Enhanced performance of bio-lubricant properties with nano-additives for sustainable lubrication

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Abstract

Purpose – The purpose of this study is to evaluate the potentials of nano-additives in enhancement of oxidation and thermal stability of biolubricants thereby, improving the resistance of dispersed nanolubricants to thermal degradation under elevated temperature.

Design/methodology/approach – This study evaluates the oxidation stability and tribological performance of nano-enhanced biolubricants. Graphene and maghemite nanoparticles at 0.1% volume concentration were dispersed into coconut oil. Oxidation stability was analysed using a thermal analyser to understand the effect of nano-additives on thermal degradation of lubricants under increasing temperature. In addition, tribological performance and viscosity of the tested lubricants were evaluated using a four-ball friction tester and viscometer according to American Society for Testing and Materials standards.

Findings – The results reveal that the oxidation stability of biolubricants dispersed with nano-additives improves due to delayed thermal degradation. The nano-enhanced biolubricants' oxidation onset temperature was delayed by 18.75 °C and 37.5 °C, respectively, for maghemite (MGCO) and graphene (XGCO) nanolubricants. This improvement imparts the performance viscosity and tribological performance positively. For graphene-enhanced nanolubricant, 10.4% and 5.6% were reduced, respectively, in coefficient of friction (COF)and wear scar diameter (WSD), whereas 3.43% and 4.3% reduction in COF and WSD, respectively, for maghemite-enhanced nanolubricant compared with coconut oil. The viscosity index of nanolubricants was augmented by 7.36% and 13.85%, respectively, for maghemite and graphene nanolubricants.

Research limitations/implications – The excellent performance of nanolubricants makes them suitable candidate as sustainable lubricants for machining with regard to environmental benefits and energy saving.

Originality/value – The effect of graphene and maghemite nanoparticles on the oxidation stability and tribological performance of biolubricants has been investigated. It is an original work and yet to be published elsewhere.

Keywords Viscosity, Nanoparticles, Tribological performance, Wear and friction, Biolubricant

Paper type Research paper

1. Introduction

Lubricants perform several functions such as friction and wear reduction, dissipation of heat and providing cooling. Lubricants application in sliding contacts lessen the possibility of metal-to-metal contact through the formation of tribo-film that separates the contacting surfaces in relative motion (Ahmed and Nassar, 2013; Mobarak *et al.*, 2014). Friction and wear reduction improve significantly with lubrication and heat dissipation from contacting surfaces and corrosion prevention (Madanhire and Mbohwa, 2016). The bulk of the lubricants consumed worldwide are from non-biodegradable and non-renewable sources such as petroleum- or mineral-based oil. The adverse effects of conventional lubricants on the health of operators and the environment, such as air pollution, contamination of the soil and groundwater and high cost of waste disposal, constitute a considerable task to sustainable manufacturing (Abdollah *et al.*, 2020; Zahid *et al.*, 2018). In addition, the need to seek alternative sources of lubricants is to compensate for the impending scarcity which may result when the hydrocarbon resources are exhausted due to volume of their current usage (Mobarak *et al.*, 2014). Due to their

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biodegradability, lesser toxicity, environmentally friendliness and excellent boundary lubrication, vegetables are considered suitable alternative to petroleum-based lubricants for sustainable manufacturing processes (Lawal *et al.*, 2014; Wickramasinghe *et al.*, 2020). Despite the seeming excellent performance of vegetable oils comparable to conventional lubricants, their poor low-temperature characteristics, poor oxidative and thermal stability are some of the challenges confronting their performance. The critical factor for the failure of lubricants while in operation, especially at elevated temperatures, is thermal degradation (Ali and Hou, 2020). These challenges can be addressed through modification of the vegetable oil chemical structure, reformulation of additives and genetic modification of oil seed crop (Shashidhara and Jayaram, 2010; Fox and Stachowiak, 2007). The use of additives is one of the ways towards addressing these challenges. Dispersion of nanoparticles in vegetable oils as a biodegradable lubricant enhance oxidative stability and thermal properties in addition to better tribological performance (Abdollah *et al.*, 2020; Darminesh *et al.*, 2017; Talib and Rahim, 2018; Padmini *et al.*, 2016). Heat transfer and anti-wear properties of base fluids enhanced by the dispersion of nanoparticles has attracted their use for the improvement of base fluid thermal and tribological properties (Sharma *et al.*, 2015; Su *et al.*, 2016a, 2016b).

Wang *et al.* (2017) affirmed that nanoparticle dispersion in palm oil improved the lubricating properties that enable the formation of the protective film, thereby reducing sliding friction between friction surfaces. The tribological properties of palm oil blended with 0.1% Vol. of 70 nm hexagonal boron nitride (hBN) was enhanced as reflected in the reduction of coefficient of friction (COF) and wear in comparison with the pure palm oil and commercially available engine oil SAE 15W40 (Abdollah *et al.*, 2020). Azman *et al.* (2016) reported that the addition of 0.05 Wt.% graphene particles in palm-oil trimethylolpropane ester blended in polyalphaolefin-blended lubricant resulted in reduction of friction and wear by 5% and 15%, respectively. The dispersion of copper oxide (CuO) and graphene nanoparticles (GNPs) in palm oil as additives improve the anti-wear and extreme pressure properties of the base palm oil by 2.77% and 12%, respectively (Azman *et al.*, 2019). Effect of molybdenum sulphide (MoS_2) on the performance of coconut oil and paraffin oil was evaluated by Koshy *et al.* (2015) on tribological and thermal performance of the base oils. They observed significant improvement of friction coefficient and anti-wear properties with application of nano-enhanced lubricants compared with the base oils. The coconut oil enhanced with MoS_2 indicated superior performance over the paraffin-based nanolubricants. Viscosity of lubricants is enhanced with nano-additives and, by extension, the viscosity index which is a critical factor in defining oil characteristics improved with addition of nano-additives (Mousavi and Heris, 2020; Esfe *et al.*, 2016). Modification of the rheological properties of palm oil-based nanolubricants will enhance the potential of their application as roller chain lubricant (Amiruddin *et al.*, 2020). Tribological performance of hBN nanoparticle dispersed in vegetable oil was evaluated by Akincioğlu and Şirin (2021) in comparison with pure base oil and dry conditions using a ball on disc test device. They reported an improvement of friction and wear under hBN nanolubricants regime compared to the pure oil and dry test condition. Su *et al.* (2015) reported the improvement of COF and anti-wear properties of vegetable oil with dispersion of graphite nanoparticles and that smaller size nanoparticle was more efficient in reduction of friction and wear. In a related study, vegetable oil LB2000 was reported to exhibit superior performance over mineral oil when both were dispersed with graphite nanoparticles as machining lubricants (Su *et al.*, 2016a, 2016b). Gulzar reported that the dispersion of MoS_2 in chemically modified palm oil resulted in friction and anti-wear properties improvement (Gulzar *et al.*, 2015).

Biolubricants in their pure form undergo instantaneous degradation under elevated temperature, and this causes deterioration in the quality of the oil and subsequently the shell life of the base oil. Thermal degradation occurs at temperatures higher than the oxidation temperature of oils and thus the usability of any lubricant is dependent on its oxidation stability (Stachowiak and Batchelor, 2013; Mannekote and Kailas, 2012). Thus, the use of nanoparticle as additives to base oils improve oxidation stability due to enhancement of their thermal properties (Rasheed *et al.*, 2016a, 2016b; Zuin *et al.*, 2020, 2017). Thermal degradation of base lubricants with dispersion of nanoparticles is retarded for about 10 min due to improved oxidation onset temperature of base oil with dispersion of GNPs (Rasheed *et al.*, 2016a, 2016b). Zuin *et al.* (2017) reported that the addition of lipophilic magnetite nanoparticles coated with stearic acid as additives in polyalphaolefin synthetic base oil (PAO8) improves thermal degradation of the blended nanolubricants due to enhance onset oxidation temperature. In addition, the improved oil retention capacity reduces friction and wear marks significantly. The use of hybrid nano-additives of Al_2O_3/TiO_2 in engine oil lubricant by Ali *et al.* (2018) resulted in a reduction by 7% of the friction power losses, thereby enhancing brake power and engine torque and improving engine mechanical efficiency. This improved performance translated to reduced fuel consumption as about 4 litres of fuel can be saved for every 100 km in the urban centre. In a related study, the frictional power losses of automobile engines can be reduced by 50% and 45% for TiO_2 and Al_2O_3, respectively, for enhanced commercial engine oil lubricants (Ali *et al.*, 2016).

Several studies on biolubricants dispersed with nanoparticles deals with tribological performance and rheological studies. However, reports on thermal degradation of biolubricants enhanced with nanoparticles are scarce in literature (Osama *et al.*, 2017), and there is need for the evaluation of oxidation and thermal stability of biolubricants enhanced with nanoparticles for sustainable application and understanding how the improvement of oxidation onset temperature with dispersion of nanoparticles affects their performance. The objective of the current study includes the formulation of vegetable oil-based nano-enhanced biolubricants with graphene and maghemite and evaluation of the effect of nano-additives on the oxidation onset temperature of the nano-enhanced lubricants, which is the basis for thermal stability of lubricants. In addition, tribological performance of the nano-enhanced lubricants was evaluated by using a four-ball friction tester and surface characterization of worn surfaces of test specimen by scanning electron microscope (SEM), energy dispersive X-ray (EDX) and atomic force microscopy (AFM).

2. Materials and methods

2.1 Nanolubricants formulation

The base coconut oil (CCO) was dispersed with graphene (xGNP) and maghemite (γFe_2O_3) nanoparticles at 0.1% volume concentration to produce nanolubricants. Properties of the nanoparticles used and coconut oil are enumerated in Tables 1 and 2. The enhanced nanolubricants were prepared in volumes of 100 mL according to a two-step method (Su *et al.*, 2015). The required quantity of nanoparticles is measured by using a precision electronic weighing balance and dispersed in the base oil. The nano dispersion was stirred using higher shear homogenizer (IKA T25 digital Ultra-Turrax, Germany) for 90 mins at 3,200 rpm. The nanolubricants were subjected to sonication process by using ultrasonication bath (RK 514 BH, Bandelin Sonorex, Berlin-Germany) with power rating and frequency of 600 W and 35 kHz, respectively, for 4 h to ensure a stable suspension and lubricants of uniform dispersion. All samples were prepared and dispersed without surfactant. The required quantity for the volume concentration of 0.1% for graphene and maghemite nanoparticles were estimated using equation (1):

$$\varnothing = \left(\frac{\frac{M_p}{\rho_p}}{\frac{M_p}{\rho_p} + \frac{M_{bf}}{\rho_{bf}}} \right) \times 100 \qquad (1)$$

Where $\varnothing$, M_p, M_{bf}, ρ_p and ρ_{bf} represent the volume concentration in percent, mass of nanoparticles, mass of base fluid, density of nanoparticles and density of base fluid, respectively.

Characterization of nanoparticles was done to determine crystal structure as well as composition using X-ray diffraction (XRD) analysis. XRD is an essential non-destructive tool to determine the material's composition and crystal structure from the positions (in degree) and relative intensities of the diffraction peaks. The XRD techniques rely on X-rays' dual wave/particle nature to obtain information about the structure of crystalline materials. XRD patterns of the nanoparticles were acquired with the aid of an automated XRD machine (Rigaku SmartLab with high-resolution X-ray diffractometer) by producing x-rays of voltage and current of 40 kV and 30 mA through copper material (*k*-beta).

Table 1 Physical and chemical properties of nanoparticles

Property	Graphene (xGNP)	Maghemite (γFe_2O_3)
Appearance	Solid	Solid
Colour	Black	brown
Average thickness (nm)	6–8	9.5 (dia.)
Density, g/cm^3	2.2	5.24
Melting point, °C	>3,600	1,565
Crystal Structure	Sheet layers	spherical

Table 2 Properties of coconut oil

Property	Value
Colour @ room temperature	Light yellow
Density, gcm^{-3} @ room temperature	0.924
Kinematic viscosity, cst at 40 °C	28.637
Kinematic viscosity, cst at 100 °C	7.226
Specific heat, J(kg°C)$^{-1}$	2100
Flash point, °C	290
Pour point, °C	21

2.2 Dispersion stability

The performance of nanolubricants is dependent on suitable dispersion stability, amongst other factors for any specific application. A stable dispersion reduces significantly or eliminates sedimentation and improves the ability of the stable lubricants to enhance wear and friction reduction (Su *et al.*, 2015). The nanoparticle suspension stability in base fluids is characterized by various techniques such as visual sedimentation, zeta potential, spectra absorbency and optical photographs (Koshy *et al.*, 2015). Dispersion stability of nano-dispersed fluid is an essential criterion for efficient performance. They are influenced by varying sonication time, preparation method and concentration loading (Su *et al.*, 2016a, 2016b). Stability tests were conducted by using Malvern Zetasizer Ultra-DiethelmKellerSiberHegner instruments in this study to determine zeta potentials.

2.3 Thermal and oxidation stability

Thermogravimetric analysis (TGA) brand thermal analyser (TA instrument, USA model TGA Q500 incorporated with software) was used for the evaluation of TGA and differential thermal analysis of the reference lubricant and nano-enhanced biolubricants to further understand the thermal degradation of nanolubricants under elevated temperature application. About 15 mg of each lubricant sample was subjected to a programmed heating process in nitrogen atmosphere from 20°C to 900°C at 10°C/min heating rate and air flow rate of 50 mL/min to evaluate inherent thermal stability of the lubricants. The onset or the initial decomposition temperature and the mass loss of the tested lubricants were extracted from the TGA and differential thermogravimetric (DTG) graphs as a measure of their thermal stability.

2.4 Viscosity measurement

Kinematic viscosity of the tested lubricants was estimated by using a rotational viscometer in accordance with American Society for Testing and Materials (ASTM) D2983. Both the pure base oil and the nano-enhanced biolubricants were subjected to gradual heating from room temperature up to 100°C and the kinematic viscosity data acquired. The viscosity index was then evaluated in according to ASTM D2270.

2.5 Tribological properties

Tribological performance of any lubricant reflects its lubricity or the ability to reduce wear and friction. In this study, lubricant samples were evaluated for wear and friction behaviour according to ASTM D4172-94 using the Ducom four ball friction tester. Specification of the standard Carbon-chromium steel (SKF) ball used as specimen for testing the lubricants, and the test condition are enumerated in Table 3. Pictorial view of the Ducom four-ball friction tester (TR 30 Series) and a schematic showing the

Table 3 Friction test parameters and composition of ball specimen

Test parameter	Value
Applied load (kg)	40 (392 N)
Rotation speed (rpm)	1,200
Temperature (°C)	75
Test duration (s)	3,600
Test ball materials	Carbon-chromium steel (SKF)
Composition (Wt.%)	92.9% Fe, 4.7% C, 1.6% Cr, 0.4% Mn, 0.3% Si
Ball diameter (mm)	12.7
Hardness (HRc)	62
Surface roughness, R_a (μm)	0.027
Lubricants	Coconut oil and 0.1%, 0.2% and 0.3% graphene-enhanced nanolubricants

arrangement of the lubricant and test ball specimen are shown in Figure 1.

The ball pot assembly containing the steel balls with a 10 mL quantity of lubricant is clamped under a rotating spindle which houses the upper ball that exerts pressure on the lower balls firmly submerged in the lubricants under evaluation. The ball pot assembly was taken out of the machine chamber at the end of the operation time with the heater turned off and the used lubricant drained off. Tint-free paper was used to wipe clean the tested steel balls after the initial cleaning with acetone. Tribological response of the lubricants were obtained by measuring wear scar diameter (WSD) of the three stationery balls with an image acquisition system and the Winducom 2010 software for acquiring the friction torque automatically. The COF was determined according to IP-239 standard from evaluation of the average tangential load and the average friction torque values of 30 readings taken per minute using the following equation (4):

$$Friction Torque, T = \frac{\mu \times 3W \times r}{\sqrt{6}} \quad (2)$$

Where T, μ, W and r represent the friction torque, COF, applied load and radius of the ball specimen, respectively. The worn surface of the test specimen were subject to further evaluation using surface profiler, AFM and EDX.

3. Results and discussion

3.1 Characterization of nanoparticles

The GNPs as shown in Figure 2(a), have a sharp peak at about 26.45° with higher intensity assigned d-002 diffraction peak and the pattern conforms with the structure reported by Rasheed *et al.* (2016a, 2016b). The orientation and structure pattern also indicate that the samples used are crystalline, which aids in high thermal conduction of the material. Similarly, the XRD pattern shown in Figure 2(b) indicates the most substantial reflection peak at about 35.6° with the highest intensity count of 311. This finding conforms with maghemite data from a previous study (Nazari *et al.*, 2014). There are no impurity peaks from maghemite analysis, which shows that the nanoparticle is of high purity. Both XRD patterns from the characterization conforms with the data reported in (JCPDS card No. 39–1346).

3.2 Stability of nanolubricants

Zeta potential is another method used to evaluate the stability test of nanolubricants and its aids in quick analysis. It is one of the quantitative methods used to evaluate the electrophoretic behaviour of dispersions. The absolute value of the zeta measurement (negative or positive) reveals the stability status of the dispersion—the higher the absolute zeta value, the better

Figure 1 (A1) Pictorial view of the Ducom four-ball friction tester (TR 30 Series) (A2) Schematic of the four-ball tester with the arrangement of the test specimens

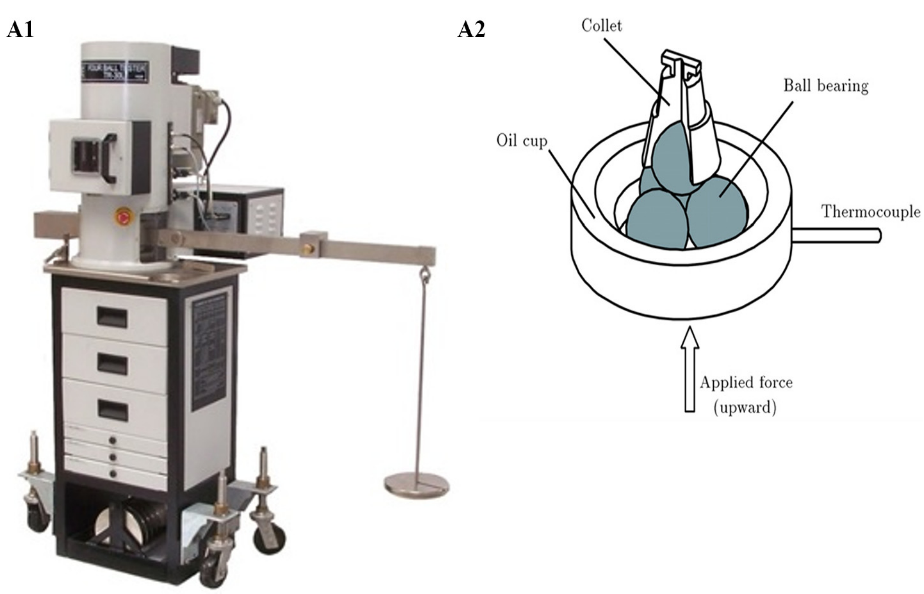
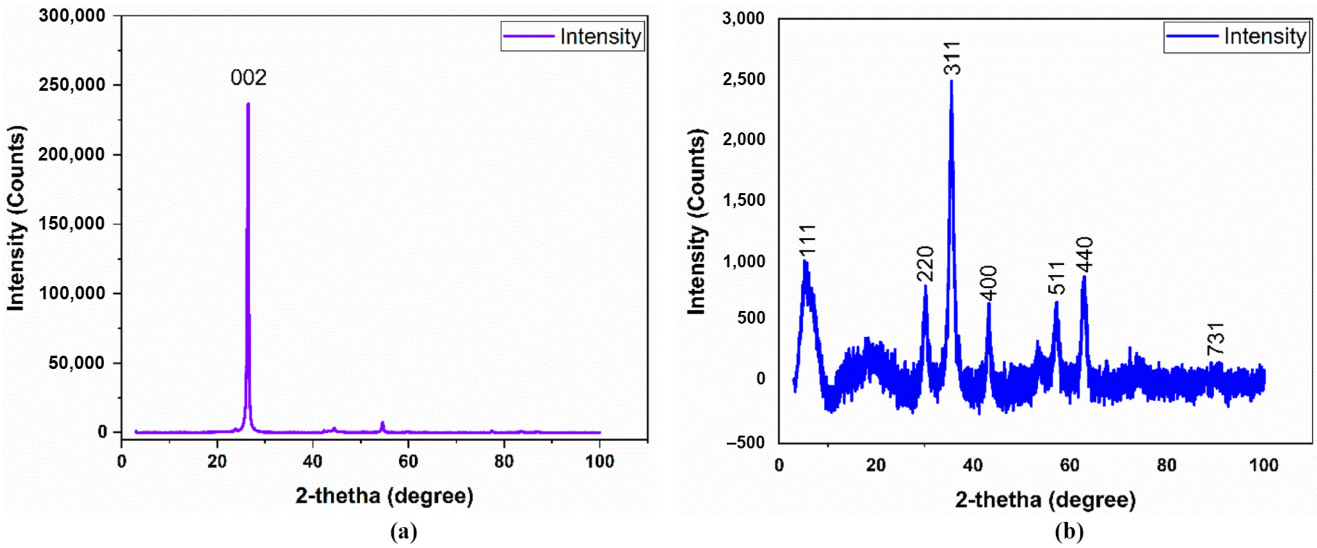


Figure 2 XRD graph for (a) graphene nanoplatelets (b) maghemite nanoparticles indicating diffraction peaks

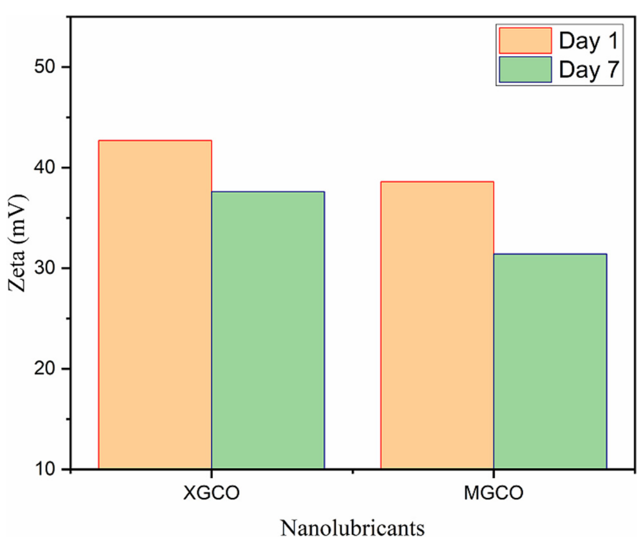


stability of the dispersion (Kong *et al.*, 2017). Zeta potential stability test was conducted for day one and day 7 of nanolubricants preparation and each concentration of nanolubricants, zeta measurement was repeated thrice. Figure 3 is a plot of the zeta potential for the evaluated nanolubricants at varying concentrations. The measurement's absolute value indicated nano-dispersion stability since the zeta potential values for all concentrations are higher than the 30 mV threshold for moderate stability, as agreed by several researchers (Kong *et al.*, 2017; Su *et al.*, 2016a, 2016b).

3.3 Thermal stability analysis

Thermal stability of lubricants was evaluated by using TGA/DTG to study the degradation and the rate of phase change throughout the heating process. Thermal degradation process of lubricant was recorded from the TGA curve as a measure of

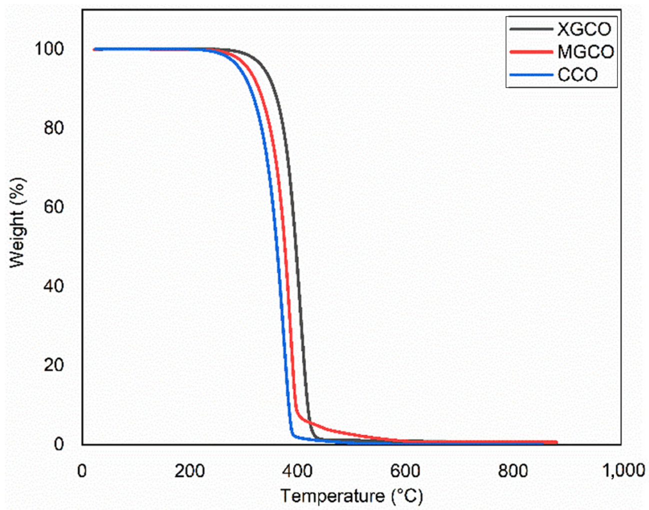
Figure 3 Zeta potential measurements for graphene- and maghemite-enhanced coconut oil nanolubricants



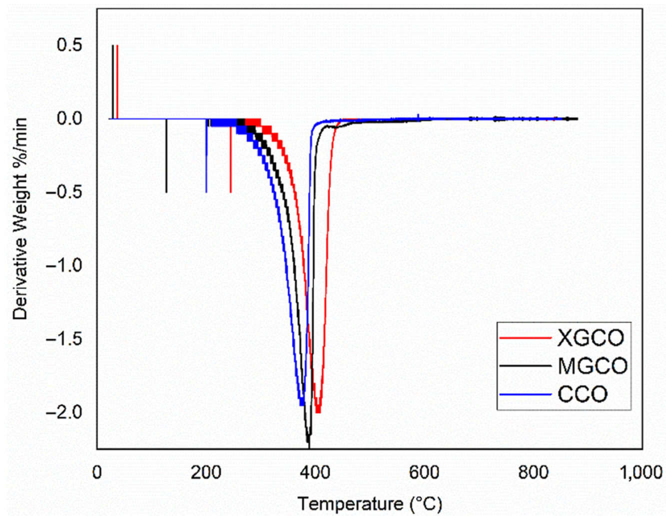
thermal stability of lubricants as shown in Figure 4(a). The weight loss appeared to be faster with CCO due to rapid deterioration compared to the nanolubricants, and this enables speedy decomposition of the base oil. The TGA curves indicates the degradation of the base lubricant (CCO), maghemite-enhanced nanolubricant (MGCO) and graphene-enhanced nanolubricant (XGCO), respectively, as temperature increases under inert atmosphere. Thus, the oxidation onset temperature for the tested lubricants are 325°C, 343.75°C and 362.5°C, respectively, for CCO, MGCO and XGCO. This implies that oxidation onset temperature in the presence of nano-additives for XGCO and MGCO can be delayed for 37.5°C and 18.75°C, respectively. The enhancement of the oxidation onset temperature with graphene nanolubricant outperforms the findings reported in previous studies (Rasheed *et al.*, 2016a, 2016b; Rashmi *et al.*, 2019) when they evaluated thermal degradation of graphene flakes-enhanced lubricants. The maghemite nanolubricant improves the oxidation onset temperature above the CCO but is lower than the enhancement with GNPs. There is an increase of mass loss for all the lubricants as temperature increases resulting in the removal of volatile substance. However, the speed of oxidation (slope of TGA curve) of the base oil without nanoparticles was observed to be much faster than that of the nanolubricants. It was observed that about 35% of total weight thermally decomposed at a temperature of 350°C for the base CCO, whereas higher energy is required for 35% of total weight decomposition of additive-enhanced MGCO and XGCO nanolubricants to occur at temperature of 366°C and 387°C, respectively. This finding is in conformity with the observation of Ali and Hou (2020) when they show that the onset temperature of lubricant with nano-additives can be delayed due to improved oil retention capacity.

Figure 4(b) shows the DTG plot of tested lubricants describing the mass loss as a function of increasing temperature under inert gas environment. The maximum rate of decomposition of the lubricants occurs at the peak points as indicated in the DTG plot. The DTG peaks (rate of weight

Figure 4 (a) TGA (b) DTG analysis of the tested reference base oil and enhanced nanolubricants



(a)



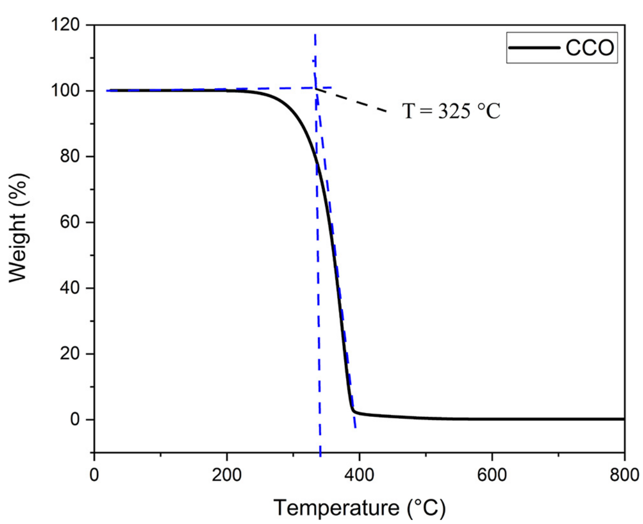
(b)

loss) of base oil CCO and nano-enhanced lubricants of MGCO and XGCO are 1.95%/min at 376.4°C, 2.2%/min at 388.2°C and 2.0%/min at 407.3°C, respectively. The results indicate that nanoparticle addition enables delayed degradation or evaporation of nanolubricant under higher temperature. This result conforms with the findings of Zuin *et al.* (2020) that addition of nanoparticles to base lubricants promotes oil retention by the enhanced nanolubricants at elevated temperature in comparison with the base oil. *Figure 5 indicates the determination of oxidation onset temperature.*

3.4 Kinematic viscosity and viscosity index

The kinematic viscosity of tested lubricants is represented in Figures 4 and 5. An improvement of kinematic viscosity was observed with the nano-enhanced lubricants over the pure base oil for the varying temperature ranges evaluated. The addition of nano-additives to the pure oil increases the viscosity of the

Figure 5 TGA of coconut oil indicating the oxidation onset temperature



nano-enhanced biolubricants. As temperature increases, viscosity decreases due to the broken down of molecular bonds between lubricants and the surface of nanoparticles under increasing temperature (Mousavi and Heris, 2020; Wang *et al.*, 2018). However, the viscosity of the nano-enhanced biolubricants at every temperature of measurement indicates an improvement over the base oil CCO as shown in Figure 6(a). The augmentation of kinematic viscosity of the base lubricant with nano-additives for selected sample temperatures are shown in Figure 6(b). From the plot, kinematic viscosity of base oil at 60°C improved by 10.2% and 18.5%, respectively, with the addition of maghemite and GNPs. The addition of nano-additives helps the strengthening the Brownian motion, thus reducing the random movement of molecules (Talib *et al.*, 2017; Zhang *et al.*, 2015). The graphene-enhanced nanolubricant exhibited the highest performance of kinematic viscosity improvement across all the range of temperatures evaluated as shown in the kinematic viscosity plot.

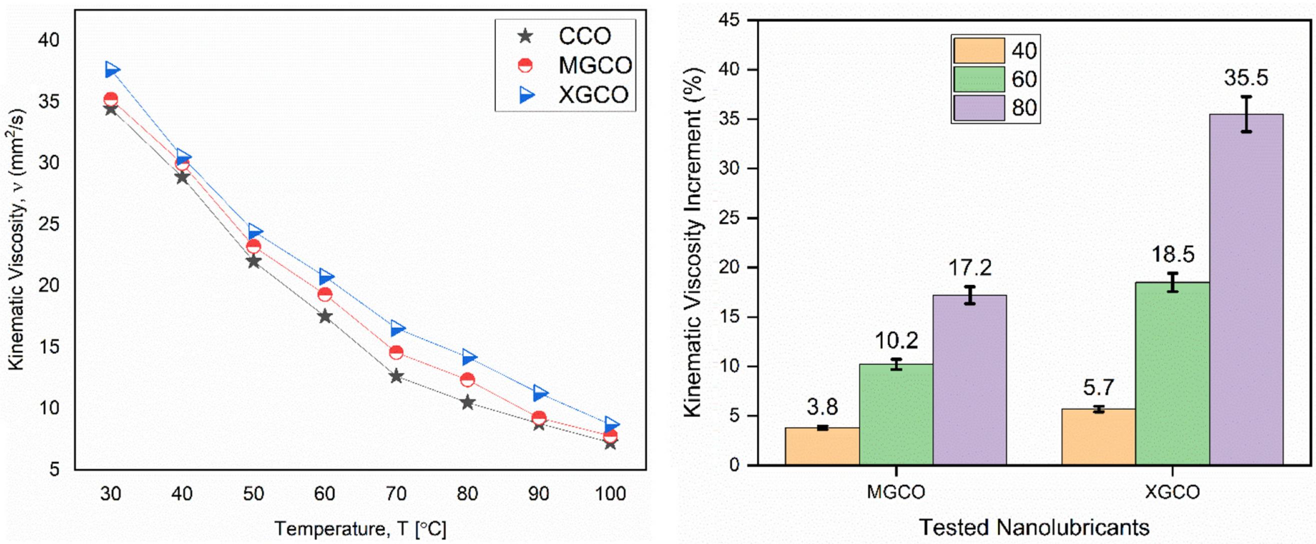
The viscosity index is a measure of change of kinematic viscosity over range of temperature. Higher viscosity index is desirable for lubricant performance as that will enhance tribo-film formation for efficient boundary lubrication under a wide range of temperatures (Rajendhran *et al.*, 2018). The viscosity index of the enhanced biolubricant was observed to be augmented by 7.39% with maghemite (MGCO) and 13.85% with graphene (XGCO) nano-additives as shown in Table 4. The XGCO nano-enhanced lubricant having higher viscosity index is an indication of providing stable lubricity over range of temperatures in comparison MGCO-enhanced nanolubricant (Azman *et al.*, 2019).

3.5 Tribological properties

3.5.1 Coefficient of friction and wear scar diameter

COF which is a measure of resistance between two bodies in contact is key tribological performance of lubricants. Figure 7 shows the friction performance for the tested lubricants under the four-ball test. Figure 7(a) indicates the variation of friction coefficient throughout the test duration. From the plot, it was

Figure 6 Kinematic viscosity of tested lubricants



(a) (b)

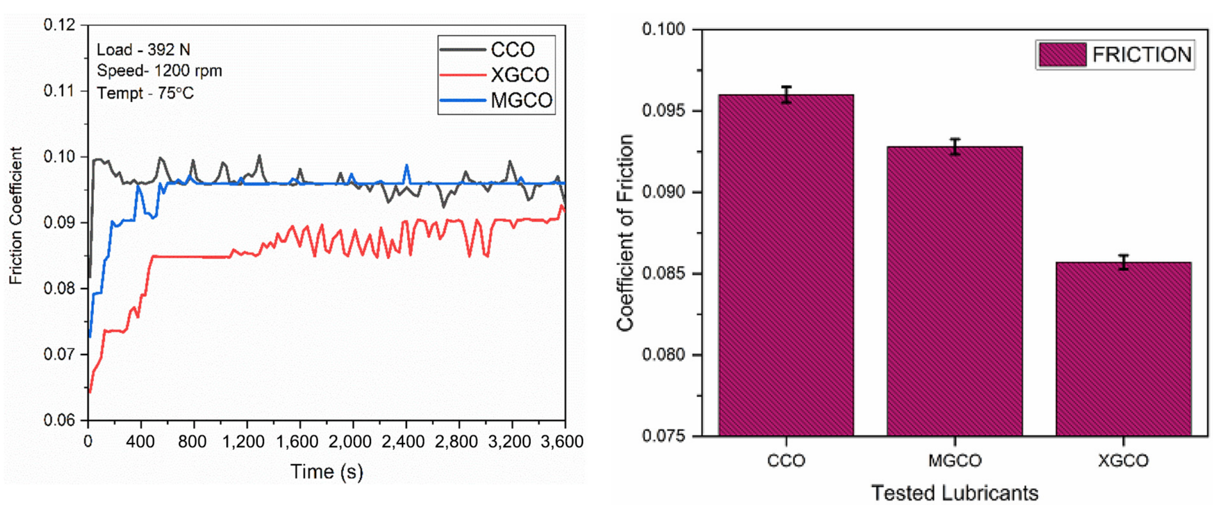
Notes: (a) Kinematic viscosity under temperature variation; (b) kinematic viscosity increment of nanolubricants in comparison with base oil

Table 4 Enhancement of viscosity index with nano-additives

Tested lubricants	Viscosity index	Viscosity index increment (%)
CCO (pure oil)	231	–
MGCO (Maghemite)	248	7.35
XGCO (Graphene)	263	13.85

noted that the base oil (CCO) has the highest friction coefficient, whereas the graphene-enhanced nanolubricant indicated the lowest friction coefficient which reflects the best performing amongst the tested lubricants. The maghemite-enhanced nanolubricant indicated better performance over the base oil but lower than the graphene-enhanced nanolubricant. The average friction coefficient for the tested lubricants are 0.0961, 0.0929 and 0.086 as shown in Figure 7(b). Thus, the addition of nanoparticles of graphene and maghemite have shown improvement of friction reduction over the pure biolubricant by 10.51% and 3.43%, respectively. The WSD is used to evaluate the tribological performance of lubricants, for they reveal the effect of the interacting surfaces in contact throughout the tribo-testing process. Figure 8 represents the WSD of tested lubricants and the results indicated that the

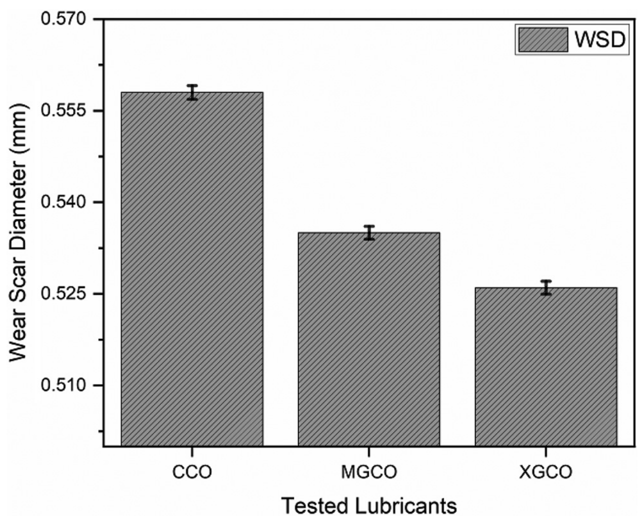
Figure 7 Coefficient of Friction of tested lubricants



(a) (b)

Notes: (a) Friction coefficient for the entire test duration; (b) average friction of four ball friction test

Figure 8 Plot of WSD of the tested lubricants



graphene-enhanced nanolubricant exhibited the best performance in terms of WSD. The pure base lubricant (coconut oil) shows higher WSD, whereas the maghemite nanoparticles and graphene-enhanced nanolubricants (MGCO and XGCO) indicated improvement of wear reduction with addition of nanoparticles. The WSD for the tested lubricants of CCO, MGCO and XGCO are 0.557 mm, 0.533 mm and 0.526 mm, respectively. This implies a reduction of WSD by 4.3% and 5.6%, respectively, for the MGCO and XGCO nanolubricants in comparison with base biolubricants (CCO). The addition of nanoparticles helps in the formation of tribo-film at the contacting surface, thereby causing rolling effect between the asperities and thus reducing friction and wear (Talib *et al.*, 2017). The graphene-enhanced biolubricant (XGCO) exhibited the best performance as anti-wear and friction reduction nanolubricant, and this can be attributed to the strong intermolecular bonding between the lamellar structures of graphene nanoplatelets. Thus, this finding reveals that lamellar sheet nanoparticles enhance better tribological performance than nanoparticles of spherical structures (Farsadi *et al.*, 2017).

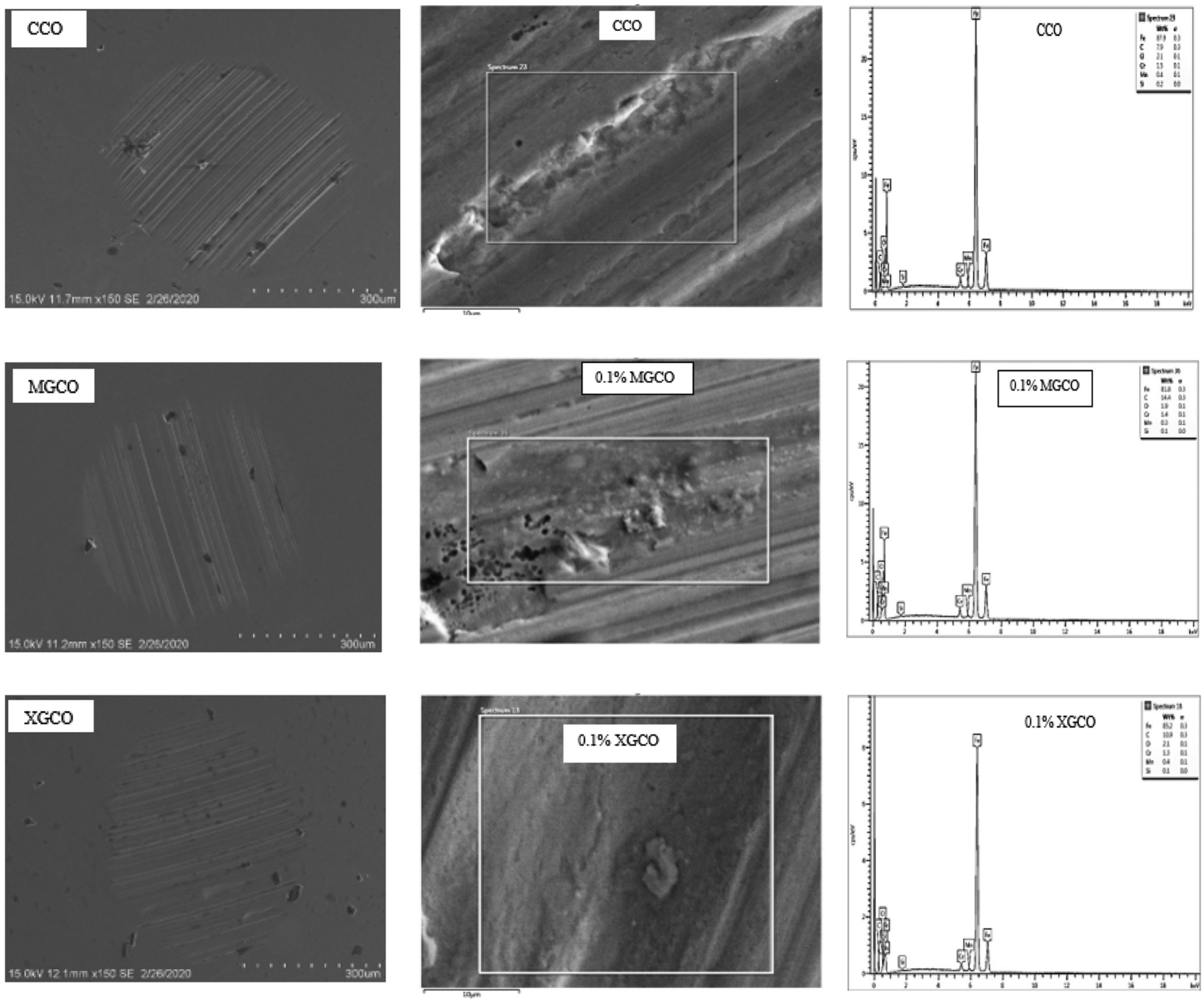
3.5.2 SEM/energy dispersive X-ray of worn surface

The surface morphology of worn surfaces of steel balls for the tested lubricants are evaluated using SEM/EDX to further understand the effect of lubrication with pure base oil and oil with additives dispersion. Surface morphology of the tested specimens were acquired at a magnification 150x are shown in Figure 9. It was noted that the breaking down of lubricant film under base oil (CCO) lubrication as shown causes adhesion of contacting surfaces resulting in adhesive wear. This phenomenon leads to transfer of material between the contacting surface as observed by Talib *et al.* (2017) due to the breaking down of the micro-joint formed as result of the adhesive wear. The surfaces lubricated with nanolubricants exhibited smoother surface compared to the pure coconut oil. Deposition of graphene flakes on the contacting surfaces lubricated with graphene-enhanced nanolubricant reduces contact between asperities by providing a protective tribo-film, reducing friction and wear between the contact surface due to effective lubrication. This finding collaborate the view expressed that protective tribo-film mechanism influence friction reduction in piston-ring assembly of automobile engine when lubricated by Al_2O_3- and TiO_2-enhanced lubricants (Ali *et al.*, 2018). The surface lubricated with maghemite-enhanced nanolubricant exhibited a smoother surface compared to the base lubricant. The roll in of nanoparticles between contacting surfaces causes a ball-bearing effect which aid the reduction of friction between contacting surface (Ali *et al.*, 2016). The EDX analysis of the worn surface reveals the elemental components and their composition as shown on the spectra in Figure 9. The variation in the chemical composition of the surface of the tested sample with nanolubricants indicated better performance. The increase of the elemental carbon content of the analysed surface confirms the deposition of graphene nanoplatelets which aid the formation of protective layer, thereby reducing the contact between asperities. The presence of oxygen could be due to material oxidation from the tribo-chemical interaction between the tribo-pairs and lubricating films during the friction testing process. The increase of carbon content of the surfaces lubricated with nanolubricants as revealed by the EDX is an indication of improved ability of the nanolubricants to bear the load at contacting surface, thereby ensuring sufficient lubrication better than the surface lubricated with pure base oil (Azman *et al.*, 2019; Koshy *et al.*, 2015).

3.5.3 Surface roughness/morphology

The roughness of the lubricated surfaces was further evaluated using surface roughness profiler and AFM, as shown in Figure 10. Surface profiler was used to measure the tested specimen for better understanding the texture of lubricated worn surfaces. The test specimen lubricated with graphene-enhanced nanolubricant exhibited the lowest Ra value of 0.14 μm compared to other samples. The smoothness of the surface is further collaborated by the AFM result as shown in Figure 10, labelled XGCO with height of ridges 30 μm on the worn surface. This could be attributed to the protective tribo-film mechanism through the formation of sufficient lubricating film between contacting surfaces to reduce or cause physical separation between asperities, significantly reducing friction and wear (Rajendhran *et al.*, 2018). The surface lubricated by biolubricant without nano-additive produces the highest Ra value of 0.18 μm. This can be attributed to the poor thermal and oxidation stability of biolubricant, which causes accelerated deterioration of lubricant without additives at higher temperatures. The breaking down of lubricant film exposes the contacting surfaces to intense interaction of surfaces leading to higher roughness, wear and friction due to adhesive wear. This finding aligns with observation of Talib *et al.* (2017) when they evaluated the performance of modified jatropha oil. The AFM result for the specimen lubricated with base lubricant indicated the height of ridges on the worn surface to be 0.53 μm. The specimen lubricated with maghemite-enhanced nanolubricant indicated enhanced surface roughness over base lubricant but below the graphene-enhanced nanolubricant lubricated specimen. The improved surface roughness was aided by converting the sliding friction

Figure 9 SEM/EDX of worn surfaces to evaluate effect of lubricant types on the wear performance

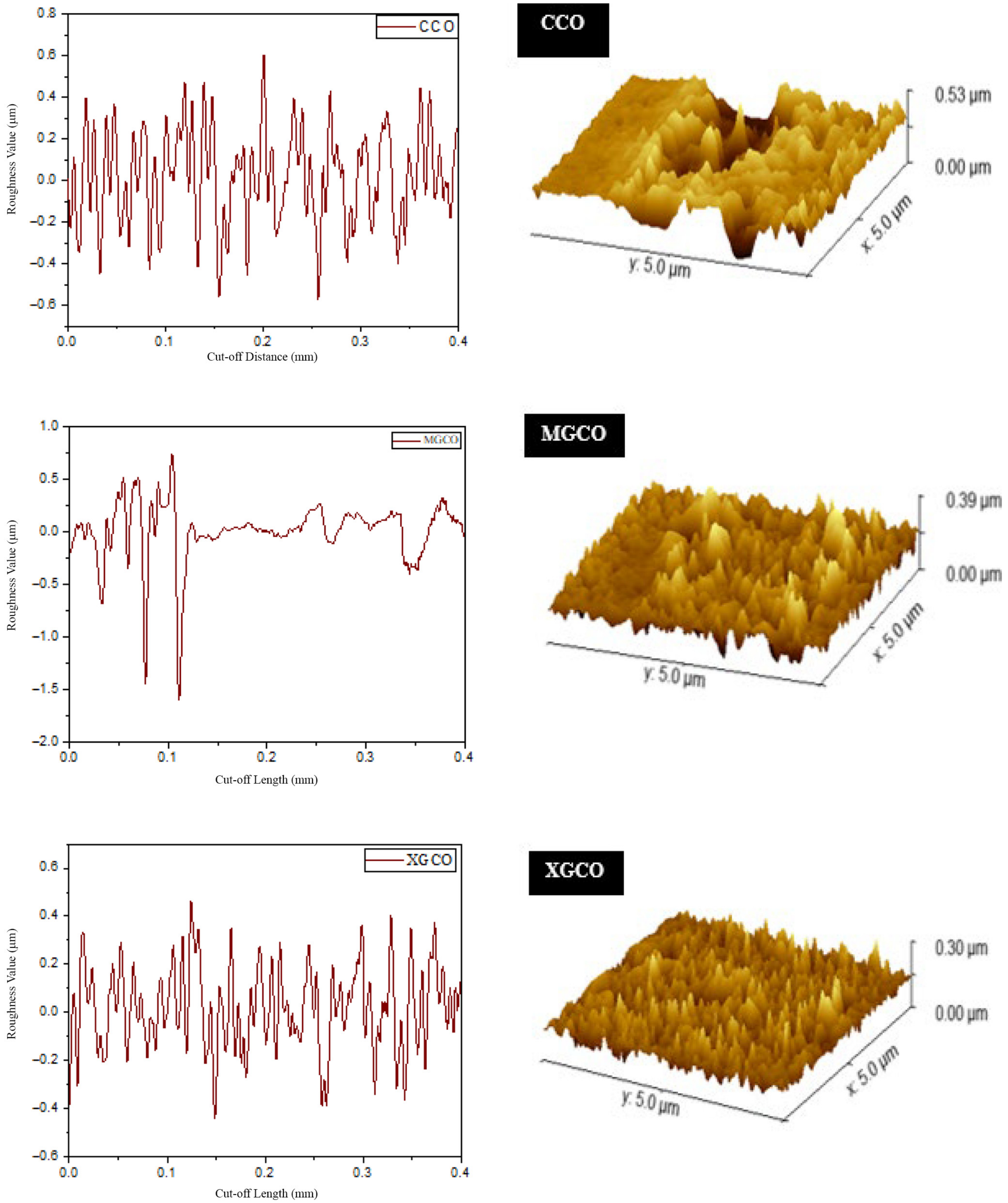


at contact surfaces into rolling friction. The formation of ball bearing effect aided the improved surface under the maghemite-enhanced nanolubricant. The worn surface has a roughness Ra value of 0.17 μm. The AFM of the worn surface reveals a height ridges of 0.39 μm.

4. Conclusion

The properties of an enhanced vegetable oil with graphene and maghemite nanoparticles have been evaluated in terms of thermal stability, viscosity and tribological properties. The oil retention capacity of the nano-enhanced biolubricants were observed to improve over the base oil and that onset oxidation temperature of the nanolubricants can be delayed by 9.09°C and 31.82°C, respectively, for maghemite and graphene nanolubricants. This implies better oil retention capacity for the nanolubricants to resist quick degradation as operating temperature increases. The graphene and maghemite nanoparticles dispersion in the base biolubricants indicated a reduction of 10.51% and 3.43%, respectively, for COF as well as 5.6% and 4.3%, respectively, in terms of WSD in comparison with the base biolubricants (CCO). The tribological performance was made possible by the protective layer formation mechanism to combat friction and wear of surface lubricated with graphene-enhanced nanolubricant. On the other hand, the maghemite-enhanced nanolubricant was instrumental in conversion of sliding friction into rolling, thereby interacting to form tribo-film on sliding contacts which aids in reduction of friction and wear at the contacting surface. The results reveal that the graphene-enhanced nanolubricant was more effective in improving the thermal stability and tribological properties of vegetable oil-based biolubricants. This performance can be attributed to its lamellar structure and the inherent properties of the graphene nanoplatelets. Thus, the addition of nanoparticles in biolubricant improves their performance, thereby making them a competitor in the lubricant market in regard to their dual potential of addressing environmental concern and energy saving when compared to the conventional lubricants.

Figure 10 Surface roughness evaluation using surface profiler and AFM



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