Preparation and Properties of Lubricant Basestocks from Epoxidized Soybean Oil and 2-Ethylhexanol

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ABSTRACT: Synthetic lubricant basestocks were prepared from epoxidized soybean oil (ESO) and 2-ethylhexanol (2-EH) to be used alone or with polyalphaolefin (PAO). Sulfuric acid-catalyzed reaction of ESO with 2-EH involves a ring-opening reaction at the epoxy group followed by transesterification at the ester group. Reaction with other catalysts including *p*-toluenesulfonic acid, Dowex 50W-8X, boron trifluoride, and sodium methoxide was also examined. Pour points of the products were observed as low as –21 and –30°C without and with 1% of pour point depressant, respectively. When the hydroxy groups in the products were esterified with an acid anhydride, lower pour points were observed. Pour point depression of the product by adding PAO has been tested. Oxidative stability of the product was examined using pressurized DSC and compared with those of synthetic lubricant basestocks, PAO, and a synthetic ester.

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KEY WORDS: Epoxidized soybean oil, 2-ethylhexanol, lubricant, oxidative stability, PDSC, pour point, synthetic lubricant.

Lubricant basestocks, especially engine oils and hydraulic fluids, are based mainly on mineral oils of fossil fuel origin. During the last decade, global industrial communities have taken a keen interest in the use of biobased fluids and have begun to explore potential areas to substitute mineral oil with these fluids. Polyol esters are excellent substitutes for mineral oils because of their low volatility, high flash point, good thermal stability, low toxicity, and excellent biodegradability (1–3). Esters in particular have better lubricity than mineral oils or polyalphaolefins (PAO) since they have high polarity due to the presence of lone pair electrons on the oxygen atom of the ester group. Such polar molecules are very effective as boundary lubricants, as they tend to form stable physical bonds with metal surfaces. In spite of their many advantages, the application of esters as lubricants at present is limited by their high price. Our research group has focused on the development of environmentally friendly ester-based lubricants from epoxidized soybean oil (ESO) and found that the ring-opening reaction of ESO followed by esterification of the resulting hydroxy group gives lubricant candidates with improved oxidative stabilities and low pour points (4).

2-Ethylhexanol (2-EH) is an intermediate in the manufacture of various esters such as plasticizers, monomers, lubricant additives, solvents, and surface treatment agents (5,6). ESO and 2-EH are readily available at low costs; therefore, we report a synthetic route for the preparation of lubricant basestocks from these two materials. The pour point, viscosity, viscosity index, and oxidative stability using pressurized DSC (PDSC) are evaluated to investigate the effect of structural variation in the oil molecules. Oxidation is the single most important reaction of oils resulting in increased acidity, corrosion, viscosity, and volatility when they are used as lubricant bases.

Several benchtop oxidation tests are available primarily as screening tools for the oxidative stability of vegetable oils and their derivatives. Oxidation is a complex phenomenon, and a fully acceptable protocol for its quantification has yet to emerge. Determination of PV can be used as an index of oxidation if the peroxides formed are stable and do not decompose after formation, which in most cases is not true (7). Two other methods for measuring the oxidative stability are the active oxygen method (AOM) (8) and the Rancimat method (9,10). In AOM, the oil is heated to 100°C, and the oxidation is followed by measuring the PV of the heated sample at regular time intervals until PV = 100 mequiv/kg is reached, which is defined as the AOM end point. For samples that form unstable peroxides, PV = 100 mequiv/kg may never be reached, and such measurements have no meaning. The Rancimat method measures the volatile acids formed during oxidation (11,12) and can be used for automated end-point detection. The Rancimat method at 100°C correlates well with oil stability measured by peroxide development during storage at 20°C (13). Another official method to measure the oxidation induction period is the oil stability index (OSI) (14). OSI values generally correspond well with AOM values if PV is 100 mequiv/kg or greater (10). However, lengthy experimental time, large errors associated with small changes in O_2/air flow rate (15), and the inability to differentiate between small changes in the vegetable oil matrix are its main disadvantages.

PDSC is currently the method of choice as it is a highly repeatable and reliable microoxidation technique that requires milligram amounts of sample. This method has been used extensively by researchers (16–18) to quantify synthetic, vegetable, and mineral oil oxidation. The PDSC procedure is highly suited for oxidation kinetic studies, additive response and optimization, and evaluation of the antioxidant activity of inhibited oils.

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EXPERIMENTAL PROCEDURES

Materials. The ESO (100% epoxidized) was purchased from Elf Atochem Inc. (Philadelphia, PA) and used as received. PAO-4 (notation 4 indicates approximate kinematic viscosity in cSt at 100°C and differentiates it from PAO-2, PAO-6, PAO-10, etc.) was obtained from Amoco (Lisle, IL). 2-EH, acetic anhydride, hexanoic anhydride, pyridine, *p*-toluenesulfonic acid, boron trifluoride, and diisododecyl adipate were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used as received. Dowex 50W-X8 was obtained from J.T.Baker Chemical Co. (Phillipsburg, NJ), washed with 1% HCl solution, and dried under vacuum just before use. All solvents were purchased from Fisher Scientific Co. (Fairlawn, NJ) and used as received.

Analysis. ^{1}H NMR spectra were obtained using an ARX 400 MHz Bruker machine (Rheinstetten, Germany). FTIR spectra were obtained with a PerkinElmer (Bucks, England) Spectrum RX FTIR System as film on NaCl plates.

Reaction with 2-EH. 2-EH (79 g, 0.61 mol, for product **1** or 183 g, 1.41 mol, for product **4**) was heated at 90°C with stirring, and sulfuric acid (12 drops) was added dropwise. ESO (60 g) was added, and the mixture was stirred at 120°C for 7 h (60 g of ESO was calculated to have 0.47 mol of functional group to react: 0.28 mol of epoxy groups and 0.19 mol of ester groups). The reaction mixture was then cooled, and saturated aqueous sodium bicarbonate (100 mL) was added. The mixture was extracted with ethyl acetate (100 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated using a rotary evaporator. Any volatile materials including the remaining solvent were evaporated overnight at 80°C under vacuum (0.3–0.5 torr) to give the product.

Esterification. Pyridine (14 mL, 0.15 mol) was added dropwise to a mixture of product **1** or **4** (50 g) and an acid anhydride (0.15 mol), and the mixture was stirred at 80°C for 2 h under a nitrogen atmosphere. The reaction mixture was cooled with ice water (200 mL) and then extracted with ethyl acetate (200 mL). The organic layer was washed successively with 5% NaOH (100 mL), 5% HCl (100 mL), and 5% aqueous sodium bicarbonate (100 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated using a rotary evaporator. The remaining solvent and other volatile components were removed under vacuum (0.3–0.5 torr) at 80°C.

Pour point measurement. Pour points were determined by ASTM method D 97 (19) with an accuracy of ±3°C. Cloud and pour point test apparatus manufactured by Petrolab Corporation (Latham, NY) was used. Test jars, thermometers, corks, and rubber rings fully met ASTM D 97 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in 3°C increments at the top of the sample until it stopped pouring.

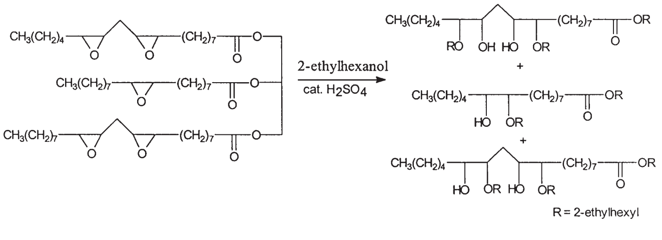
Viscosity measurement. Viscosity measurements were made at 40.0 and 100.0°C using calibrated Cannon-Fenske viscometer tubes and a Cannon CT-1000 Constant Temperature viscosity bath purchased from Cannon Instrument Co. (State College, PA). Viscosity and the viscosity index were calculated using ASTM methods D445 and D 2270, respectively (20,21). All viscosity measurements were run in duplicate, and the average value was reported.

PDSC experiment. The experiments were carried out using a PC-controlled DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically, a 1.5–2.0 mg sample resulting in less than a 1 mm thick oil film was taken in a hermetically sealed aluminum pan with a pinhole lid for gas (dry air) interaction. Controlled diffusion of gas through the hole greatly restricts volatilization of oil while still allowing for a steady blanket of air over the sample. The DSC cell was calibrated using the m.p. of indium metal (156.6°C) at a 10°C/min heating rate. The module was pressurized with dry air at 3450 kPa, and a 10°C/min scanning rate was used. The onset (T_O) and peak maximum (T_p) temperatures were calculated from the exotherm in each case. T_O is defined as the temperature when a rapid increase in the rate of oil oxidation is observed. This temperature is obtained by extrapolating the tangent drawn on the steepest slope of the reaction exotherm. T_p corresponds to the temperature at the highest point of the exothermic curve. Higher values of T_O and T_p would suggest greater oxidative stability for the oil (22).

RESULTS AND DISCUSSION

In our previous study (4) the ring-opening reaction of ESO with an alcohol followed by esterification of the resulting hydroxy groups was found to produce lubricant basestocks with improved oxidative and low-temperature stability. In this study ESO was reacted with 2-EH in the presence of a catalytic amount of sulfuric acid (12 drops for 60 g of ESO). Although the reaction may produce other minor products such as oligomers obtained by intra- and intermolecular epoxy–epoxy reactions, the ring-opening reaction at the epoxy groups and the transesterification reaction at the TAG backbone with alcohol give the major products (Scheme 1). This paper discusses the preparation, viscosity, low-temperature stability, and oxidative stability of the products; total analysis of products is not considered here.

The ring-opening reaction was confirmed by checking the disappearance of epoxy group signals at 1158, 845, and 822 cm^{-1} in the IR spectrum and also at 2.8–3.0 ppm in the ^{1}H NMR spectrum. The transesterification reaction followed the ring-opening reaction under the present reaction conditions (Fig. 1). ^{1}H NMR was used to follow the reaction at 130°C of 1.3 equivalents of 2-EH with the epoxy groups in ESO. The



SCHEME 1

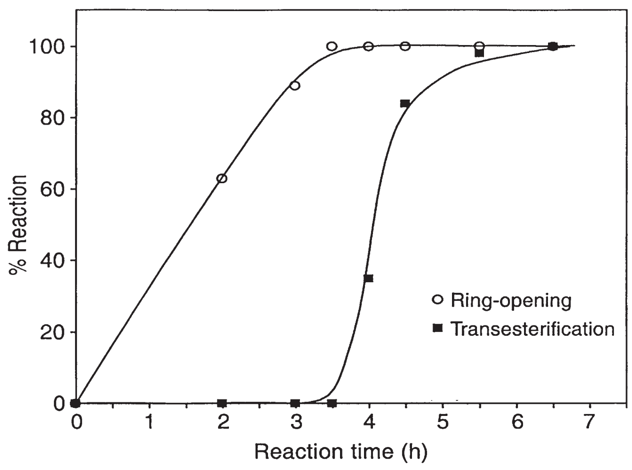


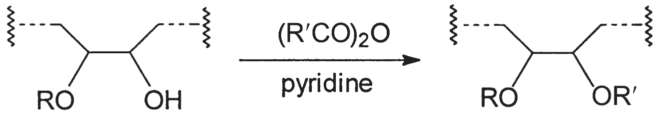
FIG. 1. Ring opening and transesterification in the reaction of epoxidized soybean oil with 2-ethylhexanol at 120°C.

percent ring-opening reaction was calculated from the relative area of the epoxy ring hydrogen signals (2.8–3.0 ppm, multiplet) compared to that of the starting material. The extent of transesterified product formation was monitored by the appearance of signals for alkyl hydrogens alpha to the ester oxygen atom derived from the alcohol portion of the newly formed ester's alpha proton (3.9 ppm, doublet) and also from the disappearance of hydrogen signals of the TAG backbone (5.2 ppm, multiplet; 4.1–4.3 ppm, multiplet).

To investigate the effect of other catalysts, *p*-toluenesulfonic acid, Dowex 50W-X8, BF_3, and a base catalyst, sodium methoxide were tested. All the reactions were carried out with 60 g of ESO and 79 g (1.3 equiv) of 2-EH. When *p*-toluenesulfonic acid (2.0 g) was used as catalyst, the reaction was so slow as to result in 82% ring opening and 0% transesterification after 22 h at 130°C. A widely used heterogeneous catalyst, Dowex 50W-8X (10 g), resulted in 100% ring-opening and 83% transesterification after 24 h at 130°C. In the reaction with sulfuric acid as catalyst, ring opening occurred prior to transesterification. When BF_3 (10 drops) was used, the ring-opening reaction was completed in 2 h at 100°C while no transesterification occurred. Even after a prolonged reaction time (24 h) and higher reaction temperature (130°C), no trace of transesterified product was found. In contrast, when a base catalyst, sodium methoxide (1% wt) was used, transesterification was completed in 2 h at 130°C and no ring opening occurred. Even after a longer reaction time (24 h), no ring-opened product was found.

The hydroxyl groups in ring-opened/transesterifed products were further esterified with acetic anhydride or hexanoic anhydride (Scheme 2). Pour points, viscosities, and viscosity indices of the products (**1**–**5**) are summarized in Table 1, which were determined by standard ASTM methods D 97, D 445, and D 2270, respectively. The ring-opened/transesterifed product (**1**) obtained by reaction with a catalytic amount of sulfuric acid at 120°C and 1.3 equivalents of 2-EH has pour points −12, −15, and −21°C without pour point depressant (PPD) and with 0.5 and 1% PPD, respectively. The ring-opened product obtained with BF_3 showed the same pour point without PPD and with 0.5% PPD while showing a higher pour point with 1% PPD (−15°C) compared to product **1**. Viscosities of product **1** at 40 and 100°C were measured as 74.4 and 9.6 cSt, respectively. The esterified product (**2**) obtained by esterification of **1** with acetic anhydride showed lower pour points, lower viscosities, and higher viscosity indices than the product before esterification. The esterification with hexanoic anhydride further lowered pour points and viscosities and increased viscosity indices (**3**).

To investigate the effect of reactant amount (2-EH) on physical properties, product **4** was prepared with 3.0 molar equivalents of 2-EH using the same reaction conditions as for product **1**. When compared with **1**, product **4** showed lower pour points and viscosities. Thus, when a smaller amount of alcohol is used, inter- and intramolecular reactions between epoxy groups are predominant, resulting in high-M.W. and high-viscosity products. The acetylated product **5** was prepared to compare its properties with parent product **4** and acetylated product **2**. Product **5** had a slightly lower pour point without PPD and pour points similar to product **4** when 0.5 and 1% PPD were added. Also, when compared to product **2**, product **5** showed the same pour points at higher additive concentrations, lower viscosities, and comparable viscosity indices.



SCHEME 2

TABLE 1
Pour Points, Viscosities, and Viscosity Indices of Products[a]

Product	R′	Pour points (°C) with 0% PPD	0.5% PPD	1% PPD	Viscosity (cSt) 40°C	100°C	Viscosity index
		Products obtained with 1.3 equiv of 2-EH					
1	H	−12	−15	−21	74.4	9.6	113
2	CH_3CO–	−18	−27	−30	57.2	8.7	127
3	$CH_3(CH_2)_4CO$–	−21	−33	−36	41.1	7.7	159
		Products obtained with 3.0 equiv. of 2-EH					
4	H	−18	−27	−30	54.4	7.89	112
5	CH_3CO–	−21	−27	−30	44.4	7.2	120

[a] PPD, pour point depressant; 2-EH, 2-ethylhexanol.

The pour point depression of product **4** was investigated by blending with PAO-4; the results are shown in Table 2. The pour points of PAO-4 used in this experiment were measured at −66 and −69°C without and with 1% PPD, respectively. The pour point of the product decreased gradually with an increasing amount of PAO-4, and the addition of 1% PPD further lowered the pour point.

PDSC was used to study the relative oxidation stability of products **4** and **5**. Product **4** was thermally more stable than product **5** (Fig. 2). The residual hydroxyl group had a lower steric interaction with the adjacent 2-ethylhexyl chains when compared to the bulky $-CH_3CO$ group in product **5**. This interaction in product **5** could lead to a thermally unstable molecule. There is a possibility of weak intermolecular H-bonding through residual –OH in product **4** (also responsible for higher viscosity at 40°C). This condition will apparently result in a high-M.W. product with higher oxidative stability when compared to product **5**. The onset temperature of oxidation (T_O) observed for product **4** (149.65°C) was almost 10°C higher than for product **5** (138.17°C).

For most practical uses, e.g., various industrial applications, synthetic lubricants are often blended with other functional fluids to match certain industry specifications. Table 3 presents the comparative thermal stabilities of a commercial synthetic ester, PAO-4, and various blends of synthetic lubricant (product **4**) and PAO-4. There is an excellent compatibility of the binary fluids in the blend, and no phase separation occurs at any concentration level. With higher PAO-4 concentration, the T_O and T_p of oxidation increase. However, with lower amounts of PAO-4 in the blend, there is a large delta (difference) increase in oxidative stability, which gradually diminishes with higher PAO concentration. The method has the potential for a rapid optimization of the thermal and oxidative stabilities of synthetic lubricants and their blends. Various structural modifications can be compared in terms of their thermal and oxidative stabilities, and their responses to other functional fluids and additive molecules can be established.

This research underlines the effect of vegetable oil derivatization to improve the low-temperature and oxidation stability of oils. Transesterification of TAG molecules using a carefully selected reagent and suitable catalyst can result in synthetic fluids with excellent physiochemical properties. It

TABLE 2
Pour Points of Blends With and Without PPD Additive Using ASTM Method D 97[a]

	Pour point (°C)	
Pure and blended fluids	Without PPD	With 1% PPD
100% product **4**	−18	−30
Product **4** + 25% PAO-4	−24	−36
Product **4** + 50% PAO-4	−30	−51
Product **4** + 75% PAO-4	−45	−60
100% PAO-4	−66	−69

[a] PAO-4, polyalphaolefin-4. See Table 1 for other abbreviation.

TABLE 3
Pressurized DSC of Vegetable Oils and Their Blends in PAO-4

Test fluids	Onset temperature[a] T_O (°C)	Peak max. temperature[a] T_p (°C)
Synthetic ester	185.94	206.20
PAO-4	187.69	204.46
Product **4** + 25% PAO-4	159.80	191.29
Product **4** + 50% PAO-4	163.73	195.08
Product **4** + 75% PAO-4	165.62	195.50

[a] Onset temperature (T_O) and peak max. temperature (T_p) data reported are the average values of three independent experiments. SE = ±0.5°C. Scanning rate = 10°C/min; constant pressure = 2450 kPa.

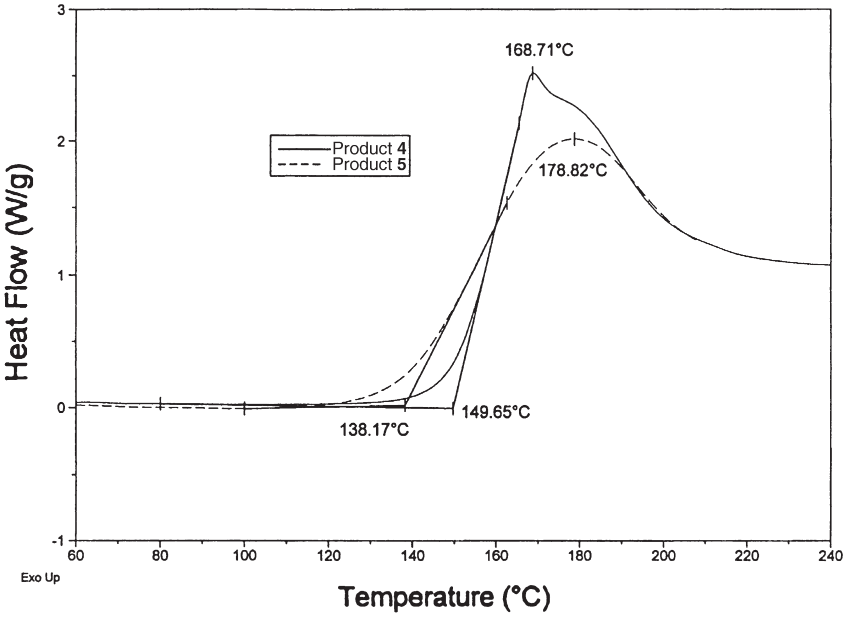


FIG. 2. Pressurized DSC exothermic plot of synthetic lubricant products **4** and **5** using a scanning rate of 10°C/min and constant air pressure of 3450 kPa.

may be concluded from this study that synthetic esters with two or three branching sites bearing C_2–C_7 chains show marked improvement in low-temperature stability with a high viscosity index. Such molecules are also thermally and oxidatively stable due to the elimination of C–C unsaturation from the ester chain. Additives and other functional fluids play a pivotal role in further improving the performance properties to match stringent industrial requirements. PDSC, viscosity, and pour point data can significantly help in the optimization process of such specialty chemicals in the final oil blend.

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