

## Effect of Saturated Fatty Acids on the Antiwear and Rheological Properties of Olive Oil

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Fatty acids  
Wear  
Viscosity  
SEM

### ABSTRACT

The study determines the effect of saturated fatty acids (coconut oil) on the rheological and tribological properties of olive oil. The olive oil is blended with different proportions of coconut oil (10%, 20%, 30%, 40%, and 50%) and the different properties (flow behaviour and antiwear) are studied on Anton Paars rheometer and Four-ball tester respectively. The study reveals that the blends depict Newtonian behaviour with a decrease in the dynamic viscosity of the olive oil. Also, WSD decreases at a higher proportion of coconut oil in the blends with an improvement of 10.74% at a 50:50 ratio. The blending of two oils for the enhancement of the lubrication properties of biolubricants can prove beneficial in making them a suitable replacement for mineral oils.

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## 1. INTRODUCTION

The replacement of petroleum-based oils has been studied extensively in recent years. One of the emerging candidates that can replace petroleum-based oils is bio-oils obtained from plant sources. Bio oils possess excellent lubricating properties like flash point, viscosity index, Fire point, and low toxicity. Further, the bio-oils also possess excellent biodegradability (90-98%) in comparison to petroleum oils [1]. However, the limitations that restrict their use as industrial lubricants are their poor thermo-oxidative properties. Bio oils are susceptible to oxidation at higher temperatures and thus modification needs to be done to make their use

as industrial lubricants. Various reports have suggested that poor oxidative properties of the bio-oils are attributed to their unsaturation [2]. The Unsaturation represents the number of double bonds in the fatty acid chain. The lubricating properties of the bio-oils are dependent on their fatty acid composition. The saturated fatty acids form strong protective films on the surface whereas the films formed by the polyunsaturated fatty acids are weaker in comparison to the saturated fatty acids [2].

Various studies have been conducted on the blending of oils to achieve satisfying lubrication properties. The blending of mineral oils with different vegetable oils has been studied by

various researchers. Jabal et al. [3] mixed palm oil with mineral oil in various blending ratios and reported that the blend of palm oil (40%) in mineral oil depicts minimum WSD of 375 $\mu$ m in comparison to 470  $\mu$ m with pure mineral oil. Bahari et al. [4] blended palm oil and soybean oil in mineral oil and reported an improvement in tribological properties equal to 25% and 27% respectively. Shahabuddin et al. [5] reported that the introduction of jatropha oil in commercial SAE40 results in an improvement in the tribological properties of SAE 40. The authors also concluded that there is an optimum blend ratio at which better lubricating properties are obtained. Loehle et al. [6] investigated the effect of different types of fatty acids (stearic acid, oleic acid, and linoleic acid) on the lubricating properties of PAO4. Authors reported that saturated fatty acid (stearic acid) depicts better lubrication properties in comparison to unsaturated fatty acids. Loehle et al. [7] further reported that the unsaturation in the oils result in the steric effect which leads to the incubation of coherent *monolayers*, consequently, increasing friction.

To develop a fully sustainable lubricant, the blending of the bio-oils has been studied more in recent years. Sajeeb et al. [8] blended coconut oil with mustard oil in blending ratios of 10-50%. Authors carried out tribological tests on four-ball tester and reported that blended oils possess better lubricating properties with blend ratios of 50:50 depicting excellent chemical and tribological properties. The saponification value of the 50:50 was reduced by 23-55% whereas the pour point improved by 159.7% in comparison to pure coconut oil. The WSD of blend 50:50 also depicted minimum WSD with an improvement of 18.45% in comparison to coconut oil. Jabal et al. [9] blended palm oil with jatropha oil in the blend ratio (60:40) and investigated the tribological properties on the four-ball tester. The author reported that blended oil depicted better lubrication properties than pure palm oil. The maximum improvement observed at a load of 300 N is equal to 43% approximately in comparison to pure palm oil.

Zapateiro et al. [10] investigated the effect of estolides derived from monounsaturated fatty acids (ricinoleic and oleic acids) on the thermophysical and tribological properties of high oleic sunflower oil and castor oil. The authors reported the estolides did not improve

the functional properties. However, the wear is significantly reduced. Gemsprim et al. [11] investigated the tribological properties of blended mahua, castor and sunflower oil. The castor oil and mahua oil are added to sunflower oil in ratios of 25-75 %. The author reported that the blends of mahua and sunflower oil performed better and attributed the improvement to the viscosity index of the blend. Further, the presence of free fatty acids in mahua-sunflower oil improves the frictional and thermal stability of the oil. Jain and Suhane [12] mixed cotton oil and malva oil in the blended ratios of 10:90, 20:80, and 30:70 respectively. The authors reported that the maximum reduction in friction and wear is observed with the blended sample and is equal to 90% and 45-65% respectively.

This study aims at determining the effect of saturated fatty acids on the rheological and antiwear properties of olive oil. Olive oil is selected as the base oil for experimentation purposes owing to its higher content of monounsaturated fatty acids and lower polyunsaturated fatty acids whereas, the coconut oil is introduced in the olive owing to the higher contents of saturated fatty acids.

## 2. EXPERIMENTAL DETAILS

The fatty acid composition of the coconut and olive oil is depicted in Table 1 [2,13,14]. Coconut oil was selected as an additive owing to its higher content (90%) of saturated fatty acid. The chemical identification of both the oils and the additivated oil is determined by Fourier-Transform Infrared spectroscopy (FTIR) analysis. As each chemical structure is associated with a distinctive spectral intensity, FTIR analysis helps in the chemical identification of the various functional groups present in the oil.

The olive oil and coconut oil are mixed in blending ratios of 90:10, 80:20, 70:30, 60:40 and 50:50 respectively depicted in Table 2 and the effect of saturated fatty acids on the antiwear and rheological properties was observed. The coconut oil was blended with olive oil on a hot plate magnetic stirrer at a temperature of 80°C and 900 RPM respectively. The blended oil was cooled at room temperature and tested for various properties.

**Table 1:** Fatty acid composition of oils.

Type of oil	Fatty Acid	Percentage (%)
Olive oil	Palmitic acid (C 16:0)	12-16
	Stearic acid (C 18:0)	2-3
	Oleic acid (C 18:1)	66-73
	Linoleic acid (C 18: 2)	9-16
	Linolenic acid (C 18: 3)	1-2
Coconut oil	Caprylic acid (C 8:0)	8-10
	Capric acid (C 10:0)	5-6
	Lauric acid (C 12:0)	49-51
	Myristic acid (C 14:0)	17-19
	Palmitic acid (C 16:0)	7-8
	Stearic acid (C 18:0)	2-3
	Oleic acid (C 18:1)	5-7
	Linoleic acid (C 18: 2)	1-2

**Table 2.** Blend ratio of oils.

Designation	Blend ratio (%)	Olive oil (ml)	Coconut oil (ml)
B1.	90:10	90	10
B2.	80:20	80	20
B3.	70:30	70	30
B4.	60:40	60	40
B5.	50:50	50	50

The antiwear investigation is carried out on Ducom's four-ball tester. The balls are procured from Ducom instruments with a standard diameter of 12.7 mm. The average surface roughness of the balls is equal to 0.016  $\mu\text{m}$  with a Rockwell hardness of 64.98. The antiwear properties of the base oils and blends are carried as per the following parameters; Load 392 N, Temperature 75°C, RPM 1800, and time 30 min. The wear scar diameter (WSD) of the balls is measured on the optical microscope and the surface analysis of balls is determined using SEM and EDX analysis. The effectiveness of the lubricating film at the tribopairs is determined by the measurement of the flash temperature parameter (FTP) that indicates the temperature where the lubricant film breaks down and is calculated using equation 1 [15]

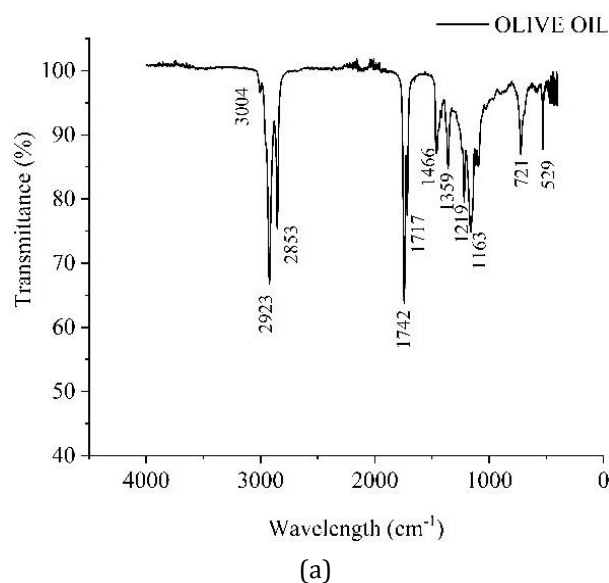
$$\text{FTP} = \frac{\text{Load}}{(\text{Average wear scar diameter})^{1.4}} \quad (1)$$

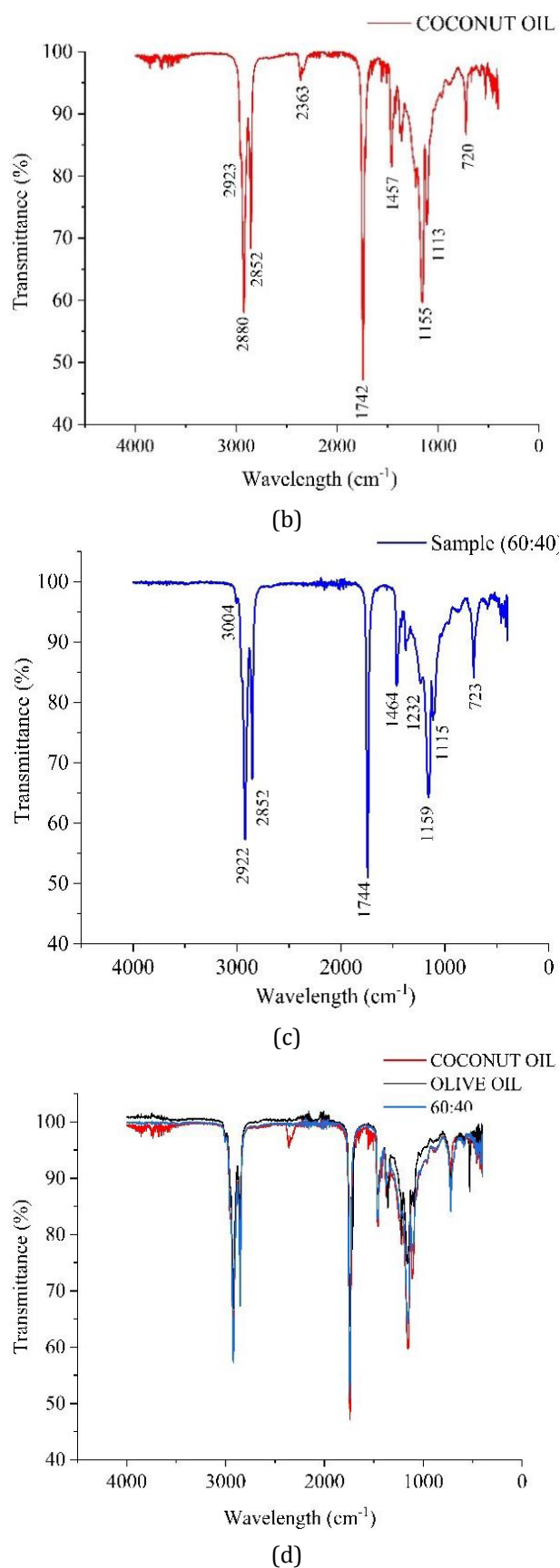
The viscosity of the pure olive oil, coconut oil and a blend of olive oil and coconut oil (60:40) is measured on Anton Paar's Rheometer (MCR 102) using a cone and plate geometry with a gap of 0.01 mm between the rotating and stationary plate. The viscosity measurement is carried out at a temperature of 75 °C with varying shear rates of 50 – 4000 per second. Further, the flow behaviour of the oils is quantified using Ostwald-de- Waele power law.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Fourier - Transform Infrared spectroscopy (FTIR) of lubricant

Fig. 1a and Fig. 1b depict the Fourier-Transform Infrared spectroscopy of olive and coconut oil. The ester structure of both oils is confirmed by the presence of C = O and C - O bond peaks between the wavelengths of 1800-1600  $\text{cm}^{-1}$  and 1300-1100  $\text{cm}^{-1}$  respectively. However, the transmittance comparison of the oils indicates the presence of higher contents of C - O in the coconut oil in comparison to olive oil. Further, the transmittance percentage of C-H bonds between 2900-2800  $\text{cm}^{-1}$  is higher for olive oil in comparison to coconut oil. This indicates that there are fewer C - H bonds present in the olive oil. The results suggest that coconut oil consists of a high content of saturated fatty acids. No adsorption peak could be detected after 3050  $\text{cm}^{-1}$  which suggests that there are no alcoholic, carboxylic or amine functional groups in the oil and confirms the ester structure of the oils. The comparative investigation of blended oils depicted in Fig. 1d reveals a high percentage of C - H bonds in the blended oil in comparison to the olive oil. Also, the C - O bonds in the blended oil are higher than the olive oil but lower than the coconut oil. Further, the transmittance percentages of blended oil at other wavelengths (1742  $\text{cm}^{-1}$ , 721  $\text{cm}^{-1}$ , 1464  $\text{cm}^{-1}$ ) is different in comparison to the olive oil. It is concluded that the blending of coconut oil with the coconut oil has changed the chemical structure of the olive oil.

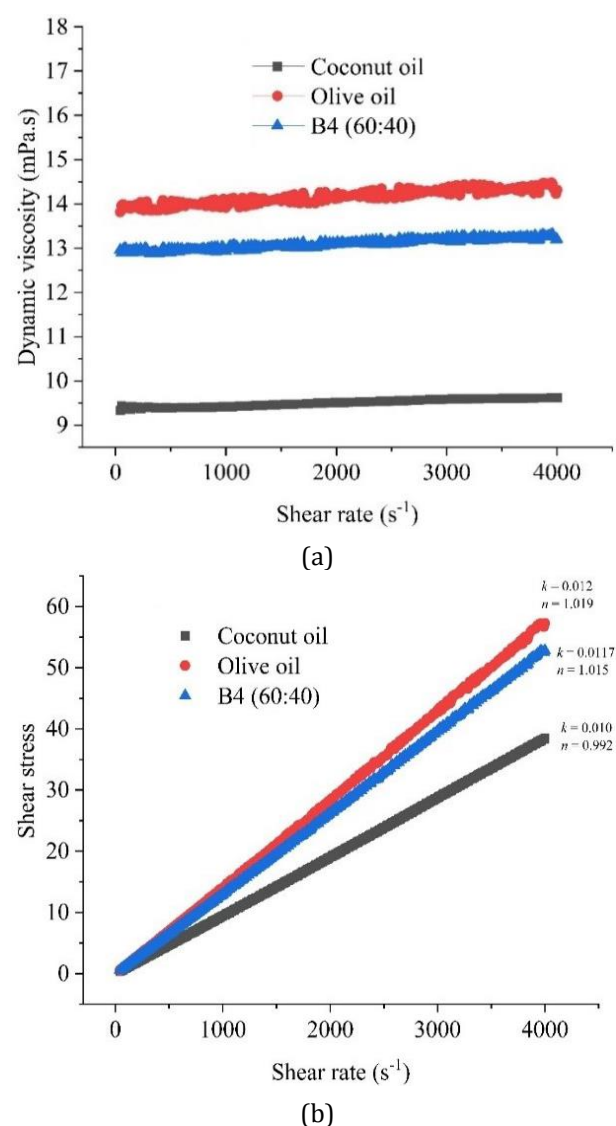




**Fig. 1.** FTIR of (a) Olive oil (b) coconut oil (c) Blend (60:40) and (d) Comparison of olive, coconut, and blend (60:40).

### 3.2 Rheological analysis of lubricants

The viscosity measurement of the pure olive oil, coconut oil and a blend of olive oil and coconut oil (60:40) is depicted in Fig. 2a. It is observed from the Fig. 2a that the olive oil depicts higher viscosity than the coconut oil and is equal to 14.2 mPa.s and 9.5 mPa.s respectively. The blended sample B4 depicts dynamic viscosity close to the olive oil and is equal to 13.1 mPa.s. Further, Fig. 2a depicts that the dynamic viscosity of olive oil and coconut oil is nearly constant with an increase in shear rate. This suggests the Newtonian behaviour of all the samples. Similar behaviour is observed with the blended sample B4 where, the dynamic viscosity is again constant with the increase in shear rate implying no effect of blending on the flow behaviour of the oils.



**Fig. 2.** Variation of (a) Dynamic viscosity with shear rate, (b) Shear stress with shear rate.

Ostwald-de-Waele power law equation is used to quantify the behaviour of fluids i.e., Newtonian and non-Newtonian behaviours of all oils, and is given by equation 2 [16]

$$\tau = k \cdot \dot{\gamma}^n \quad (2)$$

where,  $n = 1$  indicates the oil is Newtonian,  $n < 1$  indicates the shear thinning of the oils and  $n > 1$  indicates the shear thickening of oils. It is observed from Fig. 2b that the shear stress of all the samples increases linearly with an increase in the shear rate. The maximum shear stress is depicted by the olive oil followed by blended oil and coconut oil respectively. It is observed from Fig. 2b that all samples have the power law index ( $n$ ) close to 1 which implies the Newtonian behaviour of the oils. It is concluded that the blending of oils only impacts the viscosity of the oils and does not affect the flow behaviour of the oils.

### 3.3 Antiwear of pure and blended oils

Fig. 3a shows the WSD of the balls lubricated with olive oil, coconut oil and addivated oils. It is observed that the coconut oil depicts lesser WSD equal to 523.9  $\mu\text{m}$  in comparison to the olive oil. The average WSD observed with the olive oil is equal to 577.9  $\mu\text{m}$ . Further, it is observed from Fig. 3a that the blending of the oils at lower concentrations of coconut oil improves the WSD slightly. The average improvement in WSD for different blending samples B1, B2 and B3 is equal to 1.7%, 2.3% and 1.97% in comparison to the pure olive oil. The maximum reduction in the average WSD equal to 3.96% and 10.74% respectively is observed for blending samples of B4 and B5 in comparison the pure olive oil.

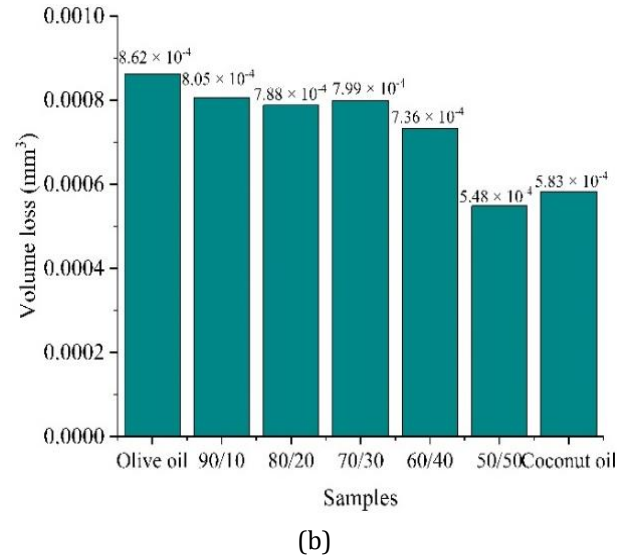
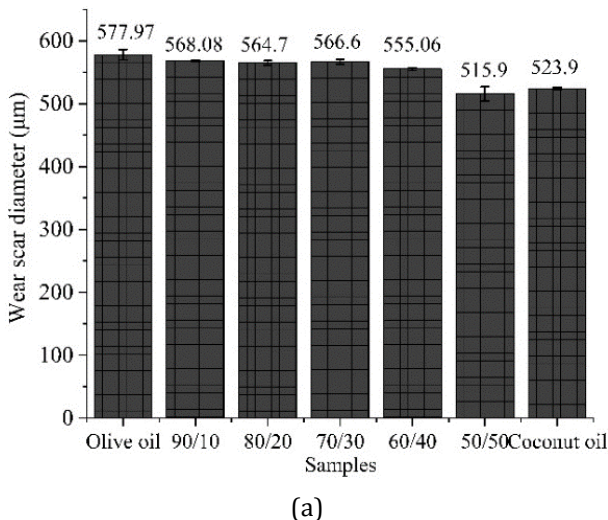


Fig. 3. (a) Variation of Wear scar diameter with different blending ratios, (b) Variation of volume loss with different blending ratios.

Fig. 3b depicts the effect of blending on the volume loss of the steel balls. The volume loss in a four-ball experiment is calculated using equation 3 [17]

$$V = \pi R^3 \left( 1 - \sqrt{1 - \frac{1}{4} \left( \frac{X}{R} \right)^2} \right)^2 \left[ 1 - \frac{1}{3} \left( 1 - \sqrt{1 - \frac{1}{4} \left( \frac{X}{R} \right)^2} \right) \right] \quad (3)$$

Where,  $V$  = volume loss of balls,  $X$  = measured WSD and  $R$  = radius of the ball.

It is observed from Fig. 3b that the balls lubricated with olive oil depict maximum volume loss equal to  $8.62 \times 10^{-4} \text{ mm}^3$ . The volume loss of balls decreases by 6.75%, 8.7%, 7.4%, and 15% at B1, B2, B3, and B4 blended ratios in comparison to the pure olive oil. The maximum improvement in the wear is observed with the blended sample B5 where the volume loss decreases by about 36.5% in comparison to the pure olive oil.

The FTP of all the samples is depicted in Fig. 4. It is observed that the coconut oil forms a strong protecting film followed by the blended sample B4 and B5. The introduction of coconut oil in the olive improves the FTP by 5.8% and 17.4% at 40% and 50% respectively. It is concluded that saturated fatty acids improve the antiwear properties of the oils.



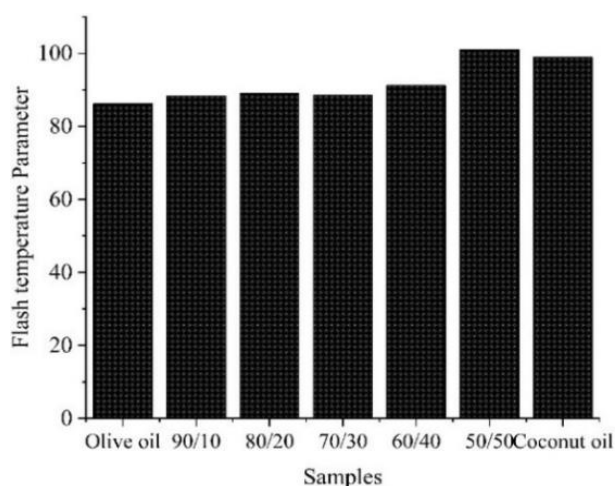
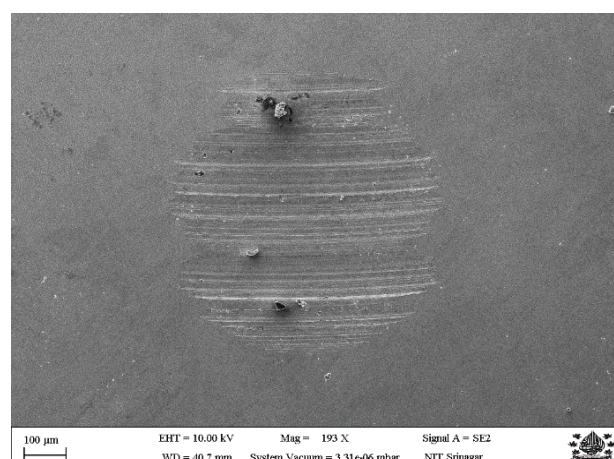


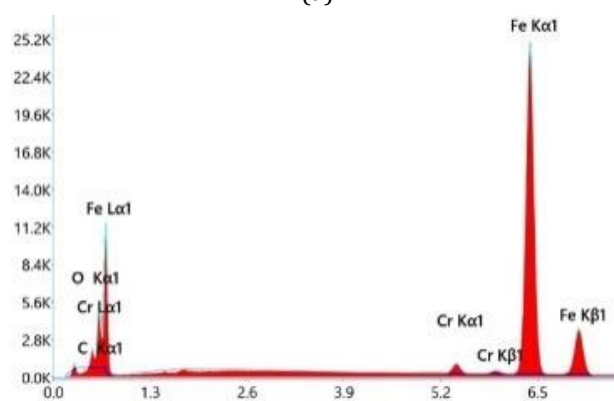
Fig. 4. Variation of FTP with different blending ratios.

### 3.4 SEM and EDX characterisation

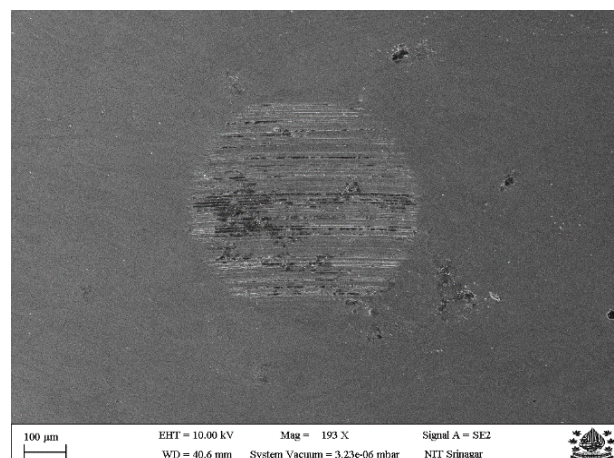
It is observed from Fig. 5a that the olive oil depicts a smoother surface than the coconut oil depicted by Fig. 5c. Coconut oil depicts a slightly higher abrasive action than pure olive oil where fine ploughing action is observed on the surface. The fine ploughing action has further reduced with the blended sample B4 and a much smoother scar is observed. The blended sample B4 depicts fine ploughing with narrow grooves on the surface. The blended sample B5 also depicts finer ploughing action with a smoother wear scar. The average WSD for all the samples is within the range for commodity oils [18]. It is concluded that the abrasive action is the main wear mechanism in all three bio-oils. The excellent lubricating properties of the bio-oils may be attributed to the chemical composition, structure, chain length and other properties of the bio-oils [2]. The presence of polar and non-polar groups in the bio-oils results in the formation of effective protective films on the tribosurface. The polar groups bind with the tribosurface and non-polar groups form molecular layers between the surfaces. The reduction in the wear scar diameter and improvement in the wear surface with an increase in the blending may be attributed to the saturated fatty acids that can form strong protective films on the tribo-surfaces. The results are in accordance with the previously established results where the saturated fatty acid improved the properties of the base oil. The EDX analysis depicted in Fig. 5b, 5d, 5e and 5f of all samples shows four major elements in the samples i.e., carbon, oxygen, chromium, and iron.



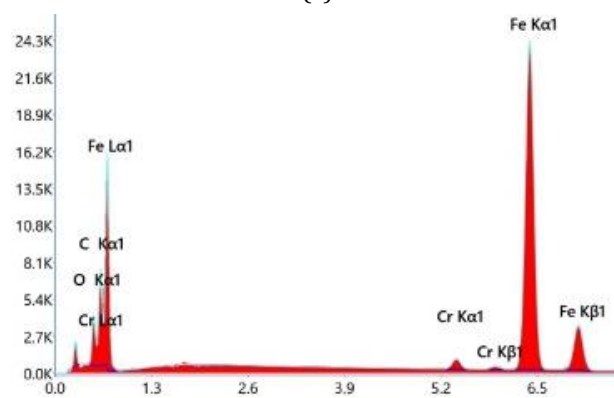
(a)



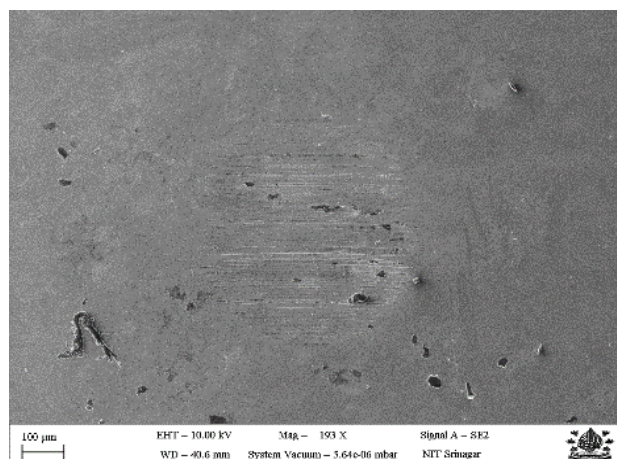
(b)



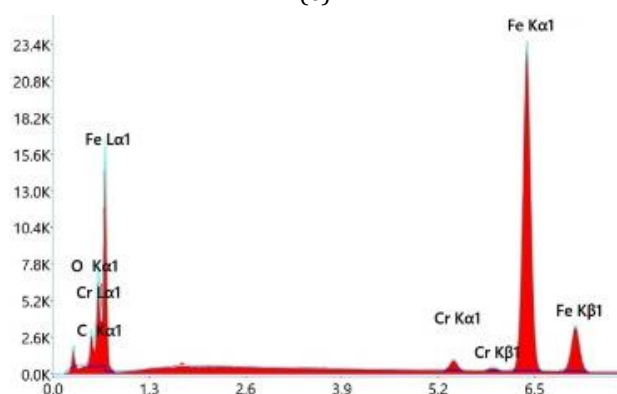
(c)



(d)



(e)



(f)

**Fig. 5.** SEM and EDX images of (a,b) Olive oil (c,d) Coconut oil (e,f) Blend oil (60:40) and Blend oil (50:50).

All the samples show iron as the major element on the wear scars. This can be attributed to the higher contents of iron in the steel tribopairs. Further, the presence of oxygen on the tribosurfaces indicates the formation of oxide films [19,20]. It is concluded that the tribochemical reactions at the contact surface form protective oxide films and result in the prevention of wear.

#### 4. CONCLUSION

The following are the deductions of the presented study:

1. The FTIR results indicated that the blending of oils changes the chemical structure of the oils.
2. The blending of coconut oil with olive oil resulted in a decrease in the dynamic viscosity of the olive oil.

3. The saturated fatty acids also have an impact on the wear scar of the balls by forming strong protective films on the tribosurfaces.
4. The maximum improvement in WSD is equal to 10.7% at a blended ratio of 50:50.

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