



Original Research Article

Performance evaluation of chemically modified vegetable oils towards development of biodegradable greener lubricant base stock

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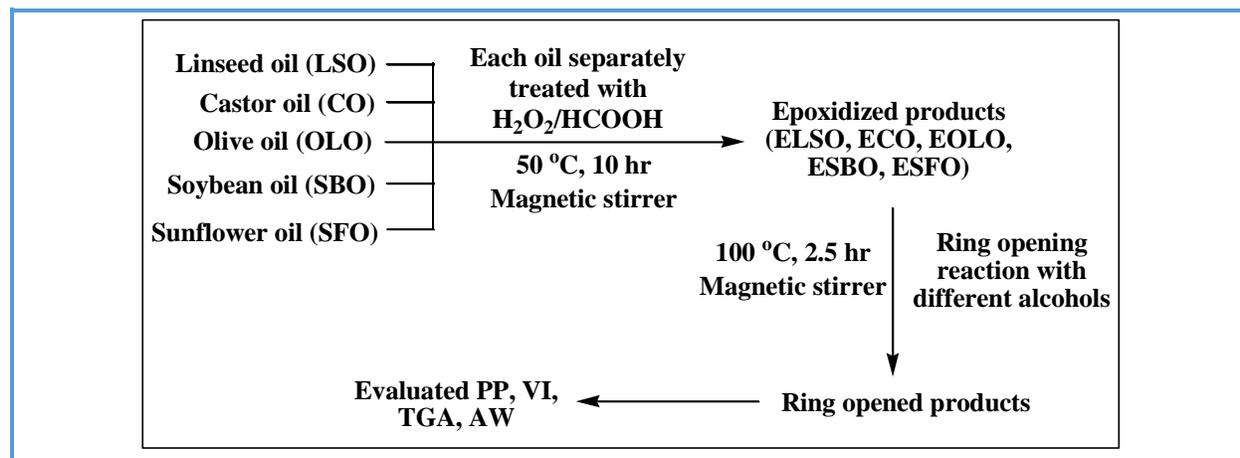
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ABSTRACT

Vegetable oils such as linseed oil (LO), castor oil (CO), olive oil (OLO), soybean oil (SBO) and sunflower oil (SFO) were epoxidized and characterized using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analysis. Reaction of epoxidized linseed oil with 2-ethylhexanol, dodecanol, n-octanol, 1-decanol and isodecanol in the presence of a catalytic amount of sulfuric acid provided ring-opened products. These ring-opened products of linseed oil exhibited better low temperature flow i.e. better pour point (PP) and high viscosity index (VI). Ring opened products with isodecanol and 2 ethyl hexanol showed better result compared to others. CO, OLO, SBO, SFO epoxide rings were also opened through the same procedure using isodecanol and the products exhibited high viscosity index and excellent low temperature flow as well. Ring opened products displayed better thermal stability when passed through thermogravimetric analysis (TGA) compared to mineral base oil. Better pour point, high viscosity index value, thermos-oxidative stability and better antiwear (AW) property make these products as an environmentally benign alternative to mineral lubricating oil.

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Graphical Abstract



Introduction

Owing to the unfavourable impact on the environment of mineral oil-based lubricants, there has been a steady increase in the demand for biodegradable, environment-friendly lubricants. However, development of a biodegradable base fluid that could replace or partially substitute conventional mineral oil is a big challenge. Vegetable oils are biodegradable and therefore good candidates for environmentally friendly base stocks. They have excellent lubricity, but poor oxidation and low temperature stabilities. The molecular composition and structure of vegetable oils has drawn huge attention of lubricant industry. The main constituents of vegetable oils are triglycerides (95–97%) and also mono- and diacylglycerides. General structure of triglyceride found in most of the vegetable oils is demonstrated in [Scheme 1](#).

Presence of unsaturated fatty acids like oleic, linoleic, linolenic etc and saturated fatty acids like tetradecanoic, palmitic, stearic has been responsible for its versatile applications such as in wall finishes [1], paints [2], electrodeposition paints [3], water thinnable primers [4] and printing inks [5] etc. Vegetable oils have high viscosity index (above 200) and high flash point

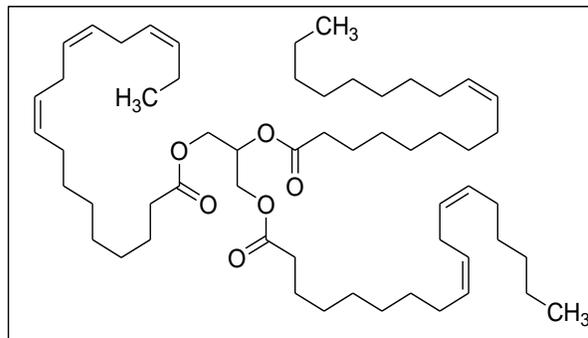
as well. In spite of having huge advantages and being biodegradable and environment friendly, vegetable oils suffer from some inherent limitations mainly low thermo-oxidative stability due to presence of polyunsaturation [6]. Therefore, untreated vegetable oils cannot be used solely as lubricant base stock.

However, this problem can be solved by some chemical modifications such as transesterification, epoxidation, selective hydrogenation, polymerization etc. Most of the vegetable oils have high contents of unsaturated fatty acid and can be converted into epoxy fatty acid by conventional epoxidation, catalytic acidic ion exchange resin, metal catalyst epoxidation or using chemoenzymatic epoxidation. Nowadays epoxidized vegetable oil is having great concern as they are obtained from sustainable, renewable natural resource and are environment friendly. Epoxidized vegetable oil can act as a raw material for synthesis of variety of chemicals including polyols, glycol, carbonyl compound, lubricants, plasticizers for polymer etc. because of their respective oxirane oxygen content and high reactivity of oxirane ring [7]. Castor oil is obtained from castor seeds which is available in nature. It contains high percentage of triacylglycerol of ricinoleic acid (85-95%)

which is a C-18 fatty acid having a double bond at C-9 and a hydroxyl group at C-12. Due to trifunctional nature of castor oil, it can be used as a monomer for the preparation of lube oil polymeric additives as well as base stock. Castor oil contains hydroxyl monounsaturated triglycerides which via hydrogen bonding raises the viscosity to a very good level. In fact castor oil has higher viscosity index compared to the super-refined mineral oils [8]. Earlier in our lab castor oil was explored towards the synthesis of multifunctional greener additives for lubricating oil [9]. Soya oil, one of the most abundant and inexpensive renewable sources towards the formulation of high molecular weight polymers, consists of poly-unsaturated fatty acids with the main component being linoleic acid (ca. 50 wt%) [10]. Hong-Sik Hwang, Sevim Z. Erhan studied the properties of synthetic lubricant basestocks from epoxidized soybean oil and Guerbet alcohols [11]. Linseed oil is also another potential candidate in this field in which the level of unsaturation for the triglyceride is somewhat greater than that for soybean oil [12]. In our previous work linseed oil based biodegradable homo and copolymers were prepared towards development of multifunctional greener additives for lube oil [13]. Bio active olive oil is also a potential candidate in lubricant industry as it is commercially available, cheap and contains about 86% of total active unsaturation. P. Ghosh et al. have conducted several studies on sunflower oil-based biolubricants and additives which accounted for its vast application in lubricant industry [14–16].

Due to high viscosity index and low pour point, these vegetable oils can be treated as a source of potential lube base stock. Lack of Thermal stability due to the unsaturation present in the triglyceride moiety is the main reason that they cannot be used directly as lube. In this context we made epoxides of vegetable

oils followed by epoxy ring opening by different alcohols and studied their properties to determine whether they can be treated as alternate lubricant base stock.



Scheme 1. General structure of triglyceride found in vegetable oil

Experimental

Materials and methods

Linseed oil, castor oil, olive oil, sunflower oil and soybean oil were bought from local market and used directly. The physical properties of the vegetable oils and the mineral base oils are given in Table 1.

The fatty acid composition of the vegetable oils is given in Table 2. H₂O₂ (30%) was bought from MERCK and used as it was. Formic acid (98% Thomas Baker Pvt Ltd Ind), Concentrated H₂SO₄ (98% MERCK), 2-ethyl hexanol (99% Sigma Aldrich), dodecanol (99% Sigma Aldrich), n-octanol (99% LOBA Chemicals Pvt Ltd Ind), 1-decanol (99% Sigma Aldich), isodecanol (99% LOBA chemical Pvt Ltd Ind) were used after distillation.

IR spectra of the vegetable oil epoxides were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe in CDCl₃ solvent and tetramethylsilane (TMS) was used

as reference material. TGA data were recorded on Shimadzu TGA-50 systems, at a heating rate of 10 °C/min. Results are summarised in Table

3. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.2\%$.

Table 1. Physical properties of base Oil (BO), linseed oil (LSO), castor oil (CO), olive oil (OLO), soybean oil (SBO), sunflower oil (SFO)

Physical properties	BO*	LSO	CO	OLO	SBO	SFO
Density (gcm ⁻³ at 25 °C)	0.95	0.93	0.88	0.92	0.86	0.91
Viscosity at 40 °C in cSt	24.211	15.220	173	41.7	28	33.8
Viscosity at 100 °C in cSt	4.47	6.33	15	8.8	7.55	8.1
Pour Point (PP in °C)	-6	-21	-27	-2	-9	-17
Flash Point (°C)	225	>280	200	316	252	245

*BO collected from IOCL, Dhakuria, West Bengal

Table 2. Fatty acid composition of vegetable oils

Vegetable oil	Palmitic acid (16:0)	Stearic acid (18:0)	Oleic acid (18:1)	Ricinoleic acid (18:1)	Linoleic acid (18:2)	Linolenic acid (18:3)
Olive	14	2	64	-	16	2
Castor	3	3	9	75	10	-
Soybean	6	5.2	20.2	-	63.7	5
Linseed	5	4	19.1	-	15.3	56.6
sunflower	6.1	5.3	21.4	-	66.4	-

Table 3. TGA data of the modified vegetable oils in comparison to the base oil

Sample	Decomposition temperature (K)	Percent weight loss (PWL)
Base Oil	393/473	38/98
ELSO + 2-Ethyl hexanol	451/573	15/90
ELSO + Dodecanol	453/571	14/93
ELSO + n-Octanol	468/608	15/92
ELSO + 1-Decanol	470/610	15/96
ELSO + Isodecanol	483/613	13/91
ECO + Isodecanol	483/603	21/95
ELO + Isodecanol	473/613	14/92
ESBO + Isodecanol	453/598	18/96
ESFO + Isodecanol	462/593	14/91

Epoxidation and purification

At first, linseed oil and formic acid (1.0:0.4) were poured to a glass set over a water bath at temperature of 50 °C and speed of 550 RPM on a magnetic stirrer. The mixture was stirred for 10 min. To start the epoxidation, hydrogen peroxide (30 %) was gradually charged into the mixture during the first 5 hr of reaction in the molar ratio of 1.0:1.7 with respect to the oil and peroxide. After charging of H₂O₂ was completed,

the reaction continued by mixing and controlling the temperature at 50 °C for further 5 h. After that, the mixture was cooled down and neutralized by water. Diethyl ether was used to enhance the separation of the oil product from water phase. The final product was dried out by heating less than 50 °C. Three replications were performed concurrently. Similarly, castor oil epoxide and epoxide of other vegetable oils were prepared. The double bonds are one of the active sites that can react with functional

groups. The epoxides were characterised by FTIR and NMR spectroscopy and used for the next step.

Epoxy ring opening reaction

A mixture of epoxidized linseed oil (ELSO) and 2-ethyl hexanol (1:5 molar ratios of epoxide and alcohols) was heated at 90 °C with stirring. Sulfuric acid (2%) was added drop wise and the mixture was stirred at 100 °C for 2.5 h. When the reaction mixture turned brownish, it was cooled by adding ice and saturated aqueous sodium bicarbonate. The mixture was extracted with ethyl acetate, dried over anhydrous magnesium. The remaining solvent was evaporated under vacuum at 80 °C to have the ring-opened product. Similar reactions were carried out using dodecanol, n-octanol, 1-decanol and isodecanol under same reaction condition stated above. Castor oil epoxide (ECO), olive oil epoxide (EOLO), soybean oil epoxide (ESBO), sunflower oil epoxide (ESFO) were treated with isodecanol in 1:2.5 molar ratio of epoxide and alcohol under same reaction condition to have the ring opened products. The ring-opening reaction was monitored by the disappearance of epoxy ring hydrogen.

Performance evaluation in respect of pour point

The pour point of the ring opened products was measured according to the ASTM D 97-09

method using cloud and pour point tester model WIL-471 (India) and a comparison was carried out against base oil. The pour point data are given in [Table 4](#).

Performance Evaluation in respect of Viscosity index

Viscosity index (VI) is an important parameter to determine the change of viscosity of the lubricant with increasing temperature. Higher the value of VI, smaller is the change of viscosity at high temperature. It was calculated according to ASTM D 2270-10. The kinematic viscosities of the lubricant composition were determined at 40 °C and 100 °C which are essential to calculate the VI. Comparison of VI data between the ring opening products of the epoxidized vegetable oils and base oil is listed in [Table 5](#).

Performance Evaluation in Respect of Antiwear Test

Antiwear performance of the ring opened products was evaluated by Four-ball Wear Test apparatus (FBWT) following the ASTM D 4172-94 methods. In this experiment the wear scar diameter (WSD), a parameter for the determination of antiwear (AW) performance of the oils, has been measured applying weld load of 392 N (40 Kg) at 75 °C for 60 min. The results are tabulated in [Table 6](#).

Table 4. Pour point data of modified vegetable oils in comparison to base oil

Sample	Pour point in °C
Base Oil	-6
ELSO + 2-Ethyl hexanol	-15
ELSO + Dodecanol	-2
ELSO + n-Octanol	-7.2
ELSO + 1-Decanol	-3.6
ELSO + Isodecanol	-18.4
ECO + Isodecanol	-22
EOLO + Isodecanol	-19.4
ESBO + Isodecanol	-18

ESFO + Isodecanol

-17

Table 5. Viscosity index data of modified vegetable oils in comparison to base oil

Sample	Viscosity index
Base Oil	89.87
ELSO + 2-Ethyl hexanol	248
ELSO + Dodecanol	256
ELSO + n-Octanol	238
ELSO + 1-Decanol	259
ELSO + Isodecanol	264
ECO + Isodecanol	138
EOLO + Isodecanol	154
ESBO + Isodecanol	268
ESFO + Isodecanol	207

Table 6. Wear Scar Diameter (WSD) values of the modified vegetable oils in comparison to the base oil

Sample	WSD x 10 ⁻³ (m)
Base Oil	1.119
ELSO + 2-Ethyl hexanol	0.868
ELSO + Dodecanol	0.835
ELSO + n-Octanol	0.856
ELSO + 1-Decanol	0.882
ELSO + Isodecanol	0.868
ECO + Isodecanol	0.616
EOLO + Isodecanol	0.989
ESBO + Isodecanol	0.776
ESFO + Isodecanol	0.798

Result and Discussion

Spectroscopic analysis

Spectral data of all the vegetable oils gave almost similar result. IR absorption band around 1745 cm⁻¹ corresponds to the C=O stretching in the ester carbonyl group in triglyceride moiety in vegetable oil, a broad peak at 3437.9 cm⁻¹ corresponds to the -OH group present in the castor oil (ricinoleic acid). Epoxydized vegetable oils produce a new absorption around 822 cm⁻¹ and 845 cm⁻¹ which indicate the presence of epoxy ring. The ring opened products have absorption ranging from 1738 cm⁻¹ to 1740 cm⁻¹ for the ester C=O group in the ring opened epoxydized vegetable oils. Broad absorption ranging from 3420 cm⁻¹ to

3450 cm⁻¹ was responsible for the -OH group in the ring opened product. Completion of ring-opening reaction was confirmed by checking the disappearance of epoxy signals at 1158, 845 and 822 cm⁻¹ in the IR spectrum. As seen in Supporting Information (Figure 1), the FTIR spectrum of ECO + isodecanol is presented as a representative of the ring opened products.

The ¹H NMR data of the epoxydized vegetable oils exhibited the presence of secondary and primary glycerol proton at δ 5.10-5.20 and 4.10-4.30 respectively. The proton signal centered at δ 3.0 is evident for the presence of epoxy protons. This is further substantiated by the disappearance of the olefinic proton signals in the region between δ 5.34-5.43. The broad intense signal observed in the region δ 1.26-

Analysis of thermal stability by TGA data

TGA data (Table 3) clearly supported that the prepared products were thermally more stable than the mineral base oil. Lower PWL value (Permanent weight loss) indicates higher thermal stability. It is clearly found that the percentage of degradation of the ring opened products of the vegetable oil epoxides at a particular temperature is lower compared to the mineral base oil. This observation simply implies that chemically modified vegetable oils are far resistant against thermal degradation than the mineral base oil under consideration. At 473 K mineral base oil degrades almost completely (PWL 98) whereas the chemically modified vegetable oils degrade almost completely (PWL around 90) above 600K. From this point of view these chemically modified vegetable oils are more reliable as lubricant base stock.

Performance evaluation in respect of pour point

From Table 4 data it is observed that ring opening product of ELSO with 2 ethyl hexanol, isodecanol; and ECO, EOLO, ESBO, ESFO with isodecanol exhibited better low temperature flow. This may be attributed to the morphology of the branched alcohol moiety that hinders the formation of wax crystal network. This result implies that at lower temperature these chemically modified vegetable oils are easier to handle than the mineral base oil.

Analysis of VI data

Viscosity may be the most important parameter for lube oil. Vegetable oil has fare viscosity index (Table 1) but due to the low thermooxidative stability they can't be directly used as lubricant. After modification of vegetable oils, they can be considered for comparison with mineral oil. Table 5 indicates

the possibility of using them as lube base stock. These data sought for the utilisation of chemically modified vegetable oils over a broad temperature range since they can sustain their viscosity at elevated temperature quite well.

Analysis of antiwear performance

The tribological properties of the lubricant compositions at different mass fractions were determined by measuring WSD values (Wear Scar Diameter) through FBWT apparatus. By analysing Table 6 data it is evident that the modified vegetable oils produce less wear in engine condition. The chemically modified vegetable oils strengthen the film through chemical and physical bonding between polar functional groups and metal atoms on the metallic surface. Due to the presence of long polar fatty ester chains, these oils showed better AW property compared to the mineral base oil. Due to polar -OH groups, the ring opened products form comparatively stronger bonds with metal atoms and exhibit better AW property. Among all the chemically modified vegetable oils under consideration, ring opened product of castor oil epoxide exhibited the best result in terms of antiwear performance.

Conclusions

Epoxidation followed by ring opening reaction with suitable alcohols have provided an efficient and easy route towards formation of vegetable oil based biodegradable and thermally stable lubricant base stock with better low temperature flow, viscometric properties and antiwear performance. These chemically modified vegetable oils can be used directly or in a mixture with mineral base lube for better performance. The above study accounts for the replacement of toxic mineral base oil with environment friendly,

biodegradable greener vegetable oil-based products as lubricant base stock.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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