meanwhile, rice bran oil is edible oil that is extracted from the brown husk outer layer of the rice. It has the smoke point at about 232 °C and often suitable for stir frying and deep frying in cooking. A brown husk of rice bran oil can be extracted up to 75% of the oil that is commonly wasted if there is no further research on it. Rice bran oil is obtained from the brown outer coating using hexane extraction and to get 8 to 16% of oil through the process of germ grinding, dehulling and polishing of rice [9]. Refined rice bran oil is often existed in light yellow liquid and highly stable due to the presence of tocopherols (vitamin E) of 320 mg/kg, oryzanols about 2% [9].

These oils are being utilized to produce bioplastic through feasible way of epoxidation process. Epoxidation is one of several reactions that can be carried out to utilize the fatty chain of edible oil in a reasonable cost. Various functional groups can be inserted into the double bond which acts as the reactive site in the vegetable oils. It was widely proven that oils with high properties of saturated fatty acid and triacylglycerol's are more suitable for the application of fuel biodiesel, while polyunsaturated acids are permitted to participate in conversion of carbon-carbon double bond alkene into epoxy compound is known as epoxidation process [10] that later can be transformed to lipid biopolymer or bioplastics. Nevertheless, epoxidation of vegetable oil has become the popular research to be done by most of the scientist as it is worth at certain values. This is a solution to substitute non-renewable resources of petroleum to act as one of the plasticizers, known as epoxide. There are four major types of methods to produce epoxidation using fatty acids such as epoxidation with percarboxylic acid or acid catalyzed or enzymatic, organic or inorganic with alkaline and nitrile hydrogen peroxide, halohydrins by using hypohalous acids and salt reagent and molecular oxygen [11]. Some of the epoxides with high oxirane oxygen contents and functional epoxy group presence in the chemical structure of epoxidized vegetable oil, it is required a hardening agent to produce bio-based polymer [12]. High viscosity of vegetable oils is commonly implemented in the applications as lubricant and additives in polymer science such as resins and coatings. Our preliminary findings show that the epoxidation reaction, this can be followed by the cross-linking polymerization could be carried out on the reactive sites. Since both oils have differences in the type of fatty acids and their degree of unsaturation, this can impose conditions on their final use for the development of new products such as bio-based polymer and resins.

Materials and Methods

Materials

The following chemicals were purchased from R&M Chemicals (Malaysia): hydrogen peroxide (H_2O_2; 35%), anhydrous sodium sulphate, crystal violet indicator, HPLC grade acetonitrile, sodium chloride and glacial acetic acid. Formic acid (HCOOH; 98%), sodium bicarbonate, hydrogen bromide solution 33 wt.% in acetic acid, 2-propanol gradient grade for liquid chromatography (LiChrosolv) and acetonitrile hypergrade for LC-MS (LiChrosolv) were all purchased from Merck (KGaA, Germany). Citric acid-1-hydrate was purchased from HmbG Chemicals (Germany). Sodium hydroxide in pellets (analytical grade) was purchased from Fisher Scientific (Malaysia). Smith filter paper 101 Qualitative 90 mm was used for filtration purpose. The chemicals used in the study were of analytical grade unless stated otherwise. Palm oil and rice bran oil were purchased from the local market.

Epoxidation of palm oil (PO) and rice bran oil (RBO)

The heating process was begun from 55 °C and monitored carefully. Hydrogen peroxide (H_2O_2; 35%) of 34 mL was dropped wisely due to its exothermic effect that may cause explosion and continuously stirred with the fastest speed. The reactions were taken about six hours to complete. The epoxidized oils were washed with n-hexane, 5% wt. sodium hydroxide (NaOH) and 5% wt. sodium chloride (NaCl). Anhydrous sodium sulphate (Na_2SO_4) of 2 g was added and filtered with Buchner funnel.

Bio-polymerization using citric acid as curing agent

Concentrated citric acid was prepared by mixing 4 parts according to the weight of CA.H_2O ($C_6H_8O_7H_2O$) and one part of distilled water and heated up to 90 °C. Poured the completely dissolved solution into the glass beaker which contained 2 g of epoxidized palm oil or rice bran oil at 90 °C. Solution was stirred to form a layer of emulsion between aqueous citric acid and epoxidized oils. The viscosity would increase as the gelation formed at the same time. The solution was constantly stirred for 10 minutes at 90 °C until it gradually turned translucent and poured into the aluminium mould. The readily samples were both put into the oven (Universal Oven UF110 Memmert). Bio-polymerisation was started for 6 hours at 90 °C and 12 hours at 110 °C. Post curing at 120 °C for an hour and low drying mode at 35 °C to remove moisture for 2 hours.

Chemical analysis of oil and epoxidized oil: Liquid chromatography-mass spectrometry for fatty acid determination

An oil aliquot of 3 g (starting material) was obtained and diluted with 10 mL of ethyl acetate. It was followed by washing with 15 mL of brine (saturated sodium chloride) solution. The mixture was left for a while and later separated into two layers. Upper layer was collected and washed with 15 mL of 1 M sodium bicarbonate ($NaHCO_3$) solution. Aqueous layer was removed and dried the upper layer with anhydrous sodium sulphate. Nitrogen evaporator (Organomation, N-EVAP 111) was used to concentrate the oils. The oils were weighted and diluted to 0.1 mg/mL in dichloromethane before LC MS/MS analysis for the analysis of fatty acid composition.

Liquid Chromatography Ion-trap Time-of-flight Mass Spectrometer (HPLC-MS-TOF, Shimadzu, Japan) is a unique combination of tandem mass spectrometer and ion trap (IT) with a time of flight (TOF) where ion trap allows MS^n capacity. A Supelco C_{18} column (250 mm x 4.6 mm i.d., particle size 5 µm) (Sigma Aldrich, ON, Canada) was used with the following linear gradient at a flow rate of 200 µL/min with an injection volume of 1 µL: Solvent A is isopropanol (IPA); Solvent B is Acetonitrile (ACN); t = 0, 20% A, hold 0.1 min; t = 25 mins 90% A. Data were acquired using ESI in the positive ion mode, with the following instrumental parameters : declustering potential (DP) at 45 V focus potential (FP) at 150 V; declustering potential 2 (DP2) at 10 V; gas (GAS 1) at 20; nebulizing gas (GAS 2) at 60; and an ion spray voltage of 5200 V [13].

Determination of oxirane oxygen content

Epoxidized oils was tested using AOCS Cd 9-57 for oxirane oxygen value. The direct titration of oils (0.5 g prepared in 10 mL glacial acetic acid) with 0.1 N 33% hydrogen bromide solution (in acetic acid) and was assisted with the use of 0.025% crystal violet indicator solution [14].

Fourier transform infrared spectroscopy (FTIR)

An amount of one-gram of each sample was used for FTIR analysis. The spectra were recorded 4 cm^{-1} resolution on IR spectrophotometer (Perkin Elmer, model FTIR Spectrum 100, Waltham, MA, USA). Data of absorbance against wavelength was generated by FTIR software (Perkin Elmer, OMNIC series suite, MA, USA). Epoxidized palm oils and epoxidized rice bran oils were recorded in transmission mode from 400 cm^{-1} to 4000 cm^{-1}.

Physicochemical analysis of of biopolymer product: Scanning electron microscopy analysis

Thin films were coated with gold using Auto Fine Coater (JFC – 1600, JEOL, Japan). The surface morphology of the bioplastic films was studied using Scanning Electron Microscopy (SEM model JSM - 6360LA, JEOL, Japan) at an accelerating voltage of 30 kV [15]. EDX analysis was done to determine the percentage of carbon and oxygen presence in the thin films.

Thermogravimetric analysis

Thermal degradation of the bioplastic films was both analysed by using thermogravimetric analyser (TGA851/LF 1100, Mettler Toledo). All samples were tested used a mass of approximately 70 mg under a nitrogen flow of 50 mL/min and heating rate of 10 °C /min within temperature range of 20 °C to 900 °C [16].

Results and Discussion

Fatty acid determination and epoxidation of edible oils

The main composition of the starting oils was determined to confirm the fatty acid profile for both starting oils and is illustrated in the Table 1. The commercial cooking oil of palm oil (olein) is made up of major of about 41.5% of C18:1 or oleic acid, followed by 40.2% of C16:0 (palmitic acid), 11.8% of C18:2 (linoleic acid), 5.3% of C18:0 (stearic acid) and 1.2% of other fatty acid constituent (e.g. lauric, myristic, palmitoleic and linolenic acids). This agreed with previous research on other commercial palm oil which usually consisting of 42-45% of palmitic acid, 40-42% of oleic acid and 9-11% of linoleic acid and very small amount of stearic and linolenic acid [17-18]. Meanwhile, rice bran oil is made up of the major composition of unsaturated fatty acids such as oleic acid (C18:1, 45.6%) and linoleic acid (C18:2, 28.3%) followed by saturated fatty acid of C16:0 (palmitic acid) at 22.1%. Previously, Purwanto (2010) and Punia et al. stated that this oil has fatty acid composition of palmitic acid (10-20%), stearic acid (1-5%), 39-43% oleic acid and 28-35% linoleic acid, depending on the method used in the oil extraction process [19-20]. The unsaturation profile of both oils was found to be suitable for further modification by epoxidation reaction.

Table 1: Major fatty acid constituent of edible oils used in the study

Fatty Acid	**Composition (%)**	
	Palm Olein	**Rice Bran Oil**
C16:0 (palmitic acid)	40.2	22.1
C18:0 (steric acid)	5.30	1.83
C18:1 (oleic acid)	41.5	45.6
C18:2 (linoleic acid)	11.8	28.3
others	1.20	2.17

Epoxidation with peracid formed *in situ* with hydrogen peroxide is a conventional method that widely used in the large-scale industry. As such, the better selection of formic acid is used in the experiment to enhance the break the unsaturated carbon double bonds into the epoxy group than acetic acid at around 60 °C [19]. There are some negative impacts of high concentration of formic acid towards the selectivity for conversion of oxirane oxygen thus reduced the final yield of epoxy group [21]. Commercialized palm oil (PO) and rice bran oil (RBO) were both underwent performic acid in situ epoxidation at 55 °C and the results shown was low epoxidation rates due to low reaction temperature, similar to the findings by Danov et al [22]. Hydrogen peroxide of 35% is dropped slowly due to its unstable reactivity and avoided adding in once the temperature exceeded higher than 85 °C. During the epoxidation process, RBO was heated to slightly viscous and turned from yellow to slight burnt brown colour in the middle of heating process. This due to the presence of phospholipid in the RBO and the antioxidant effect had caused the oil to brown darkening for several minutes during heating process. Fast stirring was continuously carried out in order to homogenize the viscous vegetable oil and but it could probably decrease the rate of epoxidation and deteriorate the formation of epoxy group [22]. Excessive epoxy ring opening reactions also would appear if the occurrence of side reactions at reaction temperature higher than 70 °C [23]. Stable oxirane rings were achieved at lower temperature and epoxidation under higher temperature was not recommended due to the exothermic effect of hydrogen peroxide that may lead to an explosion [24]. In situ generated formic acid with hydrogen peroxide was a reversible process to occur hydrolysis as it attributed by oxygen carrier from hydrogen peroxide to form peroxyformic acid. The repeatability of this method was done for several times on both PO and RBO to get the most accurate results.

A significant indication to the end of epoxidation process is the formation of light viscous liquid for both EPO and ERBO which takes about six to eight hours. This is faster than previously reported where the reaction for epoxidation process of vegetable oils could be accomplished up to 48 hours, depending on the reaction conditions and parameters [23]. Epoxidized vegetable oil (EVO) by acid generated in situ had achieved the reaction mechanism in two stages. The first step is hydrogen peroxide reacted with concentrated formic acid to form performic acid and water which is also known as hydrolysis process [24]. In the presence of water, performic acid catalysed the ring opening of unsaturated bonds of fatty acid and leading to the cleavage of oxirane rings in stage two [25]. However, a reversible process of formic acid regeneration is more likely to occur due to the unstable oxirane rings and again promote the epoxide group to undergo hydrolysis process [26].

FTIR analysis

Based on the analysis of Fourier Transform Infrared Spectroscopy (Table 1), the palm olein is converted to epoxidized palm oil. It can be seen at the C=O overtone from 3476 cm^{-1} in Figure 1(a) is changed to 3524 cm^{-1} broad stretching of OH in Figure 1(b) which resulted in ring opening of epoxy group [11, 27]. The absence of 3006 cm^{-1} at Figure 1(b) indicates the formation of epoxidation of palm oil and C=C was broken at the reaction. A missing peak of double bonds in the same figure represents that almost 100% conversion into C-O-C, epoxide group [28].

Palm oil has C=C bonds at the wavenumber of 3006 cm^{-1} at Figure 2, but the existence of epoxidation process had diminished this peak to 2927cm^{-1} CH stretching at Figure 3. In FTIR spectrum, epoxidized palm oil is shown a sharp and broader at the wavenumber of 1735 cm^{-1} C=C alkene bonding than the peak of C=O bonds at 1747 cm^{-1} in Figure 2. Stretch vibration of C-O-C ester group is noticeable at 1176 cm^{-1} [15] . Previously, it was reported that C-H rocking for epoxide band also occurred at 725 cm^{-1} in the epoxidized palm oil as proven by the wavenumber of 725 cm^{-1}. It is believed that the sensitivity of FTIR instrument lack of precision due to the disturbance of carbon dioxide because a peak of 844 cm^{-1} is not existed in the EPO, albeit small peak was observed at 831 cm^{-1}. All the functional groups of palm oil and epoxidized palm oil are tabulated in Table 2.

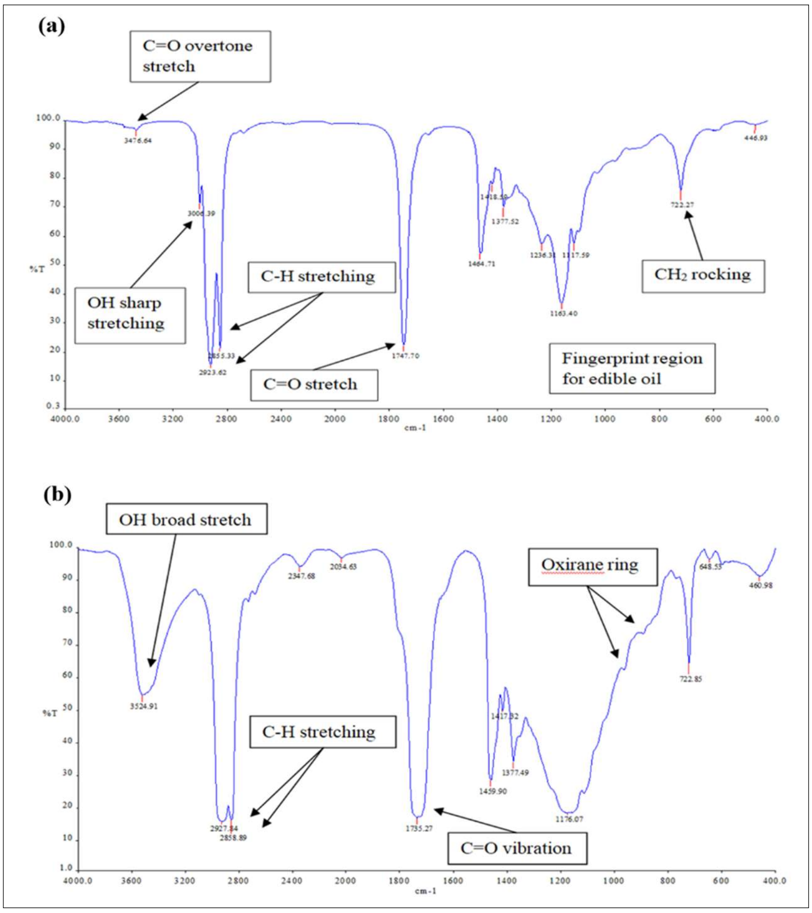

Figure 1. The FTIR spectra for (a) PO and (b) EPO

Separately, there is also an overtone of C=O at wavenumber of 3565 cm^{-1} in the RBO and a broad OH bond stretching at 3500 cm^{-1} , similarly as PO. From the IR spectrum of rice bran oil (Table 2; figure not included), it has a sharp C=O stretch at the wavenumber 1746 cm^{-1} whereas in epoxidized rice bran oil (ERBO) this peak has shifted to a lower wavelength range of 1728 cm^{-1}, similar to the infrared spectrum reported in [25]. Additionally, there is an existence of oxirane oxygen content (OOC) at the wavenumber of 773 cm^{-1} for ERBO when compares to RBO. This showed the complete conversion of C=C double bonds into C-O bonds.

Based on the infrared frequency table, the spectrum falls under the range of wavenumber from 750 cm^{-1} to 825 cm^{-1} is a monosubstituted epoxides as a proof to RBO being epoxidized. There was a disappearance of C=C at the wavenumber of 3008 cm^{-1} of rice bran oil which is extremely approximate to the 3007 cm^{-1} reported by the author Gupta et al., [29] . From the results of rice bran oil and epoxidized rice bran oil, it could be seen that the patterns and wavenumber are almost totally matched to the experimental graph in the waste rice bran oil and epoxidized waste rice bran oil [29]. Ring opening of ERBO is indicated at 3500 cm^{-1} which has minor variation to the stated wavenumber of 3440 cm^{-1} from the same study.

Table 2. The IR frequency tables for both palm oil and rice bran oil before and after epoxidation are tabulated

		PO	RBO
	Functional Group	**Wavenumber (cm^{-1})**	**Wavenumber (cm^{-1})**
Before epoxidation	C=O (overtone)	3476	3565
	C=C (sharp stretch)	3006	3008
	C-H (stretch)	2923, 2855	2925, 2854
	C=O (stretch)	1747	1746
	CH_2 (rocking)	722	722
After epoxidation	OH (broad)	3524	3500
	C-H (stretch)	2927, 2858 c	2926, 2855
	C=O (vibration)	1735	1728
	C-O-C (vibration)	1176	1175
	C-O-C (oxirane)	831	825

Oxirane oxygen content

EPO and ERBO were later tested for the epoxy weight percentage analysis by using a direct titration method with 0.1 N hydrogen bromide (HBr) solution in 33% of acetic acid. This method was successfully measured the oxirane oxygen content (OOC) and show the epoxidation state of the reaction. An equilibrium point was achieved when the crystal violet solution had changed to blue green which represented the existence of OOC [30]. The oxirane oxygen for the EPO in the first, second and third tests (triplicate) were obtained at 2.96%, 2.80% and 2.90% respectively. Hence an average result of oxirane values was calculated for EPO as 2.89%, and this is closely approximate to the range of 2.7 to 2.9 % by author Tajulruddin et al. [31]. For ERBO that has been synthesized, the oxirane oxygen were recorded at 2.98%, 2.90% and 3.28% for triplicate analysis. The RBO was synthesized originally from waste rice husk so the ERBO has an average OOC of 3.05% which is very approximate to the 3.2% reported by Gupta et al., [29]. Hence, there was an inverse relationship between the conversions of OOC to the increasing reaction time of epoxidation. However, this would not much be affecting the final yield of the product since the difference in the percentage conversion is small. The percentage of the OOC value obtained from the current study was tabulated as below in Table 3.

Table 3. Oxirane oxygen content (OOC) of both EPO and ERBO

Sample	1	2	3	Average
EPO	2.96%	2.80%	2.90%	2.89%
ERBO	2.98%	2.90%	3.28%	3.05%

Curing of films with citric acid

A recent trend of biodegradable polymerization is usually focussed on the organic weak citric acid that made up of three carboxylic acids, COOH groups. Epoxidized oils that has good heat stabilizer are very beneficial in the production of plastics. EPO and ERBO were blended separately with 2 g of citric acid and 0.5 mL of distilled water and agitated to mix well. To promote the cross-linking of epoxidized oil and citric acid to form bio polymeric film, it was heated at 90 °C to enhance the effect. Epoxide is cyclic ethers with three membered-ring that is produced from peracids with alkenes. Vegetable oils for instance PO and RBO that are composed of oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3) (Table 1) which allowed for conversion of bonds by peracids into epoxides. Asymmetric epoxides would undergo solvolysis by methanol and the ring opened by SN_2 mechanism where nucleophilic attacked at the less-substituted carbon region. In contrary, solvolysis also could be existed in acidic methanol and this reaction mechanism would be attacked at the more substituted site of carbon [32]. In the present study, citric acid acted as a curing agent and catalyst to epoxidized oils in which consisted of epoxy and triglycerides to produce polymeric films from renewable materials using vegetable oils. The reaction between epoxidized oil and citric acid was appeared in a translucent viscous gel that is known as biodegradable, non-toxic and greener biopolymer [33].

In this study, bio-polymerization process was started by mixing the epoxide oil with the curing agent at the first 6 hours (90 °C) reaction, followed by another 12 hours (110 °C) for hardening of the films in the oven. Previously, Kolanthai et al. [34] reported that the higher citric acid concentration will lead to fragility of the polymer film that might break into smaller pieces. Hence, a modified method was implemented during post-curing process. The original post-curing method by author Altuna et al. [35] was conducted at 150 °C under a monitoring period, but in the present study the temperature for post-curing was set at 120 °C for one hour to avoid the excessive burning of the samples. The biopolymer films were further dried under low oven drying mode at 35 °C for another 2 hours to remove the wettability or water content from the films. Oven dried of films were relatively carried out under a controlled environment of temperature, humidity and air circulation, thus helped to boost the water evaporation compared to the silica gel in desiccators method.

SEM-EDX analysis of bioplastic film

Scanning electron microscopy (SEM) that coupled with the function of energy dispersive X-ray (EDX) was used as a preliminary method to determine quantitative compositional data of the biopolymer film by observing the mass percentage of carbon and oxygen elements (Table 4). EPO shows that 74.72% of carbon atomic and 25.28% of oxygen atomic in the composition of its bioplastic film. While bioplastics from ERBO consists of 83.20% of carbon atomic, thus can be used to predict that the ERBO has longer chain than EPO. This is because the epoxidation will break the double bonds and increases the number of carbon single bonds as monomers repeating unit cross linked with each other in the polymerization process.

Table 4. EDX data analysis for EPO and ERBO bioplastic films produced

Sample	Element	(keV)	Mass%	Atomic%
EPO	C	0.277	68.93	74.72
	O	0.525	37.07	25.28
ERBO	C	0.277	78.80	83.20
	O	0.525	21.20	16.80

Epoxidized palm oil is suitable to cure with citric acid, as Figure 2a shows that EPO bioplastic film has a smooth and illuminating surface at 30 times of magnifications. There is a correlation to the increasing amount of citric acid blend towards the compatibility of bioplastic, similar to the previous reported findings by Ouipanich et al. [36]. Figure 2b shows the uneven surface thickness of the specimen but high miscibility due to strong hydrogen bonding interactions with epoxy, hydroxyl and carbonyl group making a smooth surface

[27]. It shows uniform vertical stripes and grid pattern under 1000 magnifications at an accelerating voltage of 10 kV. Epoxidized palm oil film is in long cross-linking shape and homogenously distributed under the boost of high temperature curing in Figure 2c. The overall of the film is concluded as very brittle due to the uneven surface thickness and fracture.

Meanwhile, epoxidized rice bran oil (ERBO) bioplastic film illustrates a clear and shiny image. It can be seen that the pattern is looked like cracked fracture dry land in Figure 3a. The crackle is short and distributed homogeneously on the entire surface of the specimen. As the numbers of crack front increasing on bioplastic film, the higher the flexibility and the ductility of the film [11]. It shows horizontal stripes at 30 times of magnification. Figure 3b is open-pores image that shows on the surface of the film and they are cross linking like bee hives, similar to the finding elsewhere [37]. The presence of voids on Figure 3b under magnification of 350 times is due to the degree of dispersion of citric acid in the polymerization of epoxidized rice bran oil. Hence, it can be explained by the increasing of natural glycerol content in vegetable oil will decrease the tendency to form void and increase the phase separation [38]. Meanwhile, in Figure 3c, a round spot is virtually observed, with the round holes shaped of the pores is noticeable at 1000 magnification of 10 kV accelerating voltage.

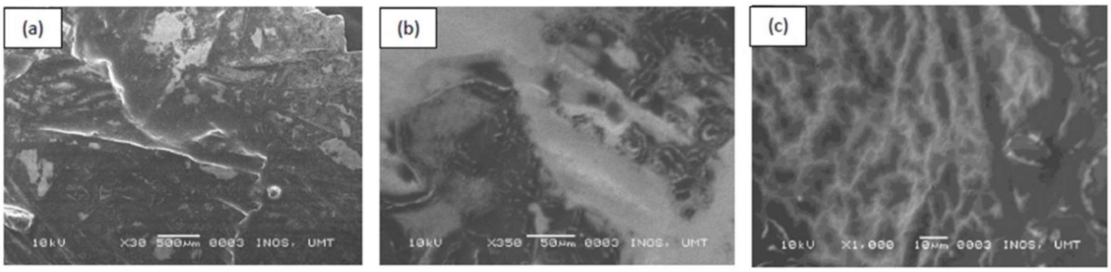

Figure 2. SEM micrograph for different magnifications of EPO bioplastic film at 10kV of (a) 30X, (b) 350X, (c) 1000X magnifications

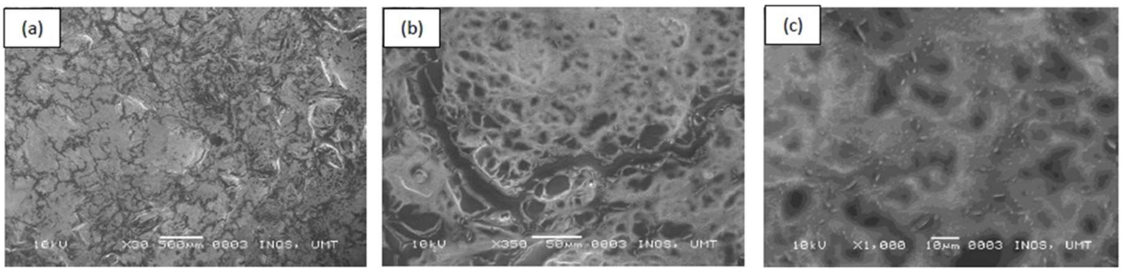

Figure 3. SEM micrograph for different magnifications of ERBO bioplastic film at 10kV of (a) 30X, (b) 350X, (c) 1000X magnifications

Thermogravimetric analysis (TGA)

Thermogravimetric is the analysis that provided information on the weight loss with the increasing of temperature in order to obtain the degradation level of biopolymeric films under an inert nitrogen environment. To observe the thermal behaviour of biopolymer films, the initial decomposition temperature, 50% degradation level and maximum decomposition rate are recorded in TGA and DTG curves. In general, the results show that the films could started degrading at higher temperature (>180 °C), thus proven that formation of biopolymers was successful. Figure 4 shows thermogravimetric analysis of biopolymer made from EPO and ERBO is illustrated as three stages according to the percentage of degradation. While, table 5 shows the thermal degradation of biopolymer films at different temperatures.

Table 5. Thermal degradation of epoxidized oil biofilms at different temperatures

Sample	T_i(°C)	Wt.%	T_{50}(°C)	Wt.%	T_{max}(°C)	Wt.%
EPO film	29.10	70.56	223.35	36.71	895.46	8.32
ERBO film	30.28	70.54	224.90	35.29	897.65	7.30

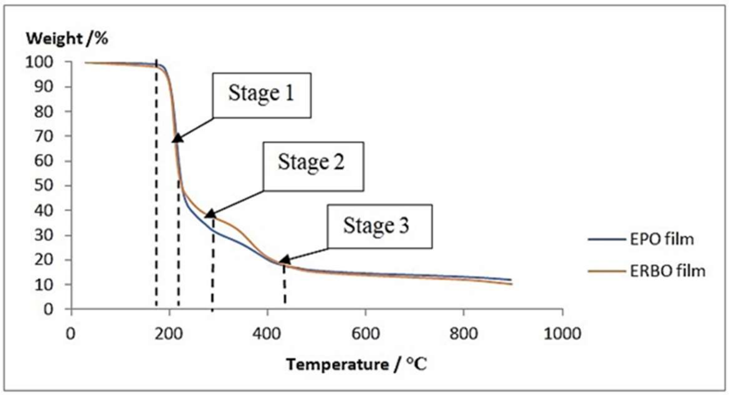

Figure 4. The thermogravimetric analysis of epoxidized palm oil (EPO) and epoxidized rice bran oil (ERBO) biopolymer films on weight percentage

From thermogravimetric analysis (TGA), the starting temperature (T_i) for biopolymer made from EPO film is 70.56 mg at 29.10 °C in Figure 5a. It is started to degrade at 182 °C and left 36.71 mg or 52% of the product at 223 °C. At 895 °C, it only contains a residue of 8.32 mg for EPO film. There is some weight loss at the initial stage of EPO biopolymer film due to the evaporation of water at the temperature between 37 °C to 176 °C, similar to the previously reported [16]. According to the first differential thermogravimetric curve (DTG), it illustrates in Figure 5b that the maximum degradation of EPO at 38% weight remained for biopolymer film at 252 °C [37].

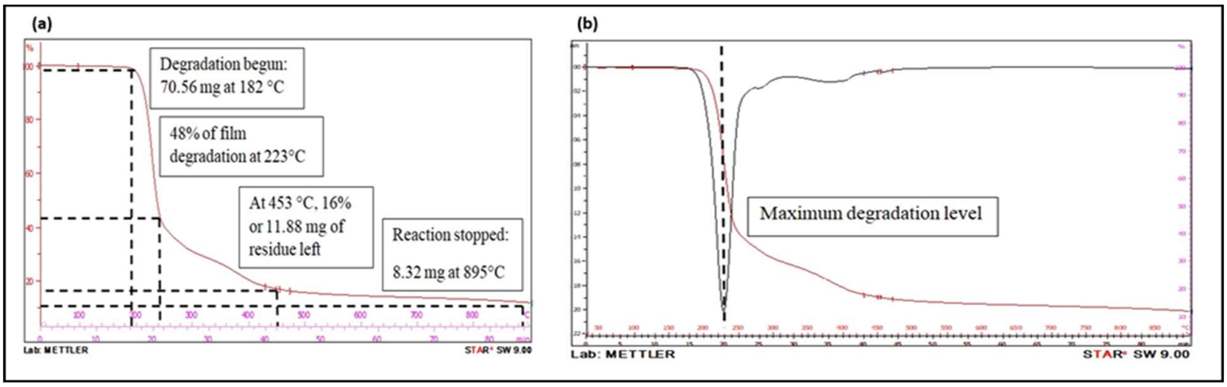

Figure 5. (a) Weight percentage of EPO from TGA curve, and (b) DTG thermograms from TGA curve of EPO

While in ERBO, it is first beginning with 70.54 mg at 30 °C in Figure 6. Then, it is started to decompose at 106 °C and remain 35.29 mg or 50% at 225 °C. At the end process of 897 °C, there is a 7.30 mg or 10% of ERBO film residue. Whilst, the differential thermogram (DTG) shows that the 257 °C is the maximum degradation level of ERBO in Figure 6 which still has 41% of the original product remained as biopolymer film. It is suggested that thermal decomposition of ERBO is well cross-linked with citric acid in order to have longer polymerization chain length, hence it is observed to degrade at slightly higher temperature compare to EPO film. This is found to be similar to the finding by an earlier study, where they reported that the contribution of network structures in enhancing the thermal stability of the biopolymer material [39].

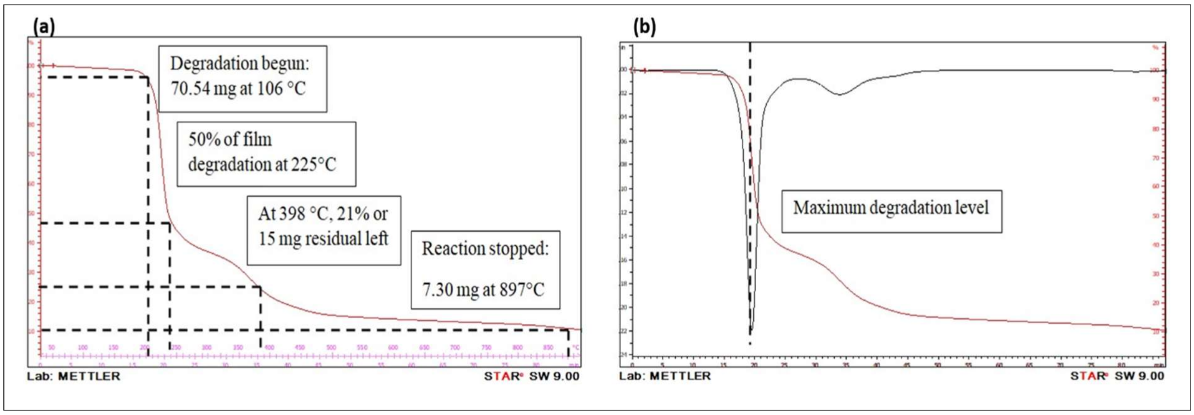

Figure 6. (a) Weight percentage of ERBO from TGA curve, and (b) DTG thermograms from TGA curve of ERBO

Conclusion

In this present study, the epoxidation process of palm oil (PO) and rice bran oil (RBO) were succesfuly converted the double bonds into epoxides that subjected for further polymerization. Oxirane oxygen content of EPO is 2.89% which is less than 3.05% of ERBO, showing that the latter has longer chain polymerization. The improvement of post-curing process shown that the cross-linking could be achieved at lower temperature while still promoting excellent polymer sturcture. From SEM analysis, bioplastic films made of EPO have smoother surface than ERBO, whilst thermogravimetric analysis (TGA) shows the degradation of both films only noticable after 180 °C, and still recorded mass residual of 10.35% (ERBO film) and 11.79% (EPO film) after 890 °C, owing to their excellent thermal stability characteristic. This shows that the PO and RBO can be used as starting material for epoxidation reaction and biopolymer transformation, and can be further explored for their degradation profile, tensile and mechanical stress as well as life-cycle assesment, thus can be used an alternative material in plastic pollution mitigation.

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