Journal of Bio- and Tribo-Corrosion (2021) 7:157
https://doi.org/10.1007/s40735-021-00593-6

Rheological and Tribological Behavior of Sunflower Oil: Effect of Chemical Modification and Tungsten DiSulfide Nanoparticles

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Received: 18 March 2021 / Revised: 8 September 2021 / Accepted: 3 October 2021 / Published online: 12 October 2021

Abstract
This paper aims to evaluate the tribological characteristics of WS_2 nanoparticles in modified sunflower oil. The modification is done by epoxidation method in order to decrease the unsaturation of the sunflower oil. Further, tungsten disulfide (WS_2) nanoparticles were added in modified sunflower oil to evaluate its effect on the rheological and tribological properties. The nanoparticles were added in 0.5 wt% and 1 wt% concentrations. The experimentation was performed on pin-on-disk tribometer with liquid metal alloy/steel contact pairs. The rheological properties were obtained with varying shear rates from 1 to 1000 1/s. Stribeck curves were generated for virgin sunflower oil, modified sunflower oil and the modified oil containing nanoparticles in mixed and boundary regimes. The modified sunflower oil results in better lubrication characteristics as compared to virgin oil. The improvement is attributed to the formation of oxirane linkage (–O–) between carbon atoms to form epoxide which leads to the formation of a stable tribofilm. A further improvement in tribological properties was observed with the addition of nanoadditives in the oil. Scanning Electron Microscopy (SEM) analysis is performed to identify the wear behavior of pin samples. It was observed that 0.5 wt% WS_2 is effective in reducing friction and wear. This is due to the lamellar structure of WS_2 nanoparticles that leads to the formation of smooth tribofilm at the interface.

Keywords Sunflower oil · Rheology · Nanofluids · Lubrication

Abbreviations

ASTM	American Society for testing and materials
CMRO	Chemically modified rapeseed oil
COF	Coefficient of friction
MSO	Modified sunflower oil
ND	Nanodiamond
PAO	Poly alpha olefin
PTFE	Poly tetra fluoro ethylene
SEM	Scanning electron microscopy
VSO	Virgin sunflower oil
WS_2	Tungsten disulfide

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1 Introduction

The importance of energy has been realized ever since the human civilization came into existence. The demand for energy has increased with the rising population, as a result of which strict standards have been brought to limit the depletion of non-renewable resources [1]. Excessive use of natural resources leads to ecological imbalance, thus affects the environment [2]. The engineering machinery in general and the automobile sector in particular heavily relies on lubricants for smooth and efficient working of machine parts, where sliding pairs are in contact with each other. Both friction as well as wear leads to energy losses and results in decreasing the effectiveness of machines and automobiles at a large [3]. The carbon emissions released from the burning of natural resources are increasing day by day leading to a climate change and global warming [4, 5]. Hence, considering the sustainability issues, the demand for eco-friendly and sustainable lubricants has been realized by researchers and lubrication engineers across the globe.

In the recent past, a lot of research has been done to evaluate the different properties of vegetable oils and other available commercial oils. Table 1 gives the details of basic

Table 1 Properties of mineral oils and vegetable oils [6, 9]

S. No	Properties	Mineral oil	Vegetable oils
1	Density	0.8–0.9 g/cm^3	> 0.9 g/cm^3
2	Viscosity Index	95–105 °C	200–260 °C
3	Flash point	200–300 °C	300–350 °C
4	Pour point	0 to − 60 °C	− 9 to − 21 °C
5	Oxidation stability limit	100–150 °C	Low
6	Biodegradability	30–40%	90–98%
7	Thermal conductivity	0.11–0.16 W/m/K	0.16–0.17 W/m/K
8	Specific heat	1.6–2.0 J/g/K	1.5–2.1 J/g/K

properties of different oils and Table 2 gives the COF of different oils under various conditions. Sajeeb et al. [6] studied the thermophysical, tribological and thermo-oxidative stabilities of coconut oil, mustard oil, and mineral oil. It was observed that the onset temperature for coconut, mustard and mineral oil is equal to 300, 334, and 290, respectively, indicating higher effectiveness of bio-oils than mineral oil. The effectiveness of mustard oil is attributed to the longer chain length present in the oil. However, the pour point of mineral oils is higher in comparison to the bio-oils. Sabarinath et al. [7] compared the physiochemical, thermo-oxidative and tribological properties of sesame oil and SAE20W40. The thermo-oxidative studies reveal that the sesame oil depicts better thermal stability but poor oxidation stability in comparison to the SAE20W40. The thermal degradation of the sesame oil and SAE20W40 begins at 295.48 C and 204.39 C, respectively. The oxidation onset temperature for the sesame and SAE20W40 is found to be equal to 182.79 °C and 277.38 °C, respectively. Cermak et al. [8] investigated the thermal, rheological, oxidative and tribological properties of commercially available petroleum-based lubricants and crop oils (pennycress, cuphea, lesquerella and meadow foam). The oxidative properties are determined by rotating pressurized vessel oxidation test (RPVOT) following ASTM 2272-98. The results from the RPVOT tests are depicted in Table 3. It is observed that commercially available lubricants depict higher oxidation stability in comparison to the bio-oils. It is concluded that the chemical modification and the use of antioxidants is a must for the application of bio-oils as lubricants at higher temperatures.

Vegetable oils possess excellent physical properties and can be further improved by transesterification,

Table 3 RPVOT values for commercially available lubricants and bio-oils [8]

S. no	Type of oil	Average time (min)
1	Aeroshell 15 W-50	552
2	Castrol synthetic 10 W-30	246
3	Valvoline 5 W-30	228
4	Valvoline SAE 30	224
5	Valvoline 10 W-30	223
6	Valvoline 20 W-50	214
7	Valvoline 10 W-40	224
8	Canola RBD + 1% lubrizol	19
9	Castor RBD 1% lubrizol	68
10	Cuphea RBD 1% lubrizol	53
11	Cuphea RBD + purified 1% lubrizol	155
12	Meadowfoam RBD 1% lubrizol	139
13	Meadowfoam RBD + purified 1% lubrizol	169
14	Soybean RBD 1% lubrizol	19
15	Pennycress RBD 1% lubrizol	26

Table 2 Frictional coefficient of bio-oils and commercial lubricants at different experimental conditions [10–12]

S. no	Type of oil	Testing parameters	COF
1	Double fractionated palm oil	1–5 m/s, 50 N and 100 N	0.01–0.025,
2	SAE 40	1–5 m/s, 50 N and 100 N	0.009–0.027,
3	Hydraulic oil	1–5 m/s, 50 N and 100 N	0.04–0.1
4	Coconut oil,	1200 rpm, 392 N, 75 °C, 3600 s	0.088
5	Mustard oil,	1200 rpm, 392 N, 75 °C, 3600 s	0.118
6	SAE20W40	1200 rpm, 392 N, 75 °C, 3600 s	0.102
7	Chaulmoogra oil	1200 rpm, 392 N, 75 °C, 3600 s	0.0588
8	Sunflower oil	1200 rpm, 392 N, 75 °C, 3600 s	0.0611
9	SAE20W50	1200 rpm, 392 N, 75 °C, 3600 s	0.08
10	Mineral oil	20 Hz, 10 N, 3600 s	0.104
11	Soybean oil	20 Hz, 10 N, 3600 s	0.053
12	Sunflower oil	20 Hz, 10 N, 3600 s	0.051
13	SAE15W40	0.52–3.14 m/s, 1.95–3.95 MPa	0.1
14	500 N base oil	150 N, 200 rpm, 75 °C	0.099
15	Coconut oil	150 N, 200 rpm, 75 °C	0.092

dimerization, epoxidation and the use of antioxidants [1]. The most commonly and widely adopted method is epoxidation in which acetic acid and hydrogen peroxide is used to form peracetic acid. The in situ formed peracetic acid is used to chemically modify the unsaturated structure in order to form epoxide having –O– linkage [13]. The tribological properties of oils can be further improved by the addition of nanoparticles. The use of nanoadditives has increased over the past few decades mainly because of their anti-friction and anti-wear properties [13]. Some of the previous studies suggest the tribological properties of various vegetable oils such as soybean, canola, avocado, olive, coconut, rapeseed, and palm oil can be improved with the addition of different nanoparticles. The various nanoparticles include Cu, h-BN, CuO, CeO_2, and MoS_2 [14, 15].

In this regard, Xu et al. [16] reported that the addition of 1 wt% MoS_2 nanoparticles in rapeseed oil led to the substantial decrease in COF when compared to base oil. In a similar study, Raina et al. investigated the lubrication performance of PAO oil containing Nano diamond (ND) using MoS_2 and WS_2 nanoparticles [17]. Authors reported that with the use of hybrid MoS_2/ND and WS_2/ND oils the COF and wear volume is almost halved in comparison to the base oil. The results obtained therein were ascribed to the polishing effect of ND which reduces the actual contact area between tribopairs. Further, exfoliation of nanoparticles results in shearing of nanoadditives layers leading to the formation of tribofilm. Koshy et al. [10] investigated the effect of MoS_2 nanoparticles on the tribological properties of coconut oil and paraffin oil, wherein it was observed that 0.53 wt% and 0.58 wt% concentration of MoS_2 nanoparticles resulted in minimum COF and wear.

Kashyap and Harsha [18] investigated the lubrication performance of chemically modified rapeseed oil mixed in different concentrations of CuO and CeO_2 particles. The authors reported that the frictional coefficient of the CMRO is lesser when compared to base oil due to the formation of oxirane ring. The frictional coefficient further resulted in a decrease with the addition of CuO and CeO_2 particles. The minimum COF was obtained with CuO nanoparticles for 0.5 wt% concentration in deoxidized rapeseed oil and for CeO_2, lowest COF was obtained at 0.1 wt% concentration. As reported by the authors this, behavior is due to the change in the nanolubrication mechanism from sliding to rolling between the friction pairs. Gupta et al. [19] investigated the effect of three nanoadditives viz CuO, CeO_2 and PTFE on lubricating properties of the rapeseed oil. The authors observed that concentration of 0.1% w/v is effective is reducing friction coefficient for all the three nanoparticles in epoxidized rapeseed oil. Further, PTFE gets adhered to the surface and forms a chemical film which reduces the COF. Reduction in wear scar diameter was due to the adherence capability of functional groups present in fatty acids of the modified oil.

Various studies pertaining to different nanoparticles with varying concentrations have been summarized in Table 4. It is evident that very less work has been carried out on sunflower oil primarily due to the manifestation of higher unsaturated fatty acid content. Based on the above discussion, the current study is focused to evaluate the rheological and tribological properties of epoxidized sunflower oil with and without the use of WS_2 nanoparticles in 0.5 wt% and 1 wt% concentrations.

2 Methodology and Materials

2.1 Bio-Lubricant and Nanoparticles

The bio-lubricant used in the study is sunflower (*Helianthus annuus*) oil. The major fatty acid present in sunflower oil is Linoleic acid (ω-6) which constitutes about 58% of the oil. Sunflower oil possesses high degree of unsaturation and these sites of unsaturation can be easily exploited using various chemical modification methods. Table 5 enlists various properties of sunflower oil used in this study. The lubricating properties of the sunflower oil in boundary lubrication regime are further enhanced with the use of WS_2 nanoparticles with varying concentration of 0.5 wt% and 1 wt% concentration. WS_2 nanoparticles owing to their lamellar structure having film formation capability were selected with an aim to minimize the coefficient friction and wear. The nanoparticles were procured from M/s Sigma-Aldrich, Bangalore and the size was of the order of 60 -90 nm. The nanoparticles possess layer-like structure and gets sheared upon the application of load. The nanoparticles get adhered to the surface resulting in the formation of a stable tribofilm. WS_2 nanoparticles were mixed in sunflower oil using bath type ultrasonicator for 8 h to obtain homogenous dispersions. Figure 1 gives the illustrative image of the oil comprising nanoparticles mixed with different concentrations of WS_2.

2.2 Chemical Treatment of Sunflower Oil

Most of the biolubricants are susceptible toto oxidation due to the presence of unsaturation. There are numerous approaches to augment the oxidation stability of oils such as epoxidation, transesterification, dimerization and use of antioxidants. In this study, epoxidation is performed in which C=C double bonds are converted into oxiranes (−O−) which tends to increase the oxidation stability of the oils. Peracetic acid is formed by the reaction of acetic acid and hydrogen peroxide in the ratio of 1:3. The desired amount of sunflower oil is added to peracetic acid in a beaker and then placed on a magnetic stirrer to ensure the complete mixing. The solution is kept at 500 rpm with

Table 4 Summary of the different studies containing nanoparticles with different concentrations

Lubricating oil	Setup/sliding pair	Nanoparticle	Concentration	Key observations
Rapeseed oil [16]	Four ball tribometer/steel–steel	MoS_2	0.5, 1.0, 1.5, 2.0 wt%	Minimum COF with 1 wt% Around 22% reduced WSD is obtained with 1 wt% MoS_2 as compared to pure Rapeseed oil
PAO [17]	Ball on disk/steel–steel	MoS_2, WS_2, nano diamond (ND)	0.2, 0.5 wt%	0.2 wt% conc. MoS_2/ND and WS_2/ND resulted in lowest friction coefficient when compared with pure oil For 20 N and 100 N load, 81.02% and 70.7% reduction in wear volume is obtained with MoS_2/ND
Coconut oil, Paraffin oil [10]	Pin-on-disk and four ball tester/aluminum alloy–steel	MoS_2	0.25, 0.50, 0.75, 1.0 wt%	For coconut oil and paraffin oil, 0.53% and 0.58 wt% MoS_2 proved to be an optimum conc. for reduced COF due to the formation of tribofilm Surface topography by AFM indicates the smoother surface roughness of the pin Around 110% and 54% increase in viscosity for coconut and paraffin oil with MoS_2 nanoparticles at 75 °C
Rapeseed oil [18]	Four ball tester/steel–steel	CuO, CeO_2	0.1, 0.2, 0.5, 0.8, 1.0 wt%	Lowest COF is obtained with 0.5 wt% CeO_2 and 0.1 wt% CuO Chemically modified rapeseed oil shows good anti-wear properties as compared to raw oil due to the presence of polar groups resulting adsorption and effective film formation
Rapeseed oil [19]	Four ball tester/steel–steel	CuO, CeO_2, PTFE	0.1, 0.25, 0.5% w/v	0.1 wt% conc. of CeO_2 and PTFE resulted in remarkable improvement in anti-wear property of Rapeseed oil Improvement in weld load capacity at 0.5% w/v of CuO and 0.25% w/v for CeO_2 For PTFE, none of the concentrations improved weld load capacity
Avocado oil [20]	Pin-on-disk tribometer/aluminum alloy–steel	Cu	0.5, 1.0 wt%	For a specific film thickness of 2.3 in mixed lubrication regime, minimum COF is observed for both the concentrations Least specific wear rate is obtained with 0.5 wt% Cu at 500 rpm speed SEM images revealed that with 0.5 wt% Cu, much smooth pin surface is obtained which is due to adhesive action of asperities
Olive oil [21]	Pin-on-disk tribometer/LM 13 alloy–Steel	Cu, h-BN	0.5, 1.0 wt%	For 0.5 wt% Cu and h-BN, least COF is obtained. It is due to the tribofilm forming capability of Cu and lamellar structure of h-BN nanoparticles For 0.5 wt% conc. of h-BN, least wear is obtained. But for 1 wt% conc. accumulation of nanoparticles acting as a barrier for lubricant resulting in increased wear which can be seen from SEM images

Table 5 Properties of sunflower oil

Properties	Sunflower Oil
Major fatty acid concentration (% age)	
Oleic acid (ω-9)	29.3
Linolenic acid (ω-3)	0.1
Linoleic acid (ω-6)	58.3
Relative density (g/cm$^{3)}$	0.91–0.93
Kinematic viscosity (at 20 °C) (mm^2/s)	33.9
Flash point (°C)	274
Iodine value	118–144

Fig. 1 Representative images of the modified oil containing 0.5 wt% WS_2 and 1 wt% WS_2

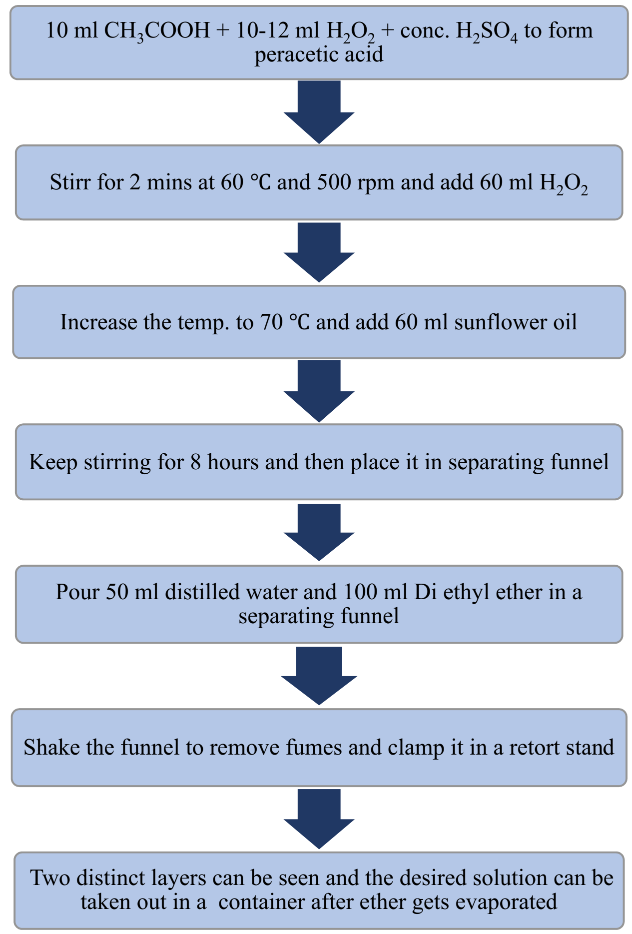
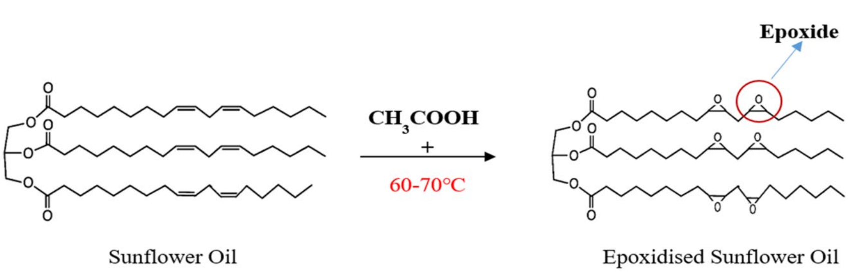


Fig. 2 Flow diagram representing the epoxidation of sunflower oil

temperature varying from 60 to 70 °C. The oil is then dissolved in di ethyl ether in a separating funnel to remove the unwanted solution from the epoxidized oil. The addition of di ethyl ether results in the formation of two layers. The bottom layer contains the unwanted solution (water, hydrogen peroxide and acetic acid), whereas the top layer is the epoxidized oil. Being volatile in nature, the di ethyl ether is then allowed to evaporate leaving the complete epoxidized oil with no impurities. Figure 2 gives the step by step method for the epoxidation of the oil and the chemical reaction [19] involved is shown below.



(1)

Table 6 Mechanical properties of Pin and Disk material

Properties	LM 13 Al alloy	EN-31 steel
Tensile strength	250 N/mm^2	750 N/mm^2
Yield stress	–	450 N/mm^2
Modulus of elasticity	70,000 N/mm^2	210,000 N/mm^2
Density	2700 kg/m^3	7800 kg/m^3
Hardness	100 HRB	63 HRC
Poisson's ratio	0.33	0.3

2.3 Tribopair

The pins were prepared from LM 13 Aluminum alloy, whereas the disks were made up of EN-31 steel. The tribopair used in the study find sits use in variety of automobile applications such as gears, connecting rods, and piston cylinder arrangement. Table 6 shows the properties of both the tribomaterials used in the study. The as received material was cut with hand hacksaw in square shapes. Thereafter, turning operation was performed on Lathe machine to form 8 mm cylindrical pins having length of 16–20 mm. The taper turning of the pins is further carried out to achieve the spherical shape at the end of the pin. The spherical shape of pins ensures the point contact geometry at the surface of tribopairs. Emery papers of different grades (200–1500) were used to obtain the polished surfaces. The disk used in the experimentation was the inbuilt disk available with the tribometer having 160 mm diameter and 15 mm thickness. The disk was polished before the start of every experiment using the emery papers of different grades followed by nano diamond polishing and cleaning with acetone in order to ensure that no foreign particles are present on the surface. Since, the hardness of the steel disk is much more than the hardness of the pins, thus no or very less damage on the surface of disk is possible and therefore the wear volume was obtained as per ASTM G-99 standards.

2.4 Experimentation

Tribological tests were conducted on a pin-on-disk tribometer (DUCOM, India) as per ASTM G-99 standards. Figure 3 shows the schematic drawing of the experimental setup used in the study. The inbuilt load cell in the tribometer measures the friction force and then the COF can be calculated by normalizing the friction force by the applied load. Wear was evaluated by calculating the mass loss from the spherical ended pins. The wear scar diameter was obtained using the optical microscope and the mass was theoretically obtained using Eq. 2 as per the ASTM G-99 standards. Tests were performed so as to obtain the Stribeck curve for boundary and mixed lubrication regimes. The Stribeck curve was obtained using the Hamrock and Dowson's equation [22]. The different parameters were selected in such a way that the

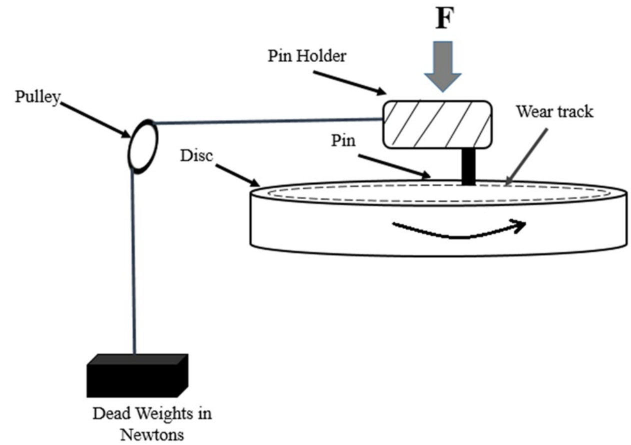


Fig. 3 Schematic diagram of Tribometer setup

Stribeck curve for boundary and mixed lubrication regimes can be obtained. The detailed testing conditions are given in Table 7. The tests were conducted for a sliding distance of 500 m.

$$W = \frac{1}{3}\pi h^2(3R - h) \tag{2}$$

where

$h = R - \sqrt{R^2 - r^2}$, r is the radius of wear scar, h is the height of worn surface and R is the radius of ball.

The rheological behavior of oils was determined on cone and plate geometry of the Anton Pars Rheometer (MCR 102). The diameter of the plate geometry is 40 mm with cone angle of 1 degree. The rheological behavior of the oils and nanofluids was determined at a temperature of 40 °C and 100 °C with variable shear rates of 1–1000 1/s. Further, the effect of nanoparticles on the dynamic viscosity and the flow behavior of the modified sunflower oil was also investigated. The testing temperatures are selected as 40 °C and 100 °C in order to determine the viscosity index of the

Table 7 Different testing conditions

Load (N)	Speed (rpm)	Sliding velocity (m/s)	λ
100	100	0.1830	0.392
80	100	0.1830	0.411
60	100	0.1830	0.437
40	100	0.1830	0.475
20	100	0.1830	0.550
10	100	0.1830	0.636
10	200	0.3665	0.999
10	300	0.5495	1.300
10	400	0.7330	1.568
10	500	0.9165	1.830

nanofluids in accordance with ASTM 2270. Viscosity index determines the change in viscosity with increase in temperature. Bio-oils have higher viscosity index than the mineral oils indicating lesser decrease in viscosity with increase in temperature. Lubricants with low V.I can depict suitable viscosity at a particular temperature but the viscosity can decrease considerably with increase in temperature. Mineral oils have V.I around 100, whereas vegetable oils have V.I even greater than 200.

2.5 Surface Analysis

The worn out surfaces of pin samples were investigated using Scanning Electron Microscopy (SAI Labs, Thapar Institute of Engineering & Technology, Patiala, Punjab). The pins were examined at different magnifications and the obtained images were evaluated in order to understand the type of wear mechanism involved.

3 Results and Discussion

3.1 Viscosity Measurement and Flow Behavior

Figure 4 depicts the relationship of dynamic viscosity with varying shear rate for modified Sunflower oil mixed with WS_2 nanoparticles. It can be observed that dynamic viscosity of MSO at both the temperature (40 °C and 100 °C) and concentrations (0.5 wt% and 1 wt%) is nearly independent of the shear rate. However, increase in the dynamic viscosity of the oils is observed with an increase in concentration of nanoparticles. The maximum viscosity was seen at a particle

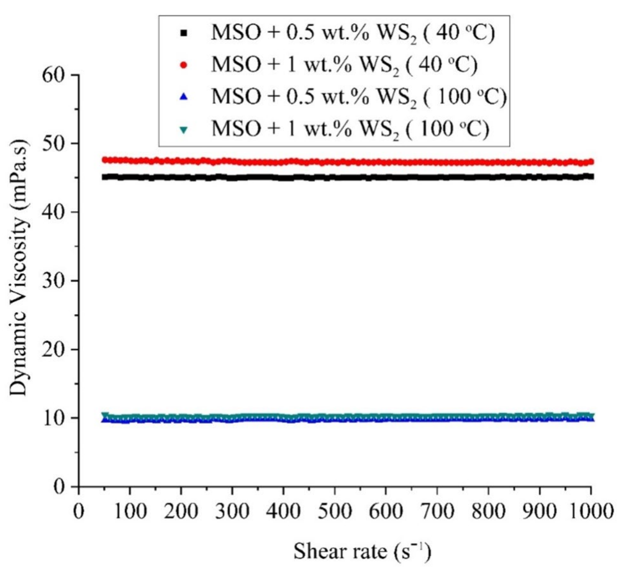


Fig. 4 Variation of Viscosity with shear rate for modified sunflower oil containing WS_2 at 40 °C and 100 °C

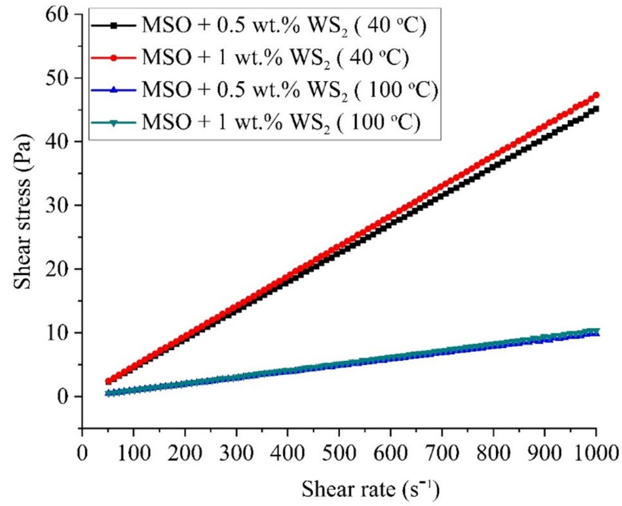


Fig. 5 Shear Stress corresponding to Shear rate for modified sunflower oil containing WS_2 at 40 °C and 100 °C

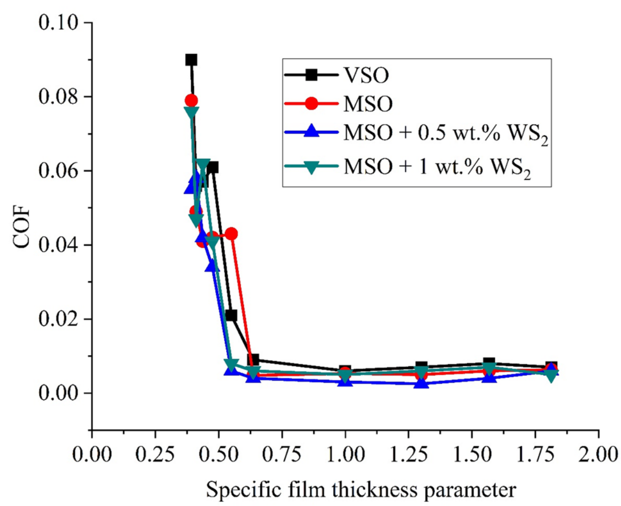


Fig. 6 Stribeck curve for sunflower oil containing WS_2 nanoparticles for LM alloy/steel contact

conc. of 1 wt%. Similar, results have been reported by various studies carried out in the recent past suggesting that particles remain in the layers of lubricating oil which increases the viscosity of oil [23]. Agglomeration of nanoparticles also have an impact on the viscosity. Higher particle concentration increases the agglomeration and sedimentation rate which consequently increases the viscosity of oils [24].

The flow behavior of nano lubricants can be observed from Fig. 5. Figure depicts the variation of shear stress with shear rate. It can be observed that the shear stress has linear relationship with shear rate. This implies that the developed nanolubricants exhibit the Newtonian behavior. Further, it can also be seen that shear stress increases with the increase in concentration of nanoparticles and maximum shear stress was observed for 1 wt% of WS_2 nanoparticles.

3.2 Stribeck Curve

The Stribeck curve obtained for all the oils can be seen in Fig. 6. It can be observed from the Figure that VSO exhibits its maximum COF for both the lubrication. The maximum COF is observed at the lowest values of λ and is equal to 0.392, whereas the minimum COF is observed just at the transition point of boundary and mixed lubrication regime at a λ of 0.997. The measured COF at $\lambda = 0.997$ is equal to 0.006. The COF in the mixed lubrication remains nearly constant. Figure also depicts the variation of COF with varying specific film thickness parameter. It was observed that MSO performs better than the VSO at each specific film thickness. The minimum COF of 0.005 with MSO was observed at λ equal to 1.3, whereas the maximum COF of 0.079 for MSO was observed at λ equal to 0.392. The maximum improvement in COF using MSO was observed in the boundary lubrication regime. This can be attributed to the protective film formation comprised of oxirane rings between C and C atoms.

Figure 6 further depicts the effect of nanoparticles on the COF. It can be observed from the figure that 0.5 wt% WS_2 nanoparticles mixed with MSO are effective in improving the COF in both boundary and mixed lubrication regimes. The COF of MSO and MSO + 1 wt% are very comparable in the boundary and mixed lubrication regime. The maximum COF observed with 0.5 wt% WS_2 is equal to 0.055 at $\lambda = 0.392$ which is 30.4% lesser than the COF observed with MSO. For same value of λ, 1 wt% WS_2 nanoparticles led to reduction of 3.8% when compared to MSO. The minimum value of COF observed with 0.5 wt% and 1 wt% is equal to 0.0025 and 0.005, respectively. It can be concluded that 0.5 wt% of WS_2 nanoparticles are most effective in reducing the COF for the modified sunflower oil.

3.3 Frictional Behavior

Figure 7 depicts the frictional behavior for VSO, MSO, MSO + 0.5 wt% WS_2 and MSO + 1 wt% WS_2 at a load of 40 N and 100 rpm. It can be observed that VSO depicts the maximum COF among all the samples. Also, the variation in COF over a period of time indicates that VSO is unable to form a stable film on the contact surfaces thereby resulting in the increased COF. However, a stable curve with less COF was observed with MSO, which indicates the effectiveness of epoxidation of sunflower oil. The frictional curve in this case remained stable throughout the number of cycles except a sharp peak which was observed after 500 number cycles. The abrupt peak may be attributed to the film breakdown caused by the wear debris at the interface. However, the epoxidation process increased the film formation capacity of VSO leading to the improved tribological performance [20].

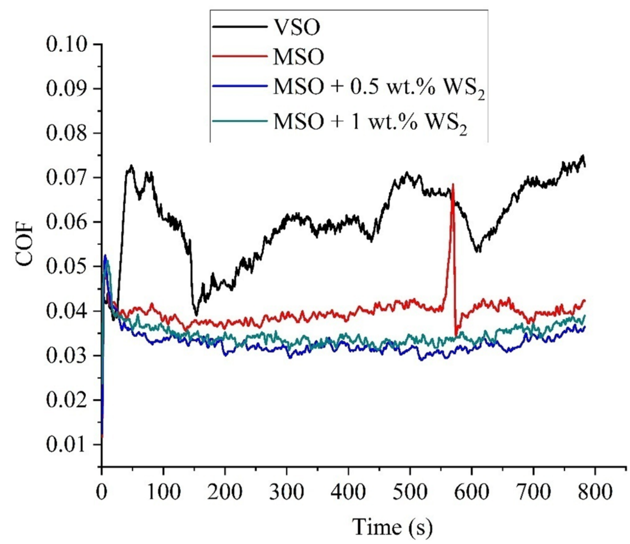


Fig. 7 Frictional characteristics of epoxidized oil mixed with nanoparticles at 40 N load and 100 rpm

The addition of nanoparticles further improved the lubricating performance of MSO with 0.5 wt% WS_2 depicting lesser COF than the VSO and MSO. The frictional curve showed a slight increase in the value of COF at the start. However, after 100 number of cycles, the steady-state condition was attained and curve remained stable thereafter. The average COF at 0.5 wt% WS_2 is equal to 0.033. The improved performance is attributed to the film formation capability of WS_2 nanoparticles. A similar behavior was also observed for the oil containing 1 wt% of WS_2 nanoparticles. The steady-state condition in this case was also attained after 100 number of cycles and no abrupt behavior or sharp peak was observed in the steady-state region. The average COF was comparatively more than the previous case. This may be attributed to the resistance being offered by the amplified conc. of nanoparticles due to the rise in viscosity of oils.

3.4 Effect of Speed on Coefficient of Friction

The effect of varying speeds on the COF for VSO, MSO, MSO + 0.5 wt% WS_2 and MSO + 1 wt% WS_2 is depicted in Fig. 8. The speeds are varied from 100 to 300 rpm at a constant load of 10 N. It can be observed from Fig. 8 that the increase in sliding speed decreases the COF for all the samples. However, the addition of WS_2 nanoparticles reduces the COF significantly at 0.5 wt% at all speeds as compared to VSO and MSO. The frictional coefficient for MSO + 0.5 wt% WS_2 is reduced by 16.6%, 43.3%, and 50% at 100, 200, and 300 rpm, respectively, in comparison to MSO without

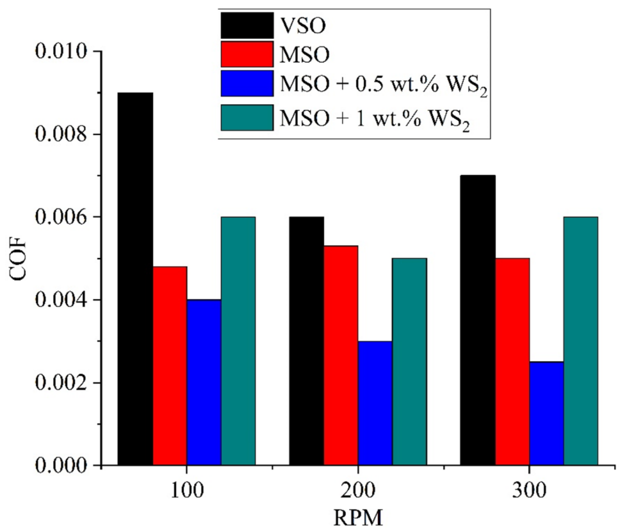


Fig. 8 Effect of speed on coefficient of friction for sunflower oil mixed with WS_2 nanoparticles

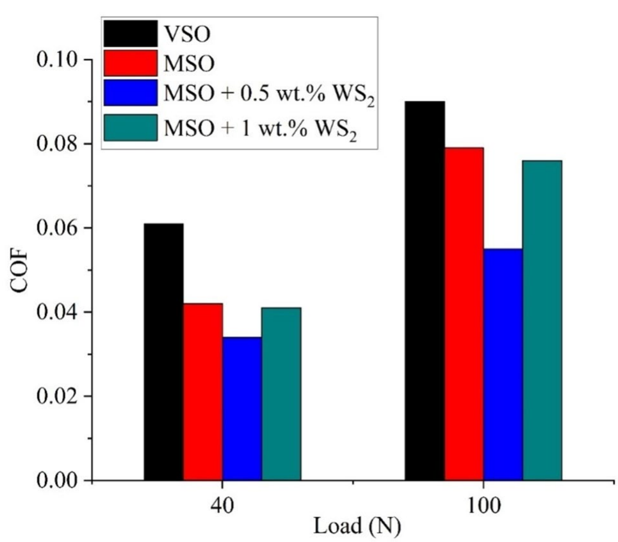


Fig. 9 Effect of load on coefficient of friction for sunflower oil mixed with WS_2 nanoparticles

nanoparticles. The reduction in friction at 0.5 wt% WS_2 in comparison to the VSO is equal to 55.5%, 50% and 64.2% at an rpm of 100, 200, and 300, respectively. This is due to the easy shearing of WS_2 nanoparticles under the application of load which leads to the adherence of WS_2 nanoparticles on the contacting surfaces that results in the formation of tribo-film at the interface [25]. Contrary to this, 1 wt% concentration of WS_2 nanoparticles are not much effective in minimizing the COF of MSO. This may be due to the agglomeration of WS_2 nanoparticles which leads to an increase in frictional resistance. However, the COF at 1 wt% nanoparticles is still lower than the VSO by 33.3%, 16.6%, and 14.3% at an rpm of 100, 200, and 300, respectively.

3.5 Effect of Load on Coefficient of Friction

The variation of COF with load (40 N and 100 N) is shown in Fig. 9. It can be observed that COF increases with an increase in load for all the oils. It can be seen from the figure that VSO depicts higher COF in comparison to the MSO. The epoxidation of VSO improves the COF by 31% and 12% for a load of 40 N and 100 N, respectively. A further improvement was observed with the oil containing 0.5 wt% WS_2 nanoparticles, whereas a decrease of 44% and 35% was observed for a load of 40 N and 100 N, respectively, with respect to the VSO. However, MSO + 1 wt% WS_2 depicted lesser improvement at both the loads but the recorded COF were still lower that the values observed for MSO.

3.6 Wear Behavior and Surface Analysis

The wear volume obtained corresponding to different speeds is shown in Fig. 10. It can be observed that there is a decrease in wear loss with the increase in sliding speed in case of the modified oil. However, an increase has been observed for virgin oil. It can also be observed that the modified oil resulted in minimum wear loss corresponding to all the speeds in comparison to the virgin oil. The addition of nanoparticles resulted in the further decrease in the wear loss and minimum wear loss was observed for 0.5 wt% WS_2 nanoparticles. This kind of pattern was also obtained from the scanning electron microscopic analysis.

Figures 11 and 12 show the SEM images of worn surfaces. Figures 11a and 12a represent the worn out image

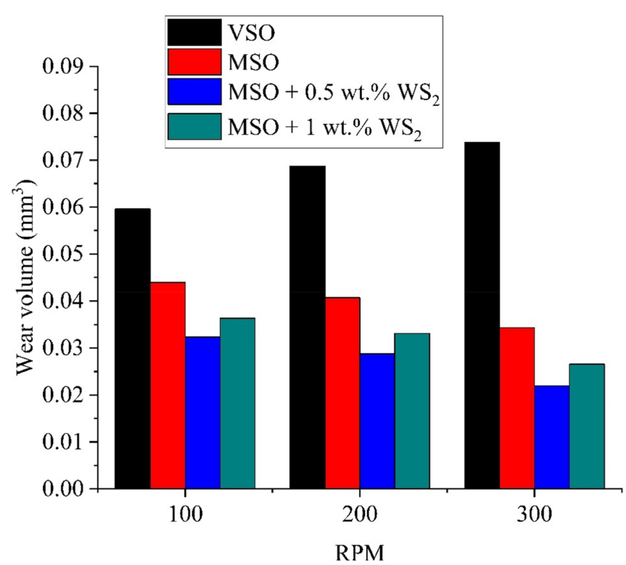


Fig. 10 Wear volume corresponding to different speeds

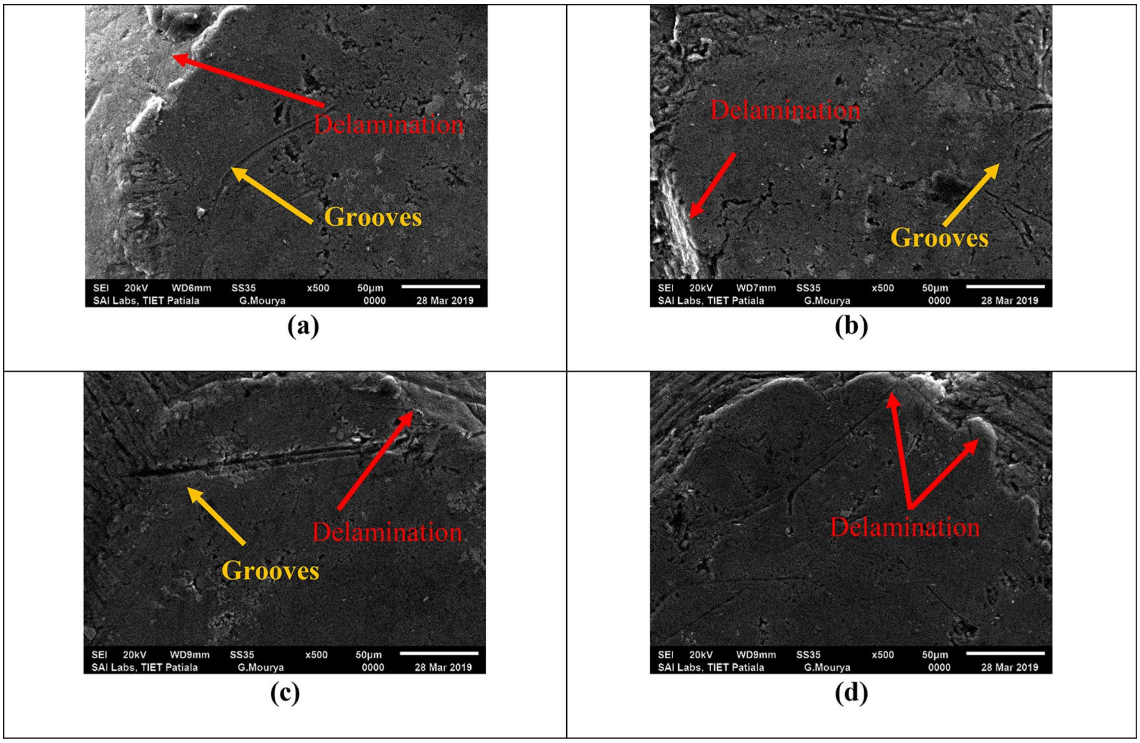


Fig. 11 SEM images of worn out samples corresponding to 10 N load at 300 rpm and at 500X for, **a** VSO, **b** MSO, **c** MSO + 0.5 wt% WS_2 and **d** MSO + 1 wt% WS_2

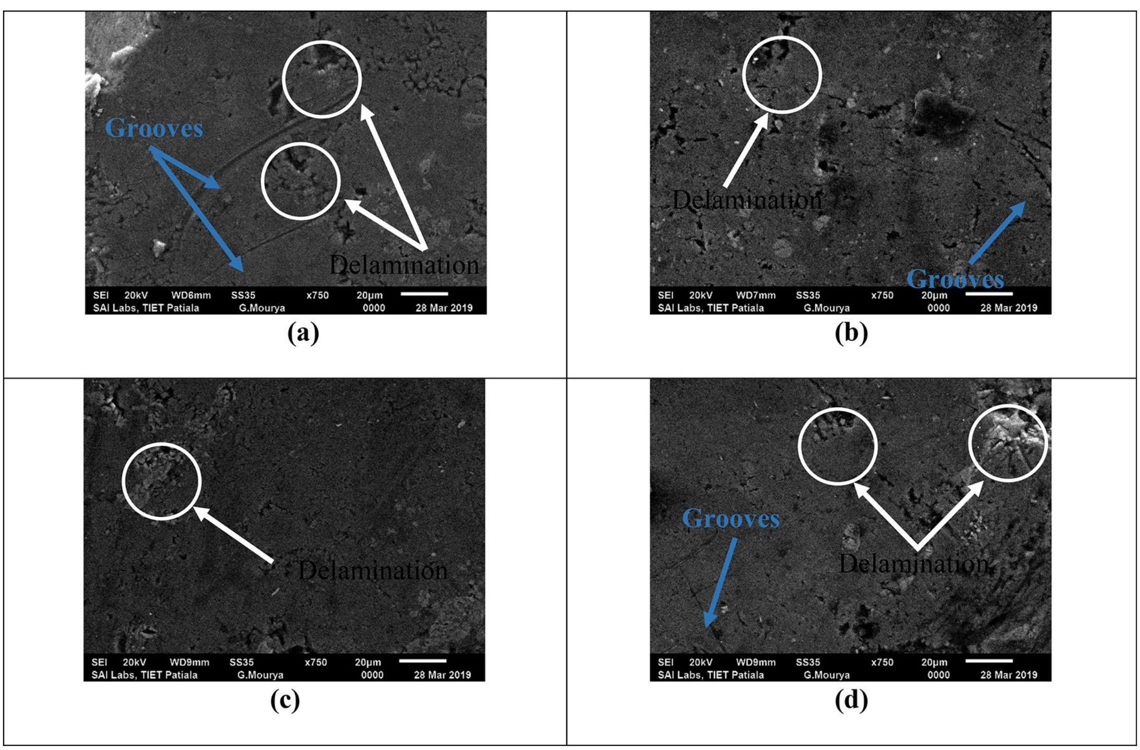


Fig. 12 SEM images of worn out samples corresponding to 10 N load at 300 rpm and at 750X for, **a** VSO, **b** MSO, **c** MSO + 0.5 wt% WS_2 and **d** MSO + 1 wt% WS_2

of VSO and it can be seen that the wear is mainly due to delamination of surfaces. This behavior may be due to the adhesion of asperities at the interface. Also, small grooves showing the abrasive wear can be observed on the surface of the material. Figures 11b and 12b show the worn surface of pin samples using MSO. The wear in this case is also evident, but in comparison to Figs. 11a and 12a, a less damage on the pin surface can be seen. This behavior is due to the −O− cross-linkage on the surface which is very effective in reducing wear. However, in this case also some grooves can be seen. This formation of grooves in both the cases is ascribed to the abrasion caused by wear debris.

Figures 11c and 12c show the worn out sample for MSO + 0.5 wt% WS_2 and it can be observed that there is reduction in wear as compared to VSO and MSO as shown in Figs. 11a,b and 12a,b. This behavior can be attributed to the formation of tribofilm at the interface that leads to smoother pin surface. Moreover, the WS_2 nanoparticles having lamellar structure also help in reducing the surface damage. The wear in this case mostly due to the adhesion of asperities. The delamination of surfaces in bulk is also absent. Moreover, the presence of grooves is not evident with the use of 0.5 wt% WS_2 in the modified sunflower oil which suggests the role of nanoparticles in improving the wear behavior. However, in Figs. 11d and 12d for MSO + 1 wt% WS_2, adhesion with minute grooves can be seen. This is due to the plowing effect where combined scuffing leads to the removal of material. The wear in this case is more than the previous case (MSO + 0.5 wt%). The increased amount of WS_2 nanoparticles leads to the formation of a lubricant barrier, which further becomes a cause of material removal. The wear in this case is also due to the delamination of surfaces and is more than the previous case (MSO + 0.5 wt%). Thus, the addition of 0.5 wt% WS_2 nanoparticles in MSO led to minimum surface damage in comparison to VSO, MSO and the MSO containing 1 wt% WS_2 nanoparticles. In addition to this, the increase in load also leads to the increased surface damage due to easy damage of the lubricant film. Under low loading conditions, the protective film remains intact for longer time in comparison to the higher loads, thereby resulting in the less damage to the pin surface. The optimum concentration of the WS_2 nanoparticles further aids in the film formation for a quite long time due to its inherent characteristics. Thus, the experimentation revealed that the developed nanofluids could serve potential engineering applications and could help to achieve the goals of sustainable development.

4 Conclusion

The sunflower oil was successfully modified by carrying out the epoxidation method. The modified oil was then mixed with WS_2 nanoparticles in 0.5 wt% and 1 wt% concentrations. The rheological studies revealed that the developed oils with and without nanoparticles exhibited the Newtonian behavior. Tribological testing was carried out on a pin-on-disk tribometer. It was observed that there is a significant decrease in COF on the addition of WS_2 nanoparticles. The minimum COF was obtained with 0.5 wt% WS_2 nanoparticles at all the loads. This is due to the easy shearing of WS_2 nanoparticles on the application of load which minimizes the resistance offered by the sliding surfaces. Scanning Electron Microscopic analysis of the worn out samples revealed that virgin oil exhibited high surface damage as compared to its modified form with both the nanoparticles. It was observed that with 0.5 wt% WS_2 nanoparticles, the damage on surface was minimum. Further, the SEM analysis also revealed that the dominant wear mechanism in all the cases was adhesive wear. The study clearly suggests the role of chemical modification and nanoparticle addition in improving the rheological and tribological behavior for sustainable lubrication.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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