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Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant applications

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Abstract For environmental reasons, as well as the dwindling source of petroleum, a new class of environmentally acceptable and renewable biolubricants based on plant oils is available. Even though plant oils possess excellent lubricant-related properties, there are some concerns about using it as biolubricant base oil. In this study we present a series of structures derived from oleic acid to be used as synthetic biolubricant basestocks. Measuring of pour point (PP), flash point, viscosity index (VI), oxidation onset temperature (OT) and signal maximum temperature (SMT) was carried out for each compound. Furthermore, the friction and wear properties were measured using a high-frequency reciprocating rig (HFRR). The resulting product structures were confirmed by NMR and FTIR spectroscopic analysis. The results showed that ethylhexyl 9-(octanoyloxy)-10-(behenoxy)octadecanoate with behenyl mid-chain ester exhibited the most favorable low temperature performance (PP −48 °C) and ethylhexyl 9-(octanoyloxy)-10-(octyloxy)octadecanoate octyl mid-chain ester exhibited higher oxidation stability (OT 142 °C) than the other synthetic ester oils. On the other hand, the highest ball wear scan diameter was obtained for ethylhexyl 9-(octanoyloxy)-10-(behenoxy)octadecanoate while the lowest value was obtained for 9-hydroxy-10-octyloxyoctadecanoic acid. Overall, it was concluded that these synthetic ester oils have potential in formulation of industrial fluids for different temperature applications.

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1. Introduction

Liquid lubricants being the predominant form of lubrication for machinery generally consist of about 70–99% of a base (base oil) and 1–30% additives. Over 95% of the lubricants in use today are petroleum-based. Environmental pollution associated with the production and application of this huge quantity of lubricants worldwide are causing environmental concern. Currently, around 50% of the lubricants sold worldwide end up in the environment via total loss applications,

volatility, spills or major accidents (Horner, 2002; Rudnick and Erhan, 2006). In view of its high ecological toxicity and low biodegradability it poses a considerable threat to the environment. In the last decade a lot of interest was developed to use 'environment friendly readily biodegradable lubricant fluids (Rudnick and Erhan, 2006). Depletion of world petroleum reserves and uncertainty in petroleum supply also stimulated the search for environmental friendly alternative to mineral oils (Rhee, 1996; Rudnick, 2003; Adhvaryu and Erhan, 2002; Erhan et al., 2006). In this scenario, plant oils have gained popularity as lubricants over the last couple of decades. Today, around 2% of the base stocks are of plant oil origin (Erhan and Adhvaryu, 2002).

The triacylglycerol structure of plant oil makes it an excellent biolubricant (Zaher and Nomany, 1988; Willing, 2001; Adhvaryu et al., 2004). Plant oils offer a number of advantages, including high biodegradability ($>95\%$), reduced environmental pollution (Salunkhe et al., 1992; Bockish, 1998; Battersby, 2000; Havet et al., 2001; Walsh, 2002) compatibility with additives, low production costs (Krzan and Vizintin, 2003), large possibilities of production, low toxicity, high flash point, low volatility, high viscosity indices and, above all, better tribological performance. It has displayed superior performance than mineral oils in terms of antiwear and fatigue resistance (Odi-Ovei, 1988; Asadauskas et al., 1997; Kozma, 1997). Also, plant oils are superior in dissolving contaminants and additives than mineral oils (Erhan and Adhvaryu, 2002). In contrast to mineral oil, plant oils are derived from a renewable source. However, it has some disadvantages: thermooxidative and hydrolytic stabilities are limited and, in some cases, there is serious limitation of low temperature fluidity (Buzas et al., 1997; Papanikolaw, 1999; Dweck and Sampaio, 2004; Fox et al., 2004; Santos et al., 2004; Petlyuk and Adams, 2004). Therefore the use of pure (i.e. unmodified) plant oils are found more in total loss applications such as chain-saw lubricants, concrete-mould release oils and hydraulic fluids with very low thermal stress (Petlyuk and Adams, 2004).

The most serious disadvantage of the usage of plant oils in biolubricants is its poor thermooxidative stability (Erhan et al., 2006). Plant oil oxidizes like hydrocarbon mineral oil following the same free radical oxidation mechanism (Hamblin, 1999) but at a faster rate. The faster oxidation of plant oils is due to the presence of unsaturated fatty acids present in it. Bisallylic hydrogens in linoleic and linolenic fatty acids are susceptible to free radical attacks, peroxide formation and production of polar oxidation products (Erhan et al., 2006).

Different modern technological approaches have been adopted to solve the problems associated with application of plant oils in lubricants, and some of them are genetic modification, additive treatment and chemical modification (Erhan, 2005). However, low resistance to oxidative degradation still remains the major drawback of plant oil application in the lubricants (Erhan and Adhvaryu, 2002). There has been slow percolation of the product technologies developed in the European and American countries to the Asian countries (Bhatia and Mahanti, 2002).

In this study, we present a novel synthetic approach for chemical modification of oleic acid derivatives to improve their oxidative stability, low temperature and other physicochemical properties. The structural modification is carried out in four stages, (i) oleic acid epoxidation, (ii) ring opening reaction, (iii) esterification of the carboxylic acid hydroxyl group, (iv) acetylation of the resulting hydroxyl group in the ring-opened products.

2. Experimental

2.1. Materials

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA) and oleic acid (99%) from Nu-Chek Prep, Inc. (Elysian, MN). All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate (Aldrich Chemical).

2.2. Characterization

The percentage compositions of the elements (CHNS) for the compounds were determined using an elemental analyzer CHNS Model Fison EA 1108. ^{1}H 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 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 neatly on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe trough in a scanning range of 650–4,000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^1.

2.3. Low temperature operability

The pour point is defined as the lowest temperature at which the sample still pours from a tilted jar. This method is routinely used to determine the low temperature flow properties of fluids. Pour point values were measured according to the ASTM D5949 method using a phase Technology Analyzer, Model PSA-70 S (Hammersmith Gate, Richmond, B.C., Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree are reported. For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Generally, materials with lower PP exhibit improved fluidity at low temperatures than those with higher PP.

2.4. Flash point values

The flash point is defined as the minimum temperature at which the liquid produces a sufficient concentration of vapor above it that it forms an ignitable mixture with air. The lower the flash point is, the greater the fire hazard is. Flash point determination was run according to the American National Standard Method using a Tag Closed Tester (ASTM D 56-79). Each sample was run in triplicate and the average values rounded to the nearest whole degree are reported.

2.5. Viscosity index measurements

Automated multi range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure viscos-

ity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 and 100.0 °C. The viscosity and viscosity index were calculated using ASTM methods D 445-97 and ASTM D 2270-93, respectively. Triplicate measurements were made and the average values were reported.

2.6. Oxidation stability

Pressurized DSC (PDSC) experiments were accomplished using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Typically, a 2-µL sample, resulting in a film thickness of < 1 mm, was placed in an aluminum pan hermetically sealed with a pinhole lid and oxidized in the presence of dry air (Gateway Airgas, St Louis, MO), which was pressurized in the module at a constant pressure of 1,378.95 kPa (200 psi). A 10 °C min^{-1} heating rate from 50 to 350 °C was used during each experiment. The oxidation onset (OT, °C) and signal maximum temperatures (SMT, °C) were calculated from a plot of heat flow (W/g) versus temperature for each experiment. Each sample was run in triplicate and average values rounded to the nearest whole degree are reported (Table 2).
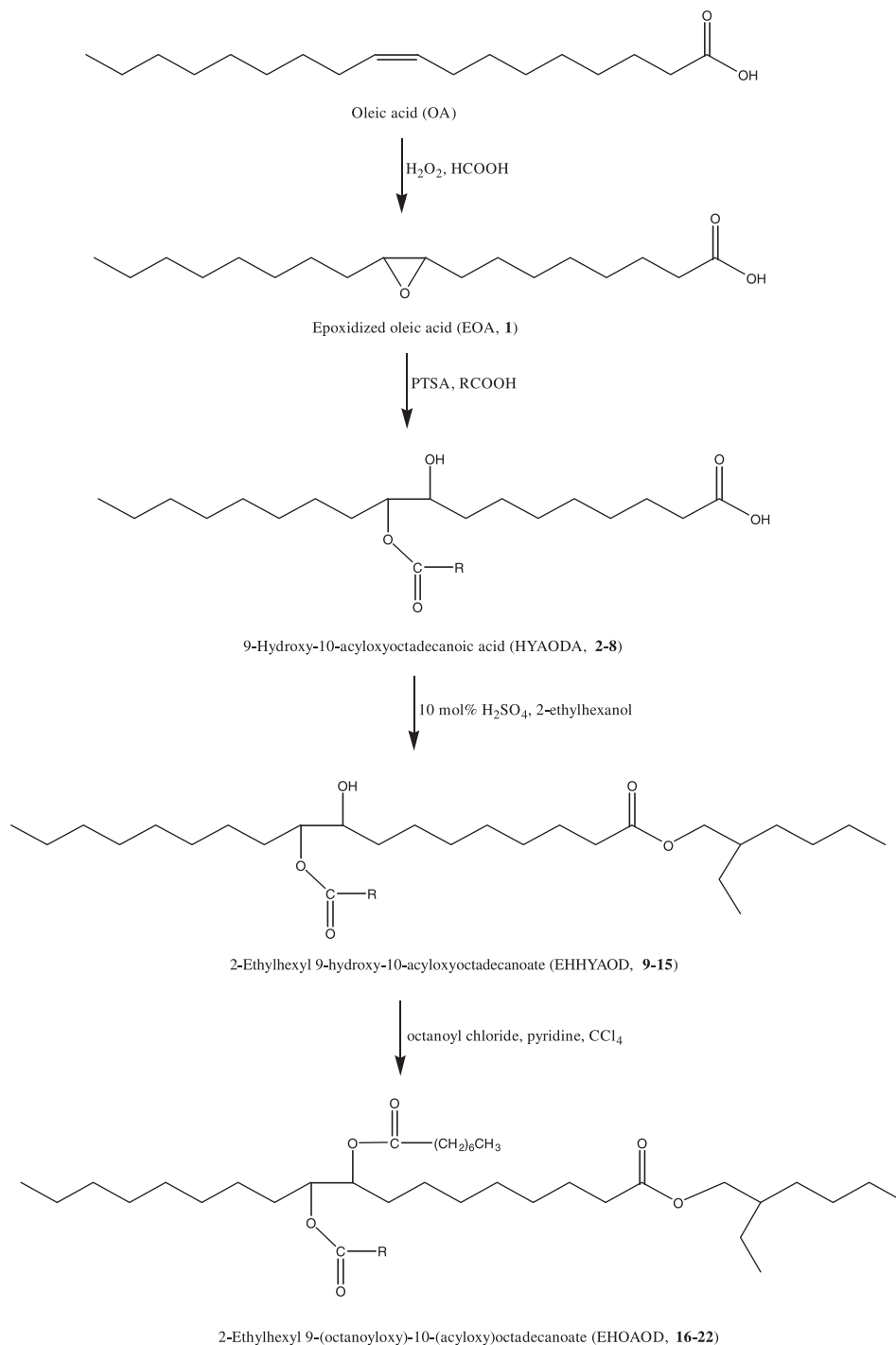

Figure 1 Triester formation.

2.7. Lubricity determination

Lubricity determinations were performed at 60 °C, according to ASTM methods D6079 using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, UK) via Laser Scientific (Granger, IN, USA). The average wear scan (μm) diameter of each replicates was determined by calculating the average of the x- and y-axis wear scar length. Each experiment was conducted in triplicate and the data are reported as mean $\pm$ SD of triplicate determinations.

2.8. Synthesis

2.8.1. Epoxidized oleic acid (EOA, 1)
Hydrogen hydroxide solution (30% in H_2O, 8.0 mL) was added slowly into a stirred solution of oleic acid (OA) (90%, 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 noticed in the reaction vessel (2–5 h). The solid was collected via vacuum filtration, washed with H_2O (chilled, 3×10 mL), and placed for 12 h under high vacuum to provide epoxidized ricinoleic acid (EOA) as a colorless, powdery solid.

2.8.2. 9-Hydroxy-10-acyloxyoctadecanoic acid (HYAODA, 2–8)
To a mixture of EOA (31 g), 5 g of p-toluenesulfonic acid (PTSA) and toluene, fatty acids (6 g) were added during

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 refluxed for 3 h. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient room temperature. The mixture was washed with the water next day. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using the vacuum evaporator.

2.8.3. 2-Ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate (EHHYAOD, 9–15)
Sulfuric acid (conc. H_2SO_4, 10 mol-%) was added into a stirred suspension of HYAODA (3.35 mmol) in the 2-ethylhexanol (3.35 mL). The suspension was heated with stirring at 60 °C for 10 h. Hexanes (5 mL) were then added, and the solution was washed with $NaHCO_3$ (sat. aq., 1×0.5 mL) and brine (2×1 mL), dried ($MgSO_4$), filtered, concentrated in vacuo and placed for 6 h under vacuum to yield the title products.

2.8.4. 2-Ethylhexyl 9-(octanoyloxy)-10-(acyloxy)octadecanoate (EHOAOD, 16–22)
The reaction scheme of triesters formation is shown in Fig. 1. Appropriate amounts of EHHYAOD, pyridine and CCl_4 were weighed into the 500 mL three-neck flask equipped with a cooler, dropping funnel and thermometer. The mixture was heated to 50 °C, with suitable aliquots of octanoyl chloride added during 1 h, and the reaction mixture was subsequently

Table 1 Elemental analysis data of synthetic ester oils.

Samples	Formula	Elemental analysis calc. (found)			
		%C	%H	%N	%S
HYOODA	$C_{26}H_{50}O_5$	70.54 (70.55)	11.38 (11.37)	–	–
HYNODA	$C_{27}H_{52}O_5$	71.01 (71.02)	11.48 (11.49)	–	–
HYLODA	$C_{30}H_{58}O_5$	72.24 (72.25)	11.72 (11.73)	–	–
HYMODA	$C_{32}H_{62}O_5$	72.95 (72.96)	11.86 (11.87)	–	–
HYPODA	$C_{34}H_{66}O_5$	73.59 (73.60)	11.99 (11.98)	–	–
HYSODA	$C_{36}H_{70}O_5$	74.17 (74.18)	12.10 (12.11)	–	–
HYBODA	$C_{40}H_{78}O_5$	75.18 (75.19)	12.30 (12.29)	–	–
EHHYOOD	$C_{34}H_{66}O_5$	73.59 (73.60)	11.99 (11.98)	–	–
EHHYNOD	$C_{35}H_{68}O_5$	73.89 (73.90)	12.05 (12.04)	–	–
EHHYLOD	$C_{38}H_{74}O_5$	74.70 (74.71)	12.21 (12.22)	–	–
EHHYMOD	$C_{40}H_{78}O_5$	75.18 (75.19)	12.30 (12.29)	–	–
EHHYPOD	$C_{42}H_{82}O_5$	75.62 (75.63)	12.39 (12.40)	–	–
EHHYSOD	$C_{44}H_{86}O_5$	76.02 (76.03)	12.47 (12.46)	–	–
EHHYBOD	$C_{48}H_{94}O_5$	76.74 (76.73)	12.61 (12.60)	–	–
EHOOOD	$C_{42}H_{80}O_6$	74.07 (74.08)	11.84 (11.85)	–	–
EHONOD	$C_{43}H_{82}O_6$	74.30 (74.29)	11.89 (11.88)	–	–
EHOLOD	$C_{46}H_{88}O_6$	74.95 (74.94)	12.03 (12.02)	–	–
EHOMOD	$C_{48}H_{92}O_6$	75.34 (75.33)	12.12 (12.11)	–	–
EHOPOD	$C_{50}H_{96}O_6$	75.70 (75.69)	12.20 (12.21)	–	–
EHOSOD	$C_{52}H_{100}O_6$	76.04 (76.05)	12.27 (12.26)	–	–
EHOBOD	$C_{56}H_{108}O_6$	76.65 (76.64)	12.41 (12.40)	–	–

HYOODA: 9-hydroxy-10-octyloxyoctadecanoic acid, HYNODA: 9-hydroxy-10-nonanoxyoctadecanoic acid, HYLODA: 9-hydroxy-10-lauroxyoctadecanoic acid, HYMODA: 9-hydroxy-10-myristoxyoctadecanoic acid, HYPODA: 9-hydroxy-10-palmitoxyoctadecanoic acid, HYSODA: 9-hydroxy-10-stearoxyoctadecanoic acid, HYBODA: 9-hydroxy-10-behenoxyoctadecanoic acid, EHHYOOD: ethylhexyl 9-hydroxy-10-octyloctadecanoate, EHHYNOD: ethylhexyl 9-hydroxy-10-nonanoxyoctadecanoate, EHHYLOD: ethylhexyl 9-hydroxy-10-lauroxyoctadecanoate, EHHYMOD: ethylhexyl 9-hydroxy-10-myristoxyoctadecanoate, EHHYPOD: ethylhexyl 9-hydroxy-10-palmitoxyoctadecanoate, EHHYSOD: ethylhexyl 9-hydroxy-10-stearoxyoctadecanoate, EHHYBOD: ethylhexyl 9-hydroxy-10-behenoxyoctadecanoate, EHOOOD: ethylhexyl 9-(octanoyloxy)-10-(octyloxy)octadecanoate, EHONOD: ethylhexyl 9-(octanoyloxy)-10-(nonanoxy)octadecanoate, EHOLOD: ethylhexyl 9-(octanoyloxy)-10-(octanoyloxy)octadecanoate, EHOMOD: ethylhexyl 9-(octanoyloxy)-10-(myristoxy)octadecanoate, EHOPOD: ethylhexyl 9-(octanoyloxy)-10-(palmitoxy)octadecanoate, EHOSOD: ethylhexyl 9-(octanoyloxy)-10-(stearoxy)octadecanoate, EHOBOD: ethylhexyl 9-(octanoyloxy)-10-(behenoxy)octadecanoate.

refluxed for 4 h. On completion, the mixture stood overnight at ambient temperature. After washing with water, the solvent extract was dried over anhydrous sodium sulfate, further filtered and vacuum distilled to remove solvent.

3. Results and discussions

3.1. Epoxidation, esterification and acetylation

Preparation of octyl 9-(lauroyloxy)-10-(acyloxy)octadecanoate **16–22** from epoxidized oleic acid is **1** an effective way of introducing branching on the fatty acid chain of plant oils. This reaction is carried out in four stages and the final products have significantly improved oxidative stability and low temperature property compared with the starting materials (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 temperature is elevated or the reaction is allowed to progress for too long.

The removal of unsaturation in the oleic acid by converting them into epoxy-groups **1** improves the oxidative stability. It has already been established that the presence of multiple double bonds in the plant oil FA chains accelerates oxidative degradation. However, the low temperature fluidity of **1** is poor and found to solidify at 0 °C (see Table 1). This would limit the application of plant oil at low operating temperature especially as automotive and industrial fluids. A suitable approach to improve the low temperature flow behavior of **1** is to attach branching sites at the epoxy carbons. This was achieved by careful ring opening to obtain the 9-hydroxy-10-acyloxyocta-

decanoic acid oils **2–8**. Then, esterification of these products was carried out using 2-ethylhexanol and sulfuric acid as catalyst to yield 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate **9–15**. The seven prepared octyl esters were used as precursors for the synthesis of modified triester-derivatives by acetylation with octanoyl chloride in an aprotic solvent.

3.2. Characterization

In the FTIR spectra of oils **2–22**, the absorption due to the epoxy group (820 and 843 cm^{-1}) is not observed. This fact suggests that **1** undergoes complete ring opening under the reaction condition. Bands representing C=O groups (724, 1740 cm^{-1}), CH_3 groups (1370–1463 cm^{-1}), OH groups (3473–3444 cm^{-1}) and also C–O–C bands in esters (999–1105 cm^{-1}) are clearly visible in the spectra (Salimon and Salih, 2010).

All synthesized oils were verified by ^1H and ^{13}C NMR spectroscopy. Significant signals in the ^1H spectrum of epoxidized oleic acid **1** between 2.6 and 2.8 ppm correspond to quaternary carbons of the oxiran ring and the doublet in the ^{13}C spectrum between 56.86 and 56.91 ppm correspond to carbons of the oxirane ring. Furthermore, ^1H spectrum of epoxidized oleic acid showed singlet signal at 9.23 ppm due to OH group. A signal in the area around 9.17–9.30 ppm, representing an OH group, and the bands at 2.05–3.68 ppm, corresponding to –CH_2– groups, are present in the ^1H spectra of monoesters, 9-hydroxy-10-acyloxyoctadecanoic acid **2–8**. The ^1H spectra of synthesized diesters, 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate **9–15**, and triesters, 2-ethylhexyl 9-(octanoyloxy)-10-(acyloxy)octadecanoate **16–22**, consist of signals of low

Table 2 Pour point, Flash point, Viscosity index, OT, SMT and Percentage yield of synthetic ester oils.

Samples	Pour point[a] (°C)	Flash point[a] (°C)	Viscosity Index[a] (°C)	OT[a] (°C)	SMT[a] (°C)	% Yield
EOA	0	113	45	75	164	91
Monoesters 2–8						
HYOODA	−20	250	71	113	123	70
HYNODA	−30	305	80	101	256	63
HYLODA	−33	176	84	91	189	80
HYMODA	−35	199	89	83	213	56
HYPODA	−39	123	93	76	209	92
HYSODA	−41	194	102	70	243	85
HYBODA	−43	232	110	64	175	76
Diesters 9–15						
EHHYOOD	−22	156	80	131	145	60
EHHYNOD	−31	178	86	125	167	72
EHHYLOD	−34	209	91	116	231	81
EHHYMOD	−37	190	102	105	216	55
EHHYPOD	−40	213	111	92	198	65
EHHYSOD	−43	146	120	85	175	75
EHHYBOD	−45	132	128	71	160	62
Triesters 16–22						
EHOOOD	−23	145	91	142	215	83
EHONOD	−33	139	105	131	147	79
EHOLOD	−35	187	113	128	189	53
EHOMOD	−38	174	122	112	209	67
EHOPOD	−41	230	130	93	214	71
EHOSOD	−44	212	139	89	187	60
EHOBOD	−48	156	145	80	193	65

[a] Mean $n = 3$, SE ± 1 °C.

intensity at about 9.22–9.40 ppm and 2.10–3.65 ppm. Broad lines at 1.41–1.77 ppm represent the CH_2 groups' hydrogen peaks. In the ^{13}C NMR spectra significant bands at about 176 ppm are present, which exhibit the characteristic signals attributed to ester groups (Sliverstien et al., 2005). Furthermore, elemental analysis was done and the obtained data are in agreement with the proposed structures (Table 1).

3.3. Products parameters

The ability of a substance to remain liquid at low temperatures is an important attribute for a number of industrial materials, such as biolubricants, surfactants and fuels. The cold flow property of plant oils is extremely poor and this limits their use at low operating temperature especially as automotive and industrial fluids. Plant oils have a tendency to form macrocrystalline structures at low temperature through uniform stacking of the 'bend' triglyceride backbone (Kleinová et al., 2008). Such macrocrystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking. Cold flow properties of these samples were determined using their pour points. In practice, the usable liquid range is limited by the pour point (PP) at low temperatures and the flash point at high temperatures. The PP should be low to ensure that the lubricant is pump-able when the equipment is started from extremely low temperatures. The flash point should be high to allow the safe operation and minimum volatilization at the maximum operating temperature. For the most demanding applications, such as aviation jet engine lubricants, an effective liquid range over 300 °C may be required (Salimon et al., 2010). The epoxidized oleic acid, synthetic mono-, di- and triesters described above were screened for

low temperature behavior through determination of their pour point (PP).

An improvement in the cold flow behavior of diesters, 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate, and triesters, 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate, was obtained over that of their monoester precursor's 9-hydroxy-10-acyloxyoctadecanoic acid. Actually there are two reasons for this behavior. The first reason is that the presence of a side chain attached to the FA backbone does not allow individual molecules to come close for easy stacking due to steric interactions. This results in the formation of microcrystalline structures rather than macro structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another resulting in better fluidity of the total matrix. Secondly, the lack of one hydroxyl group in diesters and then absence of it in triester structures mean the number of hydrogen bonds decrease, which could cause the molecules to stack together.

The efficiency of the biolubricant in reducing friction and wear is greatly influenced by its viscosity. Generally, viscosity-temperature charts are available, making a good choice of a biolubricant operation temperature. The viscosity of a biolubricant is its tendency to resist flow. A biolubricant oil of high viscosity flows very slowly. The viscosity must always be high enough to keep good oil film between the moving parts. Otherwise, friction will increase, resulting in power loss and rapid wear on the parts. The viscosity index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. A low index means a steep slope of the curve, or a great variation of viscosity with a change in temperature; high index means a flatter slope, or lesser variation of viscosity with the same

Table 3 HFRR lubricity data of synthetic ester oils.

Samples	Ball wear scar diameter (μm)	Disc wear scar width on x-axis (μm)	Disc wear length on x-axis (μm)	Film (%)	CoF
Monoesters 2–8					
HYOODA	103 ± 2	122 ± 2	1084 ± 40	97	0.075
HYNODA	114 ± 3	129 ± 3	1091 ± 36	95	0.093
HYLODA	120 ± 2	135 ± 2	1101 ± 42	96	0.064
HYMODA	127 ± 3	146 ± 2	1111 ± 49	94	0.094
HYPODA	138 ± 3	153 ± 2	1119 ± 41	93	0.092
HYSODA	149 ± 2	166 ± 3	1124 ± 45	95	0.088
HYBODA	155 ± 2	172 ± 3	1130 ± 50	96	0.095
Diesters 9–15					
EHHYOOD	130 ± 3	147 ± 2	1119 ± 55	96	0.081
EHHYNOD	139 ± 3	154 ± 2	1127 ± 53	96	0.096
EHHYLOD	144 ± 3	165 ± 2	1133 ± 48	94	0.069
EHHYMOD	150 ± 2	170 ± 3	1142 ± 51	97	0.082
EHHYPOD	158 ± 3	176 ± 3	1151 ± 57	93	0.093
EHHYSOD	160 ± 2	188 ± 2	1160 ± 50	96	0.086
EHHYBOD	168 ± 2	192 ± 2	1166 ± 52	95	0.092
Triesters 16–22					
EHOOOD	149 ± 2	196 ± 3		94	0.089
EHONOD	157 ± 2	202 ± 3	1154 ± 44	95	0.083
EHOLOD	168 ± 2	215 ± 2	1166 ± 48	93	0.092
EHOMOD	178 ± 3	222 ± 2	1173 ± 43	94	0.084
EHOPOD	188 ± 3	230 ± 3	1185 ± 52	96	0.077
EHOSOD	196 ± 3	239 ± 3	1192 ± 57	97	0.076
EHOBOD	205 ± 2	243 ± 3	1205 ± 41	94	0.097

Values are mean ± SD of triplicate determinations.

changes in temperature. Increased viscosity index (VI) of triesters is the result of their higher molar weight, and especially the altered structure of their molecules. The VI values are high, characteristic for oils of ester type (Table 2).

The ability of a substance to resist oxidative degradation is another important property of biolubricants. Therefore, epoxidized oleic acid, 9-hydroxy-10-acyloxyoctadecanoic acid, 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate and 2-ethylhexyl 9-(octanoyloxy)-10-(acyloxy)octadecanoate were screened for oxidation stability using PDSC through determination of OT and SMT. PDSC is an effective method for measuring oxidation stability of oleochemicals in an accelerated mode (Du et al., 2002). The OT is the temperature at which a rapid increase in the rate of oxidation is observed at a constant, high pressure (200 psi). A high OT would suggest high oxidation stability of the material. The SMT is the temperature at which maximum heat output is noted from the sample during oxidative degradation. A higher SMT does not necessarily correlate with improved oxidation stability. Both OT and SMT were calculated from a plot of heat flow (W/g) versus temperature that was generated by the sample upon degradation and, by definition, SMT > OT.

In the present study, as the chain length of the mid-chain ester is decreased, a corresponding improvement in oxidation stability was observed, which is because longer chains are more susceptible to oxidative cleavage than shorter chains. These results are in agreement with other studies on synthetic esters (Randals, 1999). For example, when comparing 9-hydroxy-10-acyloxyoctadecanoic acid, 2-ethylhexyl 9-hydroxy-10-acyloxyoctadecanoate and 2-ethylhexyl 9-(octanoyloxy)-10-(acyloxy)octadecanoate, an improvement in OT was noticed as the mid-chain ester length (R) was decreased (Table 2).

An important property of lubricants is their ability to maintain a stable lubricating film at the metal contact zone. Triacylglycerols of plant oils are known to provide excellent lubricity due to their ester functionality. This is because, the polar head of the triacylglycerol molecule, i.e. glycerol end attaches to metal surfaces and allows a monolayer film formation with the non-polar end of fatty acid chains sticking away from the metal surface. This prevents the metal-to-metal direct contact by providing a sliding surface. Without a good sliding surface, the two metals at the contact zones of moving parts come in direct contact with each other and results in increase in temperature causing adhesion, scuffing or even welding. The ester structures in triacylglycerols offer active oxygen sites that trigger binding on the metal surface forming a protective film. This protective film builds further with time to reduce friction.

In this work, the antiwear and friction reducing properties of synthetic ester oil basestocks were evaluated using high-frequency reciprocating rig (HFRR) lubricity tester. The HFRR method determines the lubricity or ability of a fluid to affect friction and wear between the surfaces in relative motion under load. The average ball scar diameter, width of wear track on disk at x-axis, film percentage, and coefficient of friction (CoF) for synthetic ester oils are shown in Table 3.

The high ball wear scan diameter for EHOBOD oil may be due to low amount of free fatty acids (FFA) present in it. The HYOODA oil provided the lowest ball wear scar diameter, which may be due to presence of higher amount of FFA present in it. The disk x-scar results were also similar, with biggest scar width for EHOBOD oil. The average CoF is higher (0.097) for EHOBOD, followed by EHHYNOD (0.096) and

least for HYBODA (0.095). The lower CoF in EHOSOD, EHHYLOD and HYLODA may be due to their higher viscosity compared to other oils. These results showed that lubricity properties of synthetic ester oils are on par with other plant oils (Salimon et al., 2010).

4. Conclusion

In this study we have evaluated the potential of synthetic ester oils as basestocks for biolubricant applications. The process consists a systematic approach to modify chemically oleic acid oil to yield a basestock capable of operating at low temperature. Preparation was based on epoxidation of acyl double bond, opening of the formed oxirane ring in an appropriate medium and acetylation of free hydroxyl group. Based on the results obtained, increasing the chain length of the mid-chain ester had a positive influence on the low temperature properties of diesters because they create a steric barrier around the individual molecules and inhibits crystallization, resulting in lower pour point. But the trends for PP run counter to that of OT, i.e., increasing chain length is a benefit to PP, but a detriment to OT. Also it is evident that hydrogen bonding is a critical parameter influencing the low temperature properties and oxidation stability of synthetic esters. Increasing the hydrogen bond amount will lead to increase pour point (PP) and decrease the oxidation stability of these compounds. Removal of the unstable double bonds from fatty acid acyls, increased molar weight and change in the molecular structure result in increased the viscosity index of prepared triesters. The lubricity of synthetic ester oils is similar to other plant oils. Thus, these synthetic ester oils have good potential for use as biolubricant basestocks oil.

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