Tribology Online

Japanese Society of Tribologists

https://www.tribology.jp/trol/

Vol. 18, No. 4 (2023) 103-114.
ISSN 1881-2198
DOI 10.2474/trol.18.103

Article

Tribological Performance Evaluation of Vegetable Lubricant Incorporated Ethylene Vinyl Acetate (EVA) and Tertiary-Butyl-Hydroquinone (TBHQ) Nanoparticles

Audu Ibrahim Ali [1, 2, 3]*, Mohd Kameil Abdul Hamid[1, 2], Mohd Azman Bin Abas[1], Mohd Farid Muhamad Said[1], Anthony Chukwunonso Opia[4], Izhari izmi bin Mazali[1] and Zul Hilmi bin Che Daud[1]

[1] Automotive Development Centre, Institute for Vehicle Systems & Engineering, Universiti Teknologi Malaysia, Johor Bahru 81310, Malaysia
[2] Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Johor Bahru 81310, Malaysia
[3] Department of Mechanical Engineering, Federal Polytechnic, Idah, PMB 1037 Idah, Kogi, Nigeria
[4] Faculty of Mechanical Engineering, Universiti Teknikal Malaysia, Melaka, Durian Tungal, 76100, Malaysia

*Corresponding author: Audu Ibrahim Ali (auduibrahimali@gmail.com)

Manuscript received 19 February 2023; accepted 30 May 2023; published 31 July 2023

Abstract

The adoption of vegetable oil as a basic lubricant has become increasingly prevalent due to growing environmental concerns about the harm caused by lubricants made from petroleum. As a result, many researchers are concentrating on developing new, efficient green lubricants. This current work evaluates the tribological performance of novel ficus carica (fig oil) combined with Ethylene Vinyl Acetate (EVA) viscosity modifier and Tertiary-Butyl-Hydroquinone (TBHQ) nanoparticles as an eco-friendly lubricant. The research employed a four-ball tribometer standard test (ASTM D4172-94). Field emission scanning electron microscopy (FESEM) was used for worn surface morphology examination. In the study, TBHQ was kept at 0.3 mass%, while EVA concentrations varied from 0.5, 1, 1.5, and 5 mass%. An ultrasonic homogenizer was used to combine the samples using the sonication technique. The viscometric study revealed 1 mass% EVA as optimal concentration. Thermogravimetric analysis (TGA) results showed that EVA + TBHQ inclusion resisted lubricant degradation, while oxidation time shift was at onset of 53.5 min against base oil onset of 14.1 min. The frictional results showed 100 kg of load, adding 0.9 mass% EVA + 0.3 mass% TBHQ nanoparticles gives the best reduction in wear and the coefficient of friction, although SAE-5W-30 lubricant performed better. Furthermore, the effectiveness of the added substances was determined by their ability to diffuse into the sliding contact, thereby avoiding direct contact between the sliding bodies, which, if not minimized, could result in machine damage.

Keywords

ficus carica vegetable oil, additives, lubrication, friction and wear

1 Introduction

Global environmental concerns have led to an increase in the use of biodegradable materials for a number of decades, owing to their potential to solve global warming effects [1–3]. The advent of product ecolabelling has had a considerable impact among many governmental directives addressing the preservation of the environment [4]. Fossil fuel consumption gives rise to a range of environmental worries since their emissions contain different chemicals that exacerbate environmental harm [5, 6]. Hence, there is a need to identify substitute lubricants made from sustainable sources because fossil-based lubricants will eventually run out of supply [5]. Vegetable oil-based and other bio-based lubricants can be utilized as renewable lubricants [7–9]. When evaluating bio-lubricants, vegetable oils have some outstanding qualities for their prospective usage as lubricants, including a high viscosity index, high lubricity, low volatility, and, particularly, both low toxicity and high renewability [10, 11]. Vegetable oil's quick biodegradability has in particular sped up development to the point that harvestable resource-based lubricants are now a successful reality in many regions of the world, expanding in demand and being widely used for various purposes [12, 13].

However, the availability of a narrow range of viscosity values, their thermo-oxidative stability, crystallization at relatively high temperatures, and other restrictions should all be addressed technologically [9, 14, 15]. To overcome these constraints, lubricant modification, and the inclusion of additives to lubricants with vegetable bases can assist to improve tribological characteristics and fulfil the expectation of minimize wear and friction. Azman et al. [16] investigated the use of CuO and graphite nanoparticles as an anti-wear and extreme pressure additive in palm oil. The results revealed that adding CuO and graphene nanoparticles reduced wear

Copyright © 2023 Japanese Society of Tribologists
This article is distributed under the terms of the Creative Commons BY-NC-ND 4.0 License.

and friction in comparison to the base lubricant, resulting in decreases in coefficient of friction of 3.8 and 15% and wear scar diameters of 2.77 and 6%, respectively. Compared to the base lubricant, the extreme pressure performances of CuO and graphene nano lubricants were improved by 12 and 18%, respectively. In addition, the long-chain fatty acids found in vegetable oil offer superior inherent boundary lubricating characteristics. As a result, the product provides low coefficients of friction, thereby exhibiting effective operating properties. Much research claims that even when vegetable oil is used as the boundary lubricant, friction coefficient sometimes turns low and the wear rate high.

In this research, a new lubricant, ficus carica oil (Fig oil), was employed as an alternative lubricant along with an Ethylene Vinyl Acetate (EVA) viscosity modifier and Tertiary-Butyl-Hydroquinone (TBHQ). The aim of blending the base lubricant with TBHQ and EVA is to act as an antioxidant and viscosity improver/modifier, respectively, which the base oil lacks. The fig plants are mostly found in tropical areas. Though it has long been recognized as a medicinal substance, it is currently attracting more interest as a source of bio-products. Due to negligence on the part of those involved in the cultivation and production, fig oil is an expensive and scarce product as it is an invention. As more research on fig oil is conducted and it is found to perform effectively, governments and individuals will invest in fig oil cultivation, making it a commercial product for both lubrication and biofuel production.

2 Methodology

2.1 Materials and preparation

The steel standard balls AISI E-52100 chrome alloy used in this experiment have the following characteristics: extra polish (EP) grade 25, diameter 12.7 mm, and 64-66 HRC hardness (Rockwell C Hardness). The Tertiary-Butyl-Hydroquinone (TBHQ) additive, Ethylene Vinyl Acetate (EVA), and Standard Base Fig Oil from Sigma Aldrich Company Malaysia were utilized in this study. Tert-Butylhydroquinone, often known as TBHQ or tertiary butylhydroquinone, is a powerful synthetic phenolic molecule with aromatic properties. It is a hydroquinone derivative that has had a tert-butyl group added with good anti-oxidative strength and other properties, as presented by Nazan et al., [16]. Vegetable fig oil was used in this investigation because of its new qualities with the hope of advancing bio-lubricant research and lowering friction and wear. The composition of fig oil, mineral oil, and two additives is shown in Table 1.

The mixture (oil + additive) was gradually infused with 0.5, 1, 1.5, and 2 mass% EVA NPs, as well as 0.3 mass% TBHQ, and swirled for 1.5 hours in a magnetic stirrer during preparation. Finally, the produced nano lubricants were sonicated for two hours in a bath sonicator. Figure 1 shows images of EVA and TBHQ (1a). EVA additive contains methoxy groups of aldehydes and atone, while TBHQ contains hydroxyl groups and carboxylic acid of tylenol (acetomiophen), with the black

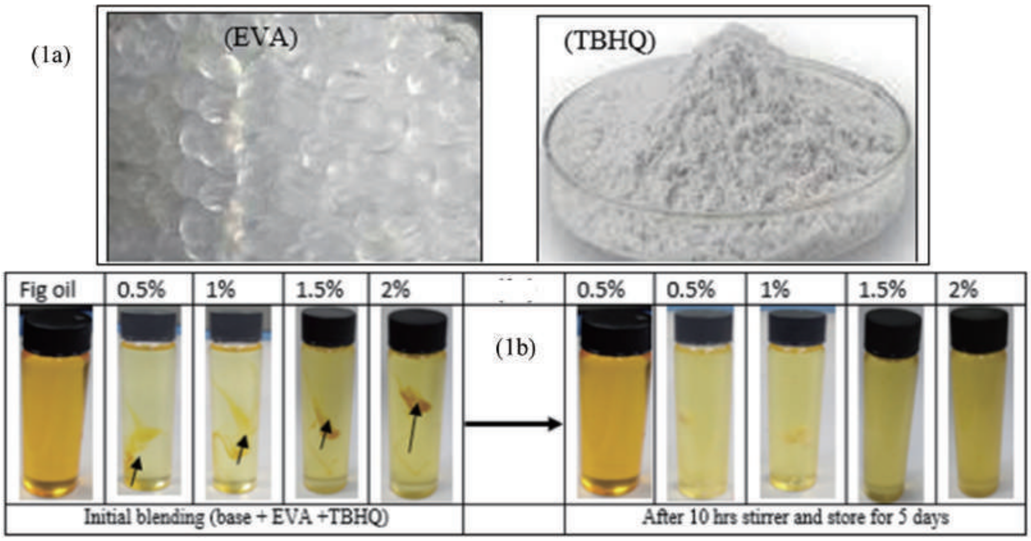

Fig. 1 Image of EVA and TBHQ (1a); and freshly prepared ficus carica oil with different concentrations of EVA and TBHQ nanoparticles, stirred for 30 mins (1b)

Table 1 Lubricant Rheological Properties

Properties	Samples			
	Ficus carica (fig oil)	Fig oil + EVA TBHQ	Commercial engine oil	Test Method
Kinematic viscosity (mm²/s) 40°C	30.91	31.32	108.2	DMA 4100M
Kinematic viscosity (mm²/s) 100°C	9.31	9.51	14.10	DMA 4100M
Density @ 40°C, g/cm³	0.8312	0.8146		DMA 4100M
Specific gravity	0.9236	0.9248	0.8660	DMA 4100M
Pour Point (°C)	4	2.8	−30	ASTM D97
°API @ 35°C	0.9206	0.9218	0.9517	DMA 4100M
Cloud Point (°C)	26	24	21.9	ASTM D2500
Flash Point (°C)	193	207.5	227	ASTM D93

arrows pointing to the key functional groups. Images taken immediately following sample preparation and ten hours later were presented in Fig. 1b. The solution observed no substantial nanoparticle sedimentation in the samples even after 10 days of preparation.

2.2 Experimental setup

In this study, a four-ball tribo-tester was employed to investigate the tribological performance of Fig oil with the selected additives. The analysis was conducted in accordance with the procedure used by Yadav et al., [17] using the standard test (ASTM D4172B) of a four-ball wear machine, the lubricant properties are carefully examined before operation. Four balls total, three at the bottom and one at the top, are used in this instrument as illustrated in Fig. 2. In a ball pot holding the lubricant under test, the three bottom balls are securely held while the top ball is forced against them. While the bottom three balls are pressing against the top ball, the top ball is made to rotate at the proper speed.

2.3 Characterization of the samples

2.3.1 FESEM and EDX analysis

The additives morphology was verified utilizing a field emission scanning electron microscope (FESEM, HITACHI SU6600). The additives particle size assessment was carried out applying a Zetasizer Nano ZS; Malvern Instruments, United Kingdom.

2.3.2 Viscometric analysis

The samples' viscosity analysis was assessed in a rotational controlled-strain rheometer, model ARES (Rheometric Scientific, UK), in a temperature range comprised of 40 and 150°C. Each test was run at minimum of two repetitions. By dividing the dynamic viscosity by the density, kinematic viscosity values were calculated. In accordance with ASTM D 2270, the viscosity index (VI) was determined.

2.3.3 Differential scanning calorimetry, FT-IR and thermogravimetric analysis (TGA) evaluation

Using 5–10 mg samples enclosed in hermetically sealed aluminum pans, differential scanning calorimetry (DSC) measurements were carried out with a Q-100 TA instrument. According to Azhari et al., [18], 10 C/min cooling and heating rates were used for all samples, which is an ideal pace that has the advantages of being quick and having more repeatable results. The temperature window selected ranged flow rate of 50 mL/min. from 65 up to 200°C. To identify the functional groups and investigate the compatibility between base fig oil as a lubricant, EVA and TBHQ additions, Fourier-transform infrared spectroscopy (FT-IR) investigation was carried out. To determine the thermal strength of the samples under the EVA and TBHQ blends with oil and pure Fig oil, was determined using TGA analysis.

2.4 Frictional analysis

The experiment ran under constant temperature at 75°C, constant load at 40, 60, 80, and 100 kg (392 N) for a 1 h duration. The variables for this experiment were the rotating speeds of 1200 rpm and 1500 rpm, which were chosen. The temperature was set at 75°C, and the speed was set at 1200 rpm and 1500 rpm. For each test, four brand-new balls were used. The balls were cleaned with acetone and dried with a brand-new lint-free industrial wipe before each test. According to ASTM D4172B standard specification, with speeds of 1200 rpm and 1500 rpm using different loads (40, 60, 80, and 100 kg), to ascertain the best additive concentrations. Friction tests were conducted three times for each sample material during the experiment to ensure that the results were repeatable.

Additionally, using a four-ball tester in accordance with the ASTM D4172B standard, the coefficient of friction and anti-wear properties of the base oils and the nano-lubricants at optimal concentrations were calculated. The tests were carried out for one hour at 1200 and 1600 rpm with loads of 80, 100, and 120 kg. A data acquisition system is used to plot the coefficient of friction against time. Utilizing FESEM, wear scar studies are conducted.

3 Results and discussion

The characterization of EVA and TQH nanoparticles was carried out using FESEM and energy dispersive spectroscopy (EDS, HORIBA-EMAX). The FESEM images of the EVA and TBHQ nanoparticles at two magnification levels are shown in Fig. 3 (a) and (b), clearly indicating their morphology and structure. Table 2 reveals the EDX analysis carried out (in terms of atomic and weight percent of constituents) on the EVA and TBQH nanoparticles, indicating the presence of carbon, oxygen, and copper. Using Zetasizer Nano ZS, a Malvern instrument, the particle distributions were conducted due to the appearance of the samples to determine the actual sizes when dissolved in base fig oil. As to know the possibility of the nanofluid passing through the machines' orifices when used. The outcome revealed that optimum dispersion was 4.2 and 4.5 nm average mean size for EVA and TBQH, respectively, as presented in

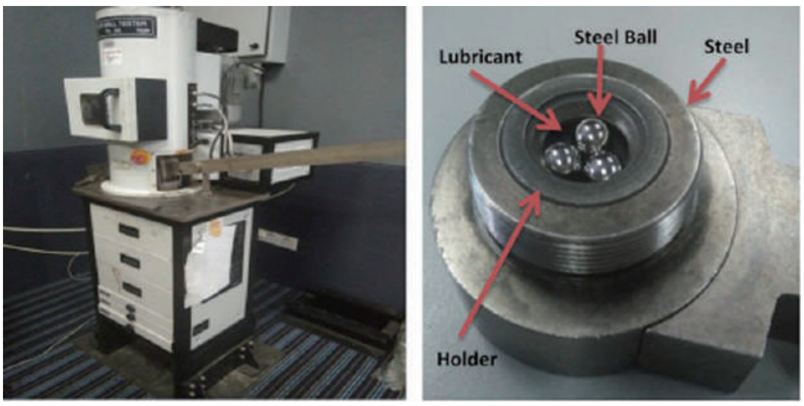

Fig. 2 Image of the Four ball tester (a) and the inner component (b) showing the ball arrangement

Fig. 4. As shown in Fig. 1, 0.5% EVA + 0.3% TBHQ and 1% EVA + 0.3% TBHQ concentrations show a similar whitish color owing to the little amount of EVA, thereby making 0.3% TBHQ dominate the color of the solution compared to 1.5% EVA + 0.3% TBHQ and 2 % EVA + 0.3% TBHQ.

Figure 5 shows the viscometric characteristics of base lubricant and the blended 0.5 mass%, 1 mass%, 1.5 mass%, and 2 mass% EVA polymer was tested in this research under specific gravities at 25°C and viscosity in centistoke at 40°C to 150°C. The viscosity indices of the lubricants are summarized in Table 3. The results indicate that viscosity decreases as temperature increases. At 100°C, the effect is much stronger than at 40°C. According to the research, the viscosity index (VI) value increases as polymers are mixed into lubricating oil. From the calculated VI values, it can be observed that the lubricants with EVA and TBHQ possess a higher viscosity index as compared to virgin fig oil. Thus, it can be established that the addition of the two additives, both single and in combination, enhanced the lubricant thermal properties. Lubricating oil's viscosity reduces as temperature rises, the polymer molecules increase [19]. The micelle becomes larger as a result, the reduced viscosity of the polymer-doped lubricating oil is balanced by the larger micelles

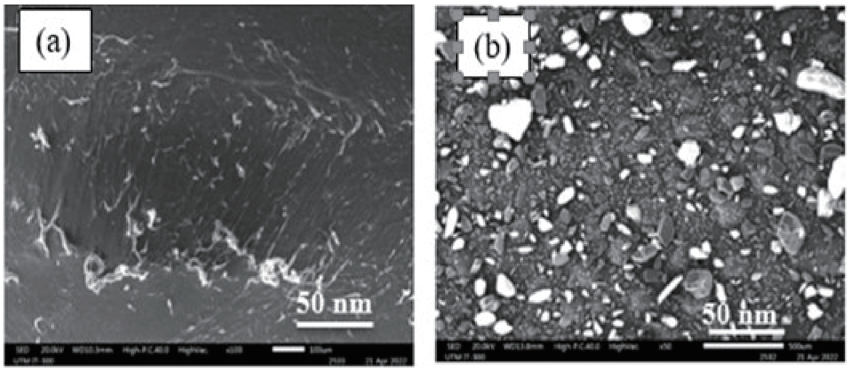

Fig. 3 FESEM characterization of EVA (a) and TBQH (b)

Table 2 Elements found EVA and TBQH under EDX analysis

Sample/Element (mass%)	C	O	Cu
TBHQ additive	77.8	22	0.2
EVA additive	88.5	11.5	

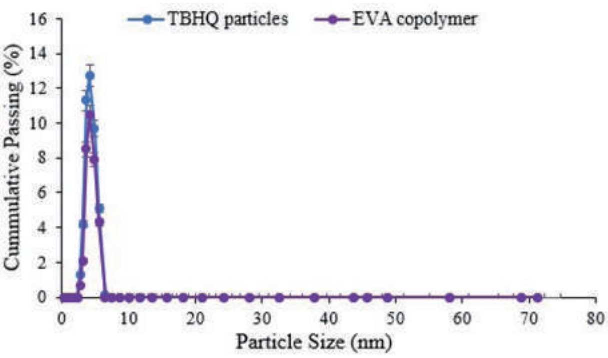

Fig. 4 Particle size distribution of EVA and TBHQ by hydrodynamic light scattering

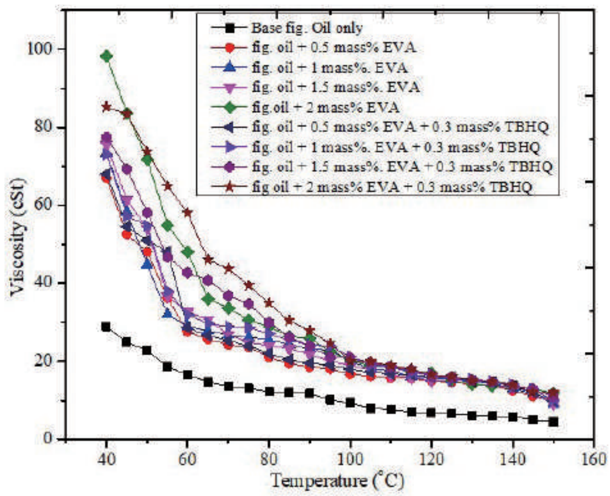

Fig. 5 Effect of temperature on viscosity for all the lubricants used

Table 3 Lubricants physical properties as used in the study

Sample	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)	Viscosity Index	Density 15°C
Fig. oil	30.91	8.91	258.73	0.8312
Fig. oil + 0.5% EVA	67.01	16.67	267.07	0.8501
Fig. oil + 1% EVA	73.34	20.15	298.76	0.8611
Fig. oil + 1.5% EVA	75.52	18.93	273.58	0.8572
Fig. oil + 2% EVA	98.21	20.01	230.23	0.8394
Fig. oil + 0.5% EVA + 0.3% TBHQ	68.01	17.97	285.09	0.8531
Fig. oil + 1% EVA + 0.3% TBHQ	73.14	21.15	313.52	0.8631
Fig. oil + 1.5% EVA + 0.3% TBHQ	77.51	20.93	296.64	0.8542
Fig. oil + 2% EVA + 0.3% TBHQ	85.21	20.31	261.33	0.8384

[19]. This behavior shows that the EVA as well as the inclusion of TBHQ exhibit the characteristics of a viscosity improver polymer capable of enhancing the tribological property of base oil when subjected to heat.

Furthermore, by analyzing the flow curve, the rheology of the utilized lubricants was examined (shear rate vs shear stress). The flow curve for various oils corresponding to two different temperatures (20, 40, and 80°C) is shown in Fig. 6 (a). For all of the lubricants employed in the study, it can be seen that the variation of shear stress with shear rate is linear and supports the Newtonian behavior of the lubricants used. Figure 6 (b) depicts the changes in lubricant viscosity corresponding to various shear speeds. The observations were similar to the findings in a previous related study [20]. The viscosity changes little with shear rate, supporting the Newtonian behavior of the lubricants studied. The implication of the result is that the inclusion of the additives resists the deformation of lubricants caused by temperature and other thermodynamic properties.

3.1 Samples oxidative stability study applying Differential Scanning Calorimetric (DSC)

The oxidative stability analysis of lubricants (fig oil and fig + TBHQ) was tested via Differential DSC techniques. The oxidative induction time (OIT), onset, and peak maximum temperatures are some of the important metrics that the DSC study may include. In the current investigation, OIT was used to test the impact of TBHQ addition to fig oil, as shown in Fig. 7 (a) and (b). The oxidation experiment was carried out in isothermal mode, following the steps used in previous works [20]. Using a Pasteur pipette, a liquid sample weighing around 12 mg was initially placed into the DSC cup. In the analysis, the time interval, referred to as the conclusion of the induction period, marks the beginning of the oxidation process, or the initiation stage, in respect to temperature according to Erhan et al., [21]. From the experiment, the base fig oil, a pronounced early oxidation on the curve was observed, showing degradation in the lubricant used at temperature of 161.3°C, as shown in Fig. 7. In the case of base fig oil incorporated with TBHQ, the oxidation initiation leading to degradation was extended to appear at temperature of 227.7°C. There was lack of much oxidation chemical reaction taking place during the operation, which in term favor the use of the blended TBHQ lubrication if used in lubrication.

Using FT-IR analysis, Fig. 8 illustrates the functional groups found in EVA polymer, TBHQ, base fig oil, and their combinations. The samples' aliphatic stretching bands (CH_3 + CH_2) are visible in the samples' spectra at 2907.13 and 2799.74 cm^{-1}. When comparing the behaviors and functional groups in

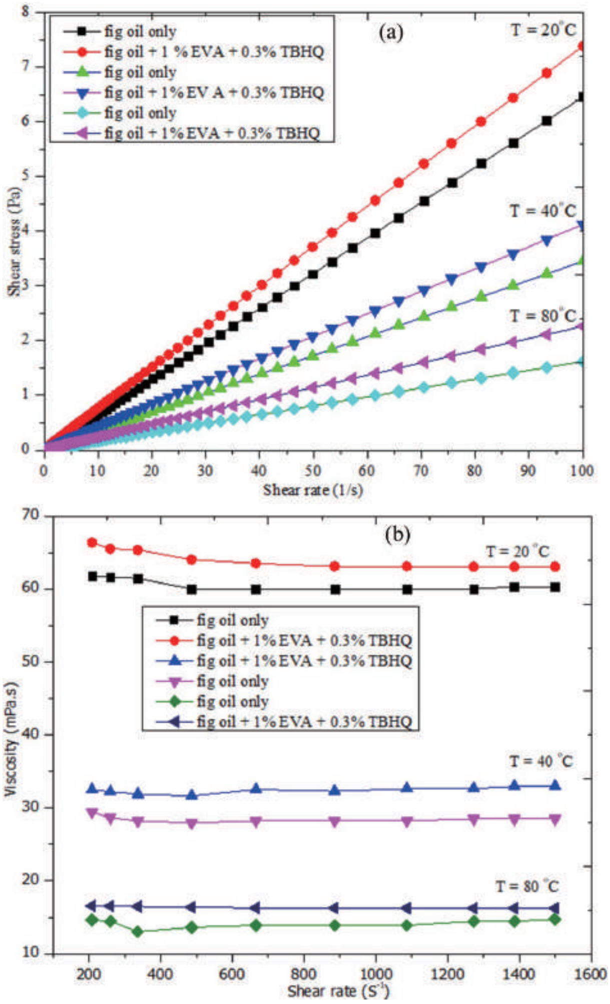

Fig. 6 Shear stress against shear rate (a) and viscosity against shear rate (b) of the various lubricants used

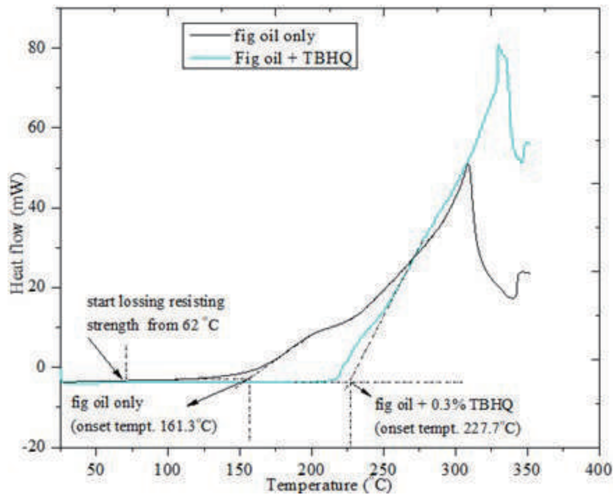

Fig. 7 Oxidative temperature for fig oil and fig oil + TBHQ

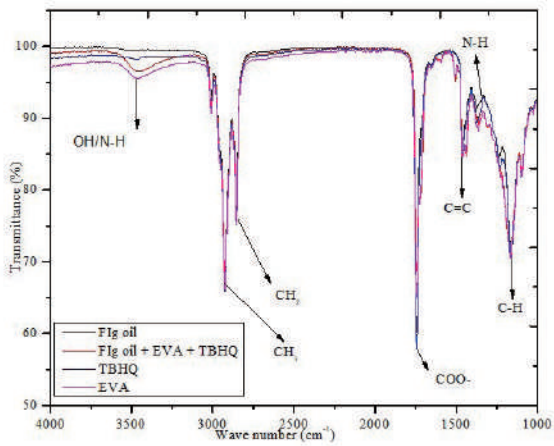

Fig. 8 FT-IR analysis of base fig oil, EVA polymer, TBHQ and oil + EVA + TBHQ

the spectra of the various samples, a wide and powerful band at roughly 3345 cm^{-1} caused by the O-H/N-H group according to Veriansyah et al., [22]. The increase in hydroxyl group due to the new molecules from the additives was seen in the new band at 3010 cm^{-1} of fig oil + EVA + TBHQ.

However, the hydroxyl group (OH) at the 3720 cm^{-1} band in the base oil spectrum exhibits a rocking vibration. This is supported by the structural formula presented in Fig. 1(b) above. When additives were added, the rocking was released. This is because, at ambient temperature and without external influence, the propagation of oil monomer components inside the polymer chains is considered a physical event; as a result, a little modification in the structure was detected [23]. With the creation of a peak at 1300 cm^{-1} for base oil, the carbonyl group C=O group's stretching vibration in the additives was seen.

Though, due to a similar and uniform concentration of the COO-group in all samples, there was a single strong peak at 1750 cm^{-1}. A developed peak between fig oil + EVA + TBHQ was found within 1470 cm^{-1} and was attributable to the presence of the C=C group. According to Asep etal., [24], the N-H group's vibration and its shared vibration with the C-H group result in the creation of peaks at 1098 cm^{-1} for EVA and a new peak at 1235 cm^{-1} for TBHQ, respectively. Finally, the homogeneity, similarity, and presence of key functional groups for a suitable lubricant in all the samples merely indicates that the formulations are anticipated to produce good results during lubrication.

The TGA results for fig oil alone, fig oil + TBHQ, fig oil + EVA, and fig oil + EVA + TBHQ are shown in Fig. 9. Data derived from thermogravimetric measurements was used to calculate the weight loss percentage [25]. The thermogravimetric curve's intersection of two tangents provided the onset degradation temperature, which was found shortly before the inclination brought on by degradation from the various tested samples. Weight loss of 38.5% was observed in fig oil, which may be related to pollutants adsorbing during formulation. Weight reduction after blending with EVA was 22%.

The modifications imply that EVA's thermal characteristics have been enhanced. A weight reduction of 17% was achieved with the modified TBHQ, while 15% was achieved with EVA + TBHA. in comparison to the fig oil foundation. Due to the heat

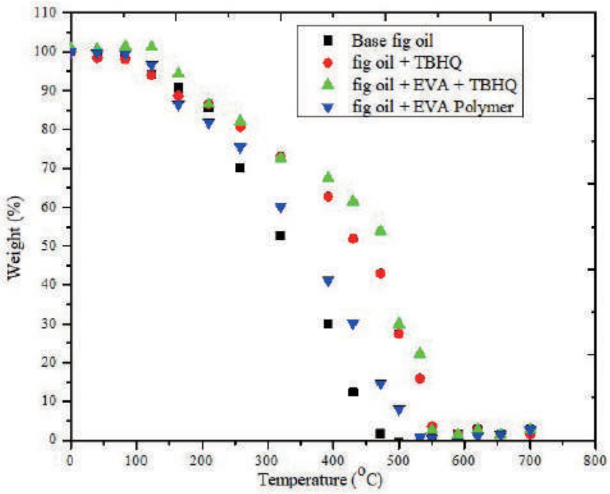

Fig. 9 Result of TGA of fig oil only, fig oil + TBHQ, fig oil + EVA + TBHQ and fig oil + EVA demonstrating the weight loss over temperature

resistance strength, which prevented lubricant degradation and resulted in considerably less weight loss for EVA + TBHQ. Shara et al. [23, 26] reported a similar observation, this led to better thermal characteristics.

3.2 Frictional characteristics

Figure 10 depicts the frictional characteristics for the various lubricants under loads of 60, 80, 100, and 120 kg under a speed of 1200 rpm. It can be seen that for base oil, the coefficient of friction increases abruptly with the increase in applied load and operating speed. Also, after 30 minutes of service in the two-speed system, a significant variation in the coefficient of friction was observed. This could be explained by a lack of effective layer development or lubricant breakdown, which would prevent direct metal to metal contact friction. With base fig oil under 1200 rpm, for 60, 80, 100, and 120 kg, the average COF was 0.182, 0.177, 0.186, and 0.247, respectively. For samples with additives, the coefficient of friction in the tested conditions was comparatively lower than the fig oil but mostly pronounced

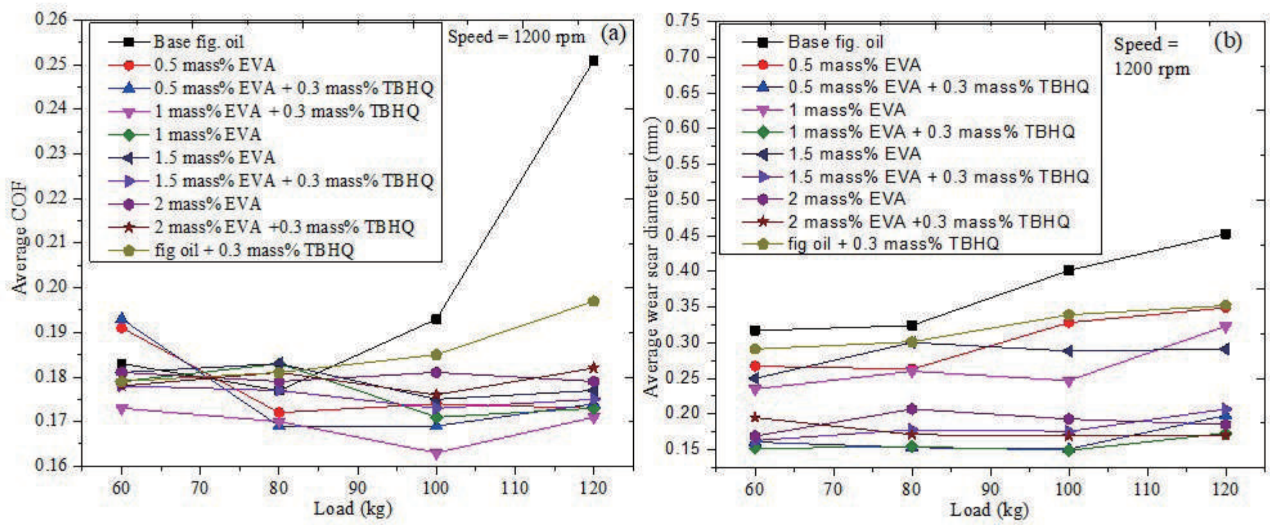

Fig. 10 Shows the variation in average coefficient of friction (a); and WSD (b) with time for various concentrations of EVA + TBHQ nanoparticles under different loads (60, 80, 100, and 120 kg) at 1200 rpm.

with the combination of the two additives, indicating synergetic effect, supported by the analysis conducted by Opia et al., [27]. This may be due to the increased ability of nanofluids to get adsorbed on metal surfaces, thereby preventing direct metal to metal contact [28]. It can be from rapid response of the additives in the formation of tribo film, which makes the sliding smoother leading to COF reduction.

For the samples with 1 mass% EVA polymer, frictional behavior is similar to that of combined additives. This can be attributed to the fact that EVA forms an effective tribo-film between moving surfaces through maintaining the viscosity when loaded, thereby reducing lubricant deformation, which could cause poor lubrication operations. The performance of 1 mass% TBHQ shows poor COF output; however, it is better than base fig lubricant (Fig. 10 (a)). When compared to the combined additives, an improved result was generated but revealed optimal output when tested with a commercially formulated lubricant in terms of COF but lower than the wear scar diameter (WSD) result. The COF reduction using 0.5, 1, 1.5 and 2 mass% EVA + TBHQ was +6%, 4.4%, 2.7%, and 1% for 60 kg; at 80 kg, it yielded 3.4%, 2.3%, 1%, and 1%; under 100 kg, it was reduced by 8.1%, 12.9%, 5.9%, and 4.3%; while at 120 kg, it gave 34%, 36%, 34.8%, and 33%, respectively. The study observed that the impact of the used additives was more pronounced at a higher load (120 kg).

The wear behavior of the tested lubricants exhibited similar trends as shown in Fig. 10 (b). For the loads of 60, 80, 100, and 120 kg under base lubricant, the average WSDs were 0.317, 0.324, 0.401, and 0.452. According to the lubricant's behavior, with only EVA lubrication exhibits a significant amount of dispersion in the average frictional values, which denotes a break in film formation. This behavior was more observed with the use of fig oil 0.3 mass% additives, which may be attributed to the lack of viscosity replenishment during lubrication, resulting in abrasives and thereby increase the third body abrasion, thus reported similar by Opia et al., [29]. Using the additive concentration of 0.5, 1, 1.5 and 2 mass% EVA + 0.3 mass%TBHQ. At 60 kg the WSD were reduced by 51%, 52.4%, 52% and 51%; at 80 kg yielded percentage reduction of 52.8%, 53.1%, 51.5% and 50.9%; at 100 kg produced 62%, 62.6%, 61.8% and 61.6%; while 120 kg gives 64.8%, 65.7%, 53.8% and 65.7%, respectively. The result indicated that effectiveness of inclusion of additives were much noticed at higher load, thus similar to that of COF.

Figure 11 illustrates the effect of nanoparticle concentrations on average friction coefficient and WSD under different loads (60, 80, 100, and 120 kg) at a speed of 1600 rpm. The operation discovered that the average friction coefficient decreases with the addition of nanoparticles in comparison to base fig oil, as shown in Fig. 11(a). However, at a specific concentration of EVA + TBHQ nanoparticles, the friction coefficient mostly rises as load increases but shows small variations compared to COF under 1200 rpm. At 60, 80, 100 and 120 kg, the COF of base fig. oil was 0.183, 0.198, 0.193 and 0.257, the use of 0.5 mass% EVA + 0.3 mass% TBHQ yielded 0.178, 0.175 and 0.177; 1 mass% EVA + 0.3 mass% TBHQ produced 0.173, 0.174 and 0.176; 1.5 mass% EVA + 0.3 mass% TBHQ gave 0.175, 0.178 and 0.179; while 2 mass% EVA + 0.3 mass% TBHQ results was 0.189, 0.177 and 0.182, respectively. However, the use of 2 mass% EVA + 0.3 mass% TBHQ resulted in poor performance with increased COF when compared to the base fig oil. The average reduction in friction coefficient caused by the addition of nanoparticles, as demonstrated in Fig. 11(a), suggested a good transition from sliding to rolling operation by the additive particles at the substrate surfaces, along with a recommended resistance to rapid viscosity degradation due to the presence of EVA copolymer in the formulated lubricant.

The average WSD as presented in Fig. 11(b), increases with increase on applied load. Reduction in WSD was recorded with addition of additives in fig oil in relative to base lubricant. Accordingly, at 60, 80 and 120 kg, the WSD of base fig.oil were 0.379, 0.452, 0.454 and 0.532; the use of 0.5 mass% EVA + 0.3 mass% TBHQ yielded 0.231, 0.250 and 0.252; 1 mass% EVA + 0.3 mass% TBHQ produced 0.213, 0.195 and 0.233; 1.5 mass% EVA + 0.3 mass% TBHQ yielded 0.242, 0.239 and 0.252; while 2 mass% EVA + 0.3 mass% TBHQ results were 0.328, 0.351 and 0.353, respectively. The research concluded that the reduction in the wear scar was due to the tiny and penetrative nature of the additives, which separate the body-body contact and transmit the sliding operation into rolling mechanism, which was reported also by Wang et al., [30].

As the COF and WSD results (optimal result concentration (1 mass% EVA + 0.3TBHQ) were not consistent, and the

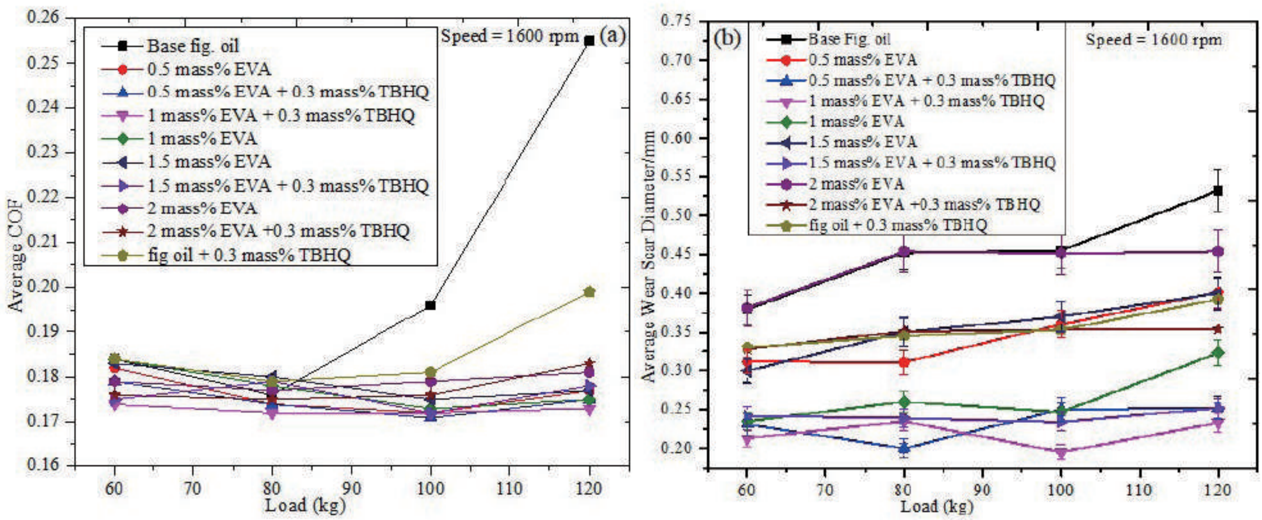

Fig. 11 Variation in average coefficient of friction (a) and WSD (b) with time for different concentration of EVA +TBHQ nanoparticles under different loads (60, 80, 100 and 120 kg) for speed 1600 rpm

first showing concentrations were much, the observed best concentrations (1 mass% EVA), which were further analyzed by forming lower and higher concentrations close to 1 mass% EVA, thus working with 0.8, 0.9, 1, and 1.1 mass% EVA, as shown in Fig. 12. The friction coefficients and wear behavior of base fig oil and 0.8, 0.9, 1, and 1.1 mass% EVA with the inclusion of 0.3 mass% TBHQ under ficus carica lubricant were tested as presented in Fig. 12. The study observed that base fig oil friction was quite high, which was about 0.28. However, as shown in Fig. 12 (a), fig oil derived from different concentrations of EVA and 0.3 mass% TBHQ had lower friction coefficients than the base fig oil friction condition.

Among the four EVA additive concentrations tested, 0.9 mass% EVA produced the best results when blended with 0.3 mass% TBHQ, followed by 1 mass% EVA and 1.1 mass% EVA, while 0.8 mass% EVA showed the least performance. This shows COF reduction by 20.4%, 57%, 72.5%, and 28.3% for 0.8, 0.9, and 1.1 mass%, respectively, while with SAE-5W-30 yielded 74.7%. The study indicated that fast and better development of frictional energy for little tribo-film formation for the reduction of friction was obtained with 0.9 mass% EVA + 0.3 mass%TBHQ. In addition to the small tribo film that resulted in low COF, the strength of the particles for facilitating rolling operation contributed an important part. The outcome was similar to what was observed from the research conducted by Singh et al., [31].

On the side of the wear resisting ability, inclusion of the additives yielded wea reduction, but SEA-5W-30 exhibited the optimal performance when compared to all the tested lubricants, as illustrated in Fig. 12 (b). The wear scar diameter under base lubricant was 0.41 mm, while the lowest WSD was 0.15 mm, recorded from a commercial reference of SAE-5W-30. The wear value of 0.9 mass% was observed to be similar to the commercial lubricant of SAE-5W-30, while 0.8 mass% shows the highest wear car diameter among the additives used, followed by 1.1 mass%. The analysis showed that the inclusion of 0.8, 0.9, and 1.1 EVA + TBHQ was reduced by 41.6%, 61%, 58.1%, and 50.8%, while the SAE-5W-30 produced 63% compared to base fig oil.

Figure 13 depicts the effect of nanoparticle concentrations on wear scar diameter for a load of 100 kg and speeds of 1400 rpm under various loads and temperatures. It was noted that the average friction coefficient reduces under different additive concentrations as load increases relative to the base lubricant, as presented in Fig. 13(a). The result displayed when tested at various temperatures demonstrated a similar trend with different loads investigated. As shown in Fig. 13(b), the average WSD increases with increasing temperature for a specific used nanoparticle. The research shows that commercial SAE 5W-30 yielded the lowest SWD, while 0.9 mass% produced the best performance among the additive concentrations tested. The finding also detected that the percentage decrement in WSD was due to the addition of nanoparticles and easy penetration within the sliding contact, thereby preventing the direct contact via transmission of sliding operation into the rolling mechanism.

3.3 Lubricants film behavior during testing

As shown in Fig. 12, the tribological analysis was performed on the tested samples so as to explore the lubricant film behavior and stability under a load of 100 kg at an operating speed of 1400 rpm. Under the motioned working condition, the lubricant was observed to display an unsteady film with a decrease from the start till about 1500 s, thus witnessing a sudden break in the formulated film between 1500 s and 1700 s and observing the same ununiform film structure till the end of the test as illustrated in the graph (Fig. 12). With the addition of additives into base oil, some levels of steady film were demonstrated during operation, but the best film stability was under 1 mass% EVA + 0.3 mass% TBHQ, followed by 0.9 mass% EVA + 0.3 mass% TBHQ, which gave the best COF. Application of 1.1 mass% EVA+0.3 mass% TBHQ and 0.8 mass% EVA+0.3 mass% TBHQ indicated unsteady film formation. The observation of unsteady film formation was due to the poor quality of developed film owing to the lack of frictional energy required for the formulation of desired film. The outcome from the results shows that lubricant with 0.9 mass% EVA + 0.3 mass% TBHQ particles exhibits good lubricity through maintaining the formulated lubricant film in terms of tribo-film stability during sliding compared to the base fig oil.

3.4 Wear surface analysis

To ascertain the nanofluid lubricating mechanism, the lubricated worn ball surface was analyzed using FESEM.

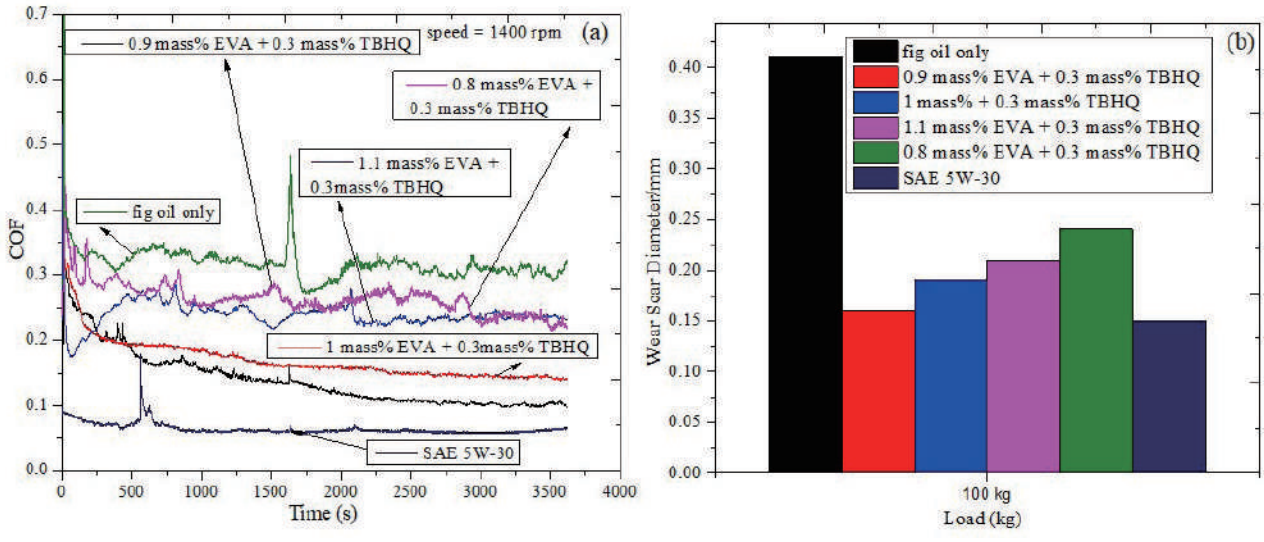

Fig. 12 Performance of various lubricants on COF (a), and WSD (b) at temperature of 75°C and load of 100 kg under uniform speed of 1400 rpm

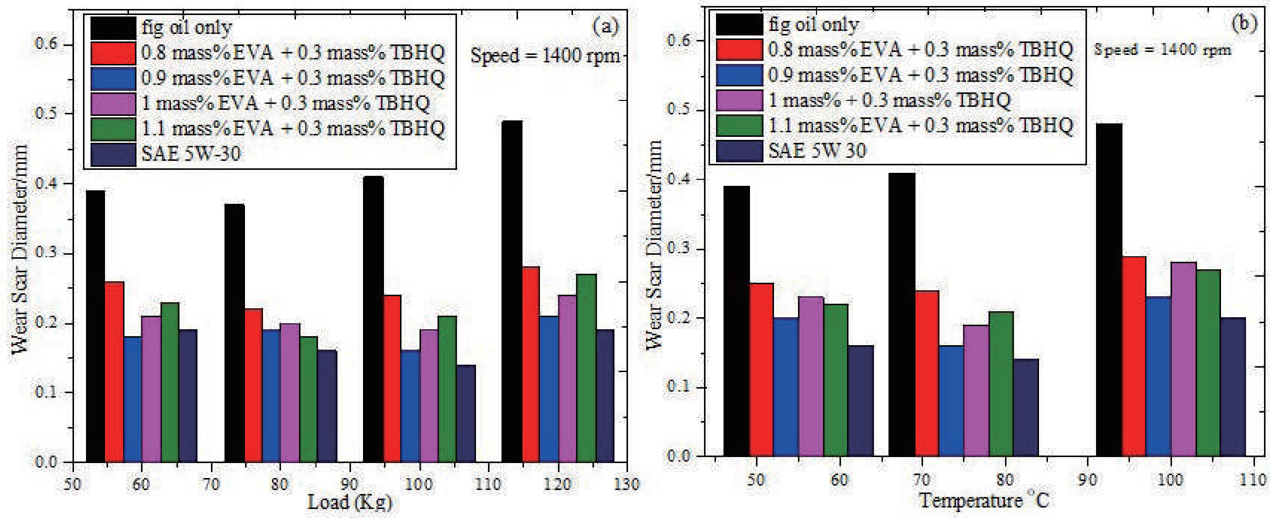

Fig. 13 Performance of various lubricants different loads at temperature of 75°C (a) and different temperatures at load of 100 kg (b) under uniform speed of 1400 rpm

Figure 14 shows the FESEM images from different lubricated surfaces (base fig oil only, 0.8%, 0.9 %, 1%, and 1.1% EVA + 0.3% TBHQ). The analysis was conducted using 100 kg of load, 75°C temperature, and a speed of 1400 rpm, which was observed to be the best performing condition. As shown in Fig. 14 (a), well pronounced rough wear can be observed similar to that of Fig. 14(b), (d) and (e), indicating ineffective lubrication leading to abrasive wear.

When compared to base oil and all other lubricants except SAE-5W-30 benchmarks (see Fig. 14(f)), the surface lubricated with 0.9% EVA + 0.3% TBHQ appears shallower and smoother (see Fig. 14(c)). Some healing effects on the grooves were observed, which are from the tribo-chemistry between the EVA + TBHQ and substrate, as seen in Fig. 14(c), (d), and (e), which indicate the point of healing by the nanoparticles. The effects of heat were seen at 1.1 mass% (Fig. 13(e), with suspected lubricant starvation due to the high concentration of additive, which is supported by previous work. by Opia et al., [32]. On investigating the surface tribo-chemistry on the surface lubricated with fig oil alone and best performance solution of 0.9% EVA + 0.3% TBHQ as shown in Fig. 15. As observed, few elements were detected on the surface with fig oil alone with high peak of Fe representing much exposure of steel tribo-pair used as shown in Fig. 15(a), while many elements like Si, high peak of oxygen and carbon) were found on the surface lubricated with 0.9% EVA + 0.3% TBHQ, indicating formation of

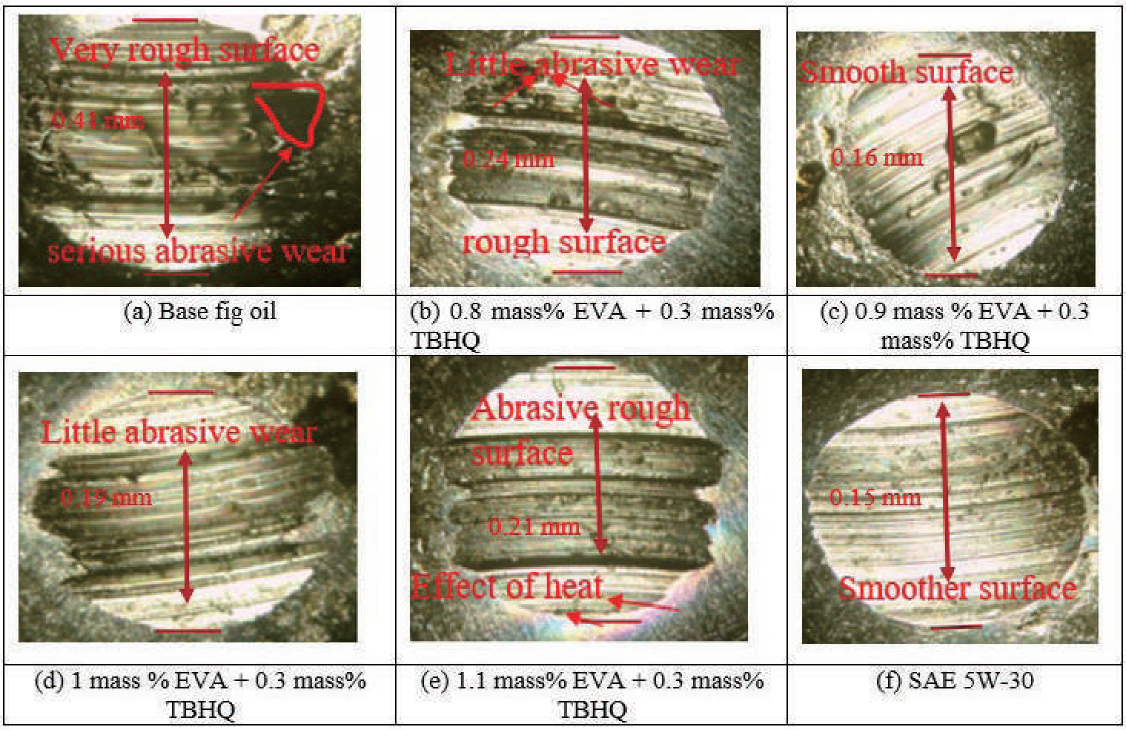

Fig. 14 FESEM images showing the wear scar of surfaces lubricated with different lubricants

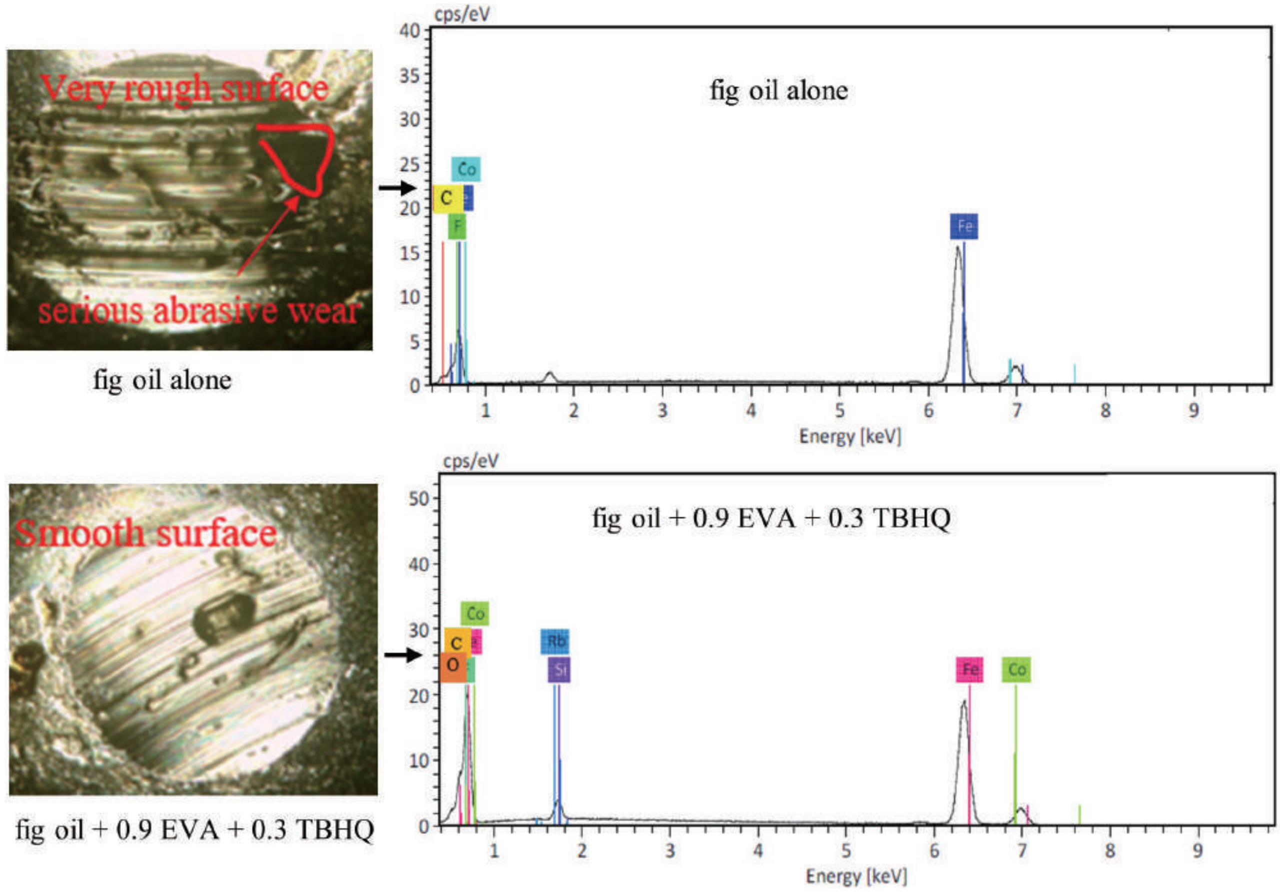

Fig. 15 FESEM images and corresponding EDX elemental tribo-chemistry on the lubricated surfaces with fig oil alone (a) and fig oil + 0.9 EVA + 0.3 TBHQ (b) additive

tribo-film. The observation of these elements was in correlation with EVA and TBHQ EDX analysis (see Table 2). The formation of these elements indicated that surface protections were observed during operation, thus reflected on the FESEM image as seen in Fig. 15(b), compared to base fig oil alone (Fig. 15(a)).

4 Conclusions

The impact of different EVA and TBHQ concentrations on the tribological behavior of fig oil was thoroughly investigated under various applied loads and sliding speeds. Analyses of worn surfaces and tribo-chemistry studies were used to explore tribological phenomena. The investigation came up with the following conclusions:

The addition of different chosen concentrations improves the tribological behavior of fig oil; as a result, it was found that the operation occurred under boundary and mixed lubrication conditions because of the type of wear produced. It was shown that the EVA + TBHQ with fig oil protected the surfaces from serious wear. Some abrasion wear patterns were still observed, but they were less severe than those from the base lubricant. The combination of 0.9 mass% EVA and 0.3 mass% TBHQ produced results comparable to those of commercial SAE-5W-30 and is therefore more effective in reducing friction and wear, perhaps because of its better hardness and abrasion resistance.

The TBHQ and EVA particles worked synergistically to lower the friction coefficient. Additionally, while sliding at moderate speeds or when the hydrodynamic influence of the oil film was minimal, the mixture showed improved wear resistance compared to the base fig oil. However, in high concentrations of EVA and TBHQ, no synergism effect was found. Designing tribo-components with oil lubrication, such as thrust sliding bearings in transmission systems, may benefit from the use of EVA + TBHQ.

During the running-in process, the surface of the subtract that was lubricated with 0.9 mass% EVA and 0.3 mass% TBHQ smoothed out to resemble that of a commercially available fully blended lubricant, which was thought to be important for reducing asperity-induced metal-metal rubbing in a mixed lubrication regime. Due to the inclusion of nano-particle additives in the base lubricant, significant tribo-chemical reactions took place during sliding as indicated by the EDX analysis, showing many elements on the lubricated surface (0.9 mass% EVA and 0.3 mass% TBHQ). The tribo-film can carry a sizable amount of load between two sliding contacts, which enhances the sliding system's boundary lubrication performance.

Acknowledgement

This study was supported by the research grant number R.J130000.7309.4B405 - Impact of Biodiesel Fuels (B30) on Selected Diesel Engine and Injector Spray Quality. This study was collaborated and sponsored by the Malaysian Palm Oil Board (MPOB).

Competing interests

The authors declare no competition nor conflict during and after the manuscript drafting.

Authors' contributions

AIA: Information curation; proper evaluation; research; main manuscript drafting. MKAH: Conceptualization; investigation; visualization; Supervision; and resources. MABA: Conceptualization; information curation, manuscript editing. MFMS: Resources and Manuscript review. ACO: Manuscript review and editing. IIBM Supervision; Manuscript review and editing. ZHBCD: Conceptualization; manuscript review.

References

[1] Quinchia LA, Delgado MA, Valencia C, Franco JM, Gallegos C. Viscosity modification of different vegetable oils with EVA copolymer for lubricant applications. Industrial Crops and Products. 2010;32(3): 607–612. https://doi.org/10.1016/j.indcrop.2010.07.011.

[2] Kowthaman CN, Arul Mozhi Selvan V. Synthesis and characterization of carbon nanotubes from engine soot and its application as an additive in schizochytrium biodiesel fuelled DICI engine. Energy Reports. 2020;6: 2126–2139. https://doi.org/10.1016/j.egyr.2020.08.003.

[3] Gad MS, Gadow SI. Enhancement of combustion characteristics and emissions reductions of a diesel engine using biodiesel and carbon nanotube. Fullerenes, Nanotubes and Carbon Nanostructures. 2021;29(4): 267–279. https://doi.org/10.1080/1536383X.2020.1837779.

[4] Khattak MA, Ayoub MAH, Manaf MAFA, Mahrul MF, Juhari MRM, Mustaffa MI, et al. Global energy security and european union: a review. Jurnal of Advanced Research in Applied Sciences and Engineering Technology. 2018;11(1): 64–81.

[5] Janakiraman S, Lakshmanan T, Chandran V, Subramani L. Comparative behavior of various nano additives in a DIESEL engine powered by novel Garcinia gummi-gutta biodiesel. Journal of Cleaner Production 2020;245: 118940. https://doi.org/10.1016/j.jclepro.2019.118940.

[6] Biddy MJ, Scarlata CJ, Kinchin CM. Chemicals from biomass: a market assessment of bioproducts with near-term potential. NREL Report 2016. https://doi.org/10.2172/1244312.

[7] Ahmed DI, Kasolang S, Dwyer-Joyce RS, Sainan KI, Roselina NRN. Formulation and physico-chemical characteristics of biolubricant. Jurnal Tribologi. 2014;3: 1–10.

[8] Rajaganapathy C, Vasudevan D, Murugapoopathi S. Tribological and rheological properties of palm and brassica oil with inclusion of CuO and TiO_2 additives. Materials Today: Proceedings. 2020;37: 207–213. https://doi.org/10.1016/j.matpr.2020.05.032.

[9] Adhvaryu A, Liu Z, Erhan SZ. Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties. Industrial Crops and Products. 2005;21(1): 113–119. https://doi.org/10.1016/j.indcrop.2004.02.001.

[10] Zulkifli NWM, Kalam MA, Masjuki HH, Shahabuddin M, Yunus R. Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant. Energy. 2013;54: 167–173. https://doi.org/10.1016/j.energy.2013.01.038.

[11] Mobarak HM, Niza Mohamad E, Masjuki HH, Kalam MA, Al Mahmud KAH, Habibullah M, et al. The prospects of biolubricants as alternatives in automotive applications. Renewable and Sustainable Energy Reviews. 2014;33: 34–43. https://doi.org/10.1016/j.rser.2014.01.062.

[12] Jain AK, Suhane A. Capability of biolubricants as alternative lubricant in industrial and maintenance applications. International Journal of Current Engineering and Technology. 2013;3(1): 179–183.

[13] Zareh-Desari B, Davoodi B. Assessing the lubrication performance of vegetable oil-based nano-lubricants for environmentally conscious metal forming processes. Journal of Cleaner Production. 2016;135: 1198–1209. https://doi.org/10.1016/j.jclepro.2016.07.040.

[14] Erhan SZ, Asadauskas S. Lubricant basestocks from vegetable oils. Industrial Crops and Products. 2000;11(2–3): 277–282.

[15] Okechukwu EH, Connolly D, Najjar YSH, Abubaker AM, Minami I, Almutairi A, et al. Physicochemical characterization of the synthetic lubricating oils degradation under the effect of vehicle engine operation. Lubricants. 2013;20: 135–138. https://doi.org/10.29333/ejac/90761.

[16] Güven N, Gökyer A, Koç A, Temiz NN, Selvi S, Koparal B, et al. Physiochemical composition of fig seed oil from turkey. Journal of Pharmacy and Pharmacology. 2019;7(10): 541–545. https://doi.org/10.17265/2328-2150/2019.10.003.

[17] Yadav G, Tiwari S, Jain ML. Tribological analysis of extreme pressure and anti-wear properties of engine lubricating oil using four ball tester. Materials Today: Proceedings. 2018;5(1): 248–253. https://doi.org/10.1016/j.matpr.2017.11.079.

[18] Azhari MA, Suffian QN, Nuri NRM. The effect of zinc dialkyldithiophosphate addition to corn oil in suppression of oxidation as enhancement for bio lubricants: a review. International Journal of Hypertension. 2020;1: 1–171.

[19] Almeida APP, de Oliveira APLR, Erbetta CDC, de Sousa RG, de Souza Freitas RF, e Silva MESR. Rheological study of polymers used as viscosity index improvers for automotive lubricant oils. Journal of Modern Physics. 2014;5(12): 1085–1093. https://doi.org/10.4236/jmp.2014.512110.

[20] Zulhanafi P, Syahrullail S. The tribological performances of super olein as fluid lubricant using four-ball tribotester. Tribology International. 2019;130: 85–93. https://doi.org/10.1016/j.triboint.2018.09.013.

[21] Erhan SZ, Sharma BK, Perez JM. Oxidation and low temperature stability of vegetable oil-based lubricants. Industrial Crops and Products. 2006;24(3): 292–299. https://doi.org/10.1016/j.indcrop.2006.06.008.

[22] Veriansyah B, Park H, Kim JD, Min BK, Shin YH, Lee YW, et al. Characterization of surface-modified ceria oxide nanoparticles synthesized continuously in supercritical methanol. Journal of Supercritical Fluids. 2009;50(3): 283–291. https://doi.org/10.1016/j.supflu.2009.06.007.

[23] Shara SI, Eissa EA, Basta JS. Polymers additive for improving the flow properties of lubricating oil. Egyptian Journal of Petroleum. 2018;27(4): 795–799. https://doi.org/10.1016/j.ejpe.2017.12.001.

[24] Saputra AH, Hapsari M, Pitaloka AB. Synthesis and characterization of CMC from water hyacinth cellulose using isobutyl-isopropyl alcohol mixture as reaction medium. Chemical Engineering, Universitas. Technology and Medicine. 2015;2020: 1–18.

[25] Fathy NA. Carbon nanotubes synthesis using carbonization of pretreated rice straw through chemical vapor deposition of camphor. RSC Advances 2017;7: 28535–28541. https://doi.org/10.1039/c7ra04882c.

[26] Faga MG, Duraccio D, Di Maro M, Pedraza R, Bartoli M, d'Ayala GG, et al. Ethylene-vinyl acetate (EVA) containing waste hemp-

derived biochar fibers: mechanical, electrical, thermal and tribological behavior. Polymers. 2022;14(9): 4171.

[27] Opia AC, Hamid MKA, Samion S, Ali AI, Johnson CN, Ibham V, et al. Tribological behavior of organic anti-wear and friction reducing additive of ZDDP under sliding condition: synergism and antagonism effect. Evergreen, 2022;9(2): 246–253.

[28] Jamaluddin NA, Talib N, Sani ASA. Tribological analyses of modified jatropha oil with hBN and graphene nanoparticles as an alternative lubricant for machining process. Journal of Advanced Research in Fluid Mechanics and Thermal Sciences. 2020;76(2): 1–10. https://doi.org/10.37934/arfmts.76.2.110.

[29] Opia AC, Hamid MKA, Syahrullail S, Johnson CC, Mamah SC, Ali AI, et al. Effect of surfactants on the tribological behavior of organic carbon nanotubes particles additive under boundary lubrication conditions. Tribology Online. 2022;17(1): 19–31. https://doi.org/10.2474/trol.17.19.

[30] Wang B, Zhong Z, Qiu H, Chen D, Li W, Li S, et al. Nano serpentine powders as lubricant additive: tribological behaviors and self-repairing performance on worn surface. Nanomaterials. 2020;10(5): 922. https://doi.org/10.3390/nano10050922.

[31] Singh Y, Chaudhary V, Pal V. Friction and wear characteristics of the castor oil with TiO_2 as an additives. Materialstoday: Proceedings. 2020;26: 2972–2976. https://doi.org/10.1016/j.matpr.2020.02.612.

[32] Opia AC, Kameil AHM, Syahrullail S, Johnson CAN, Izmi MI, Mamah SC, et al. Tribological behavior of organic formulated anti-wear additive under high frequency reciprocating rig and unidirectional orientations: particles transport behavior and film formation mechanism. Tribology International. 2022;167: 107415. https://doi.org/10.1016/j.triboint.2021.107415.

This paper is licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) License. This allows users to copy and distribute the paper, only upon conditions that (i) users do not copy or distribute such paper for commercial purposes, (ii) users do not change, modify or edit such paper in any way, (iii) users give appropriate credit (with a link to the formal publication through the relevant DOI (Digital Object Identifier)) and provide a link to this license, and (iv) users acknowledge and agree that users and their use of such paper are not connected with, or sponsored, endorsed, or granted official status by the Licensor (i.e. Japanese Society of Tribologists). To view this license, go to https://creativecommons.org/licenses/by-nc-nd/4.0/. Be noted that the third-party materials in this article are not included in the Creative Commons license, if indicated on the material's credit line. The users must obtain the permission of the copyright holder and use the third-party materials in accordance with the rule specified by the copyright holder.