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Preparation of Epoxidized Fatty Acid Ethyl Ester from Tung Oil as a Bio-lubricant Base-Stock

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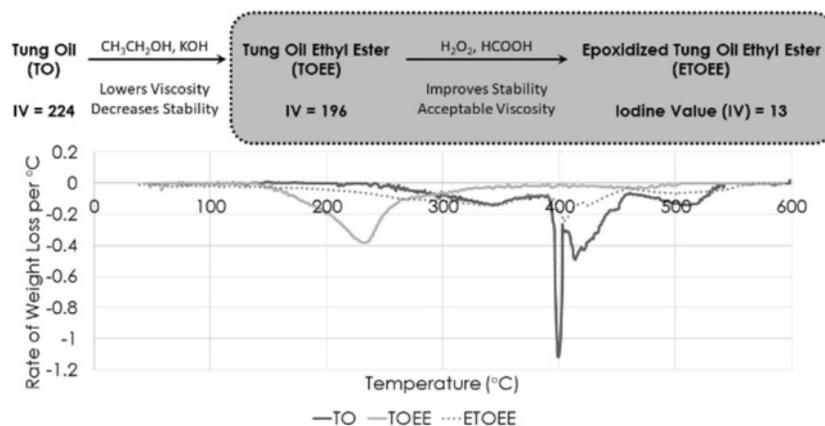
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Abstract

Preparation of epoxidized tung oil ethyl ester (ETOEE) was explored in this work via a two-step approach to produce bio-lubricant with enhanced thermal-oxidative stability. Transesterification of tung oil with ethanol was first carried out with KOH as the catalyst at 60 °C and a molar ratio of tung oil to ethanol of 1:20 for 2 h. The obtained tung oil ethyl ester (TOEE) was subjected to epoxidation in the presence of hydrogen peroxide and formic acid (FA). The highest conversion (93.6%, based on reduction of iodine value) was achieved by reacting 10 g of TOEE with 14.5 g of hydrogen peroxide and 5.86 g of FA at 50 °C for 3 h. Under these conditions, the resulting ETOEE has an oxirane number or epoxy value of 5.1%, and the presence of epoxy groups was confirmed by Fourier transform infrared spectroscopic analysis. The resulting ETOEE was further analyzed of its thermal stability under both oxidative and non-oxidative atmospheres. The viscosity index was determined and improvements in both thermal stability and lubricity were observed with the aid of a modular compact rheometer and a thermos-gravimetric analyzer, respectively. The ETOEE produced may be suitable for use as lubricating oil in gear boxes and engines.

Graphic Abstract



Keywords Bio-lubricant · Catalyst-free · Epoxidation · Tung oil · Thermal stability · Viscosity

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Statement of Novelty

Studies on the epoxidation of tung oil alkyl ester have just recently started and limited information are currently available. No work has been done using Tung oil ethyl ester as raw material to be epoxidized via simultaneous epoxidation and in situ formation of peroxyformic acid as oxygen donor without the addition of inorganic catalyst. The results in this study will serve as a baseline information for future works on the preparation of epoxidized ethyl ester from tung oil. Ethyl esters of tung oil proved to be a better starting material than its methyl counterpart previously investigated, providing better oxidative stability and lubricating properties.

Introduction

The increased awareness on the environmental impact of extracting and processing of crude oil, its fast depleting reserves, and uncertainties in supply and price, has led to the growing interest of finding alternative raw materials to produce industrially important products derived from crude oil [1]. With mechanized industrial processes and transport systems, the use of lubricants or lubricating agents has become indispensable. As a bio-based counterpart to crude oil, plant oils and animal fats have been widely explored as alternatives to various petroleum based products or as a raw material in producing renewable alternatives to petroleum derived products such as lubricants. Although plant oils and animal fats are renewable, the use of edible plant oils and animal fats can lead to negative impact on global food supply.

Tung oil is a non-edible oil extracted from mature seeds produced by tung tree of the *Aleurites fordii* and *Vernicia fordii* species, mainly grown in China. In a study by Zhang et al. [2] oil from 41 samples of tung seeds extracted using petroleum ether were found to primarily contain unsaturated fatty acids with the following average molar distribution, 77.2% α -eleostearic acid (18:3), 7.6% linoleic acid (18:2), 5.9% oleic acid (18:1), 4.2% palmitic acid (16:0), 2.3% stearic acid (18:0), and 0.4% linolenic acid (18:3). Having primarily comprises unsaturated oil, it has long been used industrially as drying oils in paints, coatings and varnishes. As a non-edible oil and a renewable resource, it has been explored as a raw material in producing fatty acid methyl ester to serve as a bio-based alternative for petroleum-based diesel fuel [3, 4]. However, owing to its high degree of unsaturation, the oxidative stability of tung oil at 110 °C (0.3 min) does not meet the current standards for biodiesel, which requires the oxidative stability to be at

least 3 min [4], making it not suitable for use as biodiesel. Fatty acid alkyl esters have generally lower viscosities, which could be 8 to 12 times less than that of its parent oil or fatty acid [3, 4] and has found applications in enhancing lubricity of low-sulfur diesel fuel when used as an additive [5]. Unfortunately, the low oxidative stability of tung oil derived methyl ester would still have limitations in its applicability as a lubricating agent owing to its low oxidative stability.

There are several approaches to improve the oxidative stability of fatty acid alkyl esters directly by reducing the number of double bond (C=C) present in ester, or indirectly by using longer chains of alcohols during the (trans)esterification of oil, thereby resulting in less amount of double bond present for a given mass of fatty acid alkyl ester. Nicolau et al. [6] investigated the thermal stability of fatty acid alkyl esters derived from soybean oil and babasu oil, ethyl esters of these oils had better oxidative stability. A 10% weight was found at 157.8 °C and 150.7 °C for soybean oil ethyl ester and soybean oil methyl ester, respectively, while babasu oil ethyl ester had a 10% weight loss at 97.8 °C and at 87.3 °C for its methyl esters [6]. A more direct means of reducing double bonds or unsaturation is to eliminate these either by hydrogenation or epoxidation. Unfortunately, hydrogenation results not only in the reduction of unsaturated carbon bonds but transforms the fatty acid alkyl esters into their fatty alcohol counter parts [7], rendering them not suitable for use as liquid fuel nor as lubricants. As for epoxidation, oxirane rings are formed at each carbon double bond (C=C) by the addition or incorporation of oxygen atom to each unsaturation in the fatty acid chain using percarboxylic acids or organic/inorganic peroxides as an oxidizing agent [8–10]. Although epoxidation also renders the alkyl ester not suitable for use as fuel, it does improve its thermal and oxidative properties allowing it to be used as bio-lubricant base-stock [9–13] or as bio-plasticizer [14]. Furthermore, epoxidized fatty acid alkyl esters also serve as a versatile raw material, which could be further modified to achieve desired lubricating properties [8, 15].

The synthesis of epoxidized methyl ester of various oils such as those obtained from soybean [14], palm [12], cotton seed [13], karanja [10], tung [11], canola [15], castor [16], grapeseed, olive oil, and avocado [9] has previously been studied. One of the challenges in the use of commonly available oils is the presence higher portions of saturated fatty acids which do not participate in the epoxidation process and are not desired for applications as bio-plasticizer [14]. Preparation of epoxidized alkyl esters was through the transesterification of available epoxidized vegetable oils, as these were more readily available in the market [17, 18]. However, the conventional approach poses a problem when it is desired to obtain higher fractions of epoxidized alkyl ester. In a related work by Galli et al. [14], two strategies

were explored, the first one is through the epoxidation of soybean oil methyl ester and fractioned through distillation to remove most of the non-reacting and unreacted methyl ester, while the second strategy was to carry out epoxidation with pre-fractioned soybean oil methyl ester (without saturated esters). The latter was found to be more preferable in avoiding the reopening of the oxirane rings during distillation. Generally, the main idea is to carry out epoxidation with oil-based materials of high iodine value (high unsaturation), while taking advantage of the lower viscosities and relatively better hydrophilicity of alkyl esters than its parent oil. In line with these, tung oil as a starting material provides the advantage of having high unsaturation of constituent fatty acids.

Previous works have also looked into the influence of phase transfer catalyst (quaternary ammonium phosphotungstate) [11], lipase (Novozyme 435) [9] and acid (sulfuric, nitric, hydrochloric, phosphoric and Amberlite IR-120H) [10, 13, 15, 16] catalyzed, as well as non-catalytic [12] epoxidation of vegetable oil methyl esters on epoxidation rate. Although the presence or use of strong acids like that of sulfuric acid in residual quantities may improve the initial epoxidation rate, but would also hasten the degradation of the epoxy groups as the reaction progresses [19]. Thus, it would be of interest to prepare epoxidized alkyl esters without the use of inorganic acids or through non-catalytic approaches.

Studies on the epoxidation of tung oil alkyl ester have just recently started and limited information are currently available. Furthermore, fatty acids esterified with ethanol as a starting material has not been previously investigated. In this work, the epoxidation of tung oil ethyl ester (TOEE) was carried out. Preliminary investigation on the effects of hydrogen peroxide and formic acid loading during simultaneous epoxidation and in situ formation of peroxyformic acid as oxygen donor without the addition of inorganic catalyst were studied. Thermal and rheological properties of the synthesized epoxidized tung oil ethyl ester (ETOEE) were also determined to initially assess its applicability as a bio-lubricant base-stock.

Materials and Methods

Tung oil, hydrogen peroxide (34.5–36.5% w/w), formic acid (98% w/w), and potassium hydroxide (85% w/w) were procured from Sigma Aldrich (Steinheim, Germany). Ethanol 95% v/v was purchased from ECHO Chemical Co., LTD, Taiwan. In this study, tung oil (TO) having low acid value (< 1 mg KOH/g oil) was transesterified to produce TOEE and was then epoxidized with hydrogen peroxide in the presence of formic acid under different reaction conditions. Iodine value and fraction of epoxy groups present in the

resulting ETOEE were measured to determine the extent of epoxidation. Density, viscosity, thermal and oxidative stabilities of the ETOEE produced were determined to see if it qualifies as a bio-lubricant and identify its potential application.

Transesterification of Tung Oil

Tung oil was transesterified according to the optimized conditions established in the work of Chen et al. [4], with slight modification. In brief, TO was transesterified with ethanol at a molar ratio 1:20 (TO:Ethanol). TO (~20 g) was heated to 60 °C. Potassium hydroxide 1% w/w (based on TO) was dissolved in ethanol and added to the preheated TO and stirred continuously at 400 rpm. The reaction was allowed to proceed for at least 2 h. After transesterification, the ethyl ester rich phase and glycerol were separated. The ethyl ester rich phase was continuously washed with deionized water until the washings has pH close to neutral. The ethyl ester rich phase was then collected, dried, and is hereafter referred to as TOEE. TOEE was analyzed of its fatty acid distribution for determining its molecular weight according to the procedures previously employed for fatty acid alkyl ester analysis [20].

Epoxidation of Tung Oil Ethyl Ester

Tung oil ethyl ester (10 g) was placed into a 250 ml flask and a predetermined amount of formic acid was added. Hydrogen peroxide, which served as the oxidizing agent, was carefully added to the mixture dropwise within 60 min so to keep reaction temperature at 50 °C. The reaction mixture was continuously stirred at 400 rpm for 3 h under open reflux condition with the condenser maintained at 4 °C. After the reaction, the product was recovered using ethyl acetate and washed with deionized water to remove formic acid and unreacted hydrogen peroxide. The ethyl acetate layer was then concentrated and dried in a rotary evaporator at 90 °C to remove residual formic acid and hydrogen peroxide removed. Epoxidation experiments were carried out in triplicates. The resulting product is then referred to as ETOEE.

The iodine value before (IV_i) and after (IV_f) epoxidation process was determined. Iodine value was determined by using titrimetric method with Wij's reagent [21], with slight modification. Oil ($m_s = 0.5$ g) was weighed into a 500 ml volumetric flask and was then dissolved in cyclohexane. The Wij's solution was mixed with the solution containing oil. The mixture was placed in a dark place for 30 min at room temperature. Potassium iodide (10% w/v, 20 ml) was then added to the flask, followed by 150 ml of distilled water. The mixture was titrated by using standardized thiosulphate solution (0.1 N) until the endpoint with starch solution (1.5 ml) as the indicator. The volume of titrant used for the samples,

S , in ml was noted. A blank titration without oil was also carried out to determine the initial amount iodine present in the Wj's reagent, the volume of titrant, B in ml, used for the blank was then recorded. The iodine value was determined by using Eq. (1) and the degree of epoxidation was calculated using Eq. (2).

$$\text{Iodine Value (IV)}, \frac{\text{g I}_2}{100 \text{ g}} = \frac{12.69 \times N \times (B - S)}{m_s} \quad (1)$$

$$\text{Degree of Epoxidation, \%} = \frac{IV_i - IV_f}{IV_i} \times 100\% \quad (2)$$

Characterization of Epoxidized Tung Oil Ethyl Ester

Epoxy Group

To verify that the epoxidation was successfully carried out it is important to determine the actual oxirane ring group present or epoxy group in ETOEE, using the method of Ahmetli and Cerit [22]. ETOEE (0.5 g) was dissolved in 25 ml of analysis reagent (1.5 ml of concentrated HCl added to 60 ml of acetone). The mixture was allowed to react under continuous stirring for 2 h at room temperature. Then, the unreacted HCl was titrated with standardized 0.1 N KOH until the endpoint was reached using phenolphthalein as indicator. The percent epoxy group present in the sample was calculated using Eq. (3), with corrections for the acid value of the sample,

$$\text{Percent Epoxy Group, \%} = \frac{(V_1 - V_2 + V_3) \times 0.0043 \times F}{m_s} \times 100\% \quad (3)$$

where V_1 is ml of 0.1 N KOH solution used in the titration of the blank, V_2 is the ml of 0.1 N KOH solution used for the sample titration, V_3 is the ml of 0.1 N KOH solution used in acid value titration for the sample being analyzed, F is the titration factor for 0.1 N KOH solution, m_s is the amount the sample measured, and 0.0043 is corresponding epoxy groups for each ml of 0.1 N KOH.

FTIR Spectroscopy

A Fourier transform infrared (FTIR) spectrophotometer (FTS-3500, Bio-Rad, Burladingen, Germany) was used to help confirm the presence of epoxy groups, double bond, hydroxyl group, and ester groups. For FTIR analysis, the sample was analyzed with pelleted KBr powder as the background and scanned over a wavenumber of 3600 to 400 cm^{-1} . The results were collected, integrated and processed using Varian Resolutions 4.1.0.101.

Viscosity and Rheological Measurements

Dynamic viscosity was determined using an Ostwald viscometer with water as the reference material. Viscosity of samples were determined at temperatures from 40 to 100 °C. The temperature of the fluid being tested and the viscometer were maintained using a temperature controlled bath. Viscosity constant at temperatures near 100 °C were obtained by extrapolating from previously measured values. The sample's dynamic (η_1) and kinematic (ν_1) viscosities were then calculated using Eq. (4) and Eq. (5), respectively.

$$\eta_1 = \eta_2 \frac{\rho_1 t_1}{\rho_2 t_2} \quad (4)$$

$$\nu_1 = \frac{\eta_1}{\rho_1} \quad (5)$$

where η_1 and η_2 are the dynamic viscosity (cP) of the sample and the reference material, respectively, ρ_1 and ρ_2 are the corresponding densities determined using a pycnometer, while t_1 and t_2 are the time required for the respective fluids to travel through the capillary of the viscometer.

The influence of shear rate on ETOEE viscosity was also investigated using a Modular Compact Rheometer (MCR 102, Anton Paar, Graz, Austria). The samples were tested under lift position, measure position, shear rate, measure points, interval and ramp profile of 30 mm, 0.7 mm, 100–1000 s^{-1} , 10 points, 100 s, and linear, respectively. The resulting shear stress in Pa was then recorded and was also used to verify the dynamic viscosity expressed in Pa s.

Viscosity Index

Since viscosity is a strong function of temperature, to provide a more objective comparison between two lubricating fluids, the kinematic viscosity is normalized and expressed as viscosity index (VI). Viscosity index was calculated by using Eqs. (6) and (7).

$$VI = \frac{(10^N - 1)}{0.00715} + 100 \quad (6)$$

$$N = \frac{\log H - \log U}{\log Y} \quad (7)$$

where U and Y are the determined kinematic viscosity (cSt) at 40 °C and 100 °C, respectively, of the sample whose VI is to be calculated, while H is the kinematic viscosity (cSt) at 40 °C of an oil having a VI of 100, while having the same kinematic viscosity (cSt) at 100 °C as the sample whose VI is to be measured. Value for H was obtained from ASTM D2270 (Table 1) [23].

Table 1 Effect of hydrogen peroxide and formic acid on epoxidation of TOEE at 50 °C for 3 h (results are average values of epoxidation experiments carried out in triplicates)

TOEE (g)	Formic acid, FA (g)	H ₂ O ₂ solution (g)	Molar ratio (TOEE:FA:H ₂ O ₂)	Molar ratio (C=C:FA:H ₂ O ₂)	Iodine value (g I ₂ /100 g)	Conversion (%)
10	1.95	3.6	1:1.3:1.1	1:0.9:0.4	90.1 ± 2.9	54.0 ± 1.5
10	1.95	7.2	1:1.3:2.3	1:0.9:0.9	90.4 ± 2.3	53.9 ± 1.2
10	1.95	10.8	1:1.3:3.4	1:0.9:1.3	80.4 ± 0.8	58.9 ± 0.4
10	1.95	14.5	1:1.3:4.5	1:0.9:1.7	83.2 ± 2.9	57.6 ± 1.5
10	1.95	17.9	1:1.3:5.7	1:0.9:2.2	90.4 ± 1.2	53.9 ± 0.6
10	5.86	3.6	1:3.9:1.1	1:2.7:0.4	91.5 ± 1.6	53.3 ± 0.8
10	5.86	7.2	1:3.9:2.3	1:2.7:0.9	69.7 ± 1.5	64.4 ± 0.8
10	5.86	10.8	1:3.9:3.4	1:2.7:1.3	48.5 ± 2.2	75.3 ± 1.1
10	5.86	14.5	1:3.9:4.5	1:2.7:1.7	12.6 ± 1.6	93.6 ± 0.8
10	5.86	17.9	1:3.9:5.7	1:2.7:2.2	20.6 ± 0.4	89.5 ± 0.2

Thermal and Oxidative Stability

Tung oil and its derivatives, ethyl ester and epoxidized ethyl ester samples were characterized thermogravimetrically using a TG/DTG analyzer (Diamond, Perkin Elmer, Massachusetts, USA) at a heating rate of 10 °C/min from room temperature to 600 °C under inert or oxidative atmosphere. Thermal stability was assessed under a continuous stream of nitrogen, as for oxidative stability a continuous stream of air was used instead.

Results and Discussion

Transesterified TO comprised fatty acid chains with the following composition: 2.1% palmitic (16:0), 7.8% linoleic (18:2), 6.9% oleic (18:1), 2.5% stearic (18:0), 1.0% linolenic (18:3), 78.2% eleostearic (18:3), 0.5% arachidic (20:0), 0.9% paullinic/gondoic (20:1), and 0.2% lignoceric (24:0) acids. The obtained partially processed TOEE contained at least 97% ethyl esters, with an estimated molecular weight of 307.4 g/mol and a theoretical iodine value of 215.5 g I₂/100 g. The TOEE obtained was then epoxidized to investigate the effect of formic acid and hydrogen peroxide loading on the degree of epoxidation and the influence of epoxidation on the rheological and thermal characteristics.

Effects of Hydrogen Peroxide and Formic Acid During Epoxidation

Partial oxidation of a double bond in a fatty acid chain requires an oxygen donor usually in the form of peroxy acid, usually performic acid or peracetic acid [10, 12, 13, 15, 16, 24]. Once peroxy acid reacts with ethylenic unsaturated group to form oxirane rings, the carboxylic acid (CA) that is originally part of peroxy acid is released [9, 12]. Thus, if hydrogen peroxide is present in the reaction system it may

then react with the released CA to produce peroxy acid to react with the remaining ethylenic unsaturated bonds. This opens the possibility of carrying out epoxidation with simultaneous or in situ peroxy acid formation. Thus, the ideal ratio of the available carbon double bonds, carboxylic acid and hydrogen peroxide should be 1:1:1. However, as can be observed from the results summarized in Table 1, increasing hydrogen peroxide near the required molar quantity only slightly improved the conversion or reduced ethylenic unsaturated bonds, with at least half of the available double bonds having been reacted. Further addition of hydrogen peroxide to twice of the required molar quantity did not result in further decrease in the iodine value (~80 g I₂/100 g) or improve conversion (~60%) of available ethylenic unsaturated bonds after a total reaction time of 4 h at 50 °C. Instead, excess addition of hydrogen peroxide resulted in the decrease in conversion. This may be due to dilution effect, since hydrogen peroxide was added as an aqueous solution contain 34 to 36 wt% hydrogen peroxide. In principle, it is expected that formic acid released after epoxidation would result in further reaction with the excess peroxide to continuously perpetuate the epoxidation process. However, this was not apparent at low formic acid loading, probably because no inorganic acid was used, resulting in peroxy acid with less reactivity and slower reaction rate.

The presence of inorganic acid not only serves as catalyst in conventional epoxidation processes, but may also form peroxy acid which directly oxidizes ethylenic unsaturated bonds. Thus, resulting in faster reaction rates and have higher conversions. In the study by Dinda et al. [13], a conversion of available double bonds to almost 60% was achieved in 4 h in the epoxidation of cottonseed oil at a C=C:CA:H₂O₂ molar ratio of 1:0.5:1.5 using 2% sulfuric acid. Despite the fact that triglycerides possess higher viscosity and using lower CA (acetic acid) loading, similar conversion of ethylenic unsaturated bonds was achieved in the presence of a catalyst. Another means to push forward

epoxidation reaction is to ensure the formation of peroxy acid as this is often considered to be the rate limiting step [9, 12]. In this study, this was achieved by adding more formic acid to push the reaction forward. Increasing formic acid loading 3 times of what was originally used resulted in significant decrease in iodine value to 12.6 g I₂/100 g at a 1:2.7 molar ratio of C=C:CA and as the ratio of H₂O₂:C=C was increased from 0.4 to 1.7 (Table 1). Further increase in hydrogen peroxide addition still resulted in a relatively lower conversion of ethylenic unsaturated bonds, which is consistent with the findings at lower formic acid loading.

Although the process has not been optimized, these initial results provide the possibility of carrying out epoxidation of ethyl esters simultaneously with in situ peroxy acid formation without the use of inorganic catalyst, making the process truly renewable. Compared to the epoxidation of tung oil methyl esters by Zheng et al. [11] where the highest oxirane number or epoxy value of 4.9 g/100 g was achieved at 50 °C at a reaction time of 3 to 4 h, with a H₂O₂:C=C of 1.6; this study did not require the use of phase transfer catalyst (quaternary ammonium phosphotungstate) while still obtaining epoxidized alkyl esters with high oxirane number (5.1 g/100 g).

Physicochemical Properties of Epoxidized Tung Oil Ethyl Ester

Shown in Table 2 are some physicochemical properties of TO and its derivatives. After epoxidation a slight increase in acid value and free fatty acid content were observed. This may be due to hydrolysis of esters in the presence of water in the reaction mixture during the epoxidation process. Iodine value decreased after epoxidation, however, the observed decrease in iodine value may partly be due to saponification which may have occurred during the transesterification step as the ethanol used was not anhydrous. The mass yield of TOEE after esterification was only ~87.2% w/w (based on weight of oil reacted) on average, indicating losses in the expected products. Nevertheless, as previously mentioned

Table 2 Some physicochemical properties of tung oil and its derivatives (results are average values of analysis and/or epoxidation experiments carried out in triplicates)

Specification	TO	TOEE	ETOEE
Acid value (mg KOH/g oil)	0.28±0.02	0.25±0.03	1.21±0.08
Free fatty acid (%w/w)	0.14±0.01	0.13±0.02	0.61±0.04
Iodine value (g I ₂ /100 g oil)	224.61±1.79	196.00±1.80	12.56±1.62
Epoxy group (%w/w)	–	–	5.09±0.08
Density at 25 °C (g/mL)	0.94±0.001	0.91±0.01	1.26±0.01

the obtained TOEE contains 97% ethyl esters, which is reasonably high for use in epoxidation studies.

Although iodine value has been significantly decreased from 196 to 12.6 g I₂/100 g, an important measure to determine the successful formation of epoxide is the determination of the presence of oxirane rings. As shown in Table 2, no oxirane rings were detected for TO and TOEE, while ETOEE has an oxirane content of 5.09 g/100 g. Theoretically the maximum oxirane oxygen that could be formed based on the available ethylenic unsaturated bond is ~10.9 g/100 g. At an ethylenic unsaturated bonds conversion of 93%, an oxirane number of 10.1 g/100 g should have been achieved. The difference observed may be because of the formation of hydroxyl groups which is one of the dominant side reactions in the presence of water & hydrogen peroxide and under acidic conditions [12, 24]. Although the relative yield of oxirane oxygen is only 46.8%, the absolute quantity of oxirane groups is higher than those reported in literatures which ranges from 2.8 to 5.8 g/100 g [10–12, 16, 24]. A marked increase in density was observed after epoxidation. The increase in density is due to the increase in molecular weight, increase in polarity and intermolecular attraction of molecules as new polar functional groups are formed or attached making the resulting molecule not only heavier but more compact [24].

To confirm the successful reduction of ethylenic unsaturated bonds, FTIR spectra of TO, TOEE and ETOEE were obtained and are presented in Fig. 1a. Tung oil and TOEE which have high fractions of ethylenic unsaturated bonds have sharp and distinct peaks at 3010 cm⁻¹ and 736 cm⁻¹, while none could be observed for ETOEE, which is consistent with findings from other works [10, 12, 16, 24]. The ETOEE sample has weak transmittance peaks at 840–915 cm⁻¹ (Fig. 1b) indicating the presence of oxirane oxygen [11, 12], while the broad peak from 3200 to 3600 cm⁻¹ indicates the presence of hydroxyl groups.

Rheological measurements for ETOEE were carried out using a rheometer to measure shear stress induced as shear rate was varied from 100 to 1000 s⁻¹ at different temperatures (40 °C, 60 °C, 80 °C, 100 °C) for later assessment in its applicability as a lubricant. As can be observed in Fig. 2, shear stress increased linearly with shear rate at all temperatures investigated, indicating that ETOEE is a Newtonian fluid. The rheological behavior exhibited by ETOEE is consistent with other epoxidized fatty acid alkyl esters such as that derived from waste cooking oil [24]. The decrease in dynamic viscosity with increasing temperature can be described by an exponential function as shown in Fig. 2b.

Thermal and Oxidative Stability of ETOEE

As previously mentioned, the elimination of double bonds by the formation of oxirane rings allows the improvement

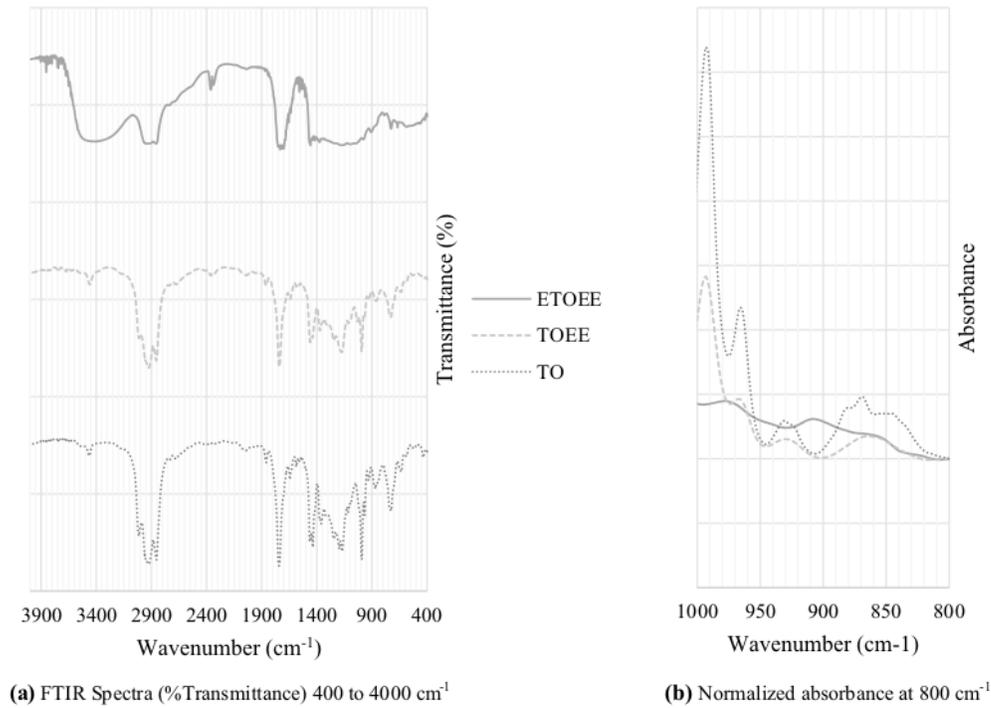
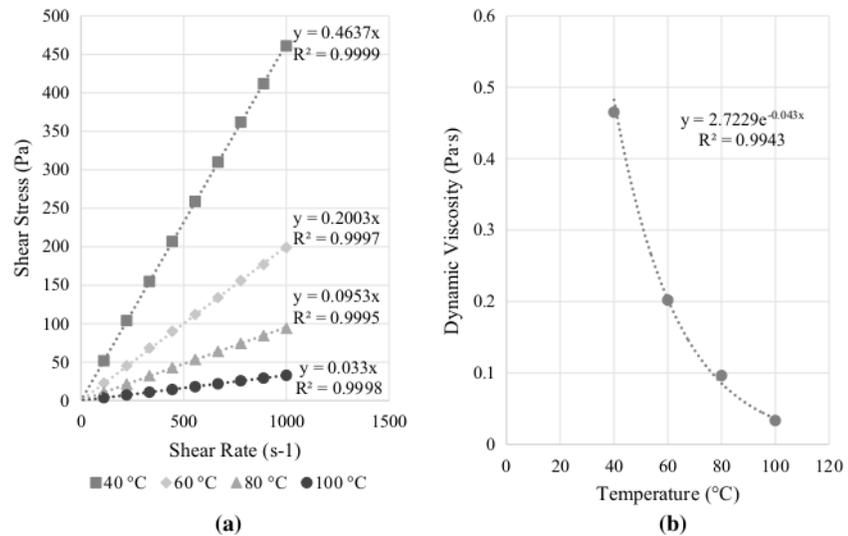


Fig. 1 Comparison of infrared spectra of tung oil (TO), tung oil ethyl ester (TOEE) and epoxidized tung oil ethyl ester (ETOEE) (Results were taken from TGA analysis of pooled samples from epoxidation reactions)

Fig. 2 Dependence of shear stress on shear rate at temperatures from 40 to 100 °C (a) and the effect of temperature on dynamic viscosity (b) of epoxidized tung oil ethyl ester (ETOEE) (Results from analysis of pooled samples from epoxidation reactions)



of thermal stability of the bio-lubricant. As shown in Fig. 3 and Table 3, thermal and oxidative stability of TO was found to be the highest, followed by ETOEE and TOEE. The same trend was observed for methyl esters and epoxidized methyl

esters from TO as reported by Zheng et al. [11]. Although the extrapolated on-set temperature for thermal degradation of ETOEE is 221 °C, changes in weigh occurred at 63 °C and significant changes of up to 5% was observed at 128 °C.

Fig. 3 Thermogravimetric profile of tung oil and its derivatives under inert (a thermogram and b differential thermogram) and oxidative atmosphere inert (c thermogram and d differential thermogram) (results were taken from TGA analysis of pooled samples from epoxidation reactions)

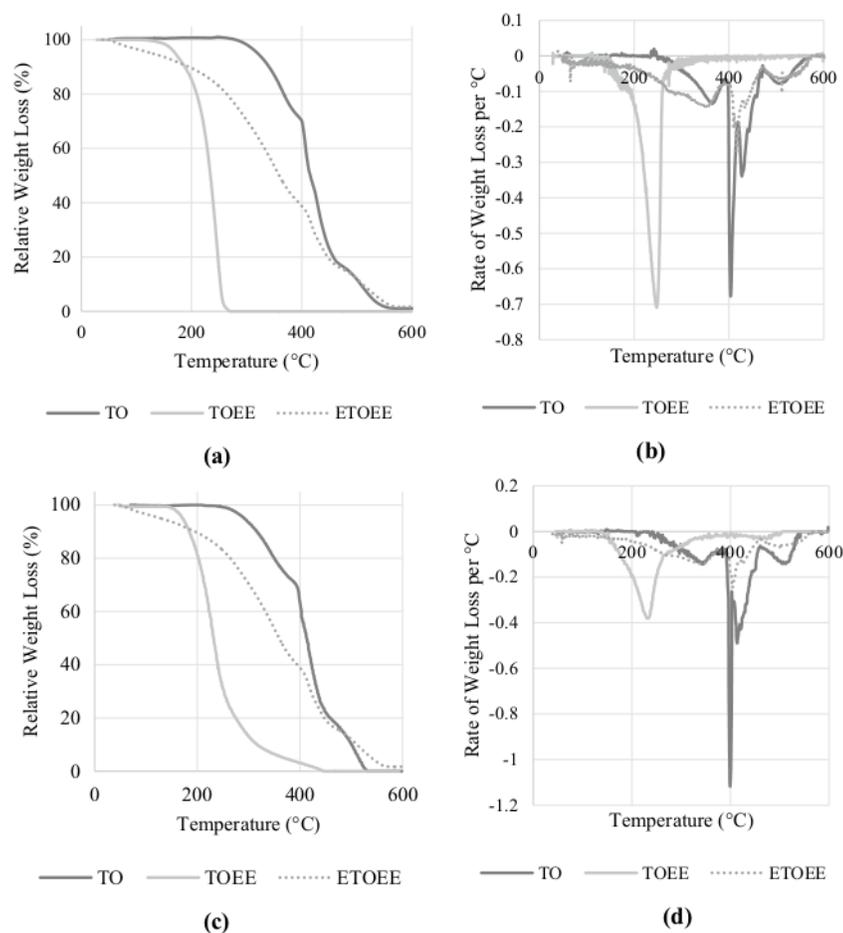


Table 3 Thermogravimetric characteristic of tung oil and its derivatives (results were taken from TGA analysis of pooled samples from epoxidation reactions)

Thermogravimetric information	Oil or lubricant		
	TO	TOEE	ETOEE
On-set temperature, °C inert atmosphere	331	190	221
On-set temperature, °C (weight loss > 1%)	293	143	63
On-set temperature, °C (weight loss > 5%)	320	171	128
On-set temperature, °C (weight loss > 50%)	415	234	359
On-set temperature, °C (highest weight loss per min)	404	249	416
Highest rate of weight loss (%/min)	-0.677	-0.702	-0.268
On-set temperature, °C oxidative atmosphere	306	175	200
On-set temperature, °C (weight loss > 1%)	255	148	63
On-set temperature, °C (weight loss > 5%)	292	172	128
On-set temperature, °C (weight loss > 50%)	413	231	358
On-set temperature, °C (highest weight loss per min)	399	231	404
Highest rate of weight loss (%/min)	-1.117	-0.380	-0.247

This may be owing to the presence of hydroxyl groups which was removed during heating, similar to dehydration process, which resulted in the observed weight loss. Similar trends were observed for analysis under oxidative atmosphere except that degradation was observed at temperatures lower by at least 20 °C.

In order to further support the positive effects of epoxidation on thermal stability, ETOEE produced under different formic acid and hydrogen peroxide loading were also studied. As shown in Fig. 4, ETOEE from reactions with higher FA loading, which corresponds to higher degree of epoxidation or better reduction in ethylenic unsaturated bonds, had higher stability based on the maximum on-set thermal degradation temperature. Increase in hydrogen peroxide resulted in the increased reduction of ethylenic unsaturated bonds, thus, resulting in better stability. Although reduction in ethylenic unsaturated bonds did not entirely result in the formation oxirane rings, the reduction of these unsaturated bonds is key to improving thermal stability.

Comparison with Other Epoxidized Fatty Acid Alkyl Esters

A summary of the physicochemical properties of ETOEE obtained in this study with those of epoxidized fatty acid alkyl esters reported in literatures is presented in Table 4. It can be concluded that epoxidized alkyl esters with longer alkyl chains, higher oxirane value and parent fatty acids of less unsaturation have better oxidative stability. The thermal stability of ETOEE (200 °C) is better than that of epoxidized methyl linolenate (131 °C) [25], which has the same number of unsaturated bonds as that of eleostearic acid (18:3), the fatty acid component in TO. The better stability of ETOEE is owing to the presence of other fatty acid chains with less unsaturation. Epoxidize tung oil ethyl ester has much higher viscosity than other epoxidized fatty acid alkyl esters. One possible cause for the observed

difference is the incorporation of longer alkyl chains. Gorla et al. [10] reported that the kinematic viscosity of epoxidized n-butyl esters of karanja oil (11.1 mm²/s) was higher than that of karanja oil methyl esters (8.9 mm²/s). However, the much higher kinematic viscosity of ETOEE (369.3 mm²/s) obtained in this work may have resulted owing to the inherent structure of ETOEE which comprises branched groups resulting from the side reaction after the oxirane ring formation. Nevertheless, the high viscosity of ETOEE may be beneficial, as additives may not be necessary to maintain high viscosities when used in applications with higher temperatures. Moreover, the viscosity index of the resulting ETOEE of 95 is within the recommended value of 80 to 120 lubricants for use in gear boxes and engines.

Conclusions

Tung oil ethyl ester was successfully produced and further epoxidized in the presence of hydrogen peroxide and formic acid (FA), without the addition of inorganic catalyst. The highest conversion of 93.6% (based on reduction of iodine value) was achieved by reacting 10 g of TOEE with 14.5 g of hydrogen peroxide and 5.86 g of FA (C=C:H₂O₂:FA=1:2.7:1.7), while the reaction was maintained at 50 °C for 3 h. Under the favorable epoxidation conditions, the resulting ETOEE has an oxirane number or epoxy value of 5.1%, an on-set oxidation temperature of 200 °C, kinematic viscosities of 369.3 mm²/s (40 °C) and 26.4 mm²/s (100 °C), and a viscosity index of 95. The resulting ETOEE behaves like a Newtonian fluid and could potentially be used as lubricant for gear box and engines. In view of the non-catalytic epoxidation process, precursor acid like formic acid should be introduced in excess to make sure that the formation of peroxyacid enough to induce the subsequent oxirane ring formation,

Fig. 4 Influence of molar ratio of ethylenic unsaturated bonds (C=C) to formic acid (FA) and hydrogen peroxide (H₂O₂) ratios on maximum decomposition temperature of epoxidized tung oil ethyl ester under inert atmosphere (results were taken from TGA analysis of pooled samples from epoxidation reactions)

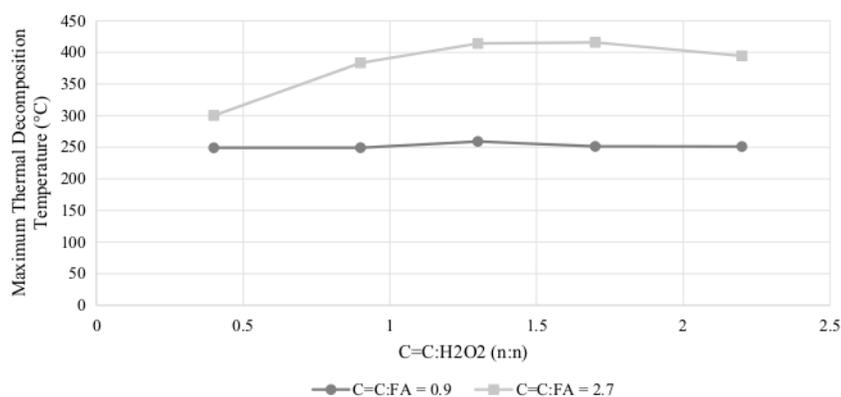


Table 4 Comparison of some physicochemical properties of different epoxidized fatty acid alkyl esters

Fatty acid source	Product	Degree of epoxidation (%)	Epoxidation number or oxirane value (g/100 g)	Oxidation on-set temperature (°C)	Kinematic viscosity at 40 °C (mm ² /s)	Kinematic viscosity at 100 °C (mm ² /s)	Viscosity index	Ref.
Tung oil	Epoxidized tung oil ethyl ester	93.6 ^a	5.1	200	369.3	26.4	95	This work
Tung oil	Epoxidized tung oil methyl ester	–	4.9	176	–	–	–	[11]
Canola Oil	Epoxidized tung oil methyl ester	–	–	160	–	–	–	[15]
Olive/avocado/ grapeseed oil	Epoxidized oil methyl ester	99	–	–	–	–	–	[9]
Karanja oil	Epoxidized karanja oil methyl ester	93.7	3.6	–	8.9	2.5	111	[10]
Karanja oil	Epoxidized karanja oil n-butyl ester	95.7	3.9	–	11.1	3.1	148	
Palm fatty acid distillate (PFAD)	Epoxidized PFAD methyl ester	93.8	2.8	–	–	–	–	[12]
Castor oil	Epoxidized castor oil methyl ester	98.5	4.8	308	35.8	–	–	[16]
Waste oil	Epoxidized waste oil methyl ester	99.8	5.8	200	10.4	3.3	214	[24]
Methyl oleate	Epoxidized methyl oleate	–	–	190	–	–	151	[25]
Methyl linoleate	Epoxidized methyl linoleate	–	–	180	–	–	132	
Methyl linolenate	Epoxidized methyl linolenate	–	–	131	–	–	63	

^aBased on iodine value reduction

while hydrogen peroxide should be added in excess, but at a quantity which would not result in the dilution of the reaction system. The reduction of double bonds owing to epoxidation and its later side reactions, as well as the use of longer alkyl chains during esterification improves not only the oxidative stability but also results in increased viscosity. Tung oil is a potential renewable raw material for the production of bio-based lubricants, which does not compete with food and fuel applications.

Compliance with Ethical Standards

Conflict of interest All author declares that they have no competing interest.

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