# Chemical Modification of Vegetable Oils for Lubricant Applications

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**ABSTRACT:** Owing to the unfavorable impact on the environment of mineral oil-based lubricants, there has been a steady increase in the demand for biodegradable, environment-friendly lubricants. However, development of a biodegradable base fluid that could replace or partially substitute conventional mineral oil is a big challenge. Vegetable oils are recognized as rapidly biodegradable and are thus promising candidates as base fluids in environment-friendly lubricants. Vegetable oils have excellent lubricity, but poor oxidation and low-temperature stability. This paper presents a series of structural modifications of vegetable oils using anhydrides of different chain lengths. The reaction was monitored and products were confirmed by NMR, FTIR, gel permeation chromatography, and thermogravimetric analysis (TGA). Experimental conditions were optimized for research quantity and for laboratory scale-up (up to 4 lb = 1.8 kg). The thermo-oxidation stability of these new lubricant base fluids was tested using pressure differential scanning calorimetry and TGA. The chemically modified base fluids exhibit superior oxidation stability in comparison with unmodified vegetable oils. These base fluids in combination with suitable additives exhibit equivalent oxidation stability compared with mineral oil-based formulations.

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**KEY WORDS:** Chemically modified vegetable oils, diester triacylglycerol, dihydroxy, epoxidized soybean oil, oxidation, pour point, vegetable oils.

In recent years, deliberate and accidental lubricant losses to the environment by means including evaporation, leakages, and spills have lead to major concerns regarding pollution and environmental health. About 5–10 million tons of petroleum products enter the environment every year, with 40% of that representing spills, industrial and municipal waste, urban runoff, refinery processes, and condensation from marine engine exhaust (1). Thus, strict specifications on biodegradability, toxicity, occupational health and safety, and emissions have become mandatory in certain applications. The enactment of these specifications, along with uncertainty in the petroleum supply for political and economic reasons, has stimulated the search for alternative energy sources. Vegetable oils, a renewable resource, are finding their way into lubricants for industrial and transportation applications (2). Waste disposal is also less of a concern for vegetable oil-based products because of their environment-friendly and nontoxic nature. Synthetic lubricant base oils are also available and offer improved stability and performance characteristics over refined petroleum oils, but at a premium price. Most of the biodegradable synthetic oils are esters that offer superior thermal and oxidative stability (3,4). Prices for these niche products are higher than for vegetable oils and are significantly higher than petroleum-based lubricants.

Currently, over 125 million metric tons of vegetable oils are produced worldwide per year. The advantages of using vegetable oils as lubricant base stocks are their excellent lubricity, favorable viscosity–temperature characteristics, high flash points, and compatibility with mineral oil and additive molecules. Their widespread use in formulating lubricants is restricted owing to insufficient thermal and oxidative stability, poor low-temperature fluidity, and hydrolytic instability. Genetic and chemical modification of vegetable oils can overcome these shortcomings, when used in combination with available additives (antioxidants, pour point depressants) and diluents or functional fluids.

The production of soybean oil ranks first (29%) among vegetable oils worldwide, and represents the cheapest readily available source of vegetable oil in the world. Other vegetable oils include canola, primarily produced in Canada; rapeseed in Europe; and sunflower, peanuts, cottonseed, coconut, palm fruits, palm kernels, linseed, castor beans, olives, sesame, corn, safflower, and the like. The TG structures of these oils have different functionalities, such as double bonds, allylic carbons, and ester groups, which are potential sites for chemical modification. The most vulnerable site is the double bond, which can be epoxidized with hydrogen peroxide, either in acetic acid or formic acid, to yield epoxidized soybean oil (ESBO), which is available in large volumes at a reasonable cost (5,6). ESBO is a promising intermediate for chemical modification, since the epoxy group is readily functionalized. Although plenty of information is available on synthesis of polymeric materials from ESBO (7–9) and oleochemical carbonates (10,11), there are few literature sources on the synthesis of lubricants from the ESBO. Hwang and Erhan (12) produced chemically modified soybean oils with improved low-temperature and oxidation stability by a ring-opening reaction of epoxidized FA esters with alcohols followed by esterification of the hydroxy groups in ring-opened product. Adhvaryu *et al*. (13) prepared synthetic lubricant base fluids by chemical modification of EBSO. Erhan *et al*. (14) converted the epoxy sites (sites of unsaturation) of

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epoxidized vegetable oils to the diester derivatives in either a one- or two-step reaction. These diester derivatives of TG were reported to have good oxidative stability and low-temperature performance properties and utility as hydraulic fluids, lubricants, metal working fluids, and other industrial fluids.

Considering the foregoing facts, in this study we report the preparation, process optimization, and characterization of diester derivatives of soybean oil with acid anhydrides of varying chain lengths from dihydroxy derivatives of soybean oil. These were prepared in an aqueous acid-catalyzed ring-opening reaction from ESBO. Both reactions were monitored using FTIR, and unreacted anhydride was determined using a thermogravimetric analyzer (TGA). Diester derivatives were characterized using FTIR, gel permeation chromatography (GPC), and $^1$H and $^{13}$C NMR. Oxidative stability of chemically modified soybean oils (CMSBO) was evaluated using pressure differential scanning calorimetry (PDSC), with and without antioxidant additive.

## EXPERIMENTAL PROCEDURES

*Materials.* The ESBO (100% epoxidized, ~4.2 epoxy groups per TAG molecule) was obtained from Elf Atochem Inc. (Philadelphia, PA) and used without further purification. All other chemicals including perchloric acid ($HClO_4$, 70%, ACS reagent) and acid anhydrides were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Polystyrene standards with M.W. of 1,700, 2,450, 5,050, 7,000, 9,200, and 10,665 (Polymer Laboratories, Ltd., Amherst, MA), and methyl oleate, methyl linoleate, monoolein, diolein, and triolein (Aldrich Chemical) with M.W. of 296.48, 294.48, 353, 619.2, and 885.4, respectively, were used for GPC calibration.

*Ring-opening reaction.* The reaction was carried out by refluxing a 2.5 L aqueous solution of 127.4 g ESBO at 100°C for 48 h in a 5-L three-necked round-bottomed flask. Perchloric acid (26.05 g) was added dropwise to the reaction mixture, which was constantly agitated by a mechanical stirrer. After the reaction was complete, the mixture was cooled to room temperature, and the organic phase was extracted with chloroform and washed three times with water to remove any traces of acid remaining in the reaction mixture. The solvent was removed under reduced pressure at 80°C, and the product (dihydroxy derivative of soybean oil: DiOH-SBO) was dried under a vacuum overnight.

*Esterification of the hydroxy groups in the dihydroxy derivative.* The DiOH-SBO (50 g) was added to 44.67 g of acetic anhydride in a 1:2 ratio (1 epoxy ring and 2 moles of anhydride), and then 21.5 g of pyridine in equimolar ratio was further added to the reaction mixture. The mixture was stirred with a mechanical stirrer in a 500-mL glass round-bottomed flask for 48 h at room temperature. Then the reaction mixture was cooled by pouring it onto ice cubes in a beaker and again stirred for 12 h. The reaction mixture was extracted three times with 100 mL of dichloromethane (chloroform or diethyl ether can also be used). Then the organic phase was washed with 75 mL of 3% HCl, 5% $NaHCO_3$, and water (each three times) and finally dried over 100 g anhydrous $MgSO_4$ for 24 h. The solvent was removed using a rotary evaporator, and unreacted anhydride was removed using Kugelrohr's distillation under reduced pressure (0.2 torr vacuum) at 80–100°C. The product (Ace-SBO) was then stored under vacuum. The above procedure was repeated using butyric, isobutyric, and hexanoic anhydride for preparation of the diester derivatives But-SBO, Isobut-SBO, and Hex-SBO, respectively.

*Analysis.* $^1$H and $^{13}$C NMR spectra were recorded using a Bruker AV-500 spectrometer (Bruker, Rheinstetten, Germany) operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA). Each spectrum was Fourier-transformed, phase-corrected, and integrated using ACD Spectrum Manager (Advanced Chemistry Development, Toronto, Canada). The integration values in $^1$H spectra were referenced to 4.00 between 4.1 and 4.4 ppm. FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) in a scanning range of 650–4000 cm$^{-1}$ for 32 scans at a spectral resolution of 4 cm$^{-1}$ with a pair of KBr crystals in thin film.

GPC profiles were obtained on a PL-GPC 120 high-temperature chromatograph (Polymer Laboratories, Amherst, MA) equipped with a column, autosampler, and in-built differential refractometer detector. The GPC was calibrated using a mixture of polystyrene (M.W. 1,700, 2,450, 5,050, 7,000, 9,200, and 10,665), methyl oleate, methyl linoleate, monoolein, diolein, and triolein in THF at 40°C.

Product purity was obtained by determining unreacted anhydrides in the final products using a TGA (model Q 500; TA Instruments, New Castle, DE), while heating the sample (3 μL) in platinum pans at 20°C/min with high-resolution sensitivity (set at 1.00) and resolution of 3.00 to 500°C in the presence of nitrogen. TGA Noack volatility was obtained as per ASTM D 6375-05 method.

*PDSC oxidation method.* The experiments were carried out using a DSC 2910 thermal analyzer from TA Instruments. Typically, a 2 μL sample, resulting in a film thickness of <1 mm, was taken in an aluminum pan hermetically sealed with a pinhole lid and oxidized in the presence of air. Dry air (Gateway Airgas, St. Louis, MO) was pressurized in the module at a constant pressure of 1378.95 kPa (200 psi) and a 10°C/min heating rate was used during the entire experiment. The onset temperature (OT) and signal maximum temperature (SM) of oxidation were calculated from the exotherm in each case. The response of the antioxidant additives (1:1 alkylated diphenylamine and antimony dialkyl dithiocarbamate) to these CMSBO fluids was studied by measuring their oxidation induction time (OIT) and signal maximum time (SMT) using an isothermal experiment at 200°C at a constant pressure of 200 psi with a flow rate of 20 mL/min.

## RESULTS AND DISCUSSION

Many nucleophilic reagents are known to add to an oxirane ring, resulting in ring opening. These ring-opening reactions in

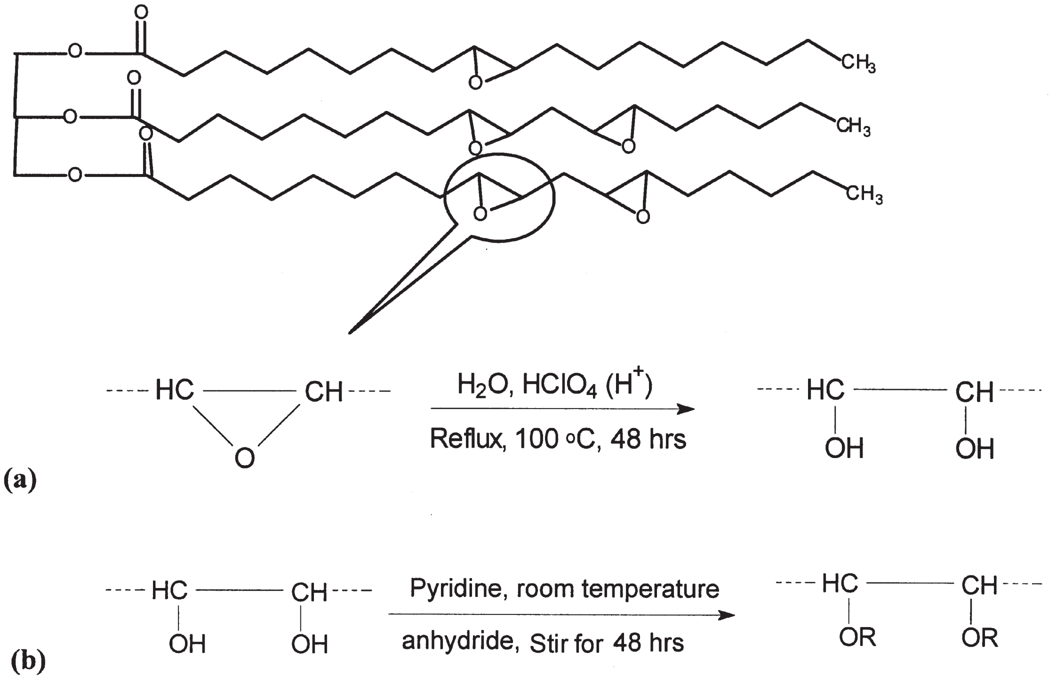

**FIG. 1.** (a) Epoxy ring opening with formation of dihydroxy derivative; (b) reaction with anhydride to form diester derivatives Ace-SBO if R = $-COCH_3$; But-SBO if R = $-COCH_2CH_2CH_3$ (R1); Isobut-SBO if R = $-COCH(CH_3)_2$ (R2); Hex-SBO if R = $-COCH_2CH_2CH_2CH_2CH_3$ (R3). SBO, soybean oil; Ace-SBO, acetate diester of SBO; But-SBO, butyrate diester of SBO; Isobut-SBO, isobutyrate diester of SBO; Hex-SBO, hexanoate diester of SBO.

ESBO could result in branching at the oxirane carbons (earlier sites of unsaturation in SBO). The appropriate branching groups would interfere with the formation of macrocrystalline structures during low-temperature applications and would provide enhanced fluidity to vegetable oils. TAG that are hydrogenated to eliminate polyunsaturation will solidify at room temperature as a result of alignment and stacking of adjacent molecules. For this reason, it is important that there should be at least one unsaturation site available for a functionalization that will generate two branching points on the chain. The ester branching groups are quite effective for attaining the desired molecular spacing. A six-carbon chain-length ester has been observed to deliver the most desired pour point properties for these oils (12). These modified vegetable oils with chain branching are reported to have superior performance properties and are promising as biodegradable lubricants in applications such as hydraulic fluids, metal-working fluids, crankcase oils, drilling fluids, two-cycle engine oils, wear-resistant fluids, and greases. A similar strategy was used for the synthesis of CMSBO with branching groups at the epoxy ring carbons.

The nucleophilic attack by water molecules on the oxirane ring of ESBO in the presence of perchloric acid results in the ring-opened product DiOH-SBO, as shown in Figure 1a. The extent of reaction was monitored by IR spectroscopy of small aliquots taken at 4-h intervals. As the ring-opening reaction progressed, the oxirane C–O twin bands at 823 and 842 $cm^{-1}$ decreased and disappeared, while a broad hump appeared at 3700–3100 $cm^{-1}$ and increased in intensity. This hump is assigned to the H-bonded O–H stretching vibrations of alcohols (Fig. 2). The presence of hydrogen-bonded OH groups results in the increased viscosity of the DiOH-SBO derivative compared with ESBO. The reaction completion was further confirmed by $^1H$ NMR spectra of the DiOH-SBO derivative (Fig. 3), where the peaks at 3.2–2.8 ppm (–**CH**– protons of the epoxy ring) completely disappeared and additional peaks appeared in the range 4.1–3.5 ppm (protons attached to carbon of –**CH**OH group) and 3.5–3.0 ppm (protons attached to oxygen of the –CHO**H** group). In addition, the disappearance of epoxy carbon peaks in the range 54–57 ppm and appearance of –**C**HOH peaks in the range 73–75 ppm in $^{13}C$ NMR spectra of DiOH-SBO confirmed the conversion of epoxy groups to the dihydroxy derivative. Ring opening of ESBO with water was done at 100°C with other catalysts such as sulfuric acid and HCl. Unfortunately, these catalysts resulted in hydrolysis of ester linkages. In perchloric acid the ring opening is predominantly the major reaction with minimal ester hydrolysis. This is observed from the retention of NMR peaks of the backbone glycerol structure in the ring-opened DiOH-SBO derivative. These are the NMR peaks at 5.2–5.3 and 4.1–4.4 ppm for the CH and $CH_2$ proton of the $-\mathbf{CH_2}-\mathbf{CH}-\mathbf{CH_2}-$ glycerol backbone, respectively. The retention of the TAG backbone is important for maintaining high biodegradability of the product. The TAG structure remains unaffected at temperatures lower than 100°C. Other $^1H$ NMR peaks that are in common in ESBO and DiOH-SBO are 2.25–2.5 ppm for $\mathbf{CH_2}$ protons α to >C=O, 1.68–1.85 ppm for $\mathbf{CH_2}$ protons in between two epoxy moieties, 1.58–1.68 ppm for $\mathbf{CH_2}$ protons β to >C=O, 1.15–1.58 ppm for all other $\mathbf{CH_2}$ protons, and 0.8–1.0 ppm for terminal $\mathbf{CH_3}$ protons.

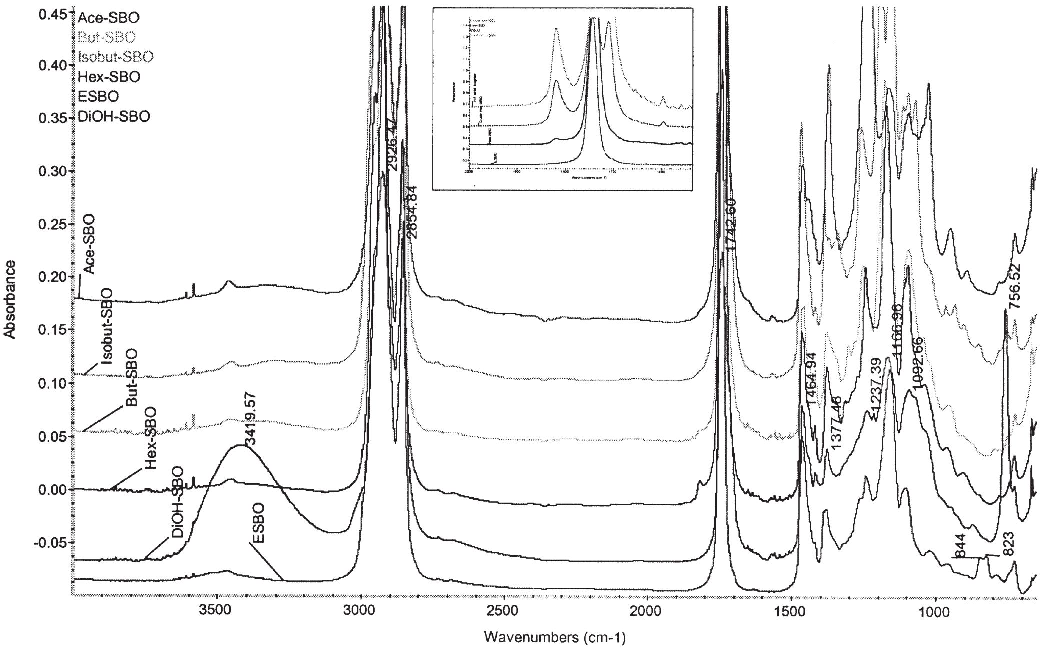

**FIG. 2.** FTIR spectra of epoxidized SBO (ESBO), DiOH-SBO, Ace-SBO, But-SBO, Isobut-SBO, Hex-SBO. Inset shows FTIR spectra of ESBO, Crude Hex-SBO (before Kugelrohr distillation), Hex-SBO (after Kugelrohr distillation), and hexanoic anhydride (HA) obtained as Kugelrohr distillate from crude Hex-SBO in the region 2000–1500 $cm^{-1}$. DiOH-SBO, dihydroxy derivatives of SBO; for other abbreviations see Figure 1.

Table 1 shows quantitative data obtained from $^1$H NMR spectra of different products. These values are computed using a reference value of four protons for peaks at 4.1–4.4 ppm corresponding to four $CH_2$ protons of –$\mathbf{CH_2}$–CH–$\mathbf{CH_2}$– in the glycerol backbone of the TAG structure. Table 1 shows the same number of $CH_3$ and $CH_2$ protons for both DiOH-SBO and ESBO molecules. Additional protons in other ranges are due to protons of –C**HOH**. A combination of time and temperature is selected for this step to ensure that the reaction goes to completion, or nearly so (at least 90%).

In the second step, the dihydroxy derivative is reacted with acetic, butyric, isobutyric, and hexanoic anhydride (HA) to

**TABLE 1**
**$^1$H NMR Data of ESBO, Dihydroxy and Diester Derivatives of SBO**

| NMR range (ppm) | Assignment | ESBO | DiOH-SBO | Ace-SBO | Isobut-SBO | But-SBO | Hex-SBO |
|---|---|---|---|---|---|---|---|
| 5.2–5.4 | CH backbone + C**H**–O–R[a] | 1 | 1 | 1.7 | 1.7 | 1.7 | 1.9 |
| 4.8–5.1 | C**H**–O–R[a] | | | 1.9 | 1.8 | 1.8 | 2.1 |
| 4.08–4.3 | $CH_2$ backbone | 4 | 5.4 | 4 | 4 | 4 | 4 |
| 3.47–4.05 | –C**H**OH dihydroxy | | 6.1 | 1.4 | 1.4 | 1.3 | 1.5 |
| 3.0–3.47 | –CHO**H** dihydroxy | | 7.7 | | | | |
| 2.83–3.2 | CH epoxy | 8.6 | | | | | 0.4 |
| 2.5–2.8 | CH isobutyric | | 0.8 | | 3.3 | 0.4 | |
| 2.23–2.5 | $CH_2$ $\alpha$ to CO | 6.2 | 7.5 | 6.1 | 6.3 | 13.5 | 14.1 |
| 1.83–2.2 | $CH_3$ acetyl | | 1.4 | 11.7 | 1.1 | 1.6 | 3.1 |
| 1.16–1.9 | $CH_2$ other | 73.2 | 73.3 | 62.4 | 61.7 | 70.1 | 83.4 |
| 1.1–1.2 | $CH_3$ isobutyric | | | | 21.8 | | |
| 0.95–1.1 | $CH_3$ butyric | 0.8 | 0.6 | | | 10.5 | |
| 0.72–0.95 | $CH_3$ | 8.8 | 9.1 | 8.5 | 8.7 | 8.1 | 18.6 |
| | nEpoxy ring[b] | 4.3 | 0 | 0 | 0 | 0 | 0.2 |
| | nSubstituents[c] | | | 3.9 | 3.6 | 3.5 | 3.2 |

[a] R = acetyl and other branching groups.
[b] Number of epoxy rings (CH epoxy protons/2).
[c] Number of substituents on SBO estimated as: for acetyl, $CH_3$ protons (1.83–2.25 ppm)/3; for isobutyric $CH_3$ protons (1.1–1.2 ppm)/6; for butyric $CH_3$ protons (0.95–1.1 ppm)/3; for hexanoic [$CH_3$ protons (0.72–1.02 ppm) – 9]/3. SBO, soybean oil; ESBO, epoxidized SBO; DiOH-SBO, dihydroxy derivative of SBO; Ace-SBO, acetate diester of SBO; Isobut-SBO, isobutyrate diester of SBO; But-SBO, butyrate diester of SBO; Hex-SBP, hexanoate diester of SBO.

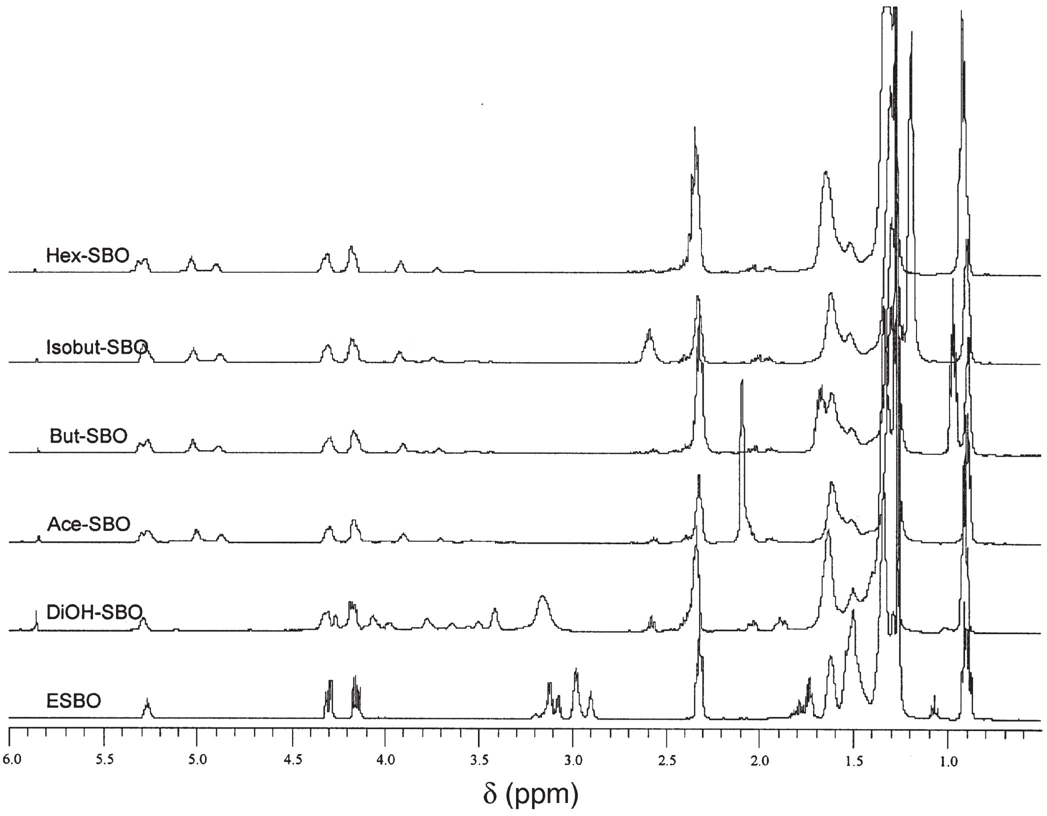

**FIG. 3.** $^1$H NMR spectra of ESBO, DiOH-SBO, Ace-SBO, But-SBO, Isobut-SBO, and Hex-SBO. For abbreviations see Figures 1 and 2.

yield the diesters Ace-SBO, But-SBO, Isobut-SBO, and Hex-SBO respectively (Fig. 1b). In this step, the reaction was monitored using FTIR for the disappearance of the O–H stretching band in the region 3700–3100 cm$^{-1}$and change in relative intensities of 1465 and 1377 cm$^{-1}$ bands in the fingerprint region (Fig. 2). The epoxy absorption band (823 and 842 cm$^{-1}$), which was present in ESBO, no longer exists in final diester products. The completion of reaction also has been confirmed by their respective $^1$H NMR spectra (Fig. 3). Peaks in the region 3.5–3.0 ppm (protons attached to the oxygen of the –CHO**H** group) have disappeared completely and new peaks at 4.8–5.4 ppm (protons at the point of substitution –CH–O–CO–R in the FA chain) appeared in all diester products. The presence of $^{13}$C NMR peaks at 173.1 ppm due to the carbonyl carbon of TAG, 68.9 and 62 ppm, respectively, for CH and CH$_2$ carbons of –**C**H$_2$–CH–**C**H$_2$– glycerol backbone and corresponding protons at 5.2–5.3 and 4.1–4.4 ppm in $^1$H NMR of all diester products confirm that the glycerol–FA linkage is intact and did not undergo any hydrolysis.

*FTIR characterization of diester products.* The FTIR spectra (Fig. 2) of all these products have some common peaks at 2926 and 2855 (methylene asymmetric stretching), 1743 (TAG carbonyl stretching), 1465 (CH$_2$ bending vibration), 1377 (CH$_3$ symmetrical bending vibration), and 724 cm$^{-1}$ (CH$_2$ rocking vibrations), and additional peaks at 1242, 1160, and 1104 cm$^{-1}$ due to stretching vibrations of the C–O group in esters (15). Formation of the Ace-SBO product was also confirmed by the increase in peak intensity ratio for 1465 vs. 1377 cm$^{-1}$. In ESBO and DiOH-SBO, the 1377 cm$^{-1}$ peak is almost half the intensity of the 1465 cm$^{-1}$ peak, while in Ace-SBO, due to addition of methyls (–COCH$_3$) in the structure, the peak at 1377 cm$^{-1}$ (CH$_3$ bending vibrations) almost doubled compared with 1465 cm$^{-1}$ (CH$_2$ bending vibration). Also the intensities of peaks such as 1743 (ester carbonyl) and 1160 cm$^{-1}$ (C–O stretching of esters) relative to 2926 cm$^{-1}$ peak increased in Ace-SBO compared with ESBO and DiOH-SBO. This is due to the increase in ester functionalities in the structure. A similar trend was observed in spectra of But-SBO, Isobut-SBO, and Hex-SBO, confirming the formation of final diester products.

*NMR characterization of diester products.* Figure 3 shows the $^1$H NMR spectra of ESBO, DiOH-SBO, Ace-SBO, But-SBO, Isobut-SBO, and Hex-SBO in CDCl$_3$, and their quantitative $^1$H NMR spectral data are recorded in Table 1. Peaks at 2.8–3.0 ppm due to the epoxy group are not present in other products except ESBO. The peaks at 3.0–3.2 ppm in DiOH-SBO due to hydroxy protons in the –CHO**H** group are also not present in diester products. The presence of additional peaks at 1.85–2.18 ppm due to methyl protons of the –COC**H$_3$** group in $^1$H NMR and corresponding methyl carbons at 21–22.6 ppm and carbonyl carbons at 171 ppm in $^{13}$C NMR confirm the formation of the Ace-SBO product. The peaks at 73.8–75.2 ppm can be assigned to the FA carbons of the branching site

–**C**H–O–Ac. The formation of the But-SBO product is confirmed by the presence of a new branching group (R1 = $–COCH_2CH_2CH_3$) in its structure. It can be shown that the increase in intensity of the peak at 2.26–2.46 ppm is due to $CH_2$ protons α to the carbonyl (Table 1), and that the appearance of new peaks at 0.95–1.06 ppm is due to methyl protons in $^1H$ NMR. The carbonyl peak of R1 group appears at 173.1 ppm, thus increasing the intensity of the already existing carbonyl peak of the base molecule. Additional peaks due to $CH_2$ carbons a to the carbonyl appeared at 36.0–36.5 ppm, and at 18.4–18.5 ppm due to $CH_2$ carbons a to the methyl of the R1 group in the But-SBO molecule. The addition of the R2 group [$–COCH(CH_3)_2$] in DiOH-SBO to yield Isobut-SBO can be confirmed by the following observations. In $^1H$ NMR, two additional peaks appeared, one at 2.5–2.68 ppm due to the CH proton a to the carbonyl, and the other at 1.10–1.23 ppm due to $CH_3$ protons of the R2 group. In addition, the appearance of new $^{13}C$ NMR peaks at 176.6 ppm due to the carbonyl carbon, and 18.8–19.0 ppm due to methyl carbons of the R2 group further confirmed the formation of the Isobut-SBO derivative. The peak due to the CH carbon of the R2 group appeared at 33.8 ppm and it merged there with other peaks. There are no additional peaks in the $^1H$ NMR spectra of Hex-SBO attributable to the addition of branching group R3 ($–COCH_2CH_2CH_2CH_2\text{-}CH_3$). The peak for $CH_3$ and the $CH_2$ proton α to the carbonyl of the R3 group resulted in intensity increase of signal at 0.83–1.01 and 2.25–2.44 ppm, respectively (Table 1). In $^{13}C$ NMR of Hex-SBO, the carbonyl carbon peak of the R3 group overlapped with the carbonyl carbon peak of base molecule (173.4 ppm), and an additional peak appeared at 35.6 ppm due to $CH_2$ carbons α to the carbonyl of the R3 group. These observations confirm the formation of diester products from DiOH-SBO and various anhydrides.

The percent conversion calculated from $^1H$ NMR data for signals in the range 2.95–3.45 ppm (hydroxy proton of the –CHO**H** group) yields values >95%. If there is only one substitution on epoxy carbons (other epoxy carbons still have –OH group), then the peak position for the remaining hydroxy proton may change, and this approach may not give accurate conversion values. Using specific $^1H$ NMR peaks arising from branching groups ($–COCH_3$, R1, R2, and R3), the number of these groups attached to the TAG structure can be calculated as shown in Table 1. In an average TAG molecule, there are 8.6 sites available for substitution; approximately four sites are substituted by these branching groups, while others retain the hydroxy group. Steric hindrance may be a possible reason, which allows only one substituent at epoxy carbons. This explanation seems valid, as the average number of substituents in diester derivatives decreases with the bulkiness (chain length) of the branching group.

The presence of hydroxy and polar ester groups in diester products may cause enhanced intermolecular interactions (9) resulting in highly viscous products. GPC was performed on ESBO, dihydroxy, and diester products to check the extent of internal polymerization. It was found that some degree of oligomerization occurred at some stage of the reaction. Apart from the main peak of expected products, there was approximately 20% oligomerized products (with higher M.W.) in the DiOH-SBO and diester products. The M.W. of the main product peaks for starting and final products are: ESBO 901; DiOH-SBO 1107; Ace-SBO 1193; But-SBO 1286; Isobut-SBO 1277; and Hex-SBO 1653, as estimated by using a calibration mixture of polystyrene, FAME, and mono-, di-, and triolein.

*Anhydride determination.* FTIR and TGA were used to check for unreacted anhydride in the final diester products. Unreacted anhydride remained in Hex-SBO and But-SBO even after vacuum distillation. The amount of unreacted anhydride was quantified using TGA. In the presence of nitrogen, the sample was heated at 20°C/min to 500°C in high-resolution mode. HA is the highest-boiling of all the anhydrides used and was found to evaporate below 200°C. No evaporation loss below 200°C was detected in ESBO. On using a solution of 20% HA in ESBO at 200°C, ~20% weight loss was detected, which can be assigned to the anhydride present in that mixture. In using TGA, unreacted anhydride in the crude Hex-SBO obtained after vacuum distillation was found to be 28% (Fig. 4). Kugelrohr's distillation was then used at 100°C under 0.2 torr vacuum to remove the unreacted anhydride. Figure 4 shows the TGA thermograms of ESBO, 20% HA in ESBO, crude Hex-SBO, HA obtained from Kugelrohr distillation of crude Hex-SBO, and the final diester product Hex-SBO. The anhydride percentages obtained using the TGA method for final diester products are Ace-SBO 2%; Isobut-SBO 1.9%; But-SBO 1.7%; and Hex-SBO 2%.

Similarly, FTIR was used to monitor the removal of unreacted anhydride. The peak for the anhydride carbonyl group appears at 1818 $cm^{-1}$ and is easily distinguishable from the ester carbonyl peak at 1743 $cm^{-1}$. In Figure 2, a peak at 1818 $cm^{-1}$ can be seen in the crude Hex-SBO. Complete removal of unreacted anhydrides using Kugelrohr distillation in final diester products (Ace-SBO, But-SBO, and Isobut-SBO) was confirmed by the absence of the 1818 $cm^{-1}$ peak in their spectra (Fig. 2).

*Oxidation and thermal stability.* The TGA profile shows that diesters are thermally as stable as ESBO even at high temperatures (Fig. 4). Noack volatilities were also determined as per ASTM D 6375 method using a TGA and are shown in Table 2. Noack volatilities for all the samples are less than 3%, which are excellent compared with 10–30% in mineral oils and synthetic esters. These diester derivatives are therefore thermally stable. PDSC experiments measured the oxidation stability of CMSBO samples. This test is widely used in the lubricant industry and considered reliable for base oils as well as finished lubricants (16). The PDSC results, onset temperature (OT), and signal maximum temperature (SM) for diester samples are shown in Table 2. The diester samples show higher oxidation stability than the dihydroxy derivative and also SBO. This shows that oxidation stability considerably improved due to the removal of unsaturation. The oxidation OT decreases with the chain length of the branching group. Ace-SBO has the highest value (174°C) of OT, while Hex-SBO has the lowest (161°C). Longer side chains are more prone to oxidative cleavage than

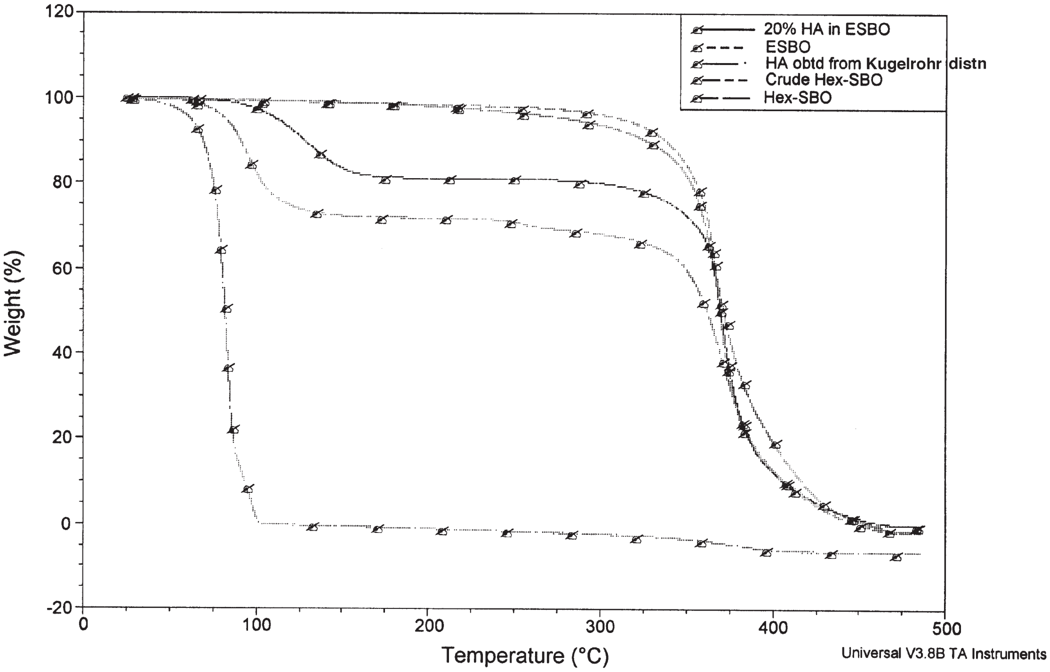

**FIG. 4.** Thermogravimetric analyzer thermograms of ESBO, 20% HA in ESBO, crude Hex-SBO, Hex-SBO, and HA obtained as Kugelrohr distillate from crude Hex-SBO, showing weight (%) loss with temperature. For abbreviations see Figures 1 and 2.

small compact ones. This observation is supported in another study on synthetic esters (4), wherein the author mentioned that short-chain acids are more stable than long.

*Additive response.* Antioxidant additives are used to improve the oxidation stability of these diester samples further. Different antioxidants were tried at varying concentrations in SBO. The best additive combination was then used 4% (w/w) in diester samples. The effect of these antioxidants was studied using PDSC temperature ramping and isothermal experiments (16). The results obtained are shown in Table 3. It was found that the antioxidant additive responded very well to these diester samples and increased their OT by 80–100°C. The isothermal PDSC experiment was done to determine oxidation induction time at 200°C under 200 psi (1380 kPa) pressure at a constant flow of 20 mL/min of air. These results also suggested that the antioxidant additive could prevent the start of oxidation for at least 50 min at 200°C. Both the OT and the oxidation induction time (OIT) of these diester samples are higher than SBO. Even mineral oil-based formulations have an OIT of 20 min at 200°C (17). This shows that chemical modification of SBO along with suitable antioxidant additives can improve their oxidation properties comparable with mineral oils. The effect of chain length on oxidation stability of diester samples with additives is similar to that for samples without additives, i.e., decreasing oxidation stability with increasing chain lengths of substituent on CMSBO.

Cold flow properties of these samples were determined using their pour points. The pour point of all these diester samples is −3°C (ESBO is 0°C). The excellent thermal and oxidative stability of diester derivatives as a result of the removal of

**TABLE 2**
**TGA Noack Volatility and PDSC Data of Dihydroxy and Diester Products at 10°C/min in Air Under 200 psi Pressure**

| Test fluids | TGA Noack volatility (%) | Onset temperature[a] (°C) | Signal maximum temperature[a] (°C) |
|---|---|---|---|
| SBO | 2.6 | 172 | 193 |
| DiOH-SBO | 3.6 | 163 | 213 |
| Ace-SBO | 2.7 | 174 | 213 |
| But-SBO | 2.5 | 169 | 208 |
| Isobut-SBO | 3 | 157 | 241 |
| Hex-SBO | 2.4 | 161 | 234 |

[a] Onset and signal maximum temperature values are the average of three experiments with SE of ±1°C. TGA, thermogravimetric analyzer; Noack Volatility, volatility as determined by the Noack Method as specified by ASTM 6375-05; PDSC, pressure differential scanning calorimetry; for other abbreviations see Table 1.

**TABLE 3**
**PDSC Temperature Ramp at 10°C/min in Air Under Static 200 psi Pressure, and Isothermal Experiment at 200°C (SBO at 170°C) Under 200 psi Pressure with 20 mL/min Flow of Air, for Diester SBO Derivatives with Additives (4% w/w)**

| Test fluids | Onset temperature (°C) | Oxidation induction time (min) |
|---|---|---|
| SBO | 192 | 25.7[a] |
| Ace-SBO | 256 | 75.3 |
| But-SBO | 247 | 51.0 |
| Isobut-SBO | 255 | 56.2 |
| Hex-SBO | 254 | 55.6 |

[a] Isothermal experiment at 170°C. For abbreviations see Tables 1 and 2.

unsaturation, however, does not significantly improve cold flow properties. Therefore, these samples are good for use in formulating high-temperature lubricants, but for use in low-temperature applications, suitable pour point depressant (PPD) along with diluents (such as polyalphaolefin, dibutyl adipate) will be required. The purpose of PPD is to hinder crystallization of CMSBO molecules at low temperature by further disrupting the stacking mechanism. Use of high-oleic sunflower oil as diluent and an additive pack containing an antioxidant, antiwear, and PPD could improve the pour point of CMSBO significantly (−18°C). This fully formulated lubricant using CMSBO as base fluid has excellent oxidation stability (PDSC onset temperature of 243°C). Rotary bomb oxidation test (RBOT, ASTM D 2272) is another rigorous measure of oxidation stability of finished lubricants, and for CMSBO-formulated lubricant, RBOT time is 135 min, which is much higher than commercially available soy-based lubricants (83 min).

This approach of chemical modification significantly improved the thermo-oxidative stability of vegetable oil, and the process technology, being cost effective, has a good potential for commercialization. The cold flow property has also been improved using a combination of PPD and suitable diluents. The basic vegetable oil structure is retained even after chemical modification of SBO, thus maintaining excellent biodegradability.

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