

THE EFFECT OF CHEMICAL STRUCTURE ON POUR POINT, OXIDATIVE STABILITY AND TRIBOLOGICAL PROPERTIES OF OLEIC ACID TRIESTER DERIVATIVES

(Kesan Struktur Kimia Pada Titik Pour, Kestabilan Pengoksidaan Dan Sifat Tribological Derivatif Triester Asid Oleik)

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Abstract

Due to the strict regulations imposed on non-biodegradable mineral oil-based lubricants, the development and applications of biolubricants are increasing daily. Plant oils are being investigated as a potential source of environmentally favorable lubricants because of their biodegradability, renewability, viscosity-temperature relationship, low volatility and excellent lubrication performance. However, the use of plant oils has some restriction, the most critical being oxidative stability and low-temperature problems. This paper presents systematic modifications to improve the physicochemical and tribological properties of plant oil derivatives. The results showed that among the oleic acid-based triester compounds, 2-ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate (**9**) had the lowest pour point (-47.19 °C) while 2-ethylhexyl 9-(caprooxy)-10-(heptanoyloxy)octadecanoate (**5**) had the highest onset temperature (103.10 °C). Overall, the data indicate that the biolubricant basestocks based on this chemical modification offer great potential for the development of industrial products application.

Keywords: Plant oils, pour point, physicochemical properties, biolubricant basestocks

Abstrak

Perkembangan dan penggunaan biopelincir telah meningkat saban hari disebabkan oleh penguatkuasaan yang lebih ketat dikenakan keatas minyak pelincir berasaskan minyak mineral yang takterbiourai. Minyak tumbuhan telah dikaji sebagai sumber yang berpotensi untuk minyak pelincir disebabkan oleh sifat terbiourai, terganti semula, hubungan kelikatan-suhu yang baik, kemeruapan yang rendah dan prestasi pelinciran yang cemerlang. Walaubagaimana pun penggunaan minyak tumbuhan mempunyai kelemahan terutamanya sifat kestabilan oksidatif and sifat suhu rendah yang rendah. Kertas kerja ini membentangkan pengubahsuaian kimia secara sistematik untuk meningkatkan sifat-sifat fizikokimia dan tribologi terbitan minyak tumbuhan. Hasil kajian menunjukkan bahawa diantara sebatian berasaskan asid oleik, 2-etilheksil 9-(miristoksi)-10-(heptanoiloksi)oktadekanoat (**9**) mempunyai takat tuang terendah (-47.19 °C) sementara 2-etilheksil 9-(kaproksi)-10-(heptanoiloksi)oktadekanoat (**5**) mempunyai suhu onset tertinggi (103.10 °C). Secara keseluruhan, hasil kajian menunjukkan stok asas biopelincir berasaskan pengubahsuaian kimia ini memberikan potensi yang tinggi untuk pembangunan produk kegunaan industri.

Kata kunci: Minyak tumbuhan, takat tuang, sifat fizikokimia, minyak asas biopelincir

Introduction

Stronger environmental concerns and growing regulations over contamination and pollution will increase the need for renewable and biodegradable lubricants [1]. Most lubricants originate from petroleum stock, which is environmentally toxic and difficult to dispose of. Because of the growing environmental concerns over petrochemical disposal, plant oils and their derivatives are finding a place as lubricants in industrial and

transportation applications. Plant oils with high oleic acid content and synthetic ester derivatives are considered to be potential candidates to replace conventional mineral oil-based lubrication oils and synthetic esters [2].

There are several reasons to use plant oils or plant oil derivatives as biolubricants. Because as much as 40% [3] of a lubricant can be lost to the environment, the inherent biodegradability of plant oils reduces their environmental impact. Other advantages include low volatility, superior lubricity and good anticorrosion properties [4].

The majority of plant oils consist primarily of triacylglycerols (TAGs), which are glycerol molecules with three fatty acid (FA) chains attached at the hydroxyl groups via ester linkages. The fatty acids vary in the length of their hydrocarbon chains and in their degree of unsaturation [5]. Triacylglycerol molecules orient themselves with their polar end at the solid surface making a close-packed monomolecular or multimolecular layer [6], which results in a surface film that is believed to inhibit metal-to-metal contact and the progression of pits and asperities on the metal surface. Furthermore, this lubricant film helps in reducing both friction and wear.

Despite the many advantages of plant oils, there are two major problems, inadequate oxidative stability and poor low-temperature properties, that restrict their use as biolubricant basestocks [7]. Low-temperature studies have shown that most plant oils undergo cloudiness, precipitation, poor flow, and solidification at $-10\text{ }^{\circ}\text{C}$, the temperature considered the benchmark for long-term exposure to cold, which is in contrast to the behavior of mineral oil-based fluids [8].

The chemical modification of plant oils is an attractive way to solve these problems. Transforming alkene groups in plant oils to other stable functional groups could improve their oxidative stability, whereas, the reducing structural uniformity of the oil by attaching alkyl side chains would improve its low-temperature performance [9].

Based on our previous research on the development of biolubricant basestocks, the ring-opening reaction of epoxidized oleic acid followed by the esterification of the resulting hydroxyl groups improved the physicochemical and tribological properties of the synthetic product oils [10]. The objective of this work was to prepare new synthetic biolubricants basestocks from epoxidized oleic acid and to study their low-temperature and thermo-oxidative properties and other physicochemical properties, such as their tribological properties. In this study, the addition of heptanoic acid to the oxirane moiety of epoxidized oleic acid (EOA) at elevated temperature ($100\text{ }^{\circ}\text{C}$) is the key step in a four-step sequential reaction (Fig. 1). The utilization both head-group manipulation and branching strategies allowed the major physical properties of these lipid-based materials to be improved.

Materials and Methods

Materials

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA) and oleic acid (92%) from ChemaR (Poland). All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI). All materials were used without further purification and all organic extracts were dried using anhydrous magnesium sulfate (Aldrich Chemical).

Characterization

^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECP 400 spectrometer operating at a frequency of 400.13 and 100.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in DMSO-d_6 (Cambridge Isotope Laboratories, Andover, MA) as the solvent. Each spectrum was Fourier-transformed, phase-corrected, and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software. FTIR spectra were recorded directly on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe over a scanning range of $650\text{--}4,000\text{ cm}^{-1}$ using 32 scans to give a spectral resolution of 4 cm^{-1} .

The pour point and the cloud point

Pour points (PP) and cloud points (CP) were measured using the ASTM D5949 [11] and ASTM D5773 [12] methods, respectively, with a Phase Technology Analyzer, Model PSA-70S (Hammersmith Gate, Richmond, B.C., Canada). The pour point of a sample is the lowest temperature at which it will pour or flow as an oil under the

prescribed conditions. It is a rough indication of the lowest temperature at which oil is readily pumpable. The cloud point is the temperature at which dissolved solids, such as paraffin wax, are no longer completely soluble, instead precipitating as a second phase giving the fluid a cloudy appearance. In the petroleum industry, the presence of solidified waxes thickens the oil, causing clogs in the fuel filters and injectors of engines. Waxes also accumulate on cold surfaces and form an emulsion with water. Therefore, the cloud point indicates the tendency of oil to plug filters or small orifices at cold operating temperatures. All runs were carried out at least in duplicate and the average values were reported with their standard deviations (\pm SD).

The flash point

The flash point (FP) measures the tendency of a specimen to form a flammable mixture with air under controlled laboratory conditions. The flash point of a volatile liquid is the lowest temperature at which it will vaporize to form an ignitable mixture in air. The lower the flash point, the easier it is to ignite the material. The flash point is an important component of a number of properties that should be considered when assessing the overall flammability hazard of a material. The flash points were determined by ASTM D56-05 [13]. All runs were carried out at least in duplicate and the average values were reported with their standard deviations (\pm SD).

Viscosity index measurements

Automated multi-range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure viscosity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 or 100.0 °C. The viscosity and the viscosity index were calculated using ASTM methods D445-97 [14] and D2270-93 [15], respectively. Triplicate measurements were made and the average values were reported with their standard deviations (\pm SD).

The pressure differential scanning calorimetry (PDSC) method

The experiments were performed using a DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically a 1.5-2.0 mg sample was taken in a hermetically sealed-type aluminum pan with a pinhole lid for interaction of the sample with the reactant gas (dry air). A film thickness of less than 1 mm was required to ensure proper oil-air interaction and eliminate gas-diffusion limitations. Dry air (Gateway Airgas, St Louis, MO) was pressurized in the module at a constant pressure of 1379 kPa. A 10 °C/min heating rate from 50 to 350 °C was used during each experiment. The onset temperature (OT, °C) and the signal maximum temperature (SMT, °C) of the oxidation were calculated from the exotherm for each sample. Each sample was run in triplicate and the average values were reported with their standard deviations (\pm SD).

The density determination method

Density determinations were made at 20 °C based on the ASTM method D1298-99 [16], using a glass hydrometer provided by Lanxi Comp., Shanghai, China.

The volatility determination method

The volatility was determined in agreement with ASTM method D6184 [17] in an electrical stove using glass pans of 4 cm in diameter.

The tribological test method

Tribological determinations were performed according to ASTM method D4172-94 [18] using the four-ball method (Anton Paar Physica MCR301, Germany) via a Rheoplus/ 32 V3.40 software. Each sample was run in triplicate and the average values were reported with their standard deviations (\pm SD).

Synthesis Procedure

Epoxidized oleic acid (EOA) (2)

Hydrogen peroxide solution (30 % in H₂O, 8.0 mL) was slowly added into a stirred solution of oleic acid (OA) (92 %, 15 g) in formic acid (88 %, 14 mL) at 4 °C (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until the formation of a powdery solid was observed in the reaction vessel (2-5 h). The solid was collected via vacuum filtration, washed with H₂O (chilled, 3×10 mL), and placed under high vacuum for 12 h to produce epoxidized oleic acid (EOA) as a colorless, powdery solid.

9-Hydroxy-10-heptanooxyoctadecanoic acid (HHODA) (3)

Heptanoic acid (6 g) was added to a mixture of EOA (31 g) and 5 g of *p*-toluenesulfonic acid (PTSA) in toluene over a period of 1.5 h in order to keep the reaction mixture temperature under 70-80 °C. The reaction mixture was subsequently heated to 90-100 °C and held there for 3 h. After termination of the reaction, the heating was stopped and the mixture was left to stand overnight at room temperature. The mixture was washed with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using a vacuum evaporator.

2-Ethylhexyl 9-hydroxy-10-heptanooxyoctadecanoate (EHHHOD) (4)

Sulfuric acid (conc. H₂SO₄, 10 mol-%) was added to a stirred suspension of 9-hydroxy-10-heptanooxyoctadecanoic acid (3.35 mmol) in 2-ethylhexanol (3.35 mL). The suspension was heated with stirring at 60 °C for 10 h. Hexanes (5 mL) was added, and the solution was washed with NaHCO₃ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried (MgSO₄), filtered, concentrated *in vacuo* and placed for 6 h under vacuum to yield the title product.

2-Ethylhexyl 9-(acyloxy)-10-(heptanoyloxy)octadecanoate (EHAHOD) (5-9)

Either caproic acid (5 g), octanoic acid (5 g), capric acid (5 g), lauric acid (5 g) or myristic acid (5 g) was added to a solution of 2-ethylhexyl 9-hydroxy-10-heptanooxyoctadecanoate (5 g) and sulfuric acid (10% H₂SO₄) in a two-neck round-bottomed flask equipped with a magnetic stir bar at room temperature; then the reaction mixture was heated to reflux with stirring for 10 h. After the reaction was transferred to a separatory funnel, the lower aqueous phase was removed and hexane (20 mL) was added to the upper oily phase. The organic phase was washed with NaHCO₃ (sat. aq., 2 × 5 mL) and brine (2 × 5 mL), dried (MgSO₄), filtered, concentrated *in vacuo*, and placed under high vacuum for 6 h to provide the triesters as clear oils, which were stored over molecular sieves to mitigate potential hydrolysis.

Results and Discussion

Synthesis

Based on our previous studies, we found that increasing the mid-chain ester group length improved the low-temperature properties but had a negative effect on oxidative stability [19]. Therefore, we continued researching chemically modified biolubricant basestocks.

In the present work, we describe the synthesis of the monoester derivative through a two-step reaction (epoxidation of oleic acid and oxirane ring opening) to afford monoester 9-hydroxy-10-heptanooxyoctadecanoic acid (**3**). Furthermore, esterification of the carboxylic acid hydroxyl group with 2-ethylhexanol gave diester 2-ethylhexyl 9-hydroxy-10-heptanooxyoctadecanoate (**4**), and finally, esterification of the resulting α -hydroxy group in diester **4** with caproic, octanoic, capric, lauric or myristic acids yielded triesters 2-ethylhexyl 9-(acyloxy)-10-(heptanoyloxy)octadecanoate **5-9**, respectively (Fig. 1). The straightforward epoxidation of oleic acid was closely monitored to avoid the synthesis of the undesired 9,10-dihydroxyoctadecanoate, which will form if the reaction is performed at elevated temperature or the reaction is allowed to progress for too long.

The low-temperature fluidity of EOA (**1**) is low, and its pour point is 0 °C (Table 1). The low pour point of plant oil prevents its use at low operating temperatures. A method to improve the low-temperature flow property is to introduce branching sites at the epoxy carbons. The branched products have significantly improved low-temperature flow characteristics and friction-wear properties compared with EOA or olefinic analogs [19]. Furthermore, the elimination of the unsaturated double bond in oleic acid through an epoxidation reaction improves the oxidation stability of the resulting products [20]. It has been established that the presence of multiple double bonds in plant oil fatty acid chains accelerates oxidative degradation. However, a balance must be obtained between improving the oxidative stability and preserving the lubricating properties of the plant oils. Too many modifications may destroy the properties that make plant oils useful in the first place.

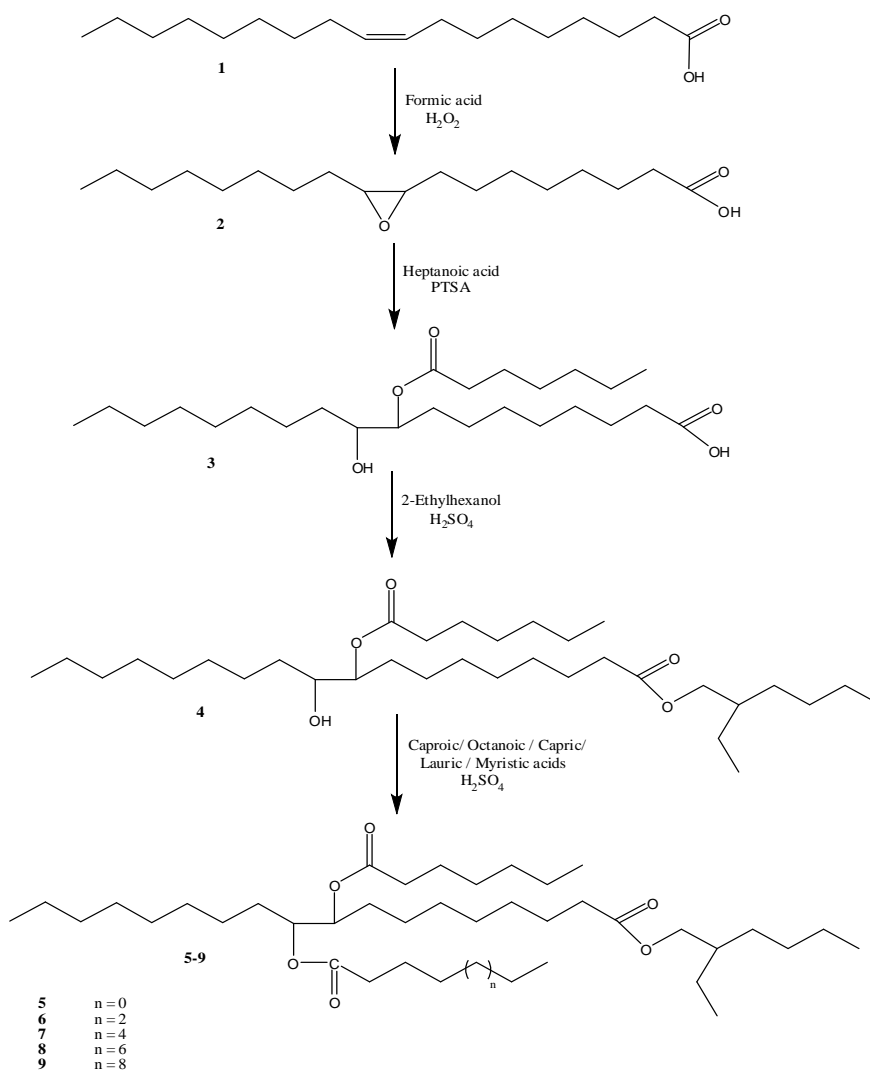


Fig. 1. The reaction scheme for triester formation.

Characterization

The FTIR spectrum of EOA (**2**) shows the characteristic peaks of an epoxy group at 826 and 845 cm⁻¹. The other important peaks observed in the FTIR spectrum are: 720 (methylene in-phase rocking); 1380 (methyl symmetric deformation); 1465 (methyl antisymmetric deformation) and 1742 cm⁻¹ (the C=O stretch) [21].

In the FTIR spectra of compounds **3-9**, the absorption bands from the epoxy group (826 and 845 cm⁻¹) are not observed. This result suggests that **2** undergoes complete ring opening under the reaction conditions. Bands representing C=O groups (~722, 1748 cm⁻¹), CH₃ groups (~1370-1462 cm⁻¹), OH groups (~3473-3450 cm⁻¹) and the C-O-C bands of esters (~998-1105 cm⁻¹) are clearly visible in the spectra [22].

The structures of all synthesized compounds were also verified by ¹H and ¹³C NMR spectroscopy. Significant signals in the ¹H spectrum of EOA (**2**) at ~2.8-2.10, ~9.26-9.29 and ~2.05-3.71 ppm were due to the quaternary hydrogens of the oxirane ring, the OH group, and the -CH₂- groups, respectively. Furthermore, in the ¹³C spectrum,

the signals at ~56.87-56.90 ppm were due to the carbons of the oxirane ring. On the other hand, in the ^1H NMR spectra of triesters 2-ethylhexyl 9-(acyloxy)-10-(heptanoyloxy)octadecanoate (**5-9**), there were no signals from an OH proton. Furthermore, in the ^{13}C NMR spectra, the signals at approximately ~174-178 ppm are attributed to the ester carbonyl groups [21]. These signals provide evidences for the proposed structures.

Low-temperature fluidity, flash point, and viscosity index measurements

The pour point (PP) and cloud point (CP) of a biolubricant are good indicators of its low-temperature fluidity. The cold flow properties of unmodified plant oils are poor and this limits their use at subzero temperatures. At low temperatures, plant oils have a tendency to form macro crystalline structures through uniform stacking of the “bent” triglyceride backbone. Such macro-crystals restrict the easy flow of the system due to the loss of kinetic energy of the individual molecules during self-stacking. Branching on the fatty acid chains may disrupt this stacking process and result in improved low-temperature properties [3]. This approach is used here to improve the low-temperature flow behavior of fatty acid triesters. The ester branching is attached at the mid- and end-sites on the fatty acid chains as shown in Fig. 2.

The attachment of an ester side chain of optimum length at the 9 or 10 position of the fatty acid chain improved the pour point significantly [23]. While EOA has a pour point of 0 °C and a cloud point of 10.24 °C; all the synthesized esters (**3-9**) have much better pour points, in the range of -16.12 to -47.19 °C, and CPs in the range -13.11 to -45.63 °C. Attachment of myristic acid to produce 2-ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate (**9**) showed the most effective decrease in the pour point and cloud point to -47.19 and -45.63 °C, respectively. It can be assumed that the presence of a large branching group at the mid-point of a fatty acid chain creates a steric barrier around the individual molecule and inhibits crystallization, the result of which is lower pour and cloud points (Table 1).

The flash point is useful in determining the volatility and fire resistance of a biolubricant. It can be used to determine the transportation and storage temperature requirements for biolubricants. The flash point should be high, to ensure the safe operation and minimum volatilization at the maximum operating temperature. For the most demanding applications, such as in aviation jet engines, an effective flash point range of greater than 300 °C may be required (Salimon et al., 2010 b). In this work, the highest flash point was 285.80 °C for 2-ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate (**9**) (Table 1).

The viscosity index (VI) of an oil indicates the effect of temperature on the viscosity of the oil. A low viscosity index signifies a relatively large change of viscosity with temperature. In other words, the oil becomes extremely thin at high temperatures and extremely thick at low temperatures. On the other hand, a high viscosity index signifies relatively little change in viscosity over a wide temperature range. Ideal oil, for most purpose, is one that maintains a constant viscosity during temperature changes. The importance of the viscosity index can be easily shown by considering automotive lubricants. Oil having a high viscosity index resists excessive thickening when the engine is cold and consequently promotes rapid starting and prompt circulation. It resists excessive thinning when the motor is hot and thus provides full lubrication and prevents excessive oil consumption. From Table 1, we can see that the viscosity index (VI) increased as the substitution of the oil increased in the order monoesters < diesters < triesters which can be rationalized by an overall increase in the molecular weight of the products with the increasing chain length from newly added ester group.

Oxidative stability measurements

Differential scanning calorimetry (DSC) is an effective technique for determining the effect of temperature on a material's properties. DSC represents these effects as an exothermic or endothermic peak that is a function of temperature. In general, chemical decomposition and oxidation cause exothermic peaks, while physical properties such as melting and boiling cause endothermic peaks. Pressure differential scanning calorimetry (PDSC) is an effective method for measuring the oxidative tendencies of biolubricant base oils, plant oils, and oleochemicals, in rapid fashion.

Table 1. The physicochemical properties of the synthesized products

Samples	Density (g/cm ³)	Volatility 120 °C (%)	Pour point/°C ^a	Cloud point/°C ^a	Flash point/°C ^a	Viscosity index (VI) ^a
2, EOA	0.804	1.05	0	10.24 ± 0.68	113.15 ± 4.78	45.10 ± 0.94
3, HHODA	0.825	0.95	-16.12 ± 0.61	-13.11 ± 0.53	145.16 ± 5.24	65.70 ± 1.67
4, EHHHOD	0.831	0.88	-24.33 ± 0.45	-21.37 ± 0.21	187.34 ± 4.89	77.89 ± 1.89
5, EHCOHOD	0.841	0.82	-31.57 ± 0.25	-27.68 ± 0.35	192.27 ± 10.78	80.57 ± 2.67
6, EHOHOD	0.848	0.73	-36.48 ± 0.77	-32.54 ± 0.64	234.79 ± 9.56	92.59 ± 3.11
7, EHCHOD	0.856	0.69	-40.40 ± 0.24	-36.42 ± 0.75	257.10 ± 6.42	156.61 ± 6.87
8, EHLHOD	0.862	0.63	-44.74 ± 0.39	-41.81 ± 0.40	277.56 ± 8.90	178.90 ± 8.38
9, EHMHOD	0.869	0.55	-47.19 ± 0.58	-45.63 ± 0.58	285.80 ± 7.46	213.53 ± 10.21

2, EOA = Epoxidized oleic acid; **3**, HHODA = 9-Hydroxy-10-heptanoxyoctadecanoic acid; **4**, EHHHOD = 2-Ethylhexyl 9-hydroxy-10-heptanoxyoctadecanoate; **5**, EHCOHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; **6**, EHOHOD = 2-Ethylhexyl 9-(octanoyloxy)-10-(heptanoyloxy)octadecanoate; **7**, EHCHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; **8**, EHLHOD = 2-Ethylhexyl 9-(lauroxy)-10-(heptanoyloxy)octadecanoate; **9**, EHMHOD = 2-Ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate.

^a Mean ± SD

Depending on the number of double bonds it has, fatty acids are categorized as saturated, monounsaturated or polysaturated. Double bonds are oxidized more easily than fully saturated hydrocarbon chains. Free radicals attack the allylic hydrogen located next to the double bond [24]. When using the PDSC technique at high air pressure, i.e., 1379 KPa, the oxygen concentration is in excess and in equilibrium with the sample. Thus, any inconsistencies due to the access rate of oxygen or the egress rate of volatile degradation products are effectively eliminated.

Epoxidized oleic acid (**2**), 9-hydroxy-10-heptanoxyoctadecanoic acid (**3**), 2-ethylhexyl 9-hydroxy-10-heptanoxyoctadecanoate (**4**) and 2-ethylhexyl 9-(acyloxy)-10-(heptanoyloxy)octadecanoate (**5-9**) were screened for oxidation stability using pressurized differential scanning calorimetry through the determination of the onset temperature (OT) and the signal maximum temperature (SMT). The onset temperature is the temperature at which we observed the rate of oxidation rapidly increase. It is obtained by extrapolating the tangent of the steepest slope of the reaction exotherm down to the baseline. A high onset temperature would suggest that the oxidation stability of oil is high. The signal maximum temperature is the temperature at which maximum heat output is observed in the sample during oxidative degradation. A higher signal maximum temperature does not necessarily correlate with improved oxidation stability.

The results in Table 2 indicate that an improvement in oxidation stability was observed as the chain length of the mid-chain ester decreased because longer side chains have more accessible sites that are prone to oxidation, which makes them more susceptible to cleavage than short chains [25].

Tribological measurements

The tribological interactions of a solid surface's exposed face with interfacing materials and the environment may result in a loss of material from the surface. The process leading to a loss of material is known as "wear". Major types of wear include abrasion, friction (adhesion and cohesion), erosion, and corrosion. Wear can be minimized by modifying the surface properties of solids by one or more "surface finishing" processes or by the use of lubricant for frictional or adhesive wear.

An important property of biolubricants is their ability to maintain a stable lubricating film at the metal contact zone. The long fatty acid chain and presence of polar groups in the structure of plant oil makes it amphiphilic in nature, therefore allowing it to be used as both boundary and hydrodynamic biolubricants. To meet the increasing demands for stability during various tribological processes, oil structures have to withstand extremes of temperature variation

and shear degradation and maintain excellent boundary lubricating properties through strong physical and chemical adsorption to the metal surface. The ester ends of the fatty acid chain adsorb to metal surfaces thus permitting monolayer film formation with the hydrocarbon end of fatty acids oriented away from the metal surface. The fatty acid chain thus offers a sliding surface that prevents direct metal-to-metal contact and the formation of pits and asperities on the metal surface. The strength of the film and the extent to which it is adsorbed on the metal surface dictate the efficiency of the biolubricant's performance. If the film is not formed, direct metal contact may result in high-temperatures at the contact zones between moving parts causing adhesion, scuffing, or even metal-to-metal welding. Under lubricated conditions, the hydroxyl and ester group of the products offers active oxygen sites that bind to the metal surface [26]. Table 3 shows the tribological results for the synthesized compounds.

The results indicated that an improvement in anti-wear properties (lower scar test values) occurred with longer mid-chain esters and increased polar ester functional group substitution, i.e., triesters > diesters > monoesters (Table 3). The branching structure of the biolubricant and increasing the polar functional groups increased the strength of the tribological film at the metal contact zone thereby increasing its efficiency at reducing wear.

Table 2. The PDSC data of the samples showing the onset of oxidation and the signal maximum temperatures

Samples	Onset temperature (OT)/°C ^a	Signal maximum temperature (SMT)/°C ^a
2, EOA	75.12 ± 1.38	164.40 ± 4.70
3, HHODA	122.67 ± 5.90	198.63 ± 6.29
4, EHHHOD	116.34 ± 4.71	122.46 ± 3.78
5, EHCOHOD	103.10 ± 4.34	203.02 ± 9.65
6, EHOHOD	97.65 ± 3.52	88.53 ± 2.24
7, EHCIHOD	90.33 ± 2.88	169.15 ± 4.90
8, EHLHOD	85.89 ± 1.93	267.69 ± 11.87
9, EHMHOD	80.46 ± 1.67	138.34 ± 4.45

2, EOA = Epoxidized oleic acid; 3, HHODA = 9-Hydroxy-10-heptanooxyoctadecanoic acid; 4, EHHHOD = 2-Ethylhexyl 9-hydroxy-10-heptanooxyoctadecanoate; 5, EHCOHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; 6, EHOHOD = 2-Ethylhexyl 9-(octanoyloxy)-10-(heptanoyloxy)octadecanoate; 7, EHCIHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; 8, EHLHOD = 2-Ethylhexyl 9-(lauroxy)-10-(heptanoyloxy)octadecanoate; 9, EHMHOD = 2-Ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate.

^a Mean ± SD

Table 3. The tribological properties of the synthesized compounds in the four-ball test

Samples	Four ball wear scar, 40 daN, 1 h (mm) ^a	Coefficient of friction (μ)
2, EOA	0.89 ± 0.11	0.58
3, HHODA	0.81 ± 0.10	0.51
4, EHHHOD	0.75 ± 0.12	0.45
5, EHCOHOD	0.62 ± 0.10	0.39
6, EHOHOD	0.50 ± 0.10	0.30
7, EHCIHOD	0.43 ± 0.11	0.24
8, EHLHOD	0.33 ± 0.10	0.16
9, EHMHOD	0.21 ± 0.10	0.12

2, EOA = Epoxidized oleic acid; 3, HHODA = 9-Hydroxy-10-heptanooxyoctadecanoic acid; 4, EHHHOD = 2-Ethylhexyl 9-hydroxy-10-heptanooxyoctadecanoate; 5, EHCOHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; 6, EHOHOD = 2-Ethylhexyl 9-(octanoyloxy)-10-(heptanoyloxy)octadecanoate; 7, EHCIHOD = 2-Ethylhexyl 9-(caproxy)-10-(heptanoyloxy)octadecanoate; 8, EHLHOD = 2-Ethylhexyl 9-(lauroxy)-10-(heptanoyloxy)octadecanoate; 9, EHMHOD = 2-Ethylhexyl 9-(myristoxy)-10-(heptanoyloxy)octadecanoate.

^a Mean ± SD

Conclusion

The present work describes a systematic approach to the chemical modification of oleic acid oils to yield basestocks capable of operating under a range of conditions. Based on the results obtained, an increase of the chain length of the mid-chain ester had a positive influence on the low-temperature properties because it created a steric barrier around individual molecules that inhibited crystallization, the result of which was an in lower pour point. An increase in the chain length of the mid-chain ester also had a positive influence on the tribological properties of the molecules. However, the trends for PP run counter to those of thermo-oxidative stability as shown in the PDSC and TFMO results, i.e., increasing the chain length is a benefit to the PP but a detriment to the thermo-oxidative stability.

Furthermore, it is evident that hydrogen bonding is a critical parameter influencing the physicochemical and tribological properties of synthetic esters. Removal of unstable double bonds from fatty acid acyls, increasing the molar weight and changing their molecular structure results in an increased of the viscosity index of the synthesized esters. In addition, the flash point and volatility values show that synthetic ester oils have a low potential as a fire hazard. Furthermore, increasing the polar functionality in the plant oil structure has a positive impact on wear protection, the result of stronger absorption potential on the metal surface and a greater lateral interaction between the ester chains. This advantage was achieved by increasing the polarity through the chemical modification of triester products. Chemical modification is necessary to improve the performance of plant oils by reducing the limitations imposed by the native oil structure. Specifically, we focus on improving the oxidative stability of these structures by eliminating the bis-allylic hydrogen functionalities in the polyunsaturated methylene chain. In general, the oleic acid-based triester derivatives have improved physicochemical and tribological properties when compared to their precursors, making them a good candidate for the general biolubricant used in chain saws, brake fluid and transmission oil. Our research suggests that these modification pathways might appreciably improve the overall properties of biolubricant basestocks.

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