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Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants☆

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Abstract

Boundary lubrication in a dynamic mechanical system is primarily governed by the formation of a stable tribochemical film. Polar functional groups in the triacylglycerol molecule of vegetable oil in conjunction with oil–additive–metal interaction during the metal rubbing process can significantly improve the wear resistance and extreme-pressure lubrication. Increasing the polar functionality of vegetable oil structure has a positive impact on wear protection resulting from stronger adsorption on metal surface as well as greater lateral interaction between the ester chains. The results reveal that ester groups of triacylglycerol molecule react with phosphate groups to form a protective fatty-phosphite layer. Antimony impregnation into the metal surface following strong complexation reaction with metal sulfide results in significant improvement in extreme-pressure characteristics due to alteration in surface metallurgy. In this case, seizure is averted even when the fluid adsorbed layer and phosphite coating is removed because of antimony induced surface hardness. The difference can be observed by analyzing the metal surface using scanning electron microscope (SEM). Selected bio fluids viz. soybean oil (SBO), thermally modified soybean oil (TMSBO) and chemically modified soybean oil (CMSBO) were investigated for potential application as industrial fluids.
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Keywords: Soybean oil; Tribology; Boundary lubrication; Chemical modification; SEM; Antiwear film

1. Introduction

Vegetable oils are renewable resources, environmentally friendly non-toxic fluids, pose no work place health hazards and are readily biodegradable [1,2]. The triacylglycerol structure of vegetable oil makes it an excellent candidate for potential use as a base stock for lubricants and functional fluids [3,4]. It makes them very attractive for industrial applications that may have potential environmental contact through accidental leakage, dripping or generating large quantities of after-use waste materials requiring costly disposal [5,6]. Vegetable oil in its natural form has limited use as industrial fluids due to poor thermal/oxidation stability [7,8 and references therein], low temperature behavior [9,10 and references therein], and other tribochemical degrading processes [11,12] that occur under severe conditions of temperature, pressure, shear stress, metal surface and environment. Independent approaches are being pursued to maximize oxidation and low temperature stability [7,13,14], however, a generalized approach is yet to evolve that will improve the over all performance properties of vegetable oils as industrial fluids.

The long fatty acid chain and presence of polar groups in the vegetable oil structure makes it amphiphilic in nature, therefore allowing them to be used as both boundary and hydrodynamic lubricants. 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 by strong physical and chemical adsorption on the metal surface in contact. Triacylglycerol molecules orient themselves with the polar end directed towards the metal surface making a close packed monomolecular [15] or multimolecular layered structure [16] 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 lubricant's

☆ 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 USDA implies no approval of the product to the exclusion of others that may also be suitable.

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performance, and it has also been observed that friction coefficient and wear rate are dependent on the adsorption energy of the lubricant [17].

The following work is based on the development of structurally modified bio-based fluids to improve their use as industrial base oils. Functional properties of seed oil improved by chemical modification are limited to oxidation, low temperature fluidity and viscosity–temperature characteristics. However, for extensive industrial applications, wear/friction resistance as well as additive response properties have considerable importance. This research provides insight on tribochemical behavior as a result of molecular structure variation using thermal and chemical modification of soybean oil. Effect of structure on friction/wear, load bearing capacity, resistance to rise in specimen temperature and varying response of antiwear/extreme-pressure additives in presence of vegetable oil/derivative structures is also discussed.

2. Materials and methods

2.1. Lubricants and additives

2.1.1. Synthesis of CMSBO #1

The reaction was carried out by refluxing a 2450 ml aqueous solution of 127.4 g epoxidized soybean oil (ESBO, Atofina, PA) at 100 °C for 48 h, in a three-neck 5000 ml round bottom flask. Perchloric acid (26.05 g) was added drop-wise to the reaction mixture that was constantly agitated by a mechanical stirrer. After the reaction was complete, the mixture was cooled to room temperature and the organic phase was extracted with chloroform ($CHCl_3$) and washed three times with water to remove any traces of acid remaining in the reaction mixture. The solvent was removed under reduced pressure at 80 °C and the product (dihydroxylated soybean oil) was stored under dry vacuum overnight. Forty grams of the above dihydroxy product was added to 40 g of hexanoic anhydride in 1:1 ratio, and 19.97 g of pyridine in equimolar ratio was further added to the reaction mixture. The mixture was stirred with a mechanical stirrer in a 500 ml glass round bottom flask for 48 h at room temperature. The reaction solution was poured into ice-water and again stirred for 12 h. The resulting mixture was extracted several times with diethyl ether. The organic phase was washed with 100 ml 3% HCl and 5% $NaHCO_3$ (each three times) and finally dried over anhydrous $MgSO_4$ for 24 h. Solvent was removed under reduced pressure at 80 °C and the product CMSBO #1 was obtained.

2.1.2. Synthesis of CMSBO #2

In a dry three-neck 500 ml round bottom flask fitted with a condenser were placed 50 g of ESBO, 46.88 g of hexanoic anhydride (1:1 equivalent ratio) and 400 ml of ethylacetate. The mixture was stirred and the temperature maintained at 50 °C under N_2 atmosphere. Boron trifluoride etherate (BF_3·ether) (8–10 drops) were added and the mixture was stirred and refluxed for 3 h. After the reaction mixture cooled to room temperature, it was washed three times with 5% $NaHCO_3$ followed by saturated brine solution. Later, the mixture was dried over anhydrous $MgSO_4$ (overnight). It was then filtered and evaporated under reduced pressure to recover the product CMSBO #2. The structural difference in CMSBO #1 and #2 is the degree of polarity in the triacylglycerol molecule and the extent of substitution on the fatty acid chains.

2.1.3. Preparative method for TMSBO

Normal refined soybean oil, SBO (fatty acid distribution: palmitic $C_{16:0} = 16\%$; oleic $C_{18:1} = 23\%$; linoleic $C_{18:2} = 53\%$ and linolenic $C_{18:3} = 8\%$) (number in the parenthesis indicate 16 or 18 carbon chain with 0, 1, 2 or 3 unsaturated sites, respectively) was heated in a three-neck 2 l glass reactor fitted with a mechanical stirrer up to 330 °C under N_2 gas purge. After 15 min of soaking at this temperature, the oil was gradually cooled to room temperature to obtain thermally modified soybean oil (TMSBO).

2.1.4. Additives

Amine phosphonate (additive A) and antimony dithiocarbamate (additive B) were obtained commercially. Each additive was blended into the vegetable oil in varying concentrations (2–8%, v/v) at room temperature. For friction measurements, the lubricant mixtures comprised 0.003–0.5 M of the above oil–additive formulations in hexadecane.

2.2. Friction measurement setup

This study designed to understand the effect of vegetable oil structure and additive components on friction and wear, was done using a ball-on-disk configuration (Fig. 1) using a friction and wear test apparatus from Falex®. 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 isopropyl alcohol and hexane prior

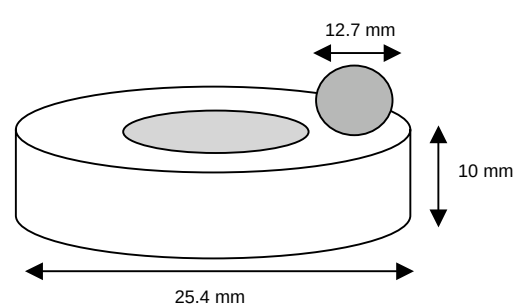


Fig. 1. Ball-on-disk friction measurement configuration.

to each experiment. The balls were: 52100 steel, 12.7 mm diameter, 64–66R_c hardness and extreme polish. The disks were: 1018 steel, 25.4 mm outer diameter, 15–25R_c hardness and 0.36–0.46 μm roughness.

The experiments were performed at room temperature with the test fluid covering the ball and the disk completely in the sample chamber. The disk and the sample chamber are 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.

2.3. Friction measurements

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 milliliters 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. 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. Data reported are average of the two tests with ±5% mean standard deviation.

The duration of friction test was 15 min at a sliding speed of 6.22 mm/s (5 rpm) and 1778 N load (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 duration.

Coefficient of friction for pure hexadecane (without vegetable oil or additive) was determined as a function of load from 444.5 to 1333.5 N (100–350 lb). It was observed that the COF increased with increasing load and leveled off at 1111.3 N (250 lb) and with an average COF of 0.5.

2.4. Disk wear track measurements

Width of the wear track on disk was measured using an optical microscope attached to a digitized moving platform. Three measurements were recorded at different position of the wear track and the average value was taken in each case. The width of the wear track is reported in millimeters.

2.5. Scanning electron micrograph

The circular wear scar left on the disk was analyzed using a SEM. The disks were not treated for any residual lubricant removal except for carefully soaking the excess oil left on the disk surface after the end of test run. Care was taken not to dislodge the metallic debris from wear track or on the edges of the track.

3. Results and discussion

3.1. Analysis of coefficient of friction

Friction coefficient is largely dependent on the concentration of vegetable oil and their derivatives in hexadecane. It is clearly observed from Fig. 2 that COF sharply decreases with increase in oil content and levels off at higher concentration. The rate of decrease in COF (as observed from the slope at low oil concentration) is largely influenced by oil structure and their ability to form thin lubricating film at the point of metal contact. It was also observed that CMSBO #1 and #2 show a higher rate of decrease in COF at lower concentration (0–0.01 M) as compared to SBO and TMSBO.

Fig. 3 presents the friction coefficient data for SBO and its derivatives at 0.07 M concentration. It is observed that SBO has the highest COF followed by TMSBO and CMSBO

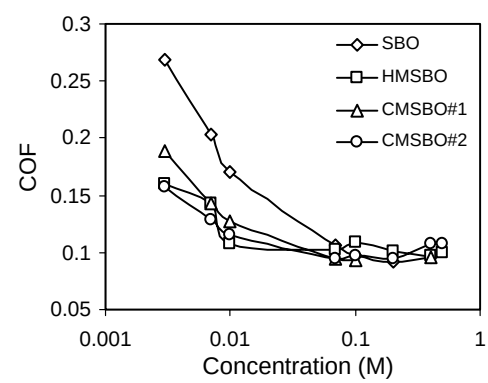


Fig. 2. Effect of vegetable oil/derivative concentration (in hexadecane) on coefficient of friction.

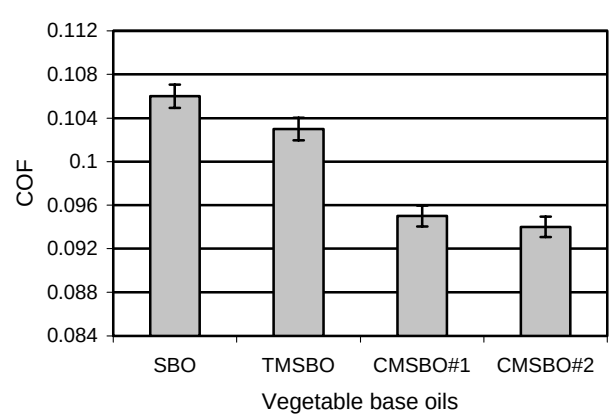


Fig. 3. Friction coefficient of vegetable based oil and derivatives at 0.07 M concentration (in hexadecane) using 6.22 mm/s sliding speed and 1778 N load (400 lb).

Table 1
Total acid number (TAN) and viscosity of the test fluids

Fluids	TAN (mg KOH/g)	Viscosity at 40 °C (cSt)
CMSBO #1	4.21	60.12
CMSBO #2	4.37	55.03
TMSBO	2.15	41.21
SBO	1.12	38.22

#1 and #2. Chemically modified oils show less than half the COF for regular and thermally treated SBO. 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 [18]. 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. Increasing the number of polar groups in the molecule through chemical modification at the fatty acid C–C unsaturated sites, improves this property. The slightly lower friction coefficient of TMSBO when compared to SBO is mainly due to its compact structure resulting from heat induced intermolecular polymerization (mainly dimers and trimers) (Table 1). The similarity in COF for CMSBO #1 and #2 (within the percentage error limit) is primarily due to the number and nature of polar groups in oil structure. The residual –OH groups in CMSBO #1 (those not converted to ester groups) contributes to polarity in the molecule but lacks the hydrocarbon chain (of ester) to provide effective molecular separation between mating surfaces. One-step synthesis of CMSBO #2 do not involve intermediate hydroxylation, and intramolecular rearrangement step converts all C–C unsaturated sites to diester functionality providing additional polarity and non-polar hydrocarbon chains to the existing molecule.

Boundary lubrication occurs when polar materials are allowed to form films to bond chemically to the metal surfaces in contact. During metal working process, for example, significant amount of heat is generated from the primary deformation zone which accounts for nearly 60% of the total heat produced in the cutting process. This heat is generated due to metal deformation and from other friction zones (tool/chip and tool/work piece interfaces). Effective removal of heat and provide lubrication to metals in contact is an important function of boundary lubricant. CMSBO #2 results in lower disk temperature when compared to CMSBO #1 under similar conditions of load and sliding speed (Fig. 4). This effectiveness holds well over a wide load range.

3.2. Analysis of wear track data

Quantification of wear scar can also lead to a better understanding of the effect of vegetable oil structure and additive on lubrication properties. Wear track width was measured for 0.003 M CMSBO #1 and #2 using additives A and B at different concentrations (0–8%, v/v) (Fig. 5). It was observed that wear track width decreased with increase in additive

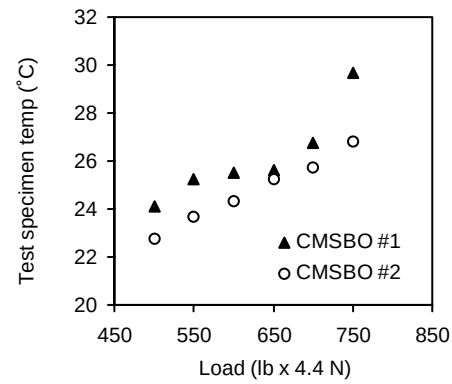


Fig. 4. Effect of load increase on disk temperature using CMSBO #1, #2 and 6% additive B with 6.22 mm/s sliding speed.

doping and reached an equilibrium at 6% (v/v) concentration (2.46 mm for CMSBO #2 + 6% additive A; 2.50 mm for CMSBO #1 + 6% additive B, at minimum value), beyond which no observable decrease in wear width was observed. The rate of decrease was more significant in CMSBO #2 and additive A combination. Therefore using similar tribological conditions, CMSBO #2 with 6% additive A provides a better wear protection at 1778.11 N load and 6.22 mm/s sliding speed, compared to CMSBO #1.

Similar wear measurements were done with varying load for 0.003 M CMSBO #1 and #2 with 6% additives A and B, separately. It was observed that CMSBO #2 demonstrates a better wear protection as compared to CMSBO #1 up to a moderate load of 2667 N (600 lb) beyond which their effects are not well distinguished. With the application of load in excess of 3334 N (750 lb), the molecules starts disintegrating and so does the oil film strength, when vegetable oil loses its lubricating property and the additive its antiwear protection.

3.3. Analysis of load experiments

The load bearing effects of additives A and B were studied on CMSBO #2. The results show (Fig. 6) that additive B

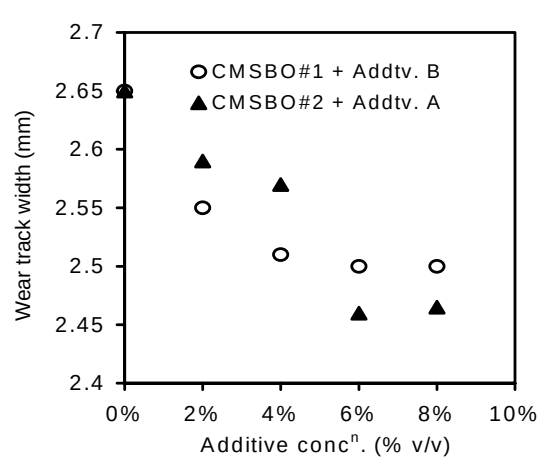


Fig. 5. Optimizing additive concentration in vegetable oil derivatives using 6.22 mm/s sliding speed and 1778 N load.

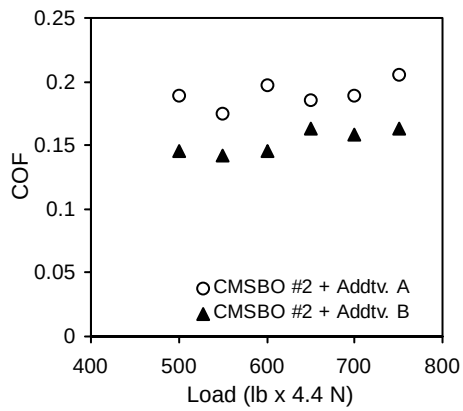


Fig. 6. Effect of load increase on friction coefficient using 6% additives A and B in CMSBO #2 with 6.22 mm/s sliding speed.

performs consistently better than additive A at all load ranges. The COF registers a slow and gradual increase up to a certain load range when the film strength is capable of holding the load increase before breaking down. Any further increase in load would result in a catastrophic rise in COF primarily due to irreversible breakdown of the vegetable oil induced lubricating film, and secondly due to additive film breakdown resulting in scuffing and welding from metal–metal contact. Fig. 7 shows that CMSBO #2 was able to maintain a stable film in the presence of additive B well into 3334 N load range, whereas CMSBO #1 shows an increase in COF beyond this point due to loss of oil and additive film. The results from Figs. 5 and 6 indicate that additive B performs better than A at higher load ranges, and CMSBO #2 shows a better response with additive B when compared to CMSBO #1.

3.4. Analysis of SEM

Metal-to-metal contact during sliding motion results in significant wear and tear of the metal surface. Analysis of worn metal's surface characteristics provides a wealth of information on the extent of wear protection by vegetable oil as boundary lubricant and metal–additive interactions. The extent of this wear is however influenced by vegetable oil and additive molecules that make a stable thin molecular film which prevents metal–metal contact [19]. This preventive mechanism is, however, lost at high load when the protective lubricant film is squeezed out from between the metals, establishing contact. Under the present experimental setup, the lubricant is allowed to flow between the metals and establish a stable film. The stability and tenacity of the film to adhere to the metal surface dictates the extent of its wear protection. Much of this stability is derived from the oil structure as observed from SEM analysis of wear track surfaces.

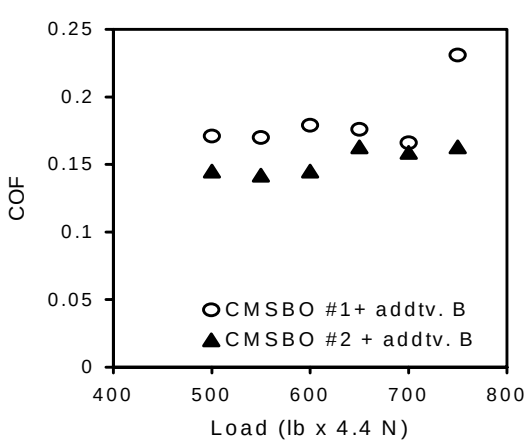


Fig. 7. Effect of load increase on friction coefficient using 6% additive B in CMSBO #1 and #2 with 6.22 mm/s sliding speed.

Fig. 8(a)–(d) present the SEM pictures of wear track obtained from 0.01 M SBO, TMSBO, CMSBO #1 and #2. The wear profile with SBO (Fig. 8(a)) and TMSBO (Fig. 8(b)) are similar showing grooving with metallic flakes dislodged from the disk surfaces. This is also supported from Fig. 3, where both SBO and TMSBO show similar friction coefficients. Higher viscosity induced by thermal polymerization in TMSBO does not improve the lubricating properties significantly. Since there is no change in the polar functional groups in TMSBO molecule, this does not translate into major improvement in boundary lubricating behavior. When compared to SBO, the slight reduction in COF (Fig. 3), groove lines and dislodged large metallic fragments in TMSBO (Fig. 8(b)) suggests that these were achieved due to its more compact molecular structure resulting in a protective film formation. The wear characteristics were further reduced in CMSBO #1 (Fig. 8(c)) and least in CMSBO #2 (Fig. 8(d)). This improvement is largely due to the presence of more polar functional groups in the chemical derivatives establishing stronger interaction with the metal surface and therefore a stable lubricant film.

Figs. 9(a) and (b) and 10(a) and (b) presents the comparative study of the wear characteristics on disk surfaces using CMSBO #1 + additive B (2, 8% concentration) and CMSBO #2+additive A (2, 8% concentration), respectively. Using similar experimental conditions (1778.11 N load and 6.22 mm/s sliding speed) and SEM magnification, CMSBO #2 shows a far greater improvement in wear protection in presence of additive A. This is also supported from the wear track width data using CMSBO with 6–8% additive concentrations (Fig. 5).

Fig. 11(a) and (b) presents the effect of additive B (2 and 8% by volume) on wear pattern while increasing the load (from 400 lb in Fig. 11(a) to 750 lb in (b)) in CMSBO #1. The SEM picture shows that nearly doubling the load in Fig. 11(b) has no significant impact on the wear profile due to additive protection. Similar effect was noticed for CMSBO #2 and additive B (2 and 8% concentration) with increasing load. It may be concluded at this stage that the antiwear protection of additive molecules exceeds the benefit derived from vegetable oil structure. This difference is primarily due to difference in their mechanism of interaction with metal surfaces.

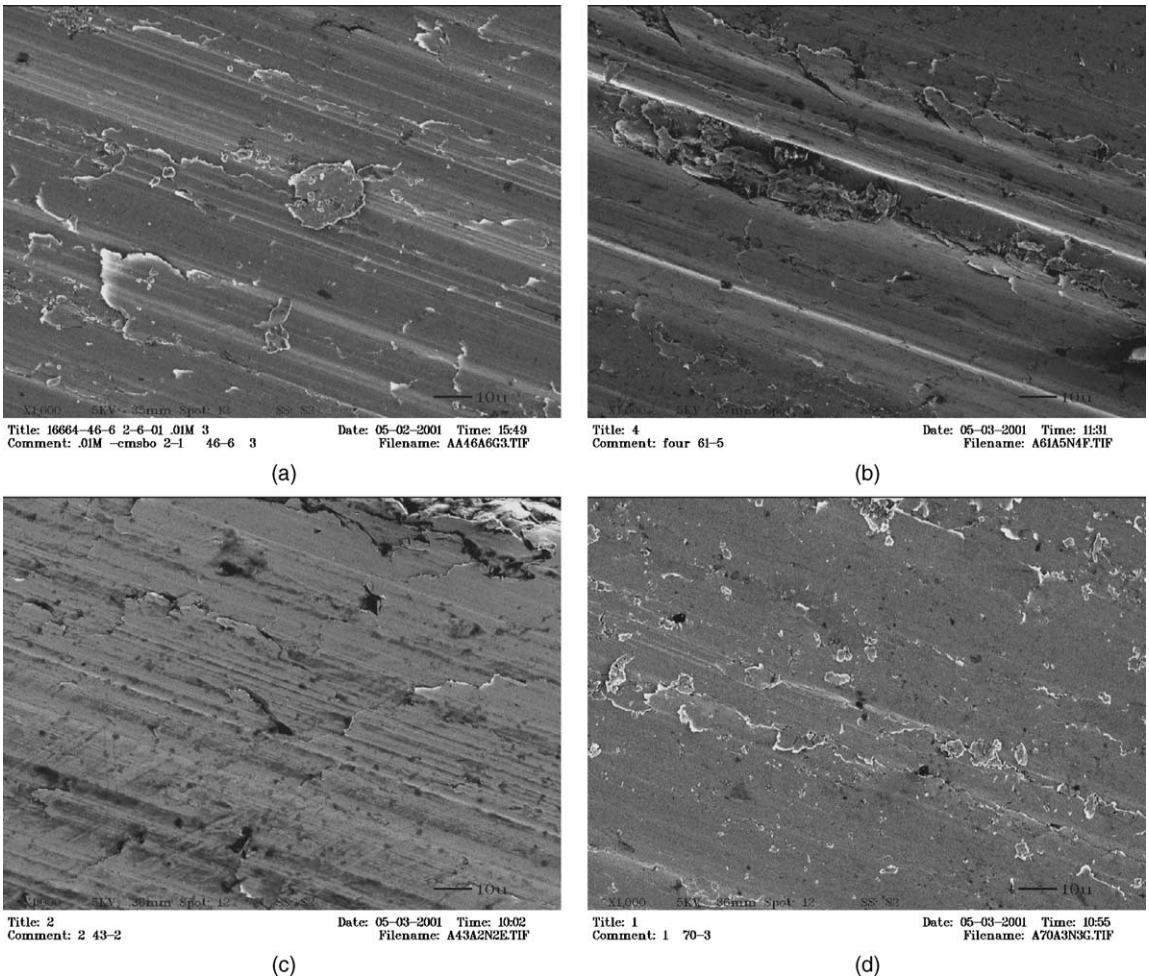


Fig. 8. SEM pictures of wear track (6.22 mm/s sliding speed and 1778 N load) obtained from 0.01 M: (a) SBO, (b) TMSBO, (c) CMSBO #1 and (d) CMSBO #2.

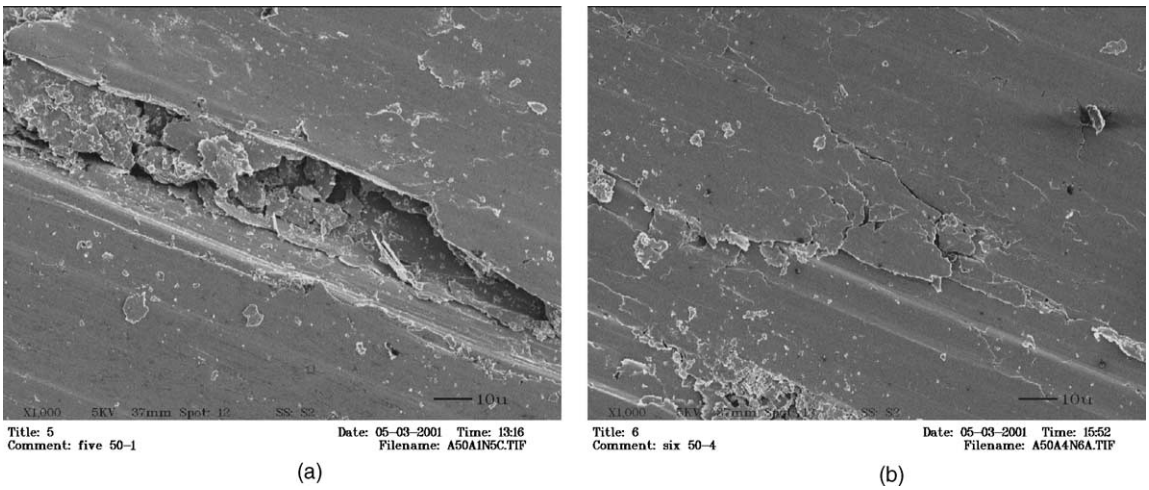


Fig. 9. Wear morphology (6.22 mm/s sliding speed and 1778 N load) of disk surface using SEM: (a) CMSBO #1 + 2% additive B and (b) CMSBO #1 + 8% additive B.

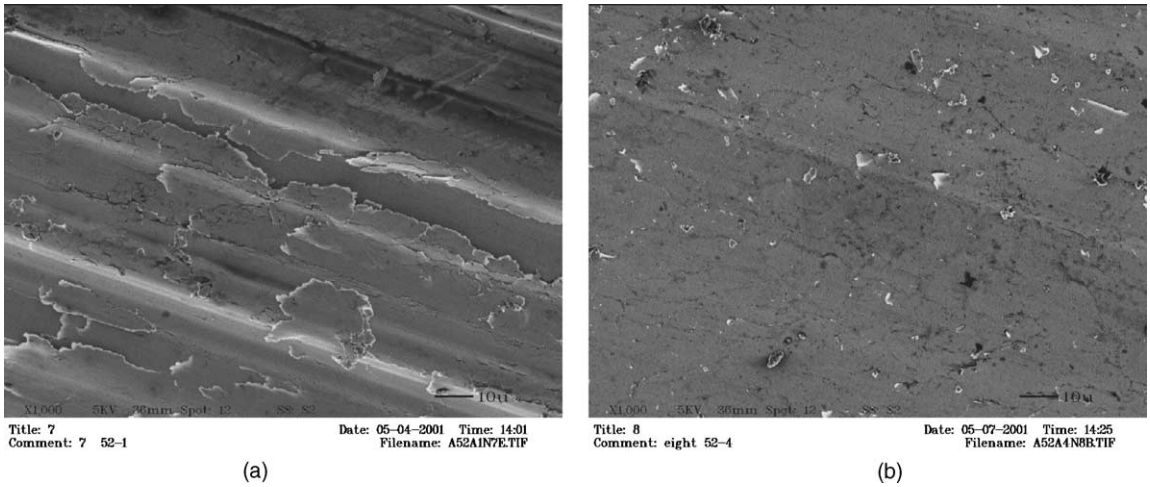


Fig. 10. Wear morphology (6.22 mm/s sliding speed and 1778 N load) of disk surface using SEM: (a) CMSBO #2 + 2% additive A and (b) CMSBO #2 + 8% additive A.

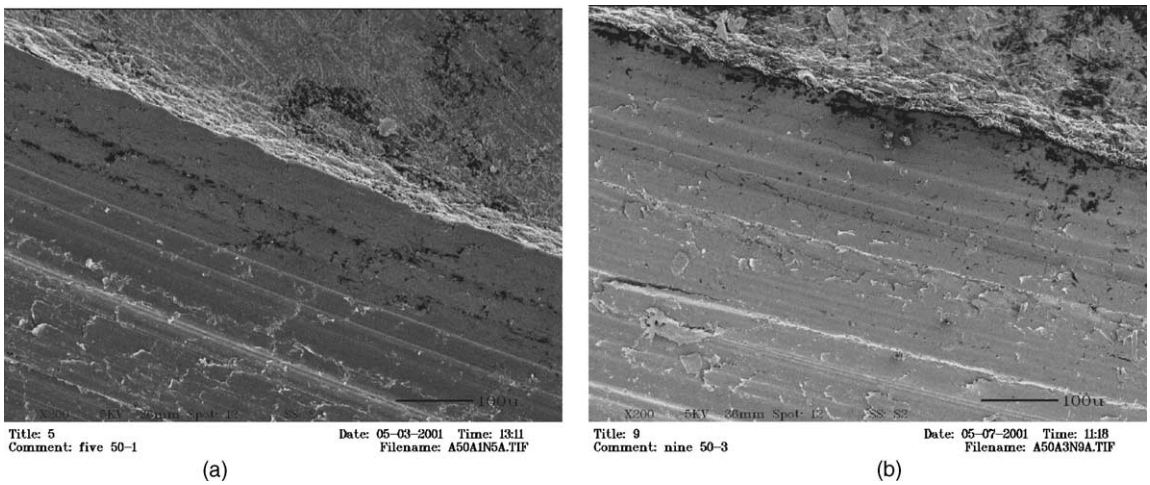
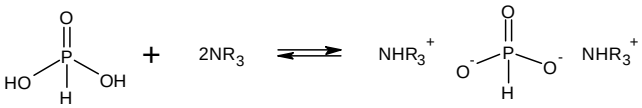


Fig. 11. Effect of additive B with load increase: (a) 1778 N (400 lb) load with 2% additive B in CMSBO #1 and (b) 3334 N (750 lb) load with 8% additive B in CMSBO #1.

3.5. Vegetable oil–additive response

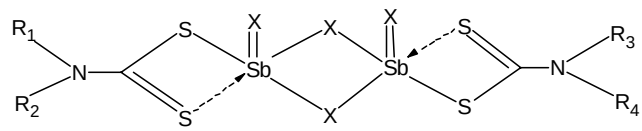
Much of the friction and wear resistance mechanism of additives results from complex chemical transformation on the metal surface [20 and references therein]. Amine phosphonate in additive A has the general structure represented by:R = mostly aliphatic groups (2-ethylhexyl, hexyl and



n-octyl); amines have *tert*-alkyl group with 10–24 carbon atoms.

The antiwear mechanism is due to the formation of an iron phosphate tribofilm on steel surface within the wear track. There are reports [21 and reference therein] available in the literature where a polyphosphate glassy material was formed on the wear track. The study revealed that low relative humidity, oxygen and temperature are necessary for effective film formation and overall useful life of the additive. The breakdown of vegetable oil molecule during tribochemical process results in the formation of fatty acids which can react with the phosphorus containing group from additive A. These fatty phosphites function as effective friction modifiers. The long hydrocarbon chain of the fatty acid provide an excellent molecular barrier while the polar group coordinate with iron to form a protective film on the metal surface.

Antimony additive B, is an interesting metal impregnant that has become very popular. The additive reduces friction/wear, and also improves the strength and thermal conductivity of the material. Typical structure of antimony dithiocarbamate is shown below:



X = S or O and R = alkyl groups (ethyl, pentyl, 2-ethylhexyl, dodecyl, tridecyl, hexadecyl) and cyclo-alkyl groups (cyclohexyl and cycloheptyl).

In a tribochemical process with sulfur containing additive, sulfur atom reacts with iron oxide on the metal surface to form iron sulfide. This formation results in a wear protective coating on the surface [22,23 and references therein]. Sulfur also allows stable complexation sites for antimony which coordinates with sulfur and leads to antimony doping into the metal. This process would lead to metallurgical changes on the metal surface making it harder than the steel core [24]. Antimony can also result in the formation of an oxide film transferred to the mating surfaces improving the tribology at the interface due to solid lubricant-like properties of the oxide film. From the above figures it is clear that additive A has good antiwear, and additive B good load bearing capacity. These properties are further accentuated in chemically modified oils due to greater number of ester chains and coordinating sites resulting in better interaction with additive molecules. The wear (Figs. 4 and 5) and load carrying capacity (Fig. 7) is further improved in CMSBO #2 when compared to CMSBO #1. This improvement is due to the availability of more polar groups in the molecule (CMSBO #2) that offer active sites for coordination with phosphorus and allow stronger adsorption on the metal surface, hence improving boundary lubrication.

4. Conclusion

This study presents the effect of chemical structure on the tribochemistry of vegetable oils for use in industrial applications. In order to qualify for broad industrial use, bio-based fluids must have high and low temperature stability as well as excellent lubricating properties. These properties are inherent weaknesses in regular seed oils. Thermal and chemical modification of oil structure can significantly influence the wear and load carrying properties under boundary lubrication regimes. Chemical modification of triacylglycerol structures has great potential in achieving a broad temperature range stability as well as excellent wear/friction characteristics.

Increasing the polar functionality in vegetable oil structure has a positive impact on wear protection resulting from stronger adsorption potential on metal surface as well as greater lateral interaction between the ester chains. This was shown by increasing the polarity by chemical modification of soybean oil.

During the tribochemical process, amine-phosphorus containing additive molecule undergo significant chemical transformation in the presence of fatty acids and enhance the antiwear properties of vegetable oil. Greater availability of ester moieties results in the formation of phosphate-esters on the wear track, which can effectively function as friction modifiers in the system.

Quantification of wear track scar width, and the coefficient of friction coupled with the analysis of the wear track by SEM gives a fairly good insight into the extent of wear protection by CMSBO when compared to SBO or TMSBO under similar experimental conditions. The experimental protocol has also been used to optimize the additive concentration (6%, v/v) in the final formulation.

The individual response of amine phosphate and antimony dithiocarbamate molecule with CMSBO #1 and #2 indicate that during the tribochemical process elemental antimony may cause metal impregnation, altering the metallurgical property of the rubbing surface which results in better load bearing capability.

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