Friction and wear behavior of thioether hydroxy vegetable oil

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This work describes the tribochemical evaluation of vegetable oil based antiwear additive obtained through chemical modification. The Sulfur was incorporated using a chemical reaction of epoxidized vegetable oil and common thiols, resulting in formation of a hydroxy thioether derivative of vegetable oils. The synthesis retains the vegetable oil structure, eliminates poly-unsaturation in the molecule, and adds polar functional groups that significantly improve adsorption on metal surfaces. These additives are obtained by chemical modification of oils originated from natural resources. The tribochemical behavior of sulfur incorporated vegetable oil was studied by measuring friction coefficient using ball-on-disk configuration and wear scar diameter using four-ball configuration. Comparative tests with commercial antiwear additives demonstrate the effectiveness of these derivatives. The derivatives were found useful as agriculturally based antiwear additives for lubricant applications.

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1. Introduction

Antiwear/antifriction lubricants typically comprise a base oil that has been blended with any number of additives that enhance the ability of the base oil to withstand the mechanical stresses of interacting working surfaces under boundary lubrication conditions. Most of the lubricants and many of the additives currently in daily use originate from petroleum base stocks that are toxic to environment, making it increasingly difficult for safe and easy disposal. There has been an increasing demand for “green” lubricants [1] and lubricant additives in recent years due to concerns about loss of mineral oil-based lubricants to the environment and increasingly strict government regulations controlling their use. A renewable resource, vegetable oil is good alternative to mineral oil because of its environmentally friendly, non toxic and readily biodegradable nature [2,3]. The triacylglycerol structure of vegetable oil is amphiphilic in character that makes it an excellent candidate as lubricants and functional fluids [4,5]. It makes them very attractive for industrial applications that have potential for environmental contact through accidental leakage, dripping or generates large quantities of after-use waste materials requiring costly disposal [6,7]. In addition double bonds present in triacylglycerol structure offer sites for additional functionalization, for further improving technical properties such as thermo-oxidative, low temperature stability and lubricity. Vegetable oil in its natural form has limited use as industrial fluids due to poor thermo-oxidation stability [8,9], low temperature behavior [10,11], and other tribochemical degrading processes [12,13] that occur under severe conditions of temperature, pressure, shear stress, metal surface and environment. To meet the increasing demands for stability during various tribochemical processes, the oil structure has to withstand extremes of temperature variations, shear degradation and maintain excellent boundary lubricating properties through strong physical and chemical adsorption with the metal. Triacylglycerol molecules orient themselves with the polar end at the solid surface making a close packed monomolecular [14] or multimolecular layer [15] resulting in a surface film believed to inhibit metal-to-metal contact and progression of pits and asperities on the metal surface. Strength of the fluid film and extent of adsorption on the metal surface dictate the efficiency of lubricants performance and it has also been observed that friction coefficient and wear rate are dependent on the adsorption energy of the lubricant [16].

The antiwear properties of commercial additives are derived from a variety of elements capable of reacting with the metal surface and establish a stable protective film. Phosphorus, sulfur, nitrogen and zinc constitute the active element in most mineral oil based
commercial antiwear additives. However due to environmental and toxicological considerations, phosphorus may phase out with time due to catalyst deactivation fitted in auto gas exhaust [17]. Biodegradable additives are indispensable for environmentally friendly lubricants. According to German ‘Blue Angel’ criteria, environmentally friendly lubricants must not contain carcinogens/mutagens, chlorine, nitrates, or metal (except potassium and calcium). Such lubricants can only contain up to 7% of potential biodegradable additives (biodegradability not less than 20% by OECD 302B method), and 2% low toxicity and non-biodegradable additives [18].

Organic sulfur compounds have been used widely in lubricating compositions for their extreme-pressure (EP) as well as their antiwear/antifriction properties [19–23]. Extensive work has been done and is reflected by the volume of literature published in characterizing and relating the structure of the organic sulfur compounds to their EP and antiwear performance [19–22]. Reports are also available where a reaction layer is formed on the metal surface containing FeS and FeS2 [24]. Elrod et al. described formulation of aqueous drilling fluid [25] consisting of essentially the reaction product of a fatty vegetable oil with 4,4'-thiodiphenol. Baldwin et al. [26] disclosed a metal working lubricant comprising a mineral or synthetic oil, and optionally a vegetable oil, and a sulfur-containing carboxylic acid (R-S-RCO2H) such as n-dodecythioacetic acid and n-butylthioacetic acid. The attempts to sulfurize vegetable oils as replacements for sulfurized sperm whale oil have resulted in products that displayed a high level of intermolecular crosslinking, and were thus characterized by unacceptable viscosities [27–29]. Previously, we have reported the synthesis of hydroxy thioether derivatives of vegetable oil using epoxidized soybean oil and common organic thiols [30]. This 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 polysan-saturation in the fatty acid chain with addition of polar functional groups that significantly improves surface adsorption on metal and also contributes to the formation of a protective film through chemical reaction during the tribochemical process. The work reported in this paper discusses the tribochemical evaluation of these thioether hydroxy derivatives of vegetable oil using ball-on-disk and four-ball test methods.

2. Experimental procedure

2.1. Synthesis of polyhydroxy thio-ether derivative of soybean oil

Epoxidized soybean oil (ESBO) was obtained with a purity level of 98% from Elf Atochem (Philadelphia, PA), and was used without any further purification. Perchloric acid (HClO4, 70%, ACS Reagent), methylene chloride, sodium bicarbonate, anhydrous magnesium sulfate from Fisher Scientific (Springfield, NJ) and 1-butanethiol from Aldrich Chemicals (Milwaukee, WI) was used as obtained. Butyl thioether of hydroxy vegetable oil (BTHV) was synthesized by reacting 1-butanethiol with epoxidized soybean oil dissolved in methylene chloride using perchorlic acid as catalyst under dry nitrogen atmosphere. Similarly, 1-decanethiol, cyclohexyl mercaptan, and 1-octadecanethiol were used to prepare the decyl thio-ether of hydroxy vegetable oil (DTHV), the cyclohexyl thio-ether of hydroxy vegetable oil (CTHV), and the octadecyl thio-ether of hydroxy vegetable oil (OTHV) respectively. The detailed description of synthesis and structural characterization using NMR and FTIR has been reported elsewhere [30]. Based on the NMR and FTIR analysis, the tentative structures of BTHV, DTHV, CTHV, and OTHV are shown in Fig. 1.

All the additive concentrations are expressed in weight percentage.

2.2. PDSC method

The experiments were done using a computer controlled DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically 2.0 mg sample, resulting in a less than 1 mm film thickness, was taken in a hermetically sealed type aluminum pan with a pinhole lid and oxidized in presence of air. Dry air (Gateway Airgas, St. Louis, MO) was pressurized in the module at a constant pressure of 1379 KPa (200 psi) and 10 C/min heating rate was used during the length of the experiment. The oxidation onset temperature (OT) was calculated from the exotherm in each case. The OT is the temperature at which a rapid increase in the rate of oxidation is observed and is obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm. A higher OT would suggest a higher oxidation stability of the sample. All samples were run in triplicate and the average OT was reported with standard deviation < 1.0.

2.3. Four-ball configuration

The experiment is designed to study the anti-wear properties of additives under sliding contact by four-ball test geometry using a Falex apparatus (Model Multi-Specimen, Falex® Corporation, Sugar Grove, IL). The test zone is a top ball rotating in the cavity of three identical balls in contact and clamped in a cup below, containing the test fluid. The resistance to the motion of the ball is measured by a load cell connected to the stationary cup on the load platform.

![Fig. 1. Average chemical structures of butyl thioether of hydroxy vegetable oil (BTHV), decyl thio-ether of hydroxy vegetable oil (DTHV), cyclohexyl thio-ether of hydroxy vegetable oil (CTHV), and octadecyl thio-ether of hydroxy vegetable oil (OTHV).](image-url)
containing the 3 balls. Appropriate load is applied from below and the top ball is rotated at a set speed for a particular length of time. The balls (52100 steel, 12.7 mm diameter, 64–66 Rc hardness and extreme polish) were thoroughly cleaned with methylene chloride and hexane before each experiment.

In four-ball geometry, the three balls are clamped together and make three-point contact with the top ball. Test fluid (10 ml of 5 wt% additive dissolved in soybean oil) 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 15 min. 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 done with new set of balls. In all cases, the coefficient of friction (CoF) increased with time and leveled off to a steady-state value. The CoF value for a particular run is the average CoF in the steady-state region.

2.4. Ball-on-disk configuration

This study was designed to evaluate the tribochemical properties of vegetable oil based additive molecules and commercial additives using a ball-on-disk configuration on a Falex friction and wear test apparatus (Model Multi-Specimen, Falex Corporation, Sugar Grove, IL). The commercial additives used for comparison were methylene-bis-dibutylthiocarbamate (V7723), amine-phosphate (V9123), antimony tris(dialkylthiocarbamate) (V73) obtained from RT Vanderbilt Co (Norwalk, CT), A8484 containing mixture of tricresyl phosphate and trixylenyl phosphate from Akzo Nobel Functional Chemicals LLC (Dobbs Ferry, NY), E833 consisting of proprietary mixture from Ethyl Petroleum Additives, Inc. (Richmond, VA), and C62 containing mixture of diithiophosphoric acid esters from Ciba Specialty Chemicals Corp. (Tarrytown, NY). The test zone was a ball moving on a stationary disk (point contact) with a specified speed. The resistance to the motion of the ball (i.e. friction force) was measured by a load cell connected to the stationary disk. The coefficient of friction (CoF) is obtained by dividing the friction force by the normal force pressing the ball against the disk. The balls and the disks were obtained from Falex and 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 diameter, 64–66 Rc hardness and extreme polish. The disks were: 1018 steel, 25.4 mm 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. Fifty ml of the test fluid was poured in the cup to totally immerse the ball and disk. The disk assembly was then raised and allowed to touch the ball attached to the shaft. The shaft holding the ball was then rotated to attain the set speed and immediately after that, the load was applied to reach the set value. The duration of 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 specimen and test fluid was 25 ± 2 °C which increased by 2–3 °C at the end of the 15 min test period. Friction and other data were recorded until the set time elapsed. A duplicate test was conducted with the same test fluid and new set of ball and disk. The CoF values reported are averages of two or three independent experiments and the standard deviation observed was ±0.02

The sample chamber is fitted with a thermocouple to record any change in temperature during the test period. The instrument is equipped with a PC and software that allows automatic acquisition and display of the following data at any selected rate: torque on the disk (friction force), vertical height change (wear), load, speed, chamber temperature (test oil), specimen temperature (stationary disk) etc. During an experiment, the coefficient of friction was calculated by the instrument and displayed in real time.

2.5. Disk wear track width and ball scar-diameter measurement

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 taken in each case. For wear scar diameter, two measurements, perpendicular to each other, were recorded for each scar on a ball and the average of six measurements for three balls was taken in each case. The standard deviation of six measurements was less than 0.04 in all the experiments. The disk WTW and scar-diameter is reported in millimeters.

3. Results and discussion

Soybean oil mainly consists of triacylglycerol molecules where the fatty acids are derived mainly from oleic (C18:1), one unsaturation in the fatty acid chain), linoleic (C18:2) and linolenic (C18:3) acids attached to a glycerol back bone. The relative distribution of fatty acids in the molecule is largely based on the seed type and its genetic makeup. Regular soybean oil fatty acid distribution typically consists of C16 = 4%, C18 = 3%, C18:1 = 22%, C18:2 = 66% and C18:3 = 5%. High polysaturation in the molecule would result in low thermal and oxidative stability, while higher degree of saturation would make the oil solid at room temperature. Synthesis of poly hydroxy thioether derivative of soybean oil (SBO) from epoxoy soybean oil (ESBO) is an effective way of introducing branching at unsaturated site as well as sulfur incorporation using a one-step intramolecular mechanism. The removal of unsaturation in SBO by converting them to epoxy groups, followed by introducing branching at the epoxy carbons, significantly improves the thermal and oxidative stability of the oil. It has already been established that the presence of multiple double bonds in the vegetable oil fatty acids (FA) chains accelerates oxidative degradation [9]. This is also supported from the PDSC data. The onset temperature (OT) of oxidation for soybean oil obtained from PDSC was 134 °C. On conversion to epoxy soybean oil, the OT has increased to 195 °C due to removal of polysaturation resulting in increased oxidation stability. Introduction of thioether groups in triacylglycerol structure also resulted in increased oxidation stability for BTHV (OT of 181 °C) compared to SBO. This shows that suitable modification of triacylglycerol structure at their double bond sites, results in elimination of polysaturation and thus results in increased oxidation stability. The use of these thioethers as antioxidant additive is also a possibility as discussed in study by Qiu et al. [31], where in they determined the antioxidant activities of several typical organic sulfides by rotary bomb oxidation test and pressurized DSC, and related the structure of sulfides to their oxidative resistance in severely hydrotreated base oil. They found that the antioxidant activity of sulfides increased with the number of sulfur atoms. Sulfides with long hydrocarbon chains, were found to have good antioxidant activity, while cyclic sulfides were poor antioxidants.

3.1. Analysis of four-ball measurement data

The function of lubricant is to protect wear between surfaces by preventing the surface from coming in contact, and the
additives present in it, provide additional protection by forming stable films and physically bonding to the metal surfaces in contact. The purpose of these tribological experiments was evaluation of such wear protection by measuring friction coefficient and wear for various thioethers of hydroxy vegetable oils BTHV, DTHV, CTHV, and OTHV along with commercial additives. A modified ASTM D 4172 four ball experiment was designed with 5% w/w solutions of additive BTHV and several other commercially used additives in soybean oil. The experimental setup for friction measurement was: 1200 rpm, 40 Kg load (88 lb) for 15 min at room temperature. Fig. 2 shows that friction coefficient is relatively less for BTHV compared to other commercial antiwear additives obtained from different sources (V7723, V9123, V73, E833, C62 and A8484). The low CoF in BTHV is due to excellent boundary lubrication property of vegetable oil structure and the ability of the sulfur atom to react with the steel surface to form stable iron sulfide surface coating. Sulfur and oxygen atoms of these additives interact with the metal surface due to attraction of lone pair of electrons present on S and O to metals partially positively charged surface. The ether linkage in BTHV molecule is easily broken under the tribochemical condition with the release of elemental sulfur that can make stable complexation in place of oxygen with the active iron surface through an exchange mechanism. Similarly scar diameter measurement of the three stationary balls, Fig. 2 presents a definitive understanding of the efficiency of iron sulfide protective film compared to commonly available commercial additive packages. In most cases scar diameter up to 0.5 mm is an acceptable limit for most industrial antiwear applications. The BTHV molecule in its current form is at par with other multi-component additive packages. The decrease in the friction coefficient and wear reduction on use of these thioether hydroxy derivatives suggests formation of boundary protective layers. During the tribochemical process, the chemical reaction between functional groups of thioether hydroxy derivatives and metal atom present in the rubbing zone results in the formation of such protective films.

3.2. Analysis of ball-on-disk measurement data

Friction coefficient is largely dependent on the concentration of additives in a base fluid (toluene in this case). In boundary lubrication regime, the base fluid is required to maintain a stable lubricating film under high load. This in conjunction with an antiwear additive component can significantly extend the life of a lubricating film under high load. It is clearly observed from Fig. 3, using a ball-on-disk test geometry, CoF sharply decreases with increasing concentration of BTHV in base fluid (in this case toluene) and levels off at higher concentration. The rate of decrease in CoF (as observed from the slope for different additive concentrations, 0–10 w/w%) at the given experimental condition (6.22 mm/s sliding speed and 181.44 Kg load), is largely influenced by additive structure and their ability to form stable tribochemical film on the metal surface during the rubbing process. Additive BTHV demonstrates significant lowering of CoF with 5 w/w concentration in sharp contrast to other commercial additive packages (Fig. 4). Commonly available commercial additives show a steady state condition at a much higher friction coefficient value than BTHV. Other thioether hydroxy derivatives such as DTHV, CTHV, and OTHV also demonstrated lower CoF at 5 w/w concentration compared to commercial ones. Among thioether hydroxy derivatives, CoF increases in the order BTHV < CTHV < DTHV < OTHV, which may be due to decreasing sulfur content in average molecule. This explanation has been corroborated by the fact that an increase in the additive concentration of thioether hydroxy derivatives decreased the CoF. By increasing the concentration of these derivatives, more sulfur containing functional groups will be available for adsorption to metal surface.

Antwear properties of thioether hydroxy derivatives and commercial additives were also evaluated at a higher load in two different concentrations. Using a ball-on-disk configuration at 6.22 mm/s sliding speed and 181.44 Kg normal load for 15 min test duration, wear track width (WTW) on the disk was measured at 4–5 different positions on the track and average value obtained. The observed wear track width (in mm) thus obtained with 1% and 5 w/w thioether hydroxy derivatives of vegetable oils and commercial additives in toluene solution are shown in Figs. 5 and 6 respectively. It was observed that thioether hydroxy derivatives of vegetable oils additive BTHV, DTHV, CTHV, and OTHV (1% w/w in toluene solution) resulted in the low WTW compared to commercial additives (Fig. 5). Using 1% additive solutions, a 15% wear reduction was obtained with BTHV and commercial additives evaluated at a higher load in two different concentrations. Using a ball-on-disk configuration at 6.22 mm/s sliding speed and 181.44 Kg normal load for 15 min test duration, wear track width (WTW) on the disk was measured at 4–5 different positions on the track and average value obtained. The observed wear track width (in mm) thus obtained with 1% and 5 w/w thioether hydroxy derivatives of vegetable oils and commercial additives in toluene solution are shown in Figs. 5 and 6 respectively. It was observed that thioether hydroxy derivatives of vegetable oils additive BTHV, DTHV, CTHV, and OTHV (1% w/w in toluene solution) resulted in the low WTW compared to commercial additives (Fig. 5).

**Fig. 2.** Friction coefficient (CoF) and observed scar diameter (mm) of BTHV and commercial additives (5% w/w concentration in soybean oil, SBO) using a modified 4-ball test method (1200 rpm, 40 Kg for 15 min duration at room temperature).

**Fig. 3.** Coefficient of friction (CoF) variation with concentration (%w/w) of BTHV in toluene using a ball-on-disk test geometry (5 rpm, 181.44 Kg for 15 min at room temperature).

**Fig. 4.** Coefficient of friction (CoF) for thioether hydroxy derivatives of vegetable oil BTHV, DTHV, CTHV, and OTHV compared with commercial additives at 1, 5, and 10% (w/w) concentration in toluene using a ball-on-disk test geometry (5 rpm, 181.44 Kg for 15 min at room temperature).
DTHV, 13% with OTHV and 12% with CTHV compared to commercial additives. The performance properties at higher additive concentration level (5% w/w in toluene solution) were slightly better than commercial additives (Fig. 6). With 5% additive solutions, 5–8% wear reduction was obtained with thioether hydroxy vegetable oils compared to commercial additive. Two of the commercial additives (C62 and A8484) showed some decrease in the disk WTW with increasing concentration, while the other two (V7723 and E833) and thioether hydroxy derivatives of vegetable oils remained relatively constant.

The friction-reducing mechanism for thioether hydroxy derivatives may be due to following four elements. The first one is that during the tribological experiment, wear causes increment of nominal surface and decrease of pressure in the friction zone, which is inversely proportional to the square of wear scar diameter [32].

Another possible friction-reducing mechanism that could be active in this case is that these thioether hydroxy derivatives of vegetable oils are characterized by high surface activity. These derivatives may be interacting with iron through the initial formation of a mercaptan at the metal surface of friction parts as one step [22]. This may be followed by formation of sulfide adsorption layer which favorably influences motion resistance. Organic molecules bound to the metal surfaces have long been recognized as effective in reducing friction. It has already been established in earlier studies that polar functional groups in the triacylglycerol molecule make physical and chemical interaction with the metallic surfaces under high load and sliding contact to perform antiwear functions [33–36]. The point of attachment to the metal is through the polar group in the molecule, with the non-polar end forming a molecular layer separating the rubbing surfaces. Previous results [33–36] and current results obtained reveal that durability of this layer depends on the structure and amount of polar functional groups present in the thioether hydroxy derivatives of vegetable oil, which are also crucial in creation of the adsorption film.

The third one for the excellent antiwear properties of thioether hydroxy derivatives may be the ability of the molecule to release sulfur to coordinate with metal (iron) atom during the tribocchemical process. This may be further evidenced by previous studies [37,38], where they have shown that the only sulfur compound found in the wear scars was sulfide while studying surface chemistry of dibenzyl-disulfide on steel. They also suggested that besides the reacted surface being sulfide, it formed the thin layer compared to oxide layer. A thin easily removed layer of this nature would act as a low shear-strength, interfacial layer in the rubbing contact and would tend to reduce friction. Such thinnest reacted layers exhibit lower friction than the thick oxide case. Iron sulfide is softer than any iron oxide and its presence would further reduce friction. Therefore, increasing the number of polar groups in the molecule through chemical modification of vegetable oil and easy availability of sulfur in the system for stable iron sulfide film formation on metal surface, demonstrated the antiwear properties of thioether hydroxy derivatives.

Finally, the triacyl structure of these additives is more ferrophilic and so hydrogen bridging may occur. Also these triacylglycerols decompose at high temperatures to form acrolein moieties during the lubrication process. The polymerized acrolein film can add strength to the sulfide film and thus show synergistic effect in improving the friction/wear/EP characteristics. These thioether hydroxy derivatives thus show synergistic effect of combination of esters and sulfur. The ester part of these molecules provides reduced friction, while sulfur provides wear and EP protection. These can be used extensively in lubricants such as metal-working fluids, industrial gear oils, tractor-transmission fluids, and greases.

4. Conclusion

The above discussion presented a detailed tribological evaluation of bio-based non-toxic additive compounds obtained through chemical modification of vegetable oils. The incorporation of sulfur through reaction of thiols with epoxidized vegetable oils retained the vegetable oil backbone, removed polyunsaturation and added more polar functional groups. The tribocchemical evaluation of these thioether hydroxy derivatives suggested that these additions in the vegetable oil molecule improved the adsorption on metal surface resulting in reduced wear and friction coefficient. The data from ball–on–disk and four ball tests demonstrated that DTHV, CTHV, and OTHV manifests similar and sometimes better anti-friction/wear characteristics compared to BTHV. All of these bio-based specialty compounds far exceed the performance level anti-wear properties of commercial additives packages. A suitably designed compound of vegetable oil origin can thus demonstrate superior antiwear additive properties compared to commercially available products. Further, the vegetable oil based composition and easy development protocols combined with their eco-friendly nature, potentially makes it safe during production, utilization and recycling.

References


