

Tribological Properties of Vegetable Oils Modified by Reaction with Butanethiol

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Abstract Corn, canola, and castor-lauric estolide oils were chemically modified by photochemical direct reaction of butanethiol with the double bonds on the hydrocarbon chains. The effect of chemical modifications on viscosity, viscosity index (VI), pour point (PP), cloud point (CP), oxidation stability (RPVOT), 4-ball anti-wear (AW), and extreme pressure (EP) were investigated. The sulfide modified (SM) corn and canola oils showed increased viscosity, increased RPVOT time (more than one order of magnitude), reduced PP (9–18 °C), and reduced VI. The SM estolide displayed similar trends in VI and RPVOT but showed no change in viscosity or cold flow. The SM oils, along with commercial mono- and polysulfide additives were also investigated as additives, at 0.6% (w/w) S concentration, in corn and polyalphaolefin (PAO) base fluids. In both fluids, the additives resulted in minor changes of PP, CP, coefficient of friction, wear scar diameter (WSD), and weld point (WP). Only the commercial polysulfide EP additive displayed large WP increases in the fluids. The additives resulted in no change of oxidation stability of corn oil, but displayed big improvement in the oxidation stability of PAO (8 to 16-fold increase in RPVOT time). The difference in the effect of the additives on the oxidation stability of PAO versus corn oil was attributed to the difference in the

reactive hydrogen contents in the two base fluids relative to those in the additives. An empirical equation, for correlating change in RPVOT time with change in bond dissociation energy of reactive protons before and after chemical modification, is proposed.

Keywords Antioxidants · Extreme pressure additives · Vegetable oils · Biodegradable oils · Oxidation resistance · Low temperature · Pour point · Viscosity · Viscosity–temperature

1 Introduction

Farm-based oils have the potential to be used as raw materials for a number of products currently manufactured from petroleum, including lubricants [1–8]. Successful development of consumer and industrial products from such oils provides a wide range of economic, environmental, and health benefits. It will also reduce the huge crop surplus, improve the income of farmers, grow the rural economy, and lead to sustainable economic growth. Farm-based oils are generally safe and non-toxic to humans, animals, and the environment, which makes their manufacture, use, and disposal non-hazardous to workers and consumers. In addition, such oils biodegrade easily, breaking down into simple and benign compounds that pose little or no risk to the environment.

In addition to their economic, environmental, and health benefits, farm-based oils have a number of physical and chemical properties that make them attractive for lubrication applications. One of the most important such properties is that they are mostly liquid at room temperature, and also have amphiphilic properties [9]. Amphiphilic materials have distinctly separated polar and non-polar regions in

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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the same molecules [10]. The farm-based seed oils have two or three ester groups in close proximity creating the polar region, which are distinctly separated from one or three non-polar hydrocarbon chains creating the non-polar region [11, 12]. Being liquids at room temperature allows seed oils to be used as base oils, while being amphiphilic allows them to be used as film-strength additives in lubricant formulations.

In spite of the above-listed benefits, development of lubricants from farm-based oils requires overcoming a number of serious scientific, engineering and development problems. One of the areas requiring major scientific breakthrough deals with overcoming a number of serious and inherent weaknesses of biobased raw materials [13–16]. These include inadequate oxidation stability, unacceptably high pour point (PP) and cloud point (CP), poor hydrolytic stability, and low biostability. The second major area requiring scientific advancement deals with building our knowledge base and improving our understanding of the tribological and tribochemical properties of farm-based raw materials. Unlike petroleum-based products, which have been studied and developed over a century, there is limited such knowledge about farm-based raw materials.

One of the methods for improving the properties of farm-based oils is through chemical modification. There are two sites on the molecule of seed oils that are amenable to such modifications and have been widely used: the ester linkages of the triglycerides, and the carbon–carbon double bonds on the hydrocarbon chains. Over the years, a number of reactions have been devised and applied to introduce chemical modifications of the oils on each of these sites [17–26]. More reactions are being developed currently and the list is expected to grow in the future.

In the work described here, corn, canola, and castor-lauric estolide [27] oils were chemically modified by direct reaction of butanethiol with the double bonds on the hydrocarbon chains. The chemically modified oils are sulfides, and will be referred henceforth as sulfide modified (SM) oils. The unmodified and the SM oils were investigated for cold flow, oxidation stability, friction and wear properties. Cold flow properties were evaluated using pour point (PP, ASTM D 97-90a) and cloud point (CP, ASTM D 2500-99) methods. Oxidation stability was evaluated using rotating pressurized vessel oxidation test (RPVOT, ASTM D 2272-98) method. Friction and wear were investigated using 4-ball anti-wear (AW, ASTM D 4172-94) and extreme pressure (EP, ASTM D 2783-88) methods. The effect of eliminating the double bond and introducing a covalently bonded organic sulfur branch on these tribological properties is discussed.

Recent critical review has identified cold flow and oxidation stability as the two most challenging hurdles preventing commercialization of biobased lubricants in such

high volume applications as engine and hydraulic oils, which together account for more than 60% of the lubricant market [1, 2, 5]. Chemical modification is one of the approaches being aggressively pursued to overcome this problem. It should be noted, however, that the success of chemical modification in improving tribological performance can be greatly enhanced with the use of predictive structure–property models. Extensive literature search produced no such models for predicting PP, CP, and RPVOT data obtained using the respective standard methods. A brief review of the surveyed literature will be given below. As it stands now, there is a need for developing relevant predictive models to improve the effectiveness of chemical modifications research.

1.1 Modeling of Lubricant Oxidation Stability Properties

A number of workers [28–32] applied autooxidation kinetic models to determine the rate constants and activation energies of auto-oxidation for a number of polyunsaturated fatty acids, their esters, and/or mixtures. The data used in these analyses were obtained from autooxidation of oil samples in a dessicator, which was kept in the dark and maintained at specified temperatures and relative humidity. Oil samples were periodically removed and the oxidation monitored by GC analysis for the unoxidized materials. The time versus fraction of unoxidized material was analyzed to determine the rate constants and activation energies of autooxidation.

Koh and Butt developed and applied kinetic model to analyze oxidation data on polyalphaolefin generated on a batch recycling trickle-bed reactor system [33]. The authors claim that their model correctly predicted the effect of catalytic material (glass, 52100 steel, brass) and additive (zinc dialkyl dithiophosphate) on rate and activation energy of oxidation.

Arrhenius model has been applied on pressurized differential scanning calorimetry (PDSC) data to estimate the rate and activation energy of oxidation for vegetable oils. This approach was used by Adhvaryu et al. [16] to estimate the relative oxidation stabilities of vegetable oils from genetically modified and unmodified seed crops (cottonseed, corn, canola, sunflower, safflower, soybean oil, high oleic sunflower, high oleic safflower, and high linoleic safflower oil). Kowalski [34] applied similar approach to study the relative oxidative stabilities of rapeseed, soybean, corn and sunflower oils.

Various types of empirical, statistical, and qualitative methods have been applied to correlate oil structure with oxidation stability [4, 16, 35–40].

Bala et al. [35] used the Groupment Francais de Coordination (GFC) procedure to investigate the oxidation

stability of organic sulfides (R–S) in hydrotreated and solvent refined base oils. In the GFC method, 300 mL of oil sample was oxidized in 500 mL flask at a specified temperature for 192 h with 10 L/h of dry air bubbling through it. Samples of oil were analyzed at the beginning, periodically and at the end for viscosity, TAN (total acid number) and insolubles. The authors reported that the oxidation stability of R–S oils was found to be a function of the bond dissociation energies (BDE) of C–S, S–S, poly-S bonds. They reported that the BDEs were found to be highly influenced by the structures of the organic groups (chain length, branching, cyclic).

Adhvaryu et al. [16] proposed a regression model for predicting the oxidation rate and activation energy of vegetable oils from the percent protons (olefinic, allylic, bis-allylic, etc.) obtained from NMR analysis.

Adhvaryu et al. [36] compared the minimum energy of derivatives of epoxidized soybean oil (ESO), which were ether–alcohols or ether–esters, with several physical and chemical properties (PDSC onset temperature, PP, insoluble deposits, kinematic viscosity). The authors claim that the compounds with minimum energy generally also have improved oxidation and cold flow properties.

Isbell et al. [37] investigated the oxidation stability of a number of crude and refined vegetable oils using oxidative stability index (OSI) method. The authors reported that the OSI of most crude and refined vegetable oils can be predicted from the ratio of total concentration of tocopherol in oil (ppm) to iodine value. A major exception to this correlation was crude and refined meadowfoam oil, whose OSI was much higher than predicted by this relationship. The authors attribute this rather high oxidation stability of meadowfoam oil to the position of the double bond (Δ -5) in its fatty acids.

Knothe and Dunn proposed a predictive equation for OSI of fatty acid compounds based on least-square regression of OSI versus bis-allylic position equivalent (BAPE) data [38, 39]. The authors claim that BAPE is better than iodine value for predicting oxidation stability by the method of OSI.

Moser et al. [40] investigated the oxidation stability of diesters of oleic acid prepared by ring opening esterification of epoxidized oleic esters. In these series of compounds, one ester group is at the end and the second in the middle of the chain. The authors provided qualitative assessment on the effect of ester group position and chemical structure on oxidative stability. They noted that the mid-chain ester plays a larger role in oxidation stability than the end-chain ester, and improved oxidation stability was achieved when the chain length of the mid-chain ester decreased.

Jayadas and Nair [4] conducted thermo-gravimetric analysis (TGA) investigations of the thermal (under

nitrogen environment) and oxidative (under oxygen environment) properties of coconut, sesame, sunflower, and a commercial mineral oil. The results of the isothermal TGA study under oxidative conditions showed weight gain due to formation of polymeric oxidation products by the vegetable oils. This weight gain was higher for sunflower and sesame oils than that for coconut oil. The authors attributed this to the higher percentage of polyunsaturated fatty acids in sunflower and sesame oils compared to that in coconut oil.

A number of workers have applied ab initio and density functional calculations to predict rates and activation energies of oxidation reactions for different species [41–47].

Chen and Bozzelli [41] applied ab initio and density functional calculations to analyze the reactions of HO₂ radical addition to the primary, secondary, and tertiary carbon–carbon double bonds of ethylene, propene, and isobutene. The authors report that calculated rate constants and activation energies using these methods show similar trends with experimental data.

Gschwender [42] applied molecular dynamic (MD) simulations to calculate the attraction energies between metals and a number of perfluoropolyalkylether base fluid and additive structures. Some of the structures were also synthesized and their tribological properties investigated. The additive structures were of interest as oxidation inhibitors/metal deactivators, lubricity additives, and anti-rust additives. The author reported that the structures that were predicted by the MD simulations to have large interaction energies with the metal surfaces were also found experimentally to have the best properties of preventing metal oxidation, rust, and improving lubricity [42].

Pfaendtner and Broadbelt [43] used experimental or quantum chemistry and transition state theory calculations to develop structure–reactivity relationship for a number of families of reactions (initiation, propagation, termination, etc) involved in free-radical oxidation of lubricating hydrocarbons oils. The authors applied the developed library of structure–reactivity relationships for estimation of all kinetic data for auto-oxidation of decane and octane [44].

Przybylski and Zambiasi [45] developed and applied Artificial Neural Network Systems (ANNW) to predict the oxidative stability of a number of vegetable oils. Oxidation stability was monitored by measuring the concentration of O₂ as a function of time, at constant temperature (35 and 65 °C), with/without light, in the headspace air of a sealed container with the vegetable oil. The data from half the oils was used to train the ANNW using composition of major and minor components of vegetable oils (major fatty acids, chlorophylls, tocopherols, tocotrienols, and metals) as inputs, and induction period and values of slopes for

initiation and propagation of oxidation as outputs. The trained ANNW was then used to predict the output parameters for the second half of the samples.

Siniawski et al. [46] calculated predicted degradation (% conversion) of vegetable oils (soybean, sunflower) and a mineral oil as a function of time, at 25 and 100 °C, under steel–steel friction, using kinetic reaction mechanism model of lubricant degradation. The kinetic rate constants for the various steps of oxidation reactions (initiation, propagation, termination) used in the predictive model were obtained from literature or were calculated using quantum chemistry and transition state theory. The predicted conversions were compared to friction versus cycle data (ball-on-disk, 2 N load, 100 rpm, 20,000 cycles) at different temperatures. The predicted degradation (% conversion) over a period of 12,000 s at 100 °C was $\gg 10\%$ for the vegetable oils but $\ll 0.1\%$ for the mineral oil. This result correlates well with the friction data at 100 °C and higher. At 100 °C, the vegetable oils experienced a marked increase in the coefficient of friction (COF) after 4,000 s that continued for the remaining duration of the sliding. At 150 °C, the transition to high COF occurred earlier, around 1,000 s, due to the increased reaction rates. The significant increase in the COF for the vegetable-based lubricants was attributed to increased lubricant degradation. The mineral oil COF data was essentially constant at both temperatures, which implies essentially non-existent conversion of the mineral oil to reaction products.

Zabarnick and Phelps [47] employed density functional theory (DFT) to calculate reaction enthalpies and activation energies for abstraction of hydrogen by peroxy radical from hydrocarbons in the autoxidation of jet fuel. They also used DFT to calculate the X–H bond strength, where X is carbon or heteroatom. The study showed that H atoms which are weakly bonded to heteroatoms including nitrogen, oxygen, and sulfur, are very reactive and can effectively compete with the bulk fuel hydrocarbon for peroxy radical species at part per million levels. In addition, benzylic hydrogens on aromatic hydrocarbons were shown to be significantly more reactive than paraffinic hydrogens so that the aromatic portions of fuel sustain the bulk of the autoxidation process.

1.2 Modeling of Lubricant Cold Flow Properties

Molecular modeling has been used to determine minimum energy conformation of molecules, which was then qualitatively related to measured cold flow data. Two such reports are by Jayadas and Nair [4] and Adhvaryu et al. [36].

Jayadas and Nair [4] conducted a differential scanning calorimetry (DSC) investigation into the low-temperature flow properties of coconut, sesame, sunflower, and a

commercial mineral oil. They also conducted MD simulations study about the effect of fatty acid degree of unsaturation on the minimum energy conformation of the triglyceride oils [4]. The simulation showed that the minimum energy conformation of triglycerides with three saturated fatty acids had its fatty acid chains nearly parallel to one another. Such structure allows close packing of the molecules during cooling leading to a gel-like structure and high PP. The simulation result is consistent with the observed high PP of coconut oil relative to sesame oil and sunflower oils, since coconut oil contains a relatively larger percentage of saturated fatty acids in its structure.

Adhvaryu et al. [36] compared the minimum energy of derivatives of ESO, which were ether–alcohols or ether–esters, with their physical properties (PDSC onset temperature, PP, insoluble deposits, kinematic viscosity) [36]. The authors reported that minimum energy conformations can be used to explain differences in PP and other properties among these derivatives.

There are several reports where cloud point curves (CPC) are used to investigate the miscibility of binary and quasi-binary blends of polymers as a function temperature and composition (volume fractions of monomers or polymers with varying chemical structure, molecular weights, etc) [48–53]. The CPC separates the homogeneous phase (miscible composition) from the inhomogeneous phase (phase separated composition) of the blend. The CPC curve can be predicted using thermodynamic models based on Flory-Huggins (F-H) theory. However, in order to accomplish this it will require knowledge of the interaction parameter for the specific blend system under investigation, and its dependence on temperature or other variables. Various experimental and computational methods have been applied to estimate the interaction parameter for use in prediction of CFC curves. Examples of blends used in such investigations are: styrene/unsaturated polyester [48], binary blends of star polymers [49], polystyrene/poly(R-methylstyrene) and polystyrene/poly(vinyl methyl ether) [50], SBR/polybutadiene elastomer [51], polystyrene/reactive epoxy monomers [52], linear poly(vinyl methyl ether)/four-armed star polystyrene [53].

Several papers provide qualitative correlations that can be used to infer cold flow properties from the structure of the oils [40, 54–56].

Govindapillai et al. [54] investigated the cold flow properties of coconut oil, with and without pour point depressant (PPD, styrenated phenol), using DSC and PP (ASTM D97) methods, and compared the results to those of other seed oils (castor, sesame, palm, groundnut, linseed, mustard, olive, sunflower). In general, coconut oil displayed endothermic DSC peaks and PP at higher temperature than the other oils. Coconut oil showed slight improvement in the cold flow properties with increased

concentration of PPD additive. The authors attribute the rather poor cold flow properties of coconut oil to the presence of large percentages of saturated fatty acids in its structures.

Letoffe et al. [55] investigated synergistic and antagonistic effects between commercial diesel fuels and cloud point depressant (CPD) or cold filter plugging point depressant (CFPPD) additives. The CPD additives were prepared by the polymerization of linear α -olefins with acrylic, vinyl, and maleic unsaturated compounds at atmospheric pressure. The CFPPD was ethylene-vinyl acetate copolymer. The result showed both antagonistic and synergistic effects by both CPD and CFPPD additives. The authors reported that the antagonistic versus synergistic effect of the CFPPD on a diesel fuel can be predicted based on the polymer glass transition temperatures and the percentage of light *n*-alkanes in the diesel fuel determined by DSC method.

Moser et al. [40] investigated the cold flow properties (CP, ASTM D 5773; and PP, ASTM D 5949) of diesters of oleic acid prepared by ring opening esterification of epoxidized oleic esters. In these series of compounds, one ester group was at the end and the second in the middle of the chain. The authors provided qualitative assessment on the effect of ester group position and chemical structure on cold flow properties. It was observed that increasing chain length of the mid-chain ester and branching in the end-chain ester had a positive influence on the low temperature properties of diesters.

Nassar and Ahmed [56] synthesized copolymers of butyl acrylate with different α -olefins (octene, dodecene, tetradecene, and octadecene) and investigated their properties as viscosity index improver (VII) and PPD additives. The copolymers were evaluated as a function of molecular weight, alkyl chain length, and concentration in SAE 30 base oil. The evaluation showed that the efficiency of the copolymers as VII additives increased with increasing concentration in the base oil and also with increasing chain length of the α -olefin alkyl groups. The efficiency of the copolymers as PPD additives improved with decreasing concentration in the base oil as well as with decreasing molecular weights.

2 Experimental

2.1 Materials

Isopropyl alcohol, hexane, castor oil, ethyl acetate, 2-ethylhexanol, lauric acid, and tin (II) 2-ethylhexanoate were obtained from Fisher Scientific Co. (Fairlawn, NJ). Hexadecyl mono-sulfide (93% purity) is a product of Acros Organics (Geel, Belgium) and was purchased from Fisher

Scientific Co. (Fairlawn, NJ). Diteriary dodecyl pentasulfide (PS) with the trade name TPS-32 was a sample from Arkema Inc. (Philadelphia, PA). Butanethiol was from Sigma-Aldrich (St. Louis, MO). Corn oil and canola oil were obtained from local supermarket. All materials were used as supplied without further purifications. PAO was from Ineos Oligomers (League City, TX). Silica gel used in flash chromatography was premium Rf grade (Cat.# 52 300-2.5) from Sorbent Technology (Atlanta, GA).

2.2 Syntheses

2.2.1 Photochemical Reactor

Sulfide modified oils were synthesized by photochemical reaction of oils with butanethiol. The reactor was assembled using parts obtained from Ace Glass, Inc. (Vineland, NJ). It consisted of a 450 W medium pressure mercury lamp (Cat# 7825-34), a power supply (Cat# 7830), low-temperature immersion well (Cat# 7858-42), and 500 mL reaction vessel (Cat# 7841-04). The immersion well was cooled to 25 °C with re-circulating water bath, and the contents of the reaction flask were mixed using a magnetic stirrer (Fisher Scientific, Pittsburgh, PA, Cat# 07-250-140).

2.2.2 Synthesis of Sulfide Modified Canola (SM Canola)

Butanethiol (350 mL) was placed in the photochemical reactor immersed in ice-water bath, and 135 mL canola oil was slowly added while the mixture was stirred with a magnetic stirrer. The mixture was irradiated in ambient atmosphere for 24 h while the temperature was being monitored and maintained between 7 and 12 °C. After the reaction, excess butanethiol was removed by distillation under vacuum, and butyl disulfide side product was removed by Kugelrohr distillation at 150 °C, 13 Pa for 8 h SM canola was obtained in 83% yield. NMR and GC-FID analysis showed 98% conversion of the canola double bonds into sulfide moieties. More details about this synthetic procedure can be found elsewhere [57].

2.2.3 Synthesis of Sulfide Modified Corn Oil (SM Corn)

Sulfide modified corn oil was synthesized following the procedure discussed above for canola oil. Excess butyl disulfide was removed by flash chromatography using premium Rf grade silica gel. SM corn oil was obtained in 61% yield. NMR and GC-FID analysis results showed 90–91% conversion of the double bonds; and elemental analysis (Galbraith, Knoxville TN) showed that the material contains 9.74% sulfur. More details about synthesis of SM corn oil can be found elsewhere [57].

2.2.4 Synthesis of Castor-lauric 2-ethylhexyl ester estolide

Castor 2-ethylhexyl ester, used in synthesis of castor-lauric 2-ethylhexyl ester estolide, was obtained using a synthesis procedure described before [27]. Details of the synthetic procedure for castor-lauric 2-ethylhexyl ester estolide have been given elsewhere [27]. A brief description of the procedure for synthesis of the estolide is as follows: 1.0 equivalents (200.0 g, 487.8 mmol) of castor 2-ethylhexyl ester and 1.5 equivalents (146.6 g, 731.7 mmol) lauric acid were combined in a three-necked round-bottom flask equipped with a magnetic stirrer, temperature probe, and a series of two connected condensers. The initial Liebig condenser, attached to a 45 °C recirculating water bath, was necessary to prevent the unreacted fatty acids from evacuating the flask. The top of the first condenser was connected to a 75° angle adapter. To the side of the adapter was connected a Friedrichs condenser, which had circulating tap water. A gas inlet adapter (vacuum line attached) and round-bottom flask to collect water were attached to the outlet of the Friedrichs condenser. The reaction was catalyzed with 0.1 wt% tin (II) 2-ethylhexanoate (0.35 g, 0.86 mmol). The reaction flask was heated at 130 °C for 24 h under vacuum (12–18 Pa). At the conclusion of the reaction, the unreacted fatty acids were removed using a Kugelrohr distillation unit at a temperature of 180–200 °C, vacuum of 6–13 Pa, for 2–4 h. The final product, castor-lauric 2-ethylhexyl ester, was vacuum filtered using #54 Whatman filter paper, which gave a light yellow product in 73% yield.

2.2.5 Synthesis of Sulfide Modified Castor-lauric estolide (SM CasLaurEst)

Sulfide modified castor-lauric 2-ethylhexyl ester estolide was synthesized according to the following procedure: 300 mL butanethiol were placed in the photochemical reactor, and 159 g of castor-lauric 2-ethylhexyl ester estolide was added drop wise with stirring over a period of 2–3 min. The photoreactor was then placed in a dry ice/acetone bath, and the reaction mixture irradiated for 3 h, during which time the temperature of the mixture was maintained between –28 and –18 °C. The product mixture was then transferred to a round bottom flask and the excess thiol removed by vacuum distillation (95 °C, 3 h). The byproduct butyl disulfide was removed using Kugelrohr distillation apparatus at 150 °C, 13 Pa, for 60 min. The SM CasLaurEst product was isolated in 96% yield. The conversion of double bonds to sulfide moieties was estimated by NMR to be 77%.

2.2.6 Spectroscopic Identification of Sulfide Modified Oils

NMR. NMR spectra of the samples were obtained in CDCl₃ on a Bruker Avance 500 NMR spectrometer (Billerica,

MA) operating at 500 MHz for ¹H and 125 MHz for ¹³C and using a 5 mm BBI probe. Chemical shifts are reported in parts per million from tetramethylsilane calculated from the lock signal. ¹H, ¹³C, ¹³C DEPT, COSY, HSQC, and HMBC were used to identify the signals.

FTIR. Neat samples were placed between two KBr disks (25 mm × 2.5 mm). Their FTIR spectra were collected using a Varian 3100 FTIR (Randolph, MA) spectrometer. Thirty-two repeat scans were averaged over a range of 600–4000 cm^{–1} at a spectral resolution of 4 cm^{–1}.

Details of the spectroscopic identification of SM canola and corn oil have been given before [57]. SM CasLaurEst was positively identified as follows. The reaction of the double bond was confirmed by the reduction in the intensity of the FTIR absorbance at 3009 cm^{–1}, and the decrease of the intensity of the olefinic ¹H NMR signals in the region 5.0–5.5 ppm. New peaks were observed at 968 cm^{–1} in FTIR (Fig. 1) and new signals appeared at 5.0–5.2 ppm in ¹H NMR, which were attributed to partial isomerization of the *cis* double bonds to *trans* double bonds. The formation of C–S bond was confirmed by the appearance of the ¹H NMR signals at 2.45 and 2.52 ppm. Additional support for the formation of C–S bonds was the appearance of ¹H NMR signals at 1.3–1.6 ppm region. The preservation of the ester bonds was confirmed by the retention of the relative areas of ¹H NMR signals at 3.97 and 4.88 ppm (Fig. 2); and by the shape and position of the FTIR absorption peak at 1739 cm^{–1}. The appearance of C–S bonds was evident also from the ¹³C spectrum signals. ¹³C: δ 174 (s, C=O, ester) 173.6 (s, C=O, ester) 133.6 (d, –CH=), 132.5 (d, –CH=), 125 (d, –CH=), 124.4 (d, –CH=), 74 (d, CH–OOCR), 73.7 (d, CH–OOCR), 73.6 (d, CH–OOCR), 66.6 (t, CH₂–OOCR), 45.6 (d, CH–S–Bu), 42.7 (d), 39.9 (t), 38.8 (d, –CH₂–CH(Et)(C₄H₉), 36.1 (t), 34.8 (t, BuSCH₂–CH₂–), 34.4 (t), 32.0 (t), 31.9 (t), 31.7 (t), 30.43 (t), 32.0 (t, –CH₂–COOR), 31.9 (t), 31.8 (t), 31.7 (t), 31.3 (t), 30.4 (t), 30.1 (t), 30.0 (t, S–CH₂–), 29.9 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 28.9 (t), 27.3 (t), 26.8 (t), 26.7 (t), 25.3 (t), 25.2 (t), 25.1 (t), 25.0 (t), 23.8 (t), 23 (t), 22.7 (t), 22.5 (t), 22.1 (t), 14.1 (q, CH₃), 14.0 (q, CH₃), 13.7 (q, CH₃ in SBU), 11.0 (q, CH₃).

2.3 Oxidation Stability

Oxidation stability determinations were conducted on a rotating pressurized vessel oxidation test (RPVOT) apparatus manufactured by Koehler (Bohemia, NY) using the ASTM Method D 2272-98 [58]. Tests were conducted at 150 °C on oil samples that were weighed to 50.0 ± 0.5 g to which 5.0 mL of reagent water was added. The copper catalyst was measured to 3 m and sanded with 220 grit silicon carbide sand paper produced by Abrasive Leaders

Fig. 1 FTIR spectra of CasLaurEst and SM CasLaurEst. The peak at 3009 cm^{-1} in the CasLaurEst spectra is characteristic for double bonds, and disappears in the SM CasLaurEst spectra, indicating that most of the double bonds have reacted

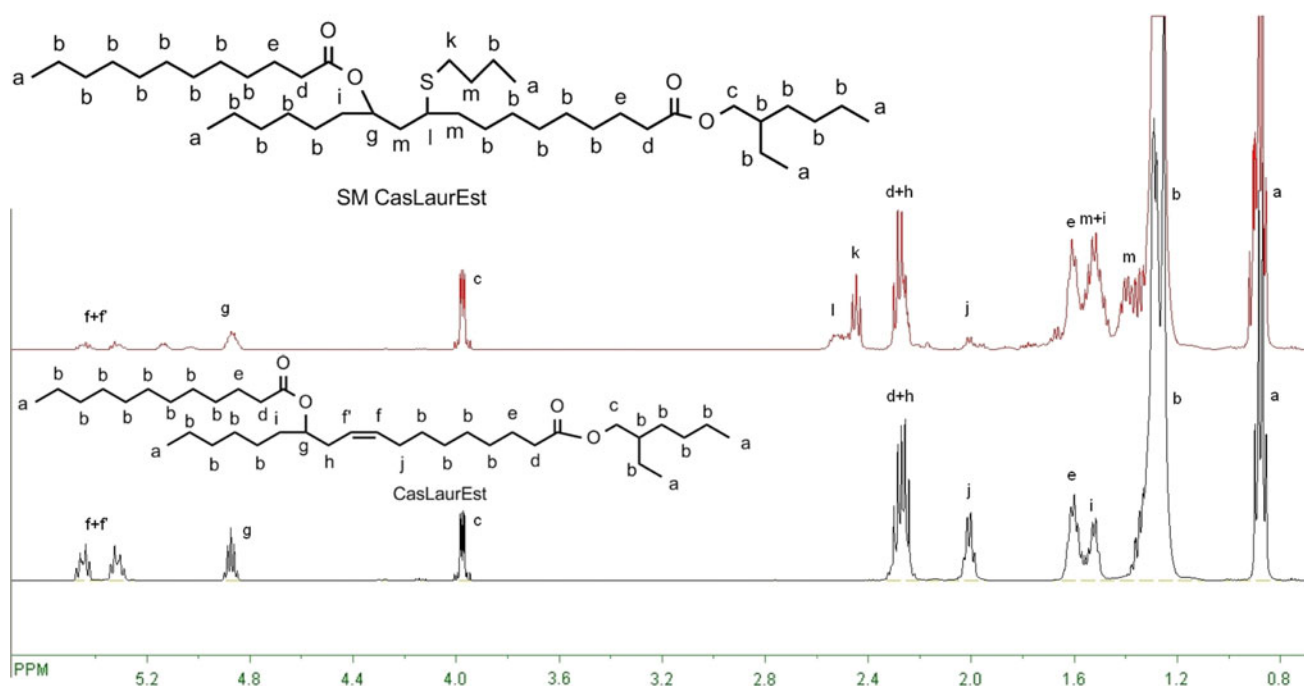
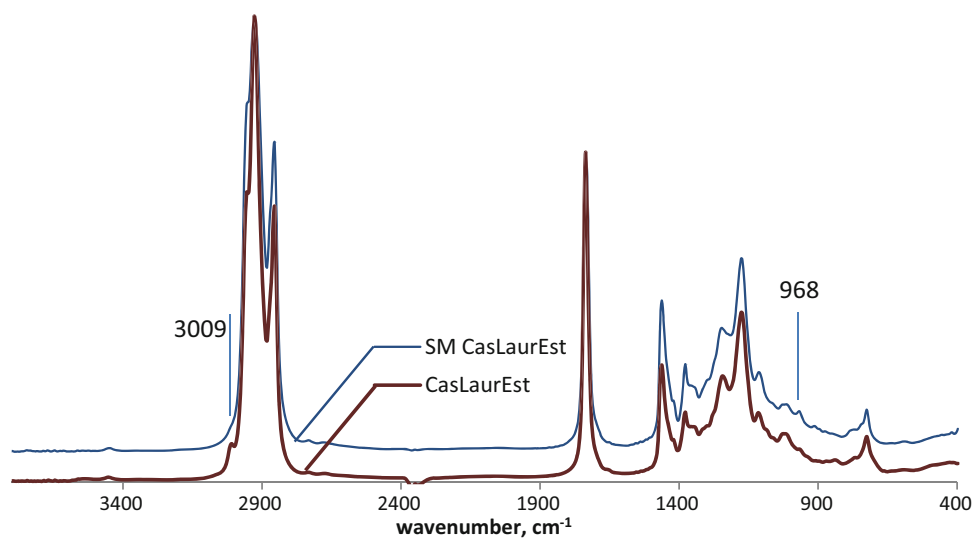


Fig. 2 ^1H NMR spectra of CasLaurEst and SM CasLaurEst

and Innovators (Fairborn, OH) and was used immediately. The wire was wound to have an outside diameter of 44–48 mm, a weight of $55.6 \pm 0.3\text{ g}$, and a height of 40–42 mm. The bomb was assembled and slowly purged with oxygen twice. The bomb was then charged with $90.0 \pm 0.5\text{ psi}$ (620 kPa) of oxygen and tested for leaks by immersing it in water. The bomb was then placed in the constant temperature bath, while its contents were continuously stirred and the pressure of the oxygen monitored.

The test was stopped when the pressure of oxygen dropped by more than 175 kPa from the initial maximum value.

2.4 Cold Flow Properties

Pour point (PP) was measured in duplicate runs to $\pm 3\text{ }^\circ\text{C}$ accuracy following ASTM Method D 97-96a [59], and average values are reported. A test jar with 50 mL of sample was placed into a cylinder submerged in a cooling

medium, whose temperature was chosen based on the expected PP of the material. Samples with PP in the range +9 to −6, −6 to −24, and −24 to −42 °C were placed in baths of −18, −33, and −51 °C, respectively. Sample temperature were measured in 3 °C increments at the top of the sample until the test material stopped flowing when held in a horizontal position for 5 s. PP is the coldest temperature at which the sample still poured.

Cloud point (CP) was measured in duplicate to an accuracy of ± 1 °C using the ASTM Method D 2500-99 [60], and average values are reported. A test jar with 50 mL of the test sample was placed into a cylinder submerged into a cooling medium. The temperature of the cooling medium was selected to be 0, −18, −33, or −51 °C for samples with expected CP range of room temperature to 10, 9 to −6, −6 to −24, or −24 to −42 °C, respectively. Sample temperatures were measured in 1 °C increments at the bottom of the sample until any cloudiness was observed at the bottom of the test jar. CP is the coldest temperature at which the sample remained opaque.

2.5 Four-Ball Tribometry

Tribometer used in 4-ball evaluations was model KTR-30L from Koehler Instrument Company, Inc. (Bohemia, New York). The balls used in 4-ball experiments were obtained from Falex Corporation (Sugar Grove, IL) and had the following specification: diameter 12.7 mm; chrome alloy steel (AISI No E52100), Grade 25 ± 0.00005 EP (Extra Polish); hardness of 64 to 66 Rockwell C. Before use, all test balls were degreased by consecutive 90 min ultrasonication in isopropyl alcohol and hexane solvents, and allowed to dry. The pot and spindle used for securing the ball were also thoroughly washed with isopropyl alcohol and hexane, wiped with Kimwipe® (Kimberly-Clark Worldwide, Inc., Roswell, GA) and allowed to dry.

Anti-wear (AW) tests were conducted according to ASTM D 4172-94 method under the following conditions [61]: load, 392 N; speed, 1200 rpm; lubricant temperature, 75°C; test duration, 60 min. Test conditions (load, speed, temperature) and frictional torque were automatically recorded as a function of time by the instrument computer during the test. The torque data was used to calculate the COF using the procedure outlined in ASTM D 5183 [62]. At the end of the test, the WSDs of the three balls in the ball pot were measured using a wear scar measurement system supplied by Koehler Instrument Company, Inc. (Bohemia, New York). The wear scar measurement system comprises a hardware (for taking digital image of the wear scar of the three balls without disassembling the ball pot) and software (ScarView, Koehler Instrument Company, Inc., Bohemia, New York) for measurement of the WSD from the analysis of the digital images. Each test lubricant

was used in at least two AW measurements and average COF and WSD values are reported.

Extreme pressure (EP) tests were conducted following ASTM D 2783-88 method [63], under the following conditions: speed, 1760 rpm; temperature, ambient; load, variable; test duration, 10 s. In the EP test, a series of tests are conducted with increasing load, starting at about 980 N, until welding is observed. New test balls and fresh lubricant are used in each test. The load at which welding occurs is the WP, and is a characteristic EP property of the lubricant. The load increments depend on the starting load and the expected WP. Finer load increments (~ 10 N) are used close to WP in order to precisely define the WP value of the test lubricant.

Data analysis was conducted using IgorPro Vesion 5.0.3.0 software (WaveMetrics, Inc., Lake Oswego, OR).

3 Results and Discussion

3.1 Synthesis and Products

Literature review shows that, in addition to the UV-initiated radical synthesis method used in this work, the thiol-ene reaction can be carried by thermo-radical initiators such as dilauroyl peroxide, AIBN or similar compounds [64–67]. We did not explore the thermo-radical synthesis method since it can introduce additional components in the product from the reaction of the initiator radicals with the double bond and from the decomposition products of the initiator. Such side product could complicate the interpretation of the data.

There was also a report that the thiol-ene synthesis can be carried out by a non-radical mechanism [68]. In this case, H₂S was added directly to double bonds by a nucleophilic addition mechanism using BF₃ as a catalyst. We have not explored the nucleophilic synthetic method either, since our lab is not equipped to handle H₂S gas.

We have not carried out cost estimates and cannot comment as to which of the three thiol-ene synthetic methods will be preferred for large volume synthesis.

The crude product mixture from reaction of butanethiol with the vegetable oils or estolides had strong sulfur odor. This was attributed to the presence of unreacted butanethiol as well as the side product butane disulfide. Distillation and/or gel chromatography purification of the crude reaction mixture gave an almost odorless product, with faint sulfur/rancid odor only if one put the bottle close to the nose. We believe that the rancid odor can be completely eliminated by bubbling nitrogen into the reaction mixture during synthesis to remove dissolved oxygen. Unfortunately, our reaction vessel and lab conditions were not

suitable for us to apply this procedure. The nitrogen purge is simple to carry out in a scaled up dedicated reactor.

The crude reaction mixture was darker than the starting oils. The products from the vegetable oils were red-brownish in color, and those from the estolide were less dark. The reaction mixture was distilled or further purified using flash chromatography. This allowed some degree of purification, but did not purify the reaction mixture to the color of the starting vegetable or estolide oils. We believe that a less dark product mixture can be obtained if the system was purged with nitrogen during the reaction. We think that it may be also possible to purify the SM estolide oils to the level of the starting materials using chromatography. However, doing so could be prohibitively expensive for large scale production.

3.2 Bulk Properties

Table 1 compares the viscosity and VI of unmodified and SM oils. Data for polyalphaolefin (PAO) of similar viscosity [69] as the unmodified vegetable oils are included for comparison. As shown in Table 1, sulfide modification has dramatically increased the viscosities at 40 and 100 °C for the vegetable oils. However, it resulted in very minor increase of the viscosity of the estolide at either temperature. Table 1 also shows that sulfide modification resulted in significant reduction of VI of vegetable oils and estolide. The reduction was particularly severe for the vegetable oils (by almost 30%) than for the estolide oil (by almost 20%). The data in Table 1 shows that, even after sulfide modification, the estolide and vegetable oils maintained higher VI than PAO.

The difference in the effect of sulfide modification on the viscosity and VI of seed oils versus estolide could be due to the difference in the degree of sulfidation between these two oils. The vegetable oils had higher degrees of unsaturation and, hence, higher degree of sulfidation than the estolide. As a result, the change in their molecular weight, and hence change in viscosity and VI, will be much

Table 1 Kinematic viscosity and viscosity index of unmodified (UM) and sulfide modified (SM) seed oils

Oil	Kinematic viscosity (cSt)				Viscosity index	
	40 °C		100 °C			
	UM	SM	UM	SM	UM	SM
PAO	31 ^a		5.9 ^a		138	
CasLaurEst	51.4	56	9.9	10.6	183	144
Corn oil	32.4	124	7.7	17.7	220	158
Canola oil	36.7	179.5	8.3	23	212	155

All data from this work unless otherwise indicated

^a Data from Ref. [69]

Table 2 Oxidation and cold flow properties of unmodified (UM) and sulfide modified (SM) seed oils

Oil	RPVOT ± sd (min)		Pour point (°C)		Cloud point (°C)	
	UM	SM	UM	SM	UM	SM
PAO	22.0 ± 0.0		<−54		<−45	
CasLaurEst	16.0 ± 0.5	224 ± 7	<−54	<−54	−36	−30
Corn oil	12.5 ± 0.7	100 ± 7	−12	−21	−1	0
Canola oil	14.5 ± 0.7	204	−21	−33	−7	<−33

All data from this work

larger than that in the estolide. Based on this mechanism, estolides with higher degrees of unsaturation are predicted to display larger changes in viscosity and VI after sulfide modification.

The oxidation stability and cold flow properties of unmodified and SM seed oils and estolide are compared in Table 2. Sulfide modification resulted in dramatic improvements in oxidation stability of both types of oils. The RPVOT times of the unmodified oils are in the same range as that of PAO (10–20 min). However, upon sulfidation, the RPVOT values increased by more than an order of magnitude. However, there were differences in the improvements of RPVOT times among the three oils, with canola and CasLaurEst estolide oils displaying the most, and corn oil the least improvements. This difference can be qualitatively correlated with the degrees of unsaturations of the unmodified oils which increase in the order: CasLaurEst < canola < corn. It is not clear how a lower degree of unsaturation of the unmodified oil results in enhanced oxidation stability of the SM oil.

The data in Table 2 shows that sulfide modification improved the PP of the seed oils but produced no change on the PP of the estolide. A reduction in PP of 9 and 18 °C for corn and canola oils, respectively, were observed after sulfide modification. Table 2 shows that sulfide modification had minor effect on CP of estolide or corn oil. However, the CP of canola oil displayed large improvement after sulfide modification. It is not clear why sulfide modification produced big change in the CP of canola but not in corn oil.

Sulfide modification eliminates unsaturation while introducing branching. In general, branching improves while unsaturation worsens cold flow properties. Based on this simplified mechanism, the net effect of sulfide modification on cold flow properties depends on which of these two factors dominate; and this will be different for different oils. For estolides, which have branches and relatively fewer unsaturations before sulfide modification, the fact that sulfide modification produced no change in PP and CP might be an indication that the effects of additional

Table 3 Effect of sulfide modified (SM) oil additive on oxidation and cold flow properties of corn and PAO oils

Oil	RPVOT \pm sd (min)	Pour point ($^{\circ}$ C)	Cloud point ($^{\circ}$ C)
Corn oil	12.5 \pm 0.7	–12	–1
2.0% (w/w) PS in corn oil	14.0 \pm 0.0	–12	–7
6.2% (w/w) SM corn oil in corn oil	13.0 \pm 0.0	–12	–5
6.3% (w/w) SM canola in corn oil	13	–12	–3
13.4% (w/w) SM CasLaurEst in corn oil	13	–12	–5
PAO	22.0 \pm 0.0	<–54	<–45
2.0% (w/w) PS in PAO6	183 \pm 23	<–54	<–45
6.2% (w/w) SM corn oil in PAO6	311 \pm 44	<–54	–33
6.3% (w/w) SM canola in PAO6	249	<–54	<–54
13.4% (w/w) SM CasLaurEst in PAO6	344	<–54	<–54

All data from this work

sd Standard deviation

branching and saturation have canceled out. For the SM seed oils, however, it appears that the effect of branching is dominant over unsaturation, especially for canola.

3.3 Additive Properties

The SM biobased oils along with reagent grade hexadecyl sulfide and a commercial EP polysulfide additive, were investigated for their additive properties in corn and PAO base oils. Each additive was dissolved to the required concentration and evaluated for the following properties: oxidation stability (RPVOT), PP, CP, AW COF and WSD, EP WP. The effect of these additives on oxidation stability, cold flow, and tribological properties will be discussed.

3.3.1 Effect of Additives on Oxidation Stability and Cold Flow Properties

The additives used in this investigation were the SM biobased oils (corn, canola, and CasLaurEst oils) and the commercial PS EP additive. Sufficient quantity of each of these additives was dissolved in corn and PAO oils so that the sulfur concentration of the blends investigated were identical at 0.6% (w/w).

Table 3 compares the effect of additives on RPVOT times, PP, and CP of corn and PAO oils. The data for corn oil indicates that these additives had no effect on the oxidation stability or PP of corn oil. However, there was a slight improvement in the CP of corn oil, a decrease of 4 to 6 $^{\circ}$ C.

The data for PAO shows that all of the additives resulted in significant improvements in the oxidative stability of PAO. The best improvement in oxidation stability was observed with the SM biobased additives, which increased the RPVOT time of PAO by more than one order of magnitude. The commercial organic sulfide also performed

well, increasing the RPVOT time eightfold relative to PAO without additive. Among the biobased additives, SM canola and CasLaurEst oils displayed superior RPVOT times over SM corn additive. Similar oxidation stability trend were observed for the neat biobased additives (Table 1), and the trend was found to correlate with the degree of unsaturation of the unmodified oils.

Table 3 shows that the presence of the organo-sulfide additives had no effect on the PP of PAO. Also, the commercial PS EP additive had no effect on the CP of PAO. On the other hand, the biobased SM additives displayed a mixed effect, slight increase or decrease of the CP of PAO. Thus, the CP of PAO increased by about 12 $^{\circ}$ C in the presence of SM corn oil additive. On the other hand, SM canola and CasLaurEst additives lowered the CP of PAO by about 9 $^{\circ}$ C. Neat PAO has a fairly good cold flow properties, and it appears that blending in these SM additives will have none (PP) or minor (CP) effect on its cold flow properties.

3.3.2 Effect of Additives on 4-Ball AW and EP Properties

The additives (and concentrations, % w/w) used in this investigation were: commercial PS EP additive (2.0%); SM corn oil (2.0 and 6.2%); SM estolide oil (13.4%); and reagent grade commercial hexadecyl mono-sulfide (3.8%). Investigations were conducted on neat canola, corn, and PAO oils as well as on blends of additives in corn and PAO oils.

The 4-ball AW and EP results are summarized in Tables 4 and 5. The AW results will be examined first. Examination of the AW data of the unmodified neat oils summarized in Table 4 shows COF increasing in the order corn oil < canola oil < PAO. The trend for the WSD of the neat oils is similar: corn \sim canola < PAO. This observation can be rationalized by considering the effect of the

Table 4 Coefficient of friction (COF) and wear scar diameter (WSD) from 4-ball anti-wear (ASTM D 4172), and weld point (WP) from 4-ball extreme pressure (ASTM D 2783) tests for unmodified oils

Oil	Anti-wear		Extreme pressure
	COF \pm sd	WSD \pm sd (mm)	WP (kgf)
PAO	0.079 \pm 0.020	0.75 \pm 0.08	120
Corn oil	0.054 \pm 0.003	0.69 \pm 0.01	140
Canola oil	0.065 \pm 0.004	0.66 \pm 0.02	140

All data from this work

sd Standard deviation

chemical structures of PAO and the biobased oils on AW COF and WSD. PAO and the seed oils have similar viscosities (Table 1) and, hence, similar hydrodynamic properties. On the other hand, only the seed oils have polar components (tri-esters) in their structure that allows them to adsorb on metal surfaces and provide boundary lubrication. The fact that the seed oils displayed lower COF and WSD than PAO implies boundary contribution by seed oils is occurring during the AW test. This also means that the AW test is occurring in the mixed film regime, where contributions from both boundary and hydrodynamic regimes are important.

Examination of the AW results of corn oil blends summarized in Table 5 indicates that, the organo-sulfur additives, with the exception of the PS additive, increased the COF and WSD of corn oil. The PS additive slightly decreased the WSD of corn oil. In addition, increasing the concentration of the sulfur modified corn oil from 2.0 to 6.2% in corn oil did not change the COF or WSD. Also,

there was no difference in the AW performance of corn oil with SM corn versus estolide additives of identical sulfur content.

Examination of the AW data of PAO blends in Table 5 shows that, within one standard deviation, the organo-sulfur additives caused no change in the COF of PAO. This was also true for the blends that have different concentrations of the SM corn oil. Similarly, no change in WSD was observed for PAO blends with SM biobased oil additives. SM corn and estolide additives of identical sulfur content displayed similar COF and WSD in PAO. On the other hand, PAO blends with the commercial mono- and poly-sulfides displayed significant increase of WSD.

Examination of the EP WP results of the blends (Table 5) shows that, with the exception of the PS additive, the organo-sulfur additives resulted in slight increase or no change in the WP of PAO and corn oil. The PS additive, however, resulted in a dramatic increase in the WP of corn and PAO oils, which is expected [70, 71]. A close examination of the EP results for the blends with PS additive indicates that the WP value for the corn oil blend was higher than that for the PAO blend. This is an indication of a better synergistic effect of the EP additive with corn than with PAO. Similar such enhancements of EP activity in biobased base stocks relative to that in petroleum based base stocks have been reported [71]. Table 5 also shows that, under identical sulfur content, SM estolide additive resulted in a higher WP than SM corn oil additive, in PAO as well as corn oil base oils. It is not clear why the SM estolide should perform better than SM corn oil under EP conditions.

Table 5 Effect of sulfide modified oil additives on 4-ball anti-wear (AW) (ASTM D 4172) coefficient of friction (COF) and wear scar diameter (WSD), and 4-ball extreme pressure (EP) (ASTM D 2783) weld point (WP) properties of corn and PAO oils

Oil	AW COF \pm sd	AW WSD \pm sd (mm)	EP WP (kgf)
Canola oil	0.065 \pm 0.004	0.66 \pm 0.02	140
Corn oil	0.054 \pm 0.003	0.69 \pm 0.01	140
2.0% (w/w) PS in corn oil	0.064 \pm 0.004	0.61 \pm 0.02	800
2.0% (w/w) SM corn oil in corn oil	0.064 \pm 0.005	0.90 \pm 0.02	140
6.2% (w/w) SM corn oil in corn oil	0.073 \pm 0.005	0.89 \pm 0.05	150
13.4% (w/w) SM CasLaurEst in corn oil	0.079 \pm 0.008	0.92 \pm 0.04	200
3.8% (w/w) hexadecyl sulfide in corn oil	0.073 \pm 0.007	0.96 \pm 0.04	120
PAO	0.079 \pm 0.020	0.75 \pm 0.08	120
2.0% (w/w) PS in PAO	0.077 \pm 0.020	0.95 \pm 0.02	740
2.0% (w/w) SM corn oil in PAO	0.089 \pm 0.010	0.72 \pm 0.05	130
6.2% (w/w) SM corn oil in PAO	0.082 \pm 0.009	0.61 \pm 0.10	140
13.4% (w/w) SM CasLaurEst in PAO	0.083 \pm 0.007	0.78 \pm 0.03	180
3.8% (w/w) hexadecyl sulfide in PAO	0.089 \pm 0.010	1.09 \pm 0.10	120

All data from this work

sd Standard deviation

3.4 Qualitative Structure–Property Analysis of the Effect of Chemical Modification

The major changes in bulk and additive properties as a result of sulfide modification of corn, canola, and Cas-LaurEst oils are: increased bulk viscosity; improved bulk oxidation stability; improved bulk PP; and improved antioxidant additive property in PAO. Each of these observations can be explained using qualitative structure–property correlations.

The observed increase in bulk viscosity is most likely due to an increase of molecular weight as a result of sulfide modification. Sulfide modification also increases the polarity of the molecule which will contribute to increased viscosity because of increased dipole-dipole intermolecular interactions. Another possible contributor to the increased viscosity could be increased entanglements between molecules caused by chain branching introduced as a result of the chemical modification.

The observed improvements in the oxidation stability of the bulk biobased oils after sulfide modification is consistent with the prevailing mechanism of reduction or total elimination of reactive hydrogen (allylic, bis-allylic) associated with the double bonds in the unmodified oils [23].

A possible reason for the improvements in bulk PP due to sulfide modification could be the introduction of branching (butyl sulfide) in the chains of the biobased oil molecules. As discussed by Jayadas and Nair [4], such change of structure will make it harder for the molecule to maintain the appropriate conformation that will allow it to crystallize, solidify, and depress its PP.

A possible explanation for the ability of SM oils to act as oxidation inhibitors in PAO but not in the unmodified corn oil (Table 3) could be due to the relative reactivity of antioxidant additives versus base fluids in a blend towards oxidation. Oxidation at initial stages occurs due to reaction of peroxy radicals with the most reactive species [35]. Antioxidants are highly reactive and their presence leads to fewer peroxy radicals available to react with base oils and cause oxidation [72]. Sulfur-containing antioxidant act by decomposing the hydroperoxides to non-radical products and decrease the generation of new radicals. The result is a decrease in the amount of hydroperoxides reacting with the C–H bond to generate new radicals. This can explain why PAO rather than corn oil would benefit more from the presence of an antioxidant. Corn oil has a number of reactive allylic and bis-allylic protons that will effectively compete against the antioxidant for the hydroperoxy radical. The next question is why do the SM biobased oils and the commercial PS additive act as antioxidants in PAO? Based on the above discussion, these materials must have more reactive species than the carbon-hydrogen bond in

PAO. The commercial PS additives comprise weak S–S [35], that are much more reactive than the C–H bonds in PAO [35], which can explain its antioxidant behavior in PAO. Similarly, the SM biobased oils comprise C–S bonds, which are weaker and, hence more reactive [35] towards hydroperoxides than the C–H bonds in PAO. Examination of the data in Table 3 shows that the SM biobased oils were more effective antioxidant additives than the commercial PS. One possible explanation is that, in addition to the C–S bond, there may be other reactive species in the SM biobased oils. It is possible that the SM biobased oils contain few unreacted double bonds and, hence, reactive allylic and bis-allylic protons. While reactive allylic and bis-allylic protons in unmodified vegetable oils do not act as antioxidants, they might, however, enhance the antioxidant properties of SM vegetable oils. However, there are no data to support or disprove such mechanism of antioxidation for SM vegetable oils. The effectiveness of an antioxidant is a function of both reactivity and concentration of the reactive species. It is clear that the reactivity toward hydroperoxides and concentration of the S–S, C–S, in these additives were no match to the high reactivity and concentrations of allylic and bis-allylic protons in unmodified corn oil.

3.5 Empirical Correlation of RPVOT with Bond Dissociation Energy of Reactive Protons

Seed oils comprise fatty acid residues with single and multiple bonds that give rise to reactive allylic and bis-allylic hydrogens. Chemical modification of seed oils such as the sulfide modification reaction used in this work, convert allylic and bis-allylic hydrogens into the relatively unreactive alkyl hydrogens. Such a phenomenon is depicted in Fig. 3.

The effect of such chemical transformation on oxidation reactivity (r) of oils can be expressed as follows:

$$r = f(z) \quad (1)$$

where z is expressed in concentration units (% w/w, etc.) and defined as follows:

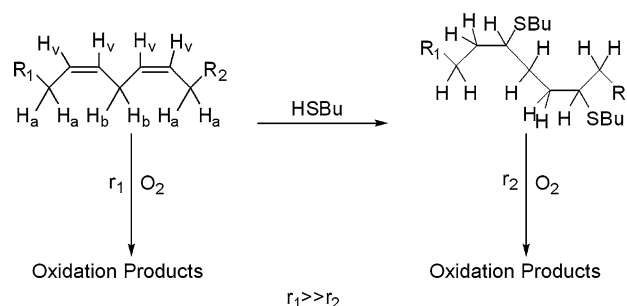


Fig. 3 Schematics showing the effect of sulfide modification on number of allylic and bis-allylic protons and oxidation rate

$$z = \sum_i [H_i] [(104 - D_i)/104]^x \quad (2)$$

$[H_i]$ in Eq. 2 is the concentration of allylic or bis-allylic protons, and is obtained from published fatty acid composition data of seed oils [73] as follows:

$$[H_i] = \sum_{i,j} w_i n_j \quad (3)$$

where w_i is the weight % of fatty acid i in the seed oil; n_j is the number of allylic or bis-allylic protons in fatty acid i .

D_i in Eq. 2 is the bond dissociation energy (BDE) of C–H bond for allylic or bis-allylic protons in kcal/mol. The value 104 corresponds to the BDE of alkyl C–H bond in kcal/mol [74].

The value of x in Eq. 2 is selected so that the reactivity of bis-allylic protons relative to allylic proton is in the range reported in the literature. This value, according to Schneider [23], is 12, which requires a value for x of between 3 and 4.

According to Eqs. 1, 2, the larger the concentration of the reactive protons and the smaller its BDE, the higher the reactivity of the unmodified oil relative to the chemically modified oil. Higher reactivity should correspond to shorter RPVOT time. Thus, the change in RPVOT time between the chemically unmodified and modified oils should be related as follows:

$$z^{-1} = |\text{RPVOT}_u - \text{RPVOT}_m| = \Delta \text{RPVOT} \text{ (min)} \quad (4)$$

where subscripts u and m denote RPVOT values for unmodified and modified oils.

The following procedure was used for calculating z^{-1} for canola and corn oils, which were used in chemical modifications in this work:

- The number of allylic and bis-allylic protons for each fatty acid in canola and corn oils were calculated. This data is shown in Table 6.
- Equation 3 was used to calculate the concentration of allylic $[H_a]$, and bis-allylic $[H_b]$ in each oil using the data in Table 6.
- Equation 2 was used to calculate z and $100 \cdot z^{-1}$ using the results from (a) and (b) above, $x = 4$, and

published BDE values for C–H of allylic and bis-allylic protons [74].

Table 7 shows the BDE and other values used in the calculation in steps (c) above as well as the results of the calculation. Also shown in Table 7 is the $\Delta(\text{RPVOT})$ data calculated from experimental results of this work. The result in Table 7 indicates that the BDE based empirical equation can predict the trend of measured RPVOT values. The result also indicates that oils with the most reactive protons will display the most improvements in RPVOT time after chemical modifications.

In order to test if Eqs. 2–4 can be applied to chemical modifications of vegetable oils other than the sulfide modification of this work, we conducted literature search that provide the following: (a) correct accounting of the concentrations of allylic and bis-allylic protons in the vegetable oils before chemical modification, (b) chemical modification that completely eliminate all double bonds and with it all allylic and bis-allylic protons, and (c) RPVOT data of the vegetable oil before and after chemical modification.

Literature search produced three cases [75–77], where similar vegetable oils were investigated using RPVOT, before and after their double bonds were completely reacted, thereby eliminating all allylic and bis-allylic protons. These were: the work by Costello et al. [75], where soybean oil was converted into ESO; work by Wu et al. [76], where rapeseed oil was converted into epoxidized rapeseed oil; and the work by Holderich et al. [77], where rapeseed oil was converted into hydroxymethoxy glyceroltristearate. The structural and RPVOT data from the unreacted and reacted oils were analyzed using Eqs. 2–4, and the resulting $\Delta(\text{RPVOT})$ vs. $100 \cdot z^{-1}$ are compared with the results from this work in Fig. 4. The data in Fig. 4 shows that the results obtained from the analysis of literature values display similar profiles as those from this work. The major difference is in the slope of the line, which was steeper for the data from this work. This difference can be explained in terms of the difference in the contribution of functional groups other than allylic and bis-allylic protons, to oxidation stability or instability of the oils. The higher slope of the butanethiol curve can be

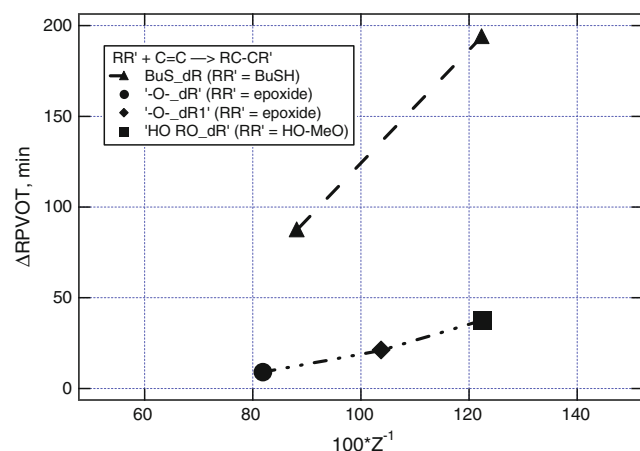
Table 6 Fatty acid composition and number of allylic and bis-allylic protons in fatty acids of canola and corn oils

FA, Chain length	14	16	18	20	22	24	16	18	20	22	18	18
FA, Double bonds	0	0	0	0	0	0	1	1	1	1	2	3
FA, % w/w in canola	0.1	4.1	1.8	0.7	0.3	0.2	0.3	60.9	1	0.7	21	8.8
FA, % w/w in corn oil	0.1	10.4	2	0.1	0.1	0.2	0.1	26.3	0.3		59	0.3
FA, # Allylic-H							4	4	4	4	4	4
FA, # Bis-allylic-H											2	4

Fatty acid composition data from Ref. [73]

Table 7 Comparison of estimated reactivity based on bond dissociation energy (BDE) with change in RPVOT time^a

Oil	[H _a] ^b	[H _b] ^b	BDE ^c (kcal/mol)		z^d	$100 \cdot z^{-1}$	$\Delta(\text{RPVOT})^e$ (min)
			C–H _a	C–H _b			
Corn	344	119.2	88	73	1.134	88.21	87.5
Canola	370.8	77.2	88	73	0.817	122.37	194

^a Subscripts a, b denote allylic, bis-allylic, respectively^b Calculated using Eq. 3 and data in Table 6^c Bond dissociation energy data from Ref. [74]^d Calculated using Eq. 2^e Calculated from experimental results of this work (Table 2)**Fig. 4** Change in oxidation stability (ΔRPVOT) vs. $100 \cdot z^{-1}$ for vegetable oils due to reactions of double bonds: *Triangle* sulfide modification (this work), *circle* epoxidation (Ref. [75]), *diamond* epoxidation (Ref. [76]), *square* hydroxymethoxylation (Ref. [77])

attributed to the antioxidation characteristics of sulfur containing groups, which is a fairly well-known phenomenon [35, 78].

4 Summary/Conclusion

Development of lubricants from farm-based oils requires major scientific breakthrough to overcome a number of serious and inherent weaknesses such as: inadequate oxidation stability; unacceptably high PP and CP; poor hydrolytic stability; and low biostability. Various approaches are being applied to counter these inherent weaknesses including modification of their structure using chemical, thermal, genetic, and/or enzymatic methods. Such modifications eliminate existing structures and/or create new structures resulting in improved properties.

In the work described here, corn, canola, and castor-lauric estolide oils were chemically modified by direct

reaction of butanethiol with the double bonds on the hydrocarbon chains. The effects of chemical modifications on the following properties were investigated: viscosity, VI, PP, CP, and oxidation stability (RPVOT).

Sulfide modification of estolide and seed oils produced similar changes in the following properties relative to the unmodified oils:

- Reduced VI, and
- Increased oxidation stability, as demonstrated by more than one order of magnitude increase in RPVOT time, which was attributed to elimination of reactive allylic and bis-allylic protons, and presence of sulfide bonds.

Sulfide modification of estolide and seed oils produced different changes in the following properties relative to the unmodified oils:

- Viscosity—SM estolide displayed slight or no change whereas SM seed oils displayed large increase of viscosity. This difference was attributed to a larger increase in molecular weight of SM seed oils, which experience a greater degree of sulfidation than the SM estolide.
- Cold flow properties—SM estolide displayed no change whereas SM seed oils displayed improvements as demonstrated by a 9 to 18 °C reduction in PP. This difference was attributed to a stronger branching effect in SM seed oils than in SM estolide.

The SM oils, along with commercial mono- and PS additives were also investigated as additives in corn and PAO base fluids at 0.6% (w/w) sulfur content. The effect of these additives on PP, CP, 4-ball AW, and 4-ball EP properties were minor. Oxidation stability results showed that these additives had no effect on corn oil but were very effective in PAO oil, displaying 8 to 16-fold increase of RPVOT time.

In the 4-ball EP test, the commercial PS EP additive performed better in corn than in PAO base fluid, which was attributed to better compatibility of EP additives with the polar biobased fluid than the non-polar petroleum-based fluids, as was reported in the literature.

The difference in the effect of the additives on the oxidation stability of PAO versus corn oil was attributed to the difference in the reactive hydrogen contents in the two base fluids relative to those in the additives.

An empirical equation for predicting change in RPVOT time with the change in BDE of reactive protons before and after chemical modification is proposed. The equation was capable of correlating data from this work and literature.

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References

- Bremmer, B.J., Plonsker, L.: Bio-based lubricants: a market opportunity study update. Omni-Tech International (Prepared for the United Soybean Board, November 2008)
- McCoy, S.: The development of an engine lubricant containing soybean oil. M. Sc. Thesis. University of Kentucky, College of Engineering (2007)
- Fox, N.J., Stachowiak, G.W.: Vegetable oil-based lubricants—a review of oxidation. *Tribol Int* **40**, 1035–1046 (2007)
- Jayadas, N.H., Nair, K.P.: Coconut oil as base oil for industrial lubricants—evaluation and modification of thermal oxidative and low temperature properties. *Tribol Int* **39**, 873–878 (2006)
- Lockwood, F.E., Dotson, O.J., Smith, D.B.: Formulating and testing of engine oils with bio-content. In: AOCs-STLE Conference on Bio-based Technologies, Cincinnati, OH, 13–18 Oct 2008
- Cermak, S., Isbell, T.: Estolides—the next biobased functional fluids. *Inform* **15**(8), 515–517 (2004)
- Schneider, M.P.: Government-Industry Forum on Non-Food Uses of Crops (GIFNFC 7/7). Case Study: Plant Oil based Lubricants in Total Loss & Potential Loss Applications. Final Report. University of York, pp. 1–54 (2002)
- Knowlton, S.: DuPont technology status report: high oleic soybean oil. In: Proceedings of United Soybean Board Technical Advisory Panel: Lubricants and Fluids, 24 and 25 Oct 2007 [CDROM]
- Biresaw, G., Adhvaryu, A., Erhan, S.Z., Carriere, C.J.: Friction and adsorption properties of normal and high-oleic soybean oils. *J. Am. Oil Chem. Soc.* **79**(1), 53–58 (2008)
- Hiemenz, P.C.: Principles of Colloid and Surface Chemistry, 2nd edn. Marcel Dekker, New York (1986)
- Bockish, M.: Fats and Oils Handbook. AOCS Press, Champaign, IL (1998)
- O'Brien, R.D.: Fats and Oils. Technomic, Lancaster, PA (1998)
- Fox, N.J., Simpson, A.K., Stachowiak, G.W., Polishuk, A.T.: Oxidation stability of vegetable oil formulations. *NLGI Spokesman* **65**(8), 32–33 (2001)
- Miles, P.: Synthetics versus vegetable oils: applications options and performance. *J. Synth. Lubr.* **15**, 43–52 (1998)
- Becker, R., Knorr, A.: An evaluation of antioxidants for vegetable oils at elevated temperatures. *Lubr. Sci.* **8**(2), 95–117 (1996)
- Adhvaryu, A., Erhan, S.Z., Liu, Z.S., Perez, J.M.: Oxidation kinetics of oils derived from unmodified and genetically modified vegetables using PDSC and NMR spectroscopy. *Thermochim. Acta* **364**(1–2), 87–97 (2000)
- Billenstein, S., Blaschke, G.: Industrial production of fatty amines and their derivatives. *J. Am. Oil Chem. Soc.* **61**(2), 353–356 (1984)
- Isbell, T.A., Kleiman, R., Plattner, B.A.: Acid-catalyzed condensation of oleic acid into estolides and polyestolides. *J. Am. Oil Chem. Soc.* **71**, 169–174 (1994)
- Dahlke, B., Hellbardi, S., Paetow, M., Zech, W.H.: Polyhydroxy fatty acids and their derivatives from plant oils. *J. Am. Oil Chem. Soc.* **72**(3), 349–353 (1995)
- Dunn, R.O., Knothe, G., Bagby, M.O.: Recent advances in the development of alternative diesel fuels from vegetable oils and animal fats. *Recent Res. Dev. Oil Chem.* **1**, 31–56 (1997)
- Biermann, U., Friedt, W., Lang, S., Lürs, W., Machmüller, G., Metzger, J.O., Rüschen, K.M.R., Schäfer, H.J., Schneider, M.P.: New syntheses with oils and fats as renewable feedstock for the chemical industry. *Angew. Chem. Int. Ed.* **39**, 2206–2224 (2000)
- Erhan, S.Z., Adhvaryu, A., Sharma, B.K.: Chemically functionalized vegetable oils. In: Rudnick, L.R. (ed.) *Synthetics, Mineral Oils, and Biobased Lubricants*, pp. 361–387. CRC Press, Boca Raton, FL (2006)
- Schneider, M.P.: Plant-oil-based lubricants and hydraulic fluids. *J. Sci. Food Agric.* **86**, 1769–1780 (2006)
- Graiver, D., Narayan, R.: Value-added chemicals from catalytic ozonation of vegetable oils. *Lipid Technol.* **18**(2), 31–35 (2006)
- Meier, M.A.R., Metzger, J.O., Schubert, U.S.: Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* **36**, 1788–1802 (2007)
- Biswas, A., Sharma, B.K., Willet, J.L., Erhan, S.Z., Cheng, H.N.: Soybean oil as a renewable feedstock for nitrogen-containing derivatives. *Energy Environ. Sci.* **1**(6), 639–644 (2008)
- Cermak, S.C., Brandon, K.B., Isbell, T.A.: Synthesis and physical properties of estolides from lesquerella and castor fatty acid esters. *Ind. Crops Prod.* **23**, 54–64 (2006)
- Adachi, S., Ishiguro, T., Matsuno, R.: Autoxidation kinetics for fatty acids and their esters. *J. Am. Oil Chem. Soc.* **72**(5), 547–551 (1995)
- Ishido, E., Minemoto, Y., Adachi, S., Matsuno, R.: Oxidation of linoleic acid and methyl linoleate mixed with saturated fatty acid or its methyl ester. *Lebensm.-Wiss. u. Technol.* **34**, 234–238 (2001)
- Minemoto, Y., Adachi, S., Shimada, Y., Nagao, T., Iwata, T., Yamauchi-Sato, Y., Yamamoto, T., Kometani, T., Matsuno, R.: Oxidation kinetics for cis-9 trans-11 and trans-10 cis-12 isomers of CLA. *J. Am. Oil Chem. Soc.* **80**(7), 675–678 (2003)
- Minemoto, Y., Kometani, T., Piao, J., Adachi, S.: Oxidation of oleoyl residue of its esters with ethylene glycol glycerol and erythritol. *LWT Food Sci. Technol.* **39**(1), 1–5 (2006)
- Sakuramoto, Y., Shima, M., Adachi, S.: Autoxidation of mono-di- and trilinoleoyl glycerols at different concentrations. *Biosci. Biotechnol. Biochem.* **71**(3), 803–806 (2007)
- Koh, C.S., Butt, J.B.: Experimental and modeling study of kinetics and selectivity in the oxidation of a poly(α -olefin) lubricant. *Ind. Eng. Chem. Res.* **34**, 524–535 (1995)
- Kowalski, B.: Determination of oxidative stability of edible vegetable oils by pressure differential scanning calorimetry. *Thermochim. Acta* **156**(2), 347–358 (1989)
- Bala, V., Hartley, R.J., Hughes, L.J.: The influence of chemical structure on the oxidative stability of organic sulfides. *Lubr. Eng.* **52**(12), 868–873 (1996)
- Adhvaryu, A., Sharma, B.K., Hwang, H.S., Erhan, S.Z., Perez, J.M.: Development of bio-based synthetic fluids: application of molecular modeling to structure-physical property relationship. *Ind. Eng. Chem. Res.* **45**, 928–933 (2006)
- Isbell, T.A., Abbott, T.P., Carlson, K.D.: Oxidative stability index of vegetable oils in binary mixtures with meadowfoam oil. *Ind. Crop Prod.* **9**(2), 115–123 (1999)
- Knothe, G., Dunn, R.O.: Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *J. Am. Oil Chem. Soc.* **80**(10), 1021–1026 (2003)
- Knothe, G.: Structure indices in FA chemistry. How relevant is the iodine value? *J. Am. Oil Chem. Soc.* **79**(9), 847–854 (2002)
- Moser, B.R., Sharma, B.K., Doll, K.M., Erhan, S.Z.: Diesters from oleic acid: synthesis, low temperature properties and oxidation stability. *J. Am. Oil Chem. Soc.* **84**, 675–680 (2007)
- Chen, C.J., Bozzelli, J.W.: Kinetic analysis for HO₂ addition to ethylene propene and isobutene and thermochemical parameters of alkyl hydroperoxides and hydroperoxide alkyl radicals. *J. Phys. Chem. A* **104**, 4997–5012 (2000)
- Gschwender, L.: Computational chemistry of soluble additives for perfluoropolyalkylether liquid lubricants. *Tribol. Trans.* **39**(2), 368–373 (1996)

43. Pfaendtner, J., Broadbelt, L.J.: Mechanistic modeling of lubricant degradation. 1. Structure-reactivity relationships for free-radical oxidation. *Ind. Eng. Chem. Res.* **47**(9), 2886–2896 (2008)
44. Pfaendtner, J., Broadbelt, L.J.: Mechanistic modeling of lubricant degradation. 2. The autoxidation of decane and octane. *Ind. Eng. Chem. Res.* **47**(9), 2897–2904 (2008)
45. Przybylski, R., Zambiasi, R.C.: Predicting oxidative stability of vegetable oils using neural network system and endogenous oil components. *J. Am. Oil Chem. Soc.* **77**(9), 925–931 (2000)
46. Siniawski, M.T., Sanial, N., Pfaendtner, J.: Tribological degradation of two vegetable-based lubricants at elevated temperature. *J. Synth. Lubr.* **24**, 167–179 (2007)
47. Zabarnick, S., Phelps, D.K.: Density functional theory calculations of the energetics and kinetics of jet fuel autoxidation reactions. *Energy Fuels* **20**, 488–497 (2006)
48. Buffa, F., Borrajo, J.: Miscibility of styrene/unsaturated polyester quasibinary systems: unsaturated polyester chemical composition and molecular weight influence. *J. Appl. Polym. Sci.* **102**(6), 6064–6073 (2006)
49. Garas, G., Kosmas, M.: Effect of chain architecture on the cloud point curves of binary blends of star polymers. *Macromolecules* **27**(22), 6671–6672 (1994)
50. Kim, J.K., Lee, H.H., Son, W.H., Han, D.C.: Phase behavior and rheology of polystyrene/poly(alpha-methylstyrene) and polystyrene/poly(vinyl methyl ether) blend systems. *Macromolecules* **31**(24), 8566–8578 (1998)
51. Maier, T.R., Jamieson, A.M., Simha, R.: Phase equilibria in SBR/polybutadiene elastomer blends: application of Flory-Huggins theory. *J. Appl. Polym. Sci.* **51**(6), 1053–1062 (1994)
52. Riccardi, C.C., Borrajo, J., Meynie, L., Fenouillot, F., Pascault, J.P.: Thermodynamic analysis of the phase separation during the polymerization of a thermoset system into a thermoplastic matrix. Part I. Effect of the composition on the cloud-point curves. *J. Polym. Sci. B: Polym. Phys.* **42**(8), 1351–1360 (2004)
53. Russell, T.P., Fetters, L.J., Clark, J.C., Bauer, B.J., Han, C.C.: Concentration fluctuations in mixtures of linear and star-shaped polymers. *Macromolecules* **23**(2), 654–659 (1990)
54. Govindapillai, A., Jayadas, N.H., Bhasi, M.: Analysis of the pour point of coconut oil as a lubricant base stock using differential scanning calorimetry. *Lubr. Sci.* **21**, 13–26 (2009)
55. Letoffe, J.M., Claudy, P., Vassilakis, D., Damin, B.: Antagonism between cloud point and cold filter plugging point depressants in a diesel fuel. *Fuel* **74**(12), 1830–1833 (1995)
56. Nassar, A.M., Ahmed, N.S.: The behavior of α -olefins butyl acrylate copolymers as viscosity index improvers and pour point depressants for lube oil. *Int. J. Polym. Mater.* **55**(11), 947–955 (2006)
57. Bantchev, G., Kenar, J., Biresaw, G., Han, M.: Free radical addition of butanethiol to vegetable oil double bonds. *J. Agric. Food Chem.* **57**(4), 1282–1290 (2009)
58. Anon.: Standard test method for oxidative stability of steam turbine oils by rotating pressure vessel. ASTM D 2272-98, vol. 05.01, pp. 780–791 (2002)
59. Anon.: Standard test method for pour point of petroleum products. ASTM D 97-96a, vol. 05.01, pp. 85–92 (2002)
60. Anon.: Standard test method for cloud point of petroleum products ASTM D 2500-99, vol. 05.01, pp. 861–866 (2002)
61. Anon.: Standard test method for wear preventive characteristics of lubricating fluid (Four-Ball Method) ASTM D 4172-94, vol. 05.02, pp. 752–756 (2002)
62. Anon.: Standard test method for determination of the coefficient of friction of lubricants using the four-ball wear test machine ASTM D 5183-95, vol. 05.03, pp. 165–169 (2002)
63. Anon.: Standard test method for measurement of extreme-pressure properties of lubricating fluids (Four-Ball Method) ASTM D 2783-88, vol. 05.02, pp. 130–137 (2002)
64. Campos, L.M., Killops, K.L., Sakai, R., Paulusse, J.M.J., Dameron, D., Drockenmuller, E., Messmore, B.W., Hawker, C.J.: Development of thermal and photochemical strategies for thiol-ene click polymer functionalization. *Macromolecules* **41**(19), 7063–7070 (2008)
65. Boyer, C., Granville, A., Davis, T.P., Bulmus, V.: Modification of RAFT-polymers via thiol-ene reactions: A general route to functional polymers and new architectures. *J. Polym. Sci. A: Polym. Chem.* **47**(15), 3773–3794 (2009)
66. Gadd, P.G., Giles, H.M., Heywood, F.W., McKenna, E.G.: Lubricating oil compositions. EU Patent 0712867 (1996)
67. Spruell, J.M., Levy, B.A., Sutherland, A., Dichtel, W.R., Cheng, J.Y., Stoddart, J.F., Nelson, A.: Facile postpolymerization end-modification of RAFT polymers. *J. Polym. Sci. A: Polym. Chem.* **47**(2), 346–356 (2009)
68. Schwab, A.W., Gast, L.E., Rohwedder, W.K.: Nucleophilic addition of hydrogen sulfide to methyl oleate, methyl linoleate, and soybean oil. *J. Am. Oil Chem. Soc.* **52**(7), 236–239 (1975)
69. Biresaw, G., Bantchev, G.: Effect of chemical structure on film-forming properties of seed oils. *J. Synth. Lubr.* **25**, 159–183 (2008)
70. Schey, J.A.: Tribology in Metalworking Friction, Lubrication and Wear. American Society of Metals, Metals Park, OH (1983)
71. Asadauskas, S.J., Biresaw, G., McClure, T.G.: Effects of chlorinated paraffin and ZDDP concentrations on boundary lubrication properties of mineral and soybean oils. *Tribol. Lett.* **37**(2), 111–121 (2010)
72. Tudos, F., Fodor, Z., Iring, M.: Kinetics and mechanism of inhibited autoxidation. In: Pospisil, J., Klemchuk, P.P. (eds.) *Oxidation Inhibition in Organic Materials*, pp. 219–247. CRC Press, Boca Raton, FL (1990)
73. Lawate, S.: Environmentally-friendly hydraulic fluids. In: Erhan, S.Z., Perez, J.M. (eds.) *Bio-based Industrial Fluids and Lubricants*, pp. 35–45. AOCS Press, Champaign, IL (2002)
74. Weast, R.C. (ed.): *Handbook of Chemistry and Physics*, vol. 53. CRC Press, Cleveland, OH (1972)
75. Costello, M.T., Riff, I., Seibert, R.F.: Method for improving the oxidative stability of industrial fluids. World Intellectual Property Organization. WO 2006/094138. International Publication Date: 8 September 2006
76. Wu, X., Zhang, X., Yang, S., Chen, H., Wang, D.: The study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *J. Am. Oil Chem. Soc.* **77**(5), 561–563 (2000)
77. Holderich, W.F., Rios, L.A., Weckes, P.P., Schuster, H.: Investigations into the epoxidation and alcoholysis of oleochemicals for use as lubricants. *J. Synth. Lubr.* **20**, 289–301 (2004)
78. Qiu, C., Han, S., Cheng, X., Ren, T.: Determining the antioxidant activities of organic sulfides by rotary bomb oxidation test and pressurized differential scanning calorimetry. *Thermochim. Acta* **447**, 36–40 (2006)

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