Lubricant Base Stock Potential of Chemically Modified Vegetable Oils

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The environment must be protected against pollution caused by lubricants based on petroleum oils.
The pollution problem is so severe that approximately 50% of all lubricants sold worldwide end up
in the environment via volatility, spills, or total loss applications. This threat to the environment can
be avoided by either preventing undesirable losses, reclaiming and recycling mineral oil lubricants,
or using environmentally friendly lubricants. Vegetable oils are recognized as rapidly biodegradable
and are thus promising candidates as base fluids in environment friendly lubricants. Lubricants based
on vegetable oils display excellent tribological properties, high viscosity indices, and flash points. To
compete with mineral-oil-based lubricants, some of their inherent disadvantages, such as poor
oxidation and low-temperature stability, must be corrected. One way to address these problems is
chemical modification of vegetable oils at the sites of unsaturation. After a one-step chemical
modification, the chemically modified soybean oil derivatives were studied for thermo-oxidative stability
using pressurized differential scanning calorimetry and a thin-film micro-oxidation test, low-temperature
fluid properties using pour-point measurements, and friction-wear properties using four-ball and ball-
on-disk configurations. The lubricants formulated with chemically modified soybean oil derivatives
exhibit superior low-temperature flow properties, improved thermo-oxidative stability, and better friction
and wear properties. The chemically modified soybean oil derivatives having diester substitution at
the sites of unsaturation have potential in the formulation of industrial lubricants.

KEYWORDS: Vegetable oils; epoxidized soybean oil; chemically modified soybean oil; oxidation; pour
point; tribological

INTRODUCTION

Most of the lubricants currently in daily use originate from
petroleum base stocks that are toxic to the environment, making
it increasingly difficult for safe and easy disposal. It is claimed
that 50% of all lubricants sold worldwide end up in the
environment via accidental spillage, nonrecoverable usage,
volatility, industrial and municipal waste, urban runoff, refinery
processes, and total loss applications, such as chainsaw oils,
two-stroke engines, concrete mold release oils, exhaust fumes
in engines, and metal cutting and forming processes (*1, 2*).
Estimates for the loss of hydraulic fluids are as high as 70−80%
(*3*). Most problematic are uncontrolled losses via broken
hydraulic hoses or accidents whereby large quantities of fluids
escape into the environment (*4*). These oils contaminate soil,
air, and drinking water and pose a threat to animal and plant
life. Thus, strict specifications on various environmental matters,
such as biodegradability, toxicity, occupational health and safety,
and emissions, have become mandatory in certain specific areas
of applications. Environmental protection from pollution can
best be performed by preventing undesirable lubricant losses
and by reclaiming and reusing mineral oil lubricants. Alterna-
tively, environmentally friendly lubricants should be used
whenever and wherever possible. Because of pollution concerns,
strict government regulations, and uncertainty in petroleum
supply, there has been an increasing demand for environmentally
friendly lubricants (*5, 6*) in recent years. Even the price of
mineral oil is increasing over the years, with crude oil prices
hovering around $130/barrel, and has already surpassed the
vegetable oil prices.

Lubricants based on vegetable oils are biodegradable and less
toxic compared to mineral oil counterparts. These are derived
from renewable resources and are low-cost alternatives to

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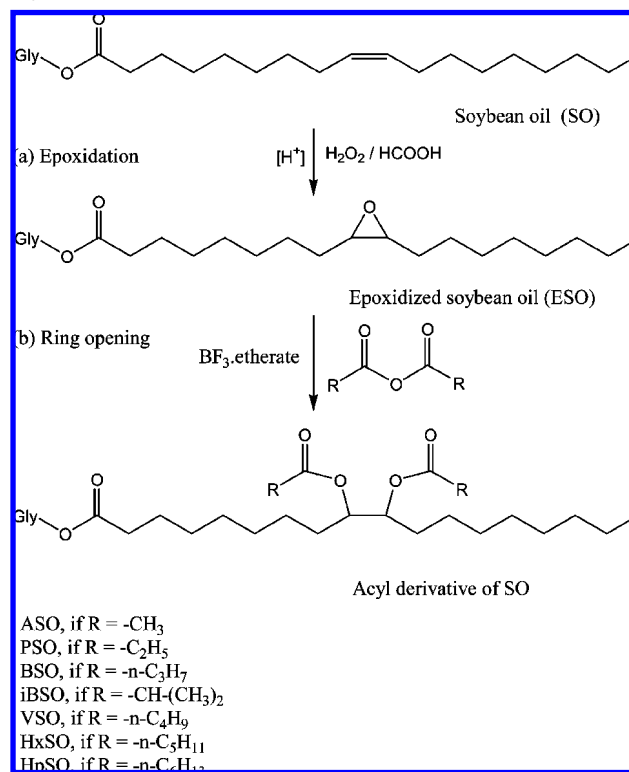   † USDA/NCAUR/ARS.
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synthetic fluids (*7*). At present, their use is limited in the area of total loss applications and those with very low thermal stress (*2, 8, 9*). Other industrial application of vegetable-oil-based lubricants is biodegradable hydraulic fluids for use in environmentally sensitive areas (excavators, earthmoving equipment, tractors, agricultural, forestry, and fresh water) (*10*). Despite considerable ecological and economical advantages, the present market share of these lubricants is relatively small (2% worldwide, with an estimated growth rate of 5−10%) (*11, 12*). To increase the market share, the acceptability must be improved. This can be performed by overcoming the inherent disadvantages of vegetable oils.

Apart from ecological advantages, vegetable oils have ideal technical properties, such as low volatility because of the high molecular weight of the triacylglycerol molecule and narrow range of viscosity change with temperature. The ester linkages deliver inherent lubricity and enable the oils to adhere to metal surfaces. Further, vegetable oils have higher solubilizing capacity for contaminants and additives than mineral base fluids. In all of these technical properties, the vegetable oils are comparable or better than mineral oils. However, they have certain disadvantages, such as poor oxidative stability (*13, 14*), primarily because of the presence of bisallylic protons. These protons are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds. This oxy-polymerization process ultimately results in insoluble deposit formation and an increase in oil acidity and viscosity. Vegetable oils also show poor corrosion protection (*15*), and the presence of ester functionality render these oils susceptible to hydrolytic breakdown (*16*). Low-temperature studies have also shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification at cold temperatures.

Some of these problems can be resolved by avoiding or modifying polyunsaturation in triacylglycerol structures of vegetable oils. Genetic (*17*) and chemical modification (*18*) of vegetable oils can overcome these shortcomings, by reducing or eliminating unsaturation in vegetable oils. Further improvements can be made by using modified vegetable oils in combination with additives (antioxidants and pour point depressants) (*19, 20*) and diluents or functional fluids. High oleic varieties of vegetable oils are considered to be potential candidates to replace conventional mineral oil-based lubricating oils and synthetic esters because of their greater oxidative stability (*21–23*). Because of a higher percentage of oleic acid, these oils require less processing to provide higher oxidative stability with relatively low *trans* and saturated fatty acid contents (*24*). The double bonds in triacylglycerols are potential sites for chemical modification and can be epoxidized with hydrogen peroxide, either in acetic or formic acid to give epoxidized soybean oil (ESO). ESO is a promising intermediate for chemical modification, because the epoxy groups are susceptible to ring-opening reactions (*8, 18, 25–35*). These epoxy sites (sites of unsaturation) of ESO were converted to the diester derivatives in either one- or two-step reaction (*26, 35, 36*).

Previously, we have reported one-step synthesis and structural characterization of chemically modified soybean oil (CMSO) derivatives (*35*). These CMSO derivatives are basically triacylglycerols with diesters at the sites of unsaturation and have been prepared using epoxidized soybean oil and common acid anhydrides (*35*). The process retains the vegetable oil structure and its associated benefits (high flash point, viscosity index, lubricity, and eco-friendly), while it allows for removal of polyunsaturation in the fatty acid chain. In this study, we report

Scheme 1. (a) Epoxidation of Triacylglycerol of Soybean Oil (SO) Resulting in Epoxidized Soybean Oil (ESO) and (b) Ring-Opening Reaction of Oxirane Rings of ESO with Acid Anhydrides To Form Acyl Derivatives of Soybean Oil[a]

ASO, if R = -CH₃
PSO, if R = -C₂H₅
BSO, if R = -n-C₃H₇
iBSO, if R = -CH-(CH₃)₂
VSO, if R = -n-C₄H₉
HxSO, if R = -n-C₅H₁₁
HpSO, if R = -n-C₆H₁₃

[a] Gly is the rest of the triacylglycerol molecule.

the thermo-oxidative stability, cold flow properties, and tribological behavior of these CMSO derivatives. The results are illustrative and may help in the development of bio-based lubricants.

EXPERIMENTAL PROCEDURES

Synthesis of Diester Triacylglycerol. The epoxidized oil (ESO, 100% epoxidized, ∼4.2 epoxy groups per triacylglycerol molecule obtained from Elf Atochem, Inc., Philadelphia, PA) was reacted in a single-step reaction with an appropriate anhydride to yield the desired diester derivatives at the sites of unsaturation. To open the oxirane ring and activate the anhydride simultaneously, boron trifluoride diethyl etherate (99.5%) was used as a catalyst in an anhydrous solvent at 50 °C for 3 h. At the completion of the reaction, some of the oxirane rings were converted to the diester derivative termed as CMSO derivatives. The anhydrides, such as acetic, propionic, butyric, valeric, hexanoic, and heptanoic, yielded corresponding diester derivatives ASO, PSO, BSO, VSO, HxSO, and HpSO, respectively. The detailed description of synthesis and structural characterization of CMSO derivatives using Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography GPC, and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) has been reported elsewhere (*35*). On the basis of the NMR and FTIR analysis, the tentative structures of CMSO derivatives ASO, PSO, BSO, VSO, HxSO, and HpSO are shown in **Scheme 1**.

Pour Point (PP) Measurements. Pour points were measured as per ASTM D-5949 method using a phase technology analyzer, Model 70X (Phase technology, Hammersmith Gate, Richmond, British Columbia, Canada). The pour point is defined as the temperature in degrees celsius when the sample still pours when the jar is tilted.

Thin-Film Micro-oxidation (TFMO). This experiment was conducted by oxidizing a small amount of selected oil samples (25 μL) under thin-film conditions on an activated high carbon steel catalyst surface with a steady flow (20 cm³/min) of dry air passing over the

heated sample. The oxidation was carried out at constant temperature (175 ± 1 °C) for 1 h by placing the coupons on the thermally equilibrated aluminum slab, covering with the bottomless impinger (*37, 38*). After 1 h, the coupons with the oxidized oil sample were removed, cooled for 2 h, and weighed. The coupons were then soaked (30 min) with tetrahydrofuran solvent to dissolve the soluble portion of oxidized oil. Finally, these coupons were dried and weighed to determine the insoluble deposit.

Pressure Differential Scanning Calorimetry (PDSC). As a measure of oxidative stability, samples were subjected to PDSC analysis. The experiments were carried out using a PC-controlled DSC 2910 thermal analyzer from TA Instruments (New Castle, DE), as described elsewhere (*20, 23, 26, 33*). A 1.5−2.0 mg of sample was placed in a hermetically sealed type aluminum pan with a pinhole lid and pressurized in the module at a constant pressure of 1378.95 KPa (200 psi) of dry air (Gateway Airgas, St. Louis, MO) in static mode. The temperature of the pressure cell was raised to 350 °C, at a scanning rate of 10 °C/min. The onset (OT) and signal maxima (SM) temperatures of oxidation were obtained from DSC exotherm. OT is obtained from extrapolating the tangent drawn on the steepest slope of the reaction exotherm. High OT and SM would suggest a high oxidative stability of the vegetable oil matrix. The response of antioxidant additives to these CMSO derivatives was studied by measuring their oxidation induction time (OIT) and signal maximum time (SMT) using an isothermal experiment at 200 °C in constant pressure mode (200 psi with a flow rate of 34 ± 5 mL/min).

Four-Ball Method. This experiment was designed to study the antiwear properties of CMSO derivatives under sliding contact using a Falex friction and wear test instrument (Model Multi-Specimen, Falex Corporation, Sugar Grove, IL) as described elsewhere in detail (*33, 39*). The balls (52 100 steel, 12.7 mm in diameter, 64−66 Rc hardness, and extreme polish) were thoroughly cleaned with methylene chloride and hexane before each experiment. Three balls were clamped together to make three-point contact with the top ball. Test fluid [15 mL of 5% (w/w) oil sample dissolved in hexadecane] was poured in the test cup to cover the stationary balls. The test sequence allowed the speed to attain a set rpm of 1200 before a normal load of 40 kg (88 lb.) was applied at room temperature for 60 min. The temperature of the test fluid was 22 °C, which increased to 27−28 °C at the end of the 15 min run. Duplicate tests were performed with a new set of balls, and the scar diameter varied within ±0.04 mm.

Ball-on-Disk Method. Boundary lubrication properties of CMSO derivatives were studied using a ball-on-disk configuration on the same Falex instrument. More details on this experiment can be found elsewhere (*33, 39*). The balls and the disks (Falex) were thoroughly degreased by sonication with fresh reagent-grade methylene chloride and hexane (Aldrich Chemical Co., Milwaukee, WI) prior to each experiment. The balls were 52 100 steel, 12.7 mm in diameter, 64−66 Rc hardness, and extreme polish. The disks were 1018 steel, 25.4 mm in outer diameter, 15−25 Rc hardness, and 0.36−0.46 μm roughness. The ball was held by the upper specimen holder to make a point contact radius of 11.9 mm on the disk. The disk was attached on the bottom specimen holder and enclosed in a fluid-tight cup. A total of 50 mL of the test fluid [5% (w/w) CMSO derivatives in hexadecane] was poured in the cup to totally immerse the ball and disk. The duration of the friction test was 15 min at a sliding speed of 6.22 mm/s (5 rpm) and normal load of 181.44 kg (400 lb.) at room temperature. The temperature of the specimen and test fluid was 25 ± 2 °C, which increased by 2−3 °C at the end of the test period. Friction and other data were recorded until the set time elapsed. The coefficient of friction (CoF) values reported are averages of two or three independent experiments with the standard deviation of ±0.02.

Disk wear track width (WTW) and scar diameter on balls is measured using an optical microscope attached to a digitized moving platform. Five measurements were recorded at different positions of the wear track, and the average value (in millimeters) was taken in each case. For wear scar diameter (in millimeters), two measurements, perpendicular to each other, were recorded for each scar on a ball. The average of six measurements for three balls was taken in each case with a standard deviation of ±0.04.

Table 1. Pour Points of Neat Chemically Modified Soybean Oil Derivatives and HxSO Formulations Using Pour-Point Depressant (PPD) and Diluent (Dibutyl Adipate)

CMSOs	PPD (%)	diluent/oil ratio	pour point (°C)
SO	0	0:100	−9
ESO	0	0:100	0
ASO	0	0:100	−3
PSO	0	0:100	−9
BSO	0	0:100	−15
VSO	0	0:100	−18
HxSO	0	0:100	−21
HpSO	0	0:100	−21
HxSO	0	0:100	−21
HxSO	1	0:100	−30
HxSO	1	30:70	−42

RESULTS AND DISCUSSION

The unsaturation in the soybean oil was removed by first converting it to epoxy groups, followed by ring opening with acid anhydrides to give diesters at the site of unsaturation (**Scheme 1a**). It has already been established that the presence of multiple double bonds in the vegetable oil fatty acid chains accelerate oxidative degradation (*26*). The epoxidation of soybean oil is a straightforward reaction (**Scheme 1a**) and is performed now on industrial scale. The resultant oxirane rings in epoxidized soybean oil were then reacted with acid anhydride to form diesters at the sites on unsaturation (**Scheme 1b**). The details of this reaction, mechanism, and products were discussed elsewhere (*35*). The diester products (ASO, PSO, BSO, iBSO, VSO, HxSO, and HpSO) were studied for their low-temperature properties, oxidation stability, and friction-wear properties.

Low-Temperature Properties. Triacylglycerols that are completely hydrogenated for the purpose of eliminating the sites of unsaturation will tend to harden at room temperature because of alignment and stacking of adjacent molecules. Therefore, it is important that there should be at least one site of unsaturation available for derivatization that will yield branching sites. This approach is used here to improve the low-temperature flow behavior of soybean oil by attaching ester branching at the double-bond sites.

The pour-point measurement provides a good estimate of low-temperature fluidity of the lubricants. Pour-point values for SO, ESO, and CMSO derivatives are given in **Table 1**. The pour point of SO is −9 °C, while that of ESO is 0 °C. The resultant modified soybean oil products are characterized by lower pour points, as demonstrated by the superior pour points for HxSO and HpSO (−21 °C). The pour points decreased with an increasing chain length of ester branching. This can be rationalized by the presence of branching groups attached at the site of unsaturation, which does not allow for individual molecules to come close for easy stacking because of steric interactions, and thus inhibiting crystallization, resulting in a lower pour point. Unmodified vegetable oils have a tendency to form macrocrystalline structures via a uniform stacking of the "bent" triacylglycerol backbone at low temperature (*40–42*). The branching groups of optimum length at the epoxy carbons not only serve to eliminate the sites of unsaturation but also impose spacing from other triacylglycerol molecules, thereby interfering with the formation of macro-crystalline structures. The ester branching groups with a chain length of at least six carbons were found to be the most effective for imposing the desired molecular spacing and thus imparting the most desired pour-point properties.

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Further improvement in the low-temperature fluidity of HxSO was attained by using pour-point depressant (PPD) additive (L7671-A from Lubrizol Corp., Wickliffe, OH), as shown in **Table 1**. Blending was carried out by stirring CMSO derivatives with an optimized additive dose at room temperature for 2 h. The purpose of the PPD additives is to sterically hinder crystallization of triacylglycerol molecules at low temperature by disrupting the stacking mechanism. In general, PPDs can lower the pour point by 30 °C in mineral oils at concentrations of only 0.1−0.4% (w/w), while in vegetable oils, a pour point reduction of only 9−12 °C can be achieved, with a high treat rate of 1%. Because the additive response of PPD in vegetable oils is not as good as in mineral oils, a higher amount of PPD is needed to lower the PP significantly. An optimum PPD additive concentration of 1% in the HxSO enabled a pour point of −30 °C. Further addition of PPD additives made no significant improvement in the pour point. To further improve the low-temperature properties of the formulation, diluents, such as polyalphaolefins, dibutyl adipate, and high oleic vegetable oils, can be used. Here, we have used a biodegradable synthetic ester, dibutyl adipate (96% purity), that was uniformly blended into the formulation as a diluent at several concentrations. The final optimized formulation HxSO + 1% PPD + diluent (70: 30 oil/diluent ratio) had a pour point of −42 °C.

The ASTM D 97 (pour-point determination) experimental setup was used for low-temperature storage stability measurements of HxSO formulation. The samples were kept at −25 °C and visually inspected every 24 h for 7 days for fluidity (similar to pour-point determination). Failing criteria consisted of crystallization, solidification, and formation of solid particles but did not include haziness and loss of transparency. The HxSO formulated with 1% PPD only, failed after 3 days at −25 °C, while the final optimized formulation of HxSO with 30% diluent and 1% PPD, which had a pour point of −42 °C, passed the 7 days storage stability test at −25 °C.

Oxidation and Thermal Stability. The thin-film micro-oxidation method provides an idea on how a lubricant will behave in various high-temperature bearing tests, under the oxidation conditions, such as a test occurring on a metal surface in an open atmosphere where evaporation can occur. The percent insoluble deposit obtained in TFMO test indicates the amount of insoluble oxidizable material in a given oil. For example, the percent insoluble deposit for soybean oil is approximately 66%. It is desirable for the lubricants to exhibit a lower amount of insoluble deposit. The conversion of double bonds to epoxy groups (ESO) also resulted in a sharp increase in the deposit formation, suggesting a catastrophic breakdown of the epoxy group, leading to an oxidative polymerization reaction through the reactive oxygen radical (38). Further conversion of ESO to CMSO derivatives (ASO, BSO, and HxSO) with branchings at the sites of unsaturation increased the initial thermal and oxidative stability compared to SO, as shown by the low deposit-forming tendency that remained constant throughout the test. The insoluble deposits of ASO, BSO, and HxSO are 9, 15, and 22%, respectively, compared to 66% of SO. High insoluble deposits in SO are because of the presence of more unsaturation in it. The double bonds are attractive sites for the reaction with primary oxidation products, which results in more polymerization (leading to more insoluble deposits) and less volatile product formation.

The PDSC test is widely used in the lubricant industry for measuring oxidative stability of base oils as well as finished lubricants (43). The onset temperature of oxidation (OT) is the temperature when a rapid increase in the rate of oxidation is

Table 2. Onset (OT) and Signal Maxima (SM) Temperatures for Chemically Modified Soybean Oil Derivatives Obtained Using Pressurized Differential Scanning Calorimetry at 10 °C/min in Air under 200 psi Pressure[a]

CMSOs	OT (°C)	SM (°C)
SO	172.2	193.0
ASO	181.0	220.9
PSO	185.0	215.1
BSO	182.8	218.0
VSO	182.7	214.8
HxSO	183.5	215.6
HpSO	181.9	215.3

[a] OT and SM values are the average of three experiments with a standard error of ±1 °C.

Table 3. Onset (OT) and Signal Maxima (SM) Temperatures Obtained Using the PDSC Temperature Ramp Method (10°C/min in Air under Static 200 psi Pressure) and Oxidation Induction (OIT) and Signal Maxima Time (SMT) Using an Isothermal Experiment (at 200°C under 200 psi Pressure with 34 ± 5 mL/min Flow of Air) for Chemically Modified Soybean Oil Derivatives with Additives [4% (w/w)]

CMSOs	OT (°C)	SM (°C)	OIT (min)	SMT (min)
SO	192.0	206.0	25.7[a]	33.0[a]
ASO	238.4	248.8	21.2	23.5
PSO	239.6	249.0	21.4	24.6
BSO	244.1	250.7	20.8	25.4
VSO	241.6	250.6	22.7	26.8
HxSO	248.0	256.9	28.5	35.4
HpSO	242.4	252.4	20.0	25.2

[a] Isothermal experiment at 170 °C.

observed in the system. The signal maximum temperature of oxidation (SM) is the temperature at which maximum heat was evolved during oxidative degradation of the sample. The PDSC results, OT and SM, for diester samples are shown in **Table 2**. The CMSO samples showed higher oxidation stability than unmodified vegetable oil (SO), as shown by their higher OT and SM values. This increase in oxidation stability is due to the removal of unsaturation. No significant change was observed with an increasing chain length of the branching group.

Antioxidant additives were used to further improve the oxidation stability of these soybean oil derivatives. Varying concentrations of different antioxidants were tried in SO (20). The best additive combination was then used, 4% (w/w), in soybean oil derivatives. The effect of these antioxidants was studied using PDSC temperature ramping and isothermal experiments, and the results are shown in **Table 3**. It was found that the response of antioxidant additives was very good in soybean oil derivatives. The presence of antioxidants in CMSO derivatives increased their OT by 60 °C and SM by 30−40 °C. In CMSO derivatives, HxSO has the highest OT (248 °C) and SM (257 °C), while ASO has the lowest values of OT (238 °C) and SM (249 °C). The isothermal PDSC experiment was performed to determine an oxidation induction time at 200 °C. These results also suggested that the antioxidant additive could prevent the onset of oxidation for 20−30 min at 200 °C. The CMSO derivative HxSO showed the highest OIT (29 min), while HpSO had the lowest OIT (20 min). The OT, SM, OIT, and SMT of CMSO derivatives are higher compared to SO. In general, OT, SM, OIT, and SMT values of additized CMSO derivatives increased with an increasing chain length of the branching up to six carbons. Some mineral-oil-based formulations were also reported to have an OIT of 20 min at 200 °C (44). The results thus showed that use of suitable antioxidant additive can bring the oxidation performance of CMSO deriva-
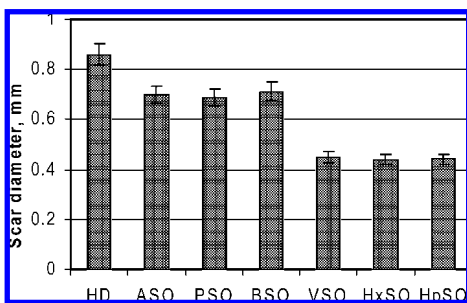
Figure 1. Four-ball wear scar diameters (WSD) on 5% (w/w) solutions of chemically modified soybean oil derivatives in hexadecane (HD) under conditions: load, 88 lbs.; speed, 1200 rpm; room temperature; time, 60 min. ASO, PSO, BSO, VSO, HxSO, and HpSO are acyl derivatives of soybean oil as shown in **Scheme 1**.

Figure 2. Coefficient of friction (CoF) data on 5% (w/w) solutions of chemically modified soybean oil derivatives in hexadecane (HD) obtained using ball-on-disk configuration under conditions: load, 400 lbs.; speed, 5 rpm; ambient temperature; time, 15 min. ASO, PSO, BSO, VSO, HxSO, and HpSO are acyl derivatives of soybean oil as shown in **Scheme 1**.

tives at par with mineral oils. The fully formulated lubricant using CMSO as a base fluid, dibutyl adipate as a diluent, PPD, and antioxidant additive has excellent oxidation stability (PDSC onset temperature of 248 °C and oxidation induction time of 28.5 min).

Friction-Wear Properties. An important property of lubricants is their ability to maintain a stable lubricating film at the metal contact zone. Vegetable oils are known to provide excellent lubricity because of their ester functionality. The four-ball wear tests were performed in a hydrocarbon base hexadecane to demonstrate their effectiveness in reducing wear. CMSO products (ASO, PSO, BSO, VSO, HxSO, and HpSO) were introduced into hexadecane base oil at a concentration of 5% (w/w). Under the experimental conditions (speed of 1200 rpm, load of 88 lbs., at room temperature for 60 min), the addition of the CMSO products as additives in hexadecane reduced the four-ball wear scar diameter of hexadecane (**Figure 1**). The addition of CMSO products, such as VSO, HxSO, and HpSO, caused ∼50% wear reduction in hexadecane base oil. The coefficient of friction obtained for hexadecane (0.095) was reduced to 0.031 upon addition of HxSO under these experimental conditions. Overall, the wear scar diameter decreased with an increasing chain length of branching in CMSO products, as shown in **Figure 1**. One possible reason may be the increased film thickness because of the increase in molecular weight as a result of long branching groups. CMSO products were analyzed as such also under four-ball conditions (speed of 1200 rpm, load of 88 lbs., at room temperature for 15 min). Under these conditions, the scar diameter of hexadecane was 0.68 mm, while the scar diameters of ASO, PSO, BSO, and HxSO were 0.48, 0.50, 0.44, and 0.43 mm, respectively.

The friction-reducing property of CMSO products as additives in hexadecane was demonstrated by the coefficient of friction (CoF) obtained using the ball-on-disk experiment. Under a high load of 400 lbs. (181.44 kg) and low speed of 5 rpm (6.22 mm s^{-1}), all of the CMSO products showed excellent reduction in CoF at a concentration of 5% (w/w) (**Figure 2**). The CoF values of all CMSO products are in the range of 0.11−0.12 and are a considerable improvement over neat hexadecane (0.46). This shows that the CMSO products can be used as friction-reducing additives also. A high proportion of these additives increased its competition at the metal surface, leading to high surface coverage and, subsequently, low CoF of the corresponding sample (*45*). The CoF values for CMSO products were also lower than the values using methyl oleate as an additive, 0.19 at the same concentration. The wear track widths (WTW) measured for certain CMSO products (ASO, PSO, BSO, and VSO) are in the range of 2.30−2.38 mm, which is considerably lower than that for hexadecane (2.59 mm). The WTW values
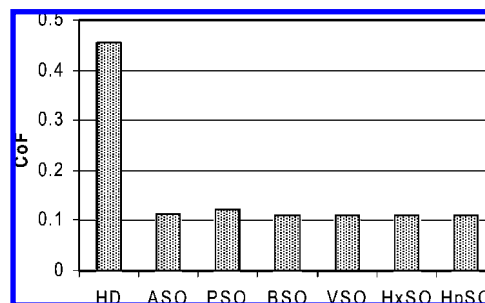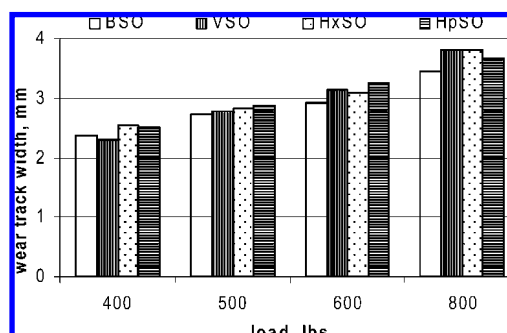

Figure 3. Effect of increasing load on wear track width (in millimeters) obtained for chemically modified soybean oil derivatives [5% (w/w) solutions in hexadecane] in ball-on-disk configuration (speed, 5 rpm; room temperature; run time, 15 min; and varying load, from 400 to 800 lbs.). BSO, VSO, HxSO, and HpSO are acyl derivatives of soybean oil as shown in **Scheme 1**.

for CMSO products [5% (w/w) solution in hexadecane] were also determined as a function of the load from 400 to 800 lbs. The measurement of WTW with increasing load helped determine the safe limits of load under which these products can be used. Any further increase in load beyond a certain point would result in a catastrophic rise in CoF as well as WTW, primarily, because of irreversible breakdown of additive film and, second, because of the loss of oil-induced lubricating film, resulting in scuffing and welding from metal contact. It was observed that the WTW values increased with increasing load (**Figure 3**). It can be concluded that all CMSO products provided better wear protection at loads up to 400 lbs., beyond which possibly the molecules start disintegrating under high loads. This translates into poor film strength and the loss of antiwear protection at higher loads.

A possible explanation for improved tribological properties of CMSO products is that there are additional polar functional groups in the triacylglycerol molecule. Active oxygen sites in the form of additional ester functionality at 9, 10; 12, 13; and 15, 16 positions on fatty acids of triacylglycerol help the molecules adhere to the metal surface more rigidly, forming monolayer film with the nonpolar end of fatty acids sticking away from the metal surface (*45–47*). This monolayer offers a sliding surface that prevents the metal−metal direct contact and thus reduces friction and wear. Without a lubricant film, metal−metal contact may result in increased temperature at the contact zones of moving parts, causing adhesion, scuffing, or even welding. During the tribochemical process, these molecules undergo chemical transformation at the metal contact zone and develop a stable tribochemical film to protect further wear of

the metal. These compounds demonstrate excellent antifriction and antiwear properties using ball-on-disk and four-ball test geometry, respectively.

The chemical modification approach has significantly improved the cold-flow properties, while thermo-oxidative stability of these chemically modified soybean oil derivatives has been improved using antioxidant additives. These CMSO derivatives have also shown superior tribological properties compared to hexadecane, a representative of mineral oils. Cold-flow property was further improved using a combination of PPD and suitable diluents. Some CMSO derivatives meet or exceed many, if not all, specifications for some lubricant end-use applications without the inclusion of conventional additives. However, for specific applications, these fluids may be formulated with other functional components, such as extreme-pressure additives, antiwear additives, pour-point depressants, other base stocks, and diluents. As demonstrated above, suitably designed CMSO derivatives have superior properties, which render them useful as base oils for various industrial lubricant applications.

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LITERATURE CITED

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