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*Article*

# Effect of Concentration on the Tribological behavior of Cyclic Heated Formulated Organic Carbon Nanotubes in Base Lubricant under Boundary Conditions

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## Abstract

The tribological enhancement of base lubricant under different concentration of formulated *Eichhornia Crassipes* carbon nanotubes (EC-CNTs) was conducted in this research. Cyclic heating approach was adopted in the formulation of EC-CNT and scientifically characterized. The characterization results confirmed the sample EC-CNTs. The effect of EC-CNT in base rapeseed oil terms of concentration, coefficient of friction (COF) and surface roughness (Ra), load carrying capacity, lubrication film stability and film mechanism were evaluated using high frequency reciprocating rig machine. The results showed that inclusion of EC-CNTs into base rapeseed oil, enhanced the tribological properties. The resultant values of COF were 0.064, 0.051 and 0.087 for rapeseed blended 1 mass%, 2.5 mass%, 4 mass% EC-CNT respectively. This is 38.5% COF reduction from 2.5 mass% EC-CNT against base oil. Under wear scar diameter, 2.5 mass% showed 47.9% reduction compared to base oil. The Ra was reduced with addition of nanoparticles, especially with 2.5 mass%. The tribological enhancement by EC-CNT is attributed from tribo-chemical reaction between the particles and the interfaces leading to formation of active protective tribo-film. The mechanism exhibited by the nanoparticles were healing and rolling from which the tribo-enhancement were achieved.

## Keywords

EC-CNTs nanoparticles, concentration, rapeseed oil, lubrication mechanism, friction and wear

## 1 Introduction

Friction and wear cause significant energy loss as well as a variety of equipment failures. One of the most effective methods for energy efficiency, friction and wear reduction is the use of lubricants. To enhance performance of lubricant, suitable additives needs to be blended with base oil during formulation. Various studies have reported that nanoparticles, like metal [1], metal sulphides, metal oxides [2], carbonate, borate [3], organic materials [4] and carbon materials [5] when applied with base lubricants has tendency of reducing friction and wear. Tribological study was conducted on CuO and graphite nanoparticles effects towards anti-wear and friction reduction enhancement of nano-lubricants [6]. The outcome revealed that CuO nano inclusion had the best anti-wear and friction reducing performance, and was attributed to their greater size together with lower bulk hardness of the nanomaterials compared the balls' content [6, 7]. Furthermore, the study [8] on nano-diamond, CuO and $TiO_2$ nanoparticles blended with API-SF engine oil as additives was investigated. CuO outperformed other nanoparticles in terms of tribological performance, indicating 18.4% and 5.8% reduction in the coefficient of friction (COF) in API-SF engine oil and base oil, respectively, with 16.7% and 78.8% decrease on the worn scar depth, respectively, when compared to tested oils without CuO nanoparticles. The outstanding performance of CuO in the area of friction and wear reduction were attributed from its excellent film mechanism [8]. On the other hand, environmental concerns have prompted researchers to look into degradable and sustainable energy resources as an alternative source to synthetic and fossil class [9, 10], as well as lubricant additives.

On this effect, chemically processed bio-based lubricants have been reported as a promising substitute to the other counterparts, thus required suitable nano-additives to enhance the anti-wear features and load carrying capacity of the bio-based lubricant [10–13]. Nano-lubricant made from rapeseed oil has been tested under sliding conditions and found to be similar to the counterparts with enormous advantages including eco-friendly features [14]. Despite the advances in research, only a few tribological studies involving base vegetable oil and bio nano additives have been reported that nanofluid of vegetable lubricant, possesses high thermal conductivity, thus enhances the frictional properties [1, 15]. Salah et al., [16] conducted tribological research using carbon nanotubes formulated from carbon-rich fly ash under different concentrations. The result shows that under 0.1 mass% concentration, yield the excellent performance with significant reduction in COF to around 58% of its original value without additive, showing good dispersion and film mechanism. Therefore, the inclusion of organic formulated *Eichhornia Crassipes* carbon nanotubes (EC-CNTs) in base rapeseed oil (rap. oil) tribo system may be beneficial due to its amphipathic property. To the best of our knowledge no research work has been reported on this topic. Therefore, this paper investigates the effect of EC-CNTs concentration as lubricant additives in vegetable base lubricant of rapeseed oil. In addition, commercial fully blended synthetic engine oil SAE 20W-40 was used as a reference. Also the film mechanism will be monitored under in-situ condition using optical microscope as suggested [17, 18]. The tribological effects of EC-CNTs will be studied using a High frequency reciprocating rig (HFRR) machine. The use of scanning electron microscope (SEM) was employed for the analysis of the worn surfaces, thereby interpret the nature of mechanisms exhibited by the various lubricants during the lubrication.

## 2 Materials and methods

### 2.1 Materials

*Eichhornia Crassipes* (EC) plant was collected from Nigeria and processed the generated Eichhornia Crassipes nanoparticles (EC-NPs) into EC-CNTs in the department of Mechanical Engineering, Option of Tribology, using cost effective method of cyclic heating approach [19]. The base rap. oil and commercial SAE 20W-40 oil were purchase from Sigma-Aldrich Co. LLC company. Rap. oil was chosen as the base oil, because of its recorded tribological characteristics and considered to be among the promising bio-lubricant, thus serves multiple purposes [20].

### 2.2 Characterisation of EC-CNTs particles

This is to ascertain the nature of the formulation, the size to enable them blend well in lubricant and easy penetration in between sliding contact region and to know the functional groups for its compatibility on application. The morphology and elemental composition characterization analysis of EC-CNT was performed using SEM fitted with EDX. Particles size distribution was conducted using a hydrodynamic light scattering of particle size machine (Zetasizer Nano ZS; Malvern instrument, United Kingdom).

### 2.3 Raman spectroscopy and Thermo-Gravimetric Analysis (TGA) study

Raman Lab RAM HR Evolution (Horiba Scientific, UK) was used to confirm the nature of CNT formulated and performed within 400-2500 $cm^{-1}$ spectral region. The study uses 633 nm solid-state laser (12 mW). Raman spectra were gathered at room temperature by concentrating the laser on the formulated sample region using a microprobe fitted with a 100x eyepiece salah et al. [16] and Costa et al. [21]. TGA was carried out using Netzsch Sta 449 F5 thermo-gravimetric analyser under 50°C to 950°C with 10°C $min^{-1}$ heating rate under nitrogen.

### 2.4 FT-IR spectroscopy analysis

Fourier Transmission Infrared Spectrum (FT-IR) was carried out on the EC-CNT, base oil with and without EC-CNT additives respectively. Mattson infinite series of Model 960 Moog ATI USA were used and operate with sample thin films of 5 mm thickness. Spacers of 13 mm and 0.025 mm diameter were used. Accordingly, little quantities of the sample were carefully placed on the diamond surface of the ATR accessory to carry out the analysis. The computer was programmed with a spectral resolution of 4 $cm^{-1}$ on a spectral wavenumber ranging from 4000-650 $cm^{-1}$. Before any test, a mandatory 100 scans (background and sample) must be done Jie et al. [22].

### 2.5 Experiment procedure

The investigation on friction and wear tribological properties of EC-CNT was conducted on sliding contact between a flat of high chromium steel (AISI 52100) and aluminium ball using HFRR under boundary lubrication conditions of highly stressed ball-on-flat contact as illustrated in Fig. 1. The testing element flat steel (40*40 mm dimension) was made of AISI 52100 steel of hardness approximately 570-750 Hv with surface roughness (Ra) 0.1 μm, while softball aluminium (10 mm diameter) was made from 190-210 Hv with Ra 0.035 μm. The Ra of the flat plate was measured using profile-meter of 0.02 μm. EC-CNTs sample concentrations (1, 2.5 and 4 mass%) were dispersed in the base rap. oil applying an ultrasonic probe for 40 minutes. The properties of the base oil with and without additives are listed in Table 1, while the lubricant preparations are stated in Table 2. Before testing, various setup elements were ultrasonically cleaned using heptane cleaning agent for 7 min, followed with ethanol before using hot air for final dry, thus done before


Fig. 1 Machine set up, a) Sliding section, b) HFRR machine, c) system monitor

Table 1 Properties of the lubricants (SAE 20W-40, Rap. oil without and with different concentration of EC-CNTs)

| Properties | SAE 20W-40 | Rap. oil | Rap. + 1 mass% EC-CNT | Rap. + 2.5 mass% EC-CNT | Rap. + 4 mass% EC-CNT |
|---|---|---|---|---|---|
| Viscosity @ 40°C | 52.1 | 40.3 | 70.1 | 72.9 | 77.4 |
| Viscosity @ 100°C | 14.3 | 7.9 | 15.0 | 16.6 | 17.2 |
| Viscosity index [ASTM D2270] | 128 | 220 | 183 | 175 | 172 |
| Pour point [ASTM D97] | -21 | -18 | -15 | -13 | -13 |
| Specific gravity @ 15°C [ASTM D287] | 0.87 | 0.913 | 0.95 | 0.93 | 0.93 |
| Flashpoint [ASTM D92] | 230 | 320 | 243 | 223 | 231 |

Table 2 Samples/lubricant and additive preparation

| Samples | Standard oil | Additives/oil solution |
|---|---|---|
| SAE 20W-40 | 100% | SAE 20W-40 (100%) |
| Rap. oil | 100% | Rap. base oil (100%) |
| EC-CNT (10%) | 90% | 1 mass% EC-CNTs in 99% Rap. oil solution |
| EC-CNT (25%) | 75% | 2.5 mass% EC-CNTs in 97.5% Rap. oil solution |
| EC-CNT (40%) | 60% | 4 mass% EC-CNT in 96% Rap. oil solution |

and after each tests. The friction tests due repeated three times for each additive sample to ensure that the experiments were reproducible. Prior to the test, little model was fabricated with a white flat plate and ball of the same dimension with that of main experiment. It was set into operation and uses microscopic machine to observe the film formation and behavior with the sliding ball. This technique was adopted in the main work for the film mechanism analysis.

2.5.1 Friction and wear tests

The investigation was carried on the sliding between the ball and flat under the frequency of 5 Hz, normal load of 100 N, linear stroke of 10 mm, temperature of 75°C for time duration of 15 min. The COF was recorded via the WINDOCUM 2010 softwear. The study was first conducted on base rap. oil, followed the oils blended with EC-CNT (1, 2.5 and 4 mass%) before testing with SAE 20W-40 as reference. Also, different normal applied loads of 40 N, 60 N and 80 N were used to analyse the load carrying capacity of EC-CNT concentrations and to confirm the best candidate. Further analysis was conducted using the best candidate with different quantities of base lubricant (60, 120 and 180 ml) under load of 120 N while other working conditions remain constant. The use of atomic force microscope, Scanning Electron Microscopy (SEM) and EDX were imployed to determine the Ra, Wear scar diameter (WSD), elmental distribution on the lubricated surface and the additive mechanism of operation.

## 3 Results and discussions

3.1 Characterization of EC-CNTs additive

Figure 2 shows the morphology of EC-CNTs and EC-NPs nanostructures examined using SEM. The result indicated the tube-like nature of the EC-CNTs (Fig. 2 (a)), while little of big tube-like structure were shown in EC-NPs (Fig. 2 (b)). The elemental composition of both EC-CNT and EC-NPs are shown in Table 3, indicating different elements, with percentage of carbon (C) and oxygen (O) in EC-CNTs were 70.4% and 17.4%,

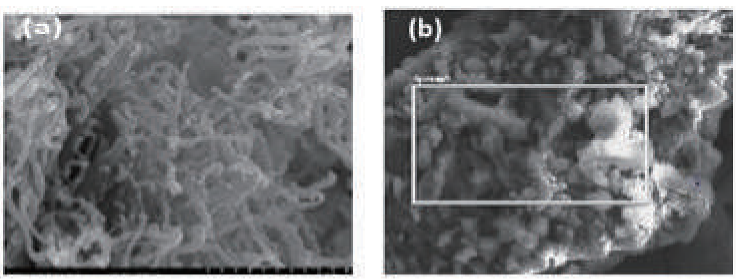


Fig. 2 SEM images, a) EC-CNTs modified and b) EC-NPs unmodified

Table 3 Elemental composition in EC-CNT and EC-NPs samples by EDX

| Sample/Element (mass%) | C | O | Si | K | Al | Cl | Cu | Ca | Mo | Mg | Co | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EC-CNT | 70.4 | 15.4 | 5.3 | 1.8 | 1.6 | 1.5 | 1.3 | 1.3 | 0.5 | 0.4 | 0.3 | 0.2 |
| EC-NPs | 58.5 | 35.2 | 0.6 | 0.2 | 0.8 | 0.5 | 1.4 | 1.1 | 0.6 | 0.4 | 0.5 | 0.2 |

while EC-NPs contain 64.5 and 29.2 mass% respectively. The detected values are similar with the presentation on EC material [23]. Some of these elements found in EC-CNTs is based on its physiochemical properties especially from the root as presented by Rezania et. al, [24] and Angela et. al, [25].

Figure 3 shows the particles size distribution measured with a hydrodynamic light scattering of particle size analyser. The results show optimal dispersion of EC-CNTs in polar/non-polar solution of N-Methyl-2-pyrrolidone with average mean size of 74.8 nm (Fig. 4). Other properties of EC-CNTs detected include; bulk density value of 0.67 * $10^3$ kg/$m^3$, with shape of nearly spherical and colour of Metallic Silver.

Figures 4 (a) and (b) shows the images of EC-CNTs and EC-NPs Raman spectroscopy and TGA analysis respectively. The graph in Fig. 4 (a) indicated two pronounced peaks at 1375.31 and 1601.37 $cm^{-1}$ for D-band and G-band respectively, attributed to the carbon atom vibrations in graphene layer. In contrast to modified EC-CNT samples, the Raman change of the G-band and D-band were less pronounced on EC-NPs, due to no purification (HCL) and cyclic heating unlike EC-CNTs. The treatments resulted in $sp^3$ carbon hybridization accessibility [26]. These values are similar to the carbon nanotube analysis results conducted by Bakshi et al. [27]. It clearly depicts higher intensity on G-band than D-band, indicates a defect in graphene sheet [21]. However, the Raman intensity nature of the two bands (D and G) was used to ascertain the crystalline order of the carbon constituents and useful to ascertain the CNTs defectiveness in application. The graph shows that $I_D < I_G$, simply indicate CNTs of the prepared sample of EC-CNTs. Figure 4 (b) shows the results of TGA of EC-NPs and EC-CNTs. The weight loss of EC-NPs was 34.5%, which could be from formulation adsorbed contaminants. After modification, the EC-CNTs weight loss was 18.1%. The weight loss of EC-CNT decreases substantially when compared to EC-NPs thus ascribed to the synthesis treatment leading to thermal properties enhancement [28]. The changes show that EC-CNTs has been modified with better thermal feature.

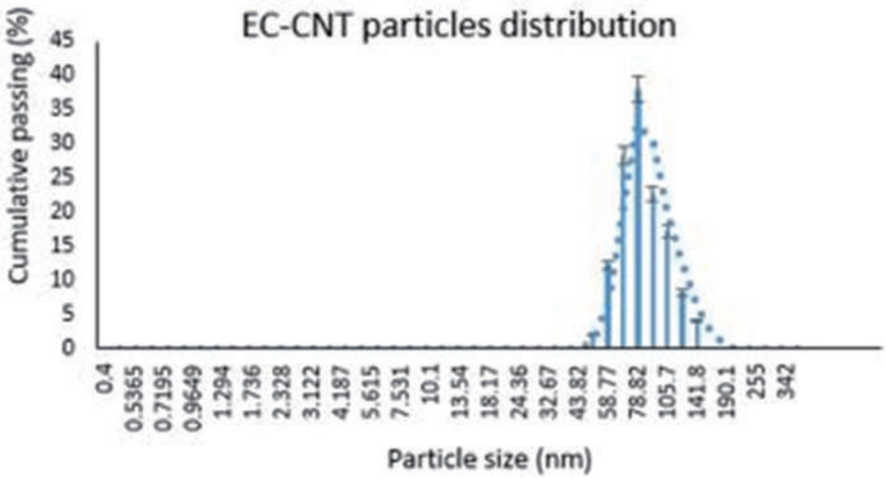


Fig. 3 Particle Size distribution of EC-CNTs by hydrodynamic light scattering

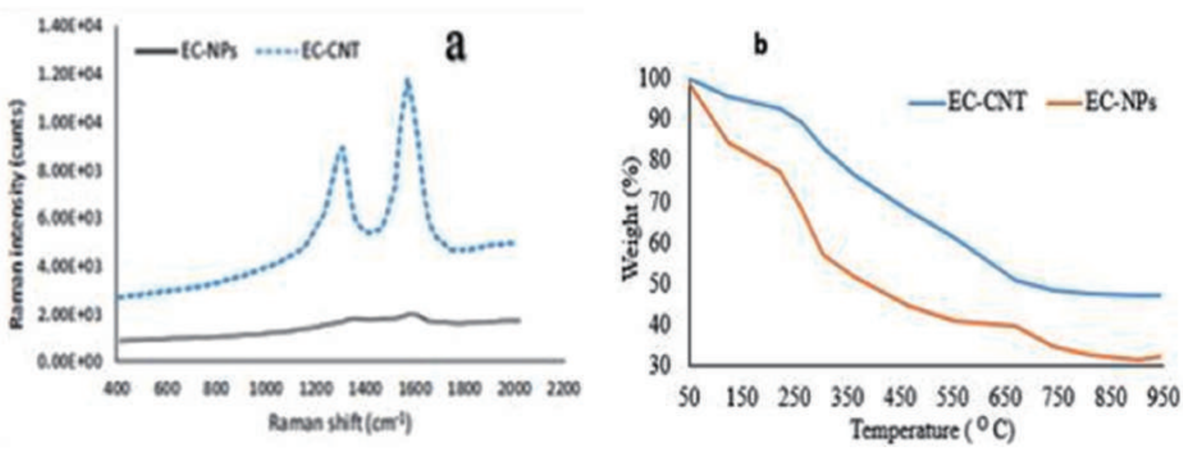


Fig. 4 Raman spectroscopy of EC-CNTs and EC-NPs showing D and G bands (a), TGA

Figure 5 shows the functional groups and compatibility analysis of EC-CNTs in a base oil using FT-IR. In Fig. 5, absorption peaks at 2925 and 2848 $cm^{-1}$ were observed, resulting from asymmetric and symmetric stretching of $CH_2$ of oleic acid found in the respective samples [29]. Again, another two peaks were detected within 1662 and 1632 $cm^{-1}$, attributed to the vibrations shift on COO- groups found in base oil and oil + EC-CNTs with asymmetric and symmetric stretching [30]. Also, significant shift in EC-CNTs sample were observed around 1593 $cm^{-1}$, account from weak concentration of COO-group [31], with much absorption peak around 1170 $cm^{-1}$ leading to stretching of the N-H bond of the organic compound [31].

The effect of band 1007 $cm^{-1}$ is from C-O-C stretch behavior related with -OH bending of constituents of cellulose, lignin and hemicellulose, whereas the peak of 779 $cm^{-1}$ is the product of aromatic C-H out of plane bends [31]. However, in Fig. 5, EC-CNTs + base oil, witnessed change in the intensity of band with a shift to the new value around 1744 $cm^{-1}$, as a result of ester cleavage and formation of a carboxyl group [32]. The similar graph train between base oil and EC-CNTs inclusion proofs good compatibility between the additives and the base oil and recommend for lubrication application.

### 3.2 Frictional characteristics

Figure 6 shows the COF and wear volume of SAE 20W-40, base rapeseed oil and rapeseed oil with EC-CNTs of different concentrations (1, 2.5 and 4 mass%) operating under load of 100 N, frequency of 5 Hz for 15 minutes. With the operating frequency, COF recorded according to the lubrication index value for lambda ($\lambda$) is less than 1, thus, considered boundary lubrication regime at the Stribeck Curve [33]. Figure 6(a) indicates that as concentration increases, the COF decreases but shows increase with 4 mass% EC-CNT. The start of the operation with inclusion of EC-CNT shows significant decrease in COF from higher values, which reflected on the higher value of samples (EC-CNTs candidates) viscosity (Table 1) but decrease by heat due to lack of viscosity improver. The maximum COF of 0.087 was obtained with 4 mass% EC-CNT lubricant, while base lubricant has 0.083. This is 38.5% COF reduction by 2.5 EC-CNTs against base lubricant. Meanwhile, the control (SEA 20W-40) shows the lowest COF among all the lubricants. With application of Rap. oil + 2.5 mass% EC-CNT, the temperature was reduced due to lower friction, leading to increase in viscosity with resultant effect on low COF. Therefore, 2.5 mass% EC-CNT concentration gives the optimal performance. Figure 6 (a) clearly show the zig-zag pattern exhibited by Rap. oil + 4 mass% EC-CNT, indicating sharp destruction on the formulated film with increase in COF line at around 580 to 620 s before became stable till the end. This observation was suspected to be from agglomeration of the EC-CNT in the lubricant [34, 35], also could be of higher acidity from high concentration of EC-CNT, leading to sharp break-off of the formed tribo-film with weakening of molecules of lubricating film, resulting in COF increase [36]. Again, could be from poor dispersion due to high

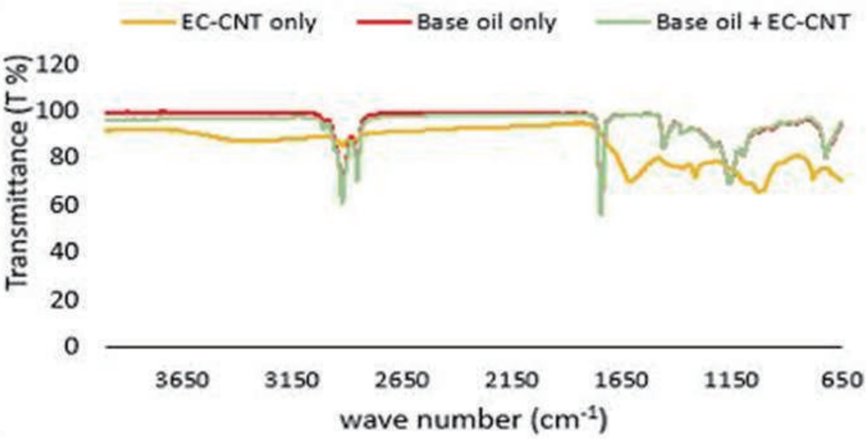


Fig. 5 FT-IR spectra analysis of EC-CNTs + base Oil (together)

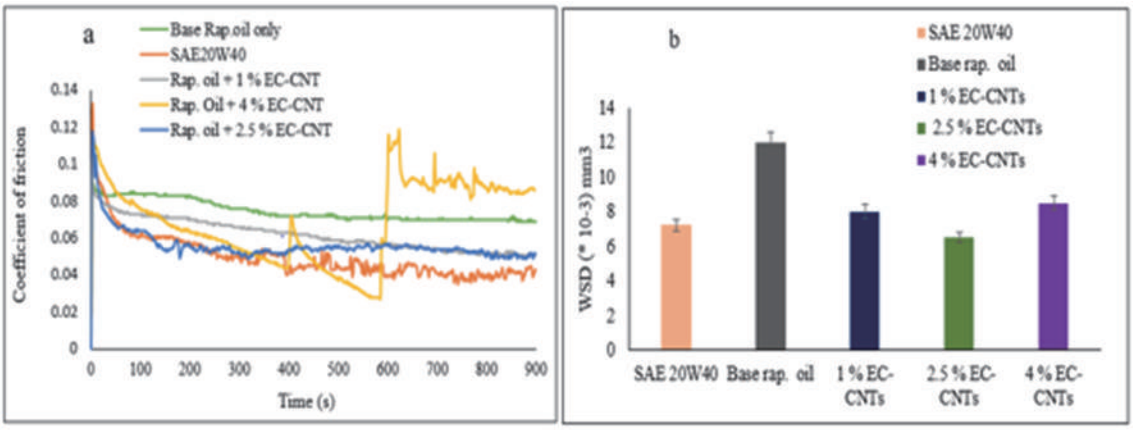


Fig. 6 Friction coefficients against time (a) and wear Scar diameter (b); on SAE 20W-40, base rapeseed oil and rapeseed blended with EC- CNT (1, 2.5 and 4%) concentrations. (100 N, 5 Hz, 15 min)

concentration leading to formation of aggregates between the sliding surfaces thereby causing non-homogeneous lubrication.

A lubricant's effectiveness is not determined only from its low COF during operation but also characterized by its strength in minimizing surface wear. As provided in Fig. 6 (b), as EC-CNTs concentration increases, sliding wear scar diameter (WSD) gradually reduces against base lubricant, until lowest value obtained with 2.5 mass% EC-CNT, and increased with 4 mass% but lesser than base oil value. The result shows that 2.5 mass% concentration yield the minimum wear diameter of 6.2 x $10^{-3}$ $mm^3$ against 11.9 x $10^{-3}$ $mm^3$ of base rap. oil. This is 47.9% reduction in the wear diameter. Therefore, the findings reveal that optimal concentration was with 2.5 mass%, yielding the maximum tribological performance with base oil. This result on COF increase with high concentration is similar with previous report using CuO additive in PAO6 base oil [37]. The results clearly show that during sliding operation, EC-CNT particles penetrate into the friction zone and undergo tribo-chemistry reaction on the metal surface leading to formulation of tribo-films with high effective healing and protective effect [35].

3.3 Lubricants load carrying capacity

The effect on the load carrying capacity (40, 60, 80 and 100 N) of the different EC-CNT additive concentrations on their tribological performance was studied at 5 Hz for 15 min. The operation average COF are presented in Fig. 7 (a). The result indicated that with the inclusion of EC-CNT nanoparticles in the base rapeseed oil, gives significant reduction on COF, compared to base rapeseed, though had poor tribological performance with EC-CNT 4 mass%. Figure 7 (a) shows that base rapeseed oil exhibited steady increase in COF when increasing applied load, with maximum COF of 0.062 at 40 N to 0.083 at 100 N. More so, the COF on rapeseed blended EC-CNTs (2.5 mass%) decreases from 0.054 at 40 N to 0.031 at 100 N and appears similar behavior to that of SAE 20W-40. With these results obtained, it is good to say that EC-CNT nanoparticles and rapeseed oil are compatible and more effective at higher load, i.e., the greater the load, the lower the COF generated. The findings concluded that the tribo-film formation is a dependent of energy built during sliding process [34]. With small applied load, sliding friction energy is little to enhance tribo-reaction between nanofluid (EC-CNT) and the metal surface [34, 35]. Increasing the applied load, nanofluid ie additive acquired more energy to react with the working element friction pair, thereby produces strong tribo-film which is responsible for friction reduction [35]. As shown in Fig. 7 (b), the anti-wear effect of the various lubricants was investigated at different temperatures under constant applied load of 100 N. the result shows that average WSD decreased significantly relative to base lubricant as the temperature rises from 50-120°C. The average WSD were reduced by 12.4% at 50°C to 43.7% at 120°C, 20.3% at 50°C to 50.6% at 120°C, 11.2% at 50°C to 39.9% at 120°C for 1 mass%, 2.5 mass%, 4 mass% respectively compared to base lubricant, but SAE 20W-40 lubricant exhibited better result at 120°C. The result shows that tribo-chemistry for the film formation activated at higher temperature and normally occur between the nano particles and the interfaces. However, the nano particles show more decomposition at 120°C, thereby makes lubricating film difficult to replenish, thus lead to increase in wear.

3.4 Frictional properties of 2.5 mass% EC-CNT under different volume of base oil (60 ml, 120 ml 180 ml base oil) and the stability of the formulated tribo-film (120 N)

In order to ascertain the suitable volume of lubricant for 2.5 mass% EC-CNT, different volume of base lubricants was investigated under 2.5 mass%, and compared to base lubricant and commercial (SAE 20W-40) in terms of friction coefficient and film stability. Figure 8 gives the variation of COF on the different lubricants (SAE 20W-40, base rap. oil and 2.5 mass% EC-CNTs with 60 ml, 120ml and 180 ml of rap. oil) with respect to time during the tribological test. The result shows that COF enhanced under EC-CNT blends with 60 ml and 120 ml base oil but shows poor performance with 180 ml. The poor outcome from 180 ml could be attributed from weak and insufficient constituents of EC-CNT leading to poor tribo-chemistry reaction for the formation of tribo-film layer. On testing 60 and 120 ml with equal 2.5 mass% additive, the friction decreases at the beginning and stabilizes from around 80 s till the end of the test, though the COF value was higher than that of SEA 20W-40 tested early, while 150 ml shows much of high amplitude wave, showing lack of tribo-layer. This is similar with previous presentation [36, 37]. Although 180 ml exhibits different behavior, however, the COF decreases like other samples (60 ml, 120 ml, 180 ml and SAE 20W-40) with respect to time unlike only base oil sample. This is because of presence of active functional groups [31] which contributes in lubricating film creation for the enhancement of lubricant lubricity. These results strongly point out the enhanced effect from EC-CNT as lubricant additive. This is confirmed owing to its pronounced lubricating tribo-film stability which was not found in base oil

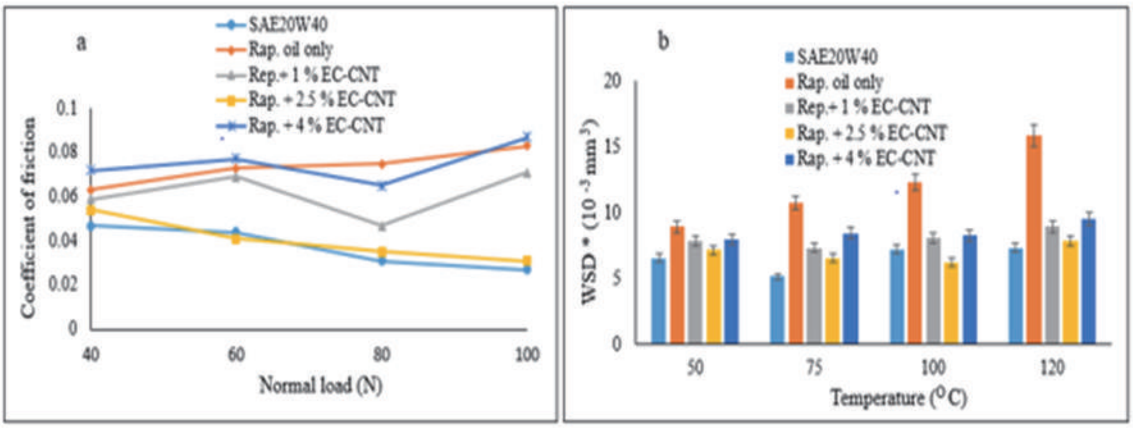


Fig. 7 Effect of different load on average COF at constant temperature 75°C, (a), and WSD against different tempt. (50°C, 75°C, 100°C, 120°C) (b), for the various lubricants (SEA 20W-40, Base oil, 1% EC-CNTs, 2.5% EC-CNTs and 4% EC-CNTs) under 5 Hz,15 min.

sample leading to increase in the COF as shown in Fig. 8. The study observed that stability and dispersability of 2.5 mass% EC-CNT were found optimal with 120 ml than every other lubricant apart from SEA 20W-40 but appear too similar, thus show more protection on the surface contact.

3.5 The wear scars micrographs and lubrication mechanism of the tribo-film of nanoparticles

For better understanding on the mechanism of nanofluid, the lubricated surfaces were analysed using SEM as to ascertain the nature of the worn surfaces. Figure 9 shows the SEM images of the lubricated surfaces and optical tribo-film images (base

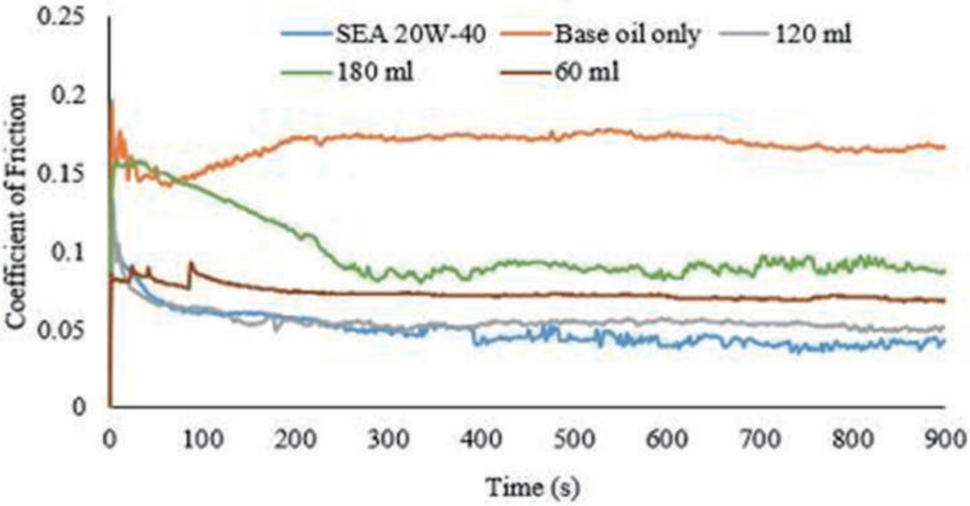


Fig. 8 Effect on film stability from lubricants; SAE 20W-40, base oil and EC-CNT 2.5 mass% under 60 ml, 120 ml, 150 ml volume of base oil (120 N, 5 Hz 15 min)

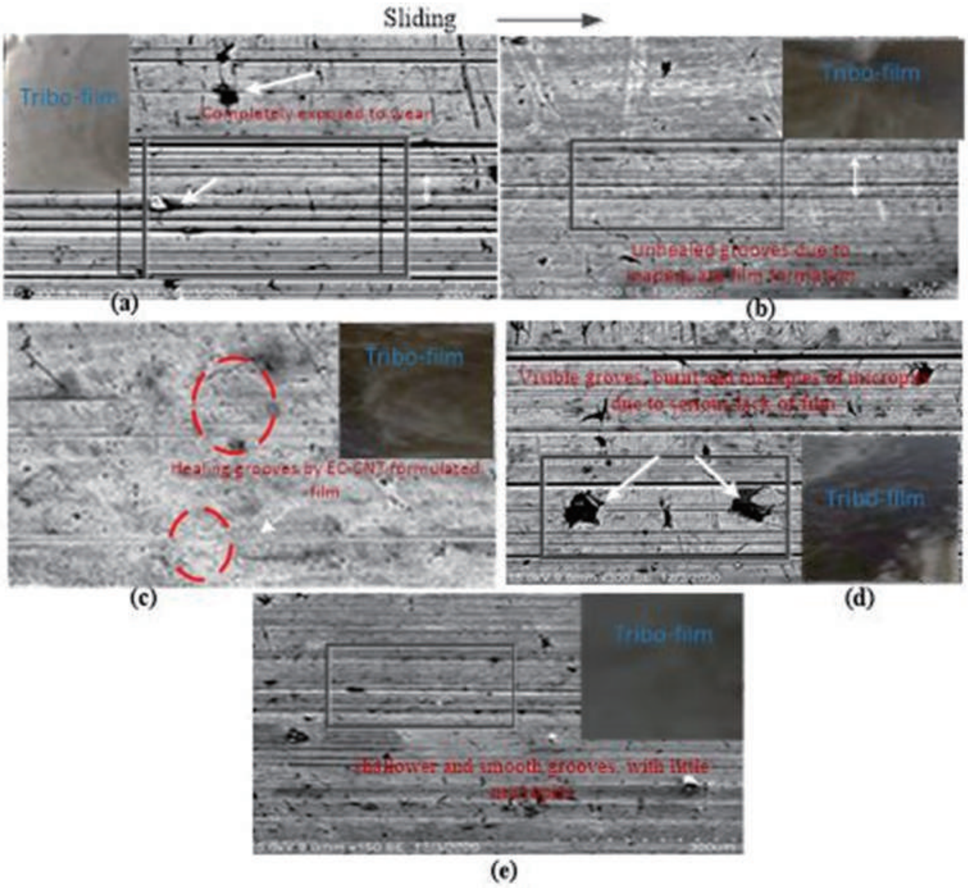


Fig. 9 SEM images of the worn surfaces and tribo-films from different lubricants (a) base Rap. oil only, (b) 120 ml base Rap. + 2.5 mass% EC-CNT, (c) 60 ml base Rap. + 2.5 mass% EC-CNT, (d) 180 ml base Rap. + 2.5 mass% EC-CNT, (e) SAE 20W-40, (120 N, stroke 10 mm, 75°C, 5 Hz, 15 min)

lubricant and base lubricant of 60, 120 and 180 ml blended with 2.5 mass% additive) under high load 120 N and 5 Hz for a period of 15 min. As presented in Fig. 9 (a), a long narrow visible trench is seen, showing abrasive wear manner from the sliding contact under the base lubricant. Furthermore, testing 60 ml, 120 ml and 180 ml with 2.5 mass% EC-CNT respectively, the lubricated surfaces appears shallower and smooth, compared to base lubricant (Fig. 9 (a)) but that of 120 ml gives smoothest surface, followed by 80 ml before 120 ml as shown in Fig. 9 (b, c, d). Again, the wear scar from 60 ml and 120 ml nanofluid shows unevenly distributed along the sliding direction on the wear surface. The results are similar to the presentation by Hie et al., [35] on nano-additives tribological performance on steel–steel contacts. As for 40 ml nanofluid, show some serious effect like burnt with rough appearance of many micro-pits. The evidence of tribo-film formation between the nanoparticles and the interface are listed in EDX as shown in Table 4.

As stated in section 3.2 that the lubricant effectiveness is not only measured by COF but also the ability to minimize the wear effect. Figure 10 showcases the 3D topography images and profile wear volume of the lubricated surfaces (base oil, 60 ml, 120 ml and 180 ml) measured by AFM machine. As provided the image, lubricated surface without EC-CNT particles($a_1$-$a_2$) has the highest value of wear. The lubricated surfaces with EC-CNTs shows great wear reduction with best result recorded from120 ml ($C_1$-$C_2$), followed by 60 ml ($d_1$-$d_2$) before 180 ml ($b_1$-$b_2$) as shown in Fig. 10. This result strongly support the observations in section 3.2 Fig. 6 (b).

Nanofluid mechanisms for friction reduction are mostly affected by their intrinsic properties like poor molecular bond formation. However, some other mechanisms towards tribological enhancement through friction reduction on applying additives of nano forms have been reported [5] such as healing/self-mending, rolling effect through sliding, protective film formation, third body impact etc. Therefore, the mechanism of EC-CNT nanoparticles for the formation of tribo-film are modelled from Figs. 9, 10 and analyse in Fig. 11. The behavior of EC-CNT is dependent on operational conditions such as load, temperature, frequency as well as the additive concentration and viscosity. Viscosity affects the flow of the nanofluid, if viscous causing delay in filling the swept fluids during sliding. The result of this phenomenon lead to lubricant starvation in the system which causes increase in temperature and friction. As early stated (section 3.2), with optimal operational parameters, the greater the load, the better the COF generated through frictional energy. This causes fast formation of film layer between the surface contact [35]. Figure 11, summarizes occurrences during EC-CNT nanofluid lubrication under HFRR operation. In addition, good tribological performance from EC-CNT was as a result of nano-scale, thus easily penetrate at the contact region thereby introduce rolling and prevent metal-to-metal contact.

Using 120 ml base Rap. oil with 2.5 EC-CNT as the best candidate in this study. Nanoparticles in the lubricant experiences some excited energy and tend to move towards the point of their higher affinity in order to annul the effect as shown in Fig. 11 (a). In this process, some enters into available valleys along the sliding surfaces as seen in Fig. 11 (b). Because of the amphipathic nature of EC-CNTs via functional groups, revealed by FT-IR analysis, during the crushing, EC-CNT additives undergoes tribo-chemical reactions and stick strongly on the contact surfaces as shown in Fig. 11 (d). The connectivity of nanoparticles with distribution through Stokes' law provides the flexibility to connect the size with controls of nano-lubricant. According to the simple concept, the tiny the size, the greater the diffusion stability, as a result, the improved tribological characteristics [38]. The film structure of EC-CNT was discovered to be suitable for lowering friction via tribo-film formation. But in excess concentration of EC-CNT, base lubricant or incompatibility, aggregates or clusters of nanoparticles were observed leading to poor performance ie high COF and wear as shown in Fig. 11 (c1) (c2), Fig. 10 (d) (also see Fig. 6 (b)). This could possibly lead to lubricant starvation due to high accumulation of aggregates at the sliding contact front, distort of particle penetration to the contact region (Fig. 11 (c2)). Although some of these films formed, clustered without contributing fully in friction reduction as expected as shown Fig. 11 (e).

## 4 Conclusion

Based on the outcome of the experiment on friction, wear, surface roughness, tribo-film behavior and micrographs trace from the friction pairs with EC-CNT as lubricating oil additives, the study drawn conclusion as follows.

(1) The inclusion of nano-additive of EC-CNT in base rap. oil exhibit good lubrication features compared with base rap. oil under HFRR steel contacts. Concentration of 2.5 mass% EC-CNT showed optimal performance under all the tested condition.

(2) Under load carrying capacity test, positive effect with EC-CNT were more pronounced. However, detected poor result from high concentration (4 mass%). During the study, it obviously shows that with increase on applied load, increases the tribological behavior especially with 2.5 mass% EC-CNT. But on comparing with SEA 20W-40, 2.5 mass% EC-CNT shows similar behavior. Base rap. oil shows the worst result while 4 mass% EC-CNT exhibited the same behavior trend with 1 mass% EC-CNT but the results of 1 mass% EC-CNT is better.

(3) Film stability of the various lubricants (2.5 mass% EC-

Table 4 EDX measurement of lubricated surfaces (base oil, and 2.5 mass% EC-CNT with 60 ml, 120 ml, 180 ml base oil

| Samples/elements (at. %) | Fe | C | O | Cr | Mn | Si | Ca | Al | Co | Na | Cl | Total (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Base rap. Oil | 95.23 | 1.36 | 1.05 | 0.51 | 0.6 | 0.09 | - | - | 0.7 | | - | 100 |
| 60 ml nanofluid | 67.63 | 15.04 | 5.43 | 0.57 | 1.70 | 1.96 | 4.58 | 0.86 | 0.97 | 2.03 | 0.23 | 100 |
| 120 ml nanofluid | 62.85 | 16.01 | 7.54 | 1.82 | 1.04 | 2.67 | 2.91 | 1.13 | 1.15 | 2.05 | 0.83 | 100 |
| 180 ml nanofluid | 73.18 | 12.00 | 3.67 | 0.84 | 0.93 | 2.07 | 4.03 | - | 0.68 | 1.77 | 1.03 | 100 |

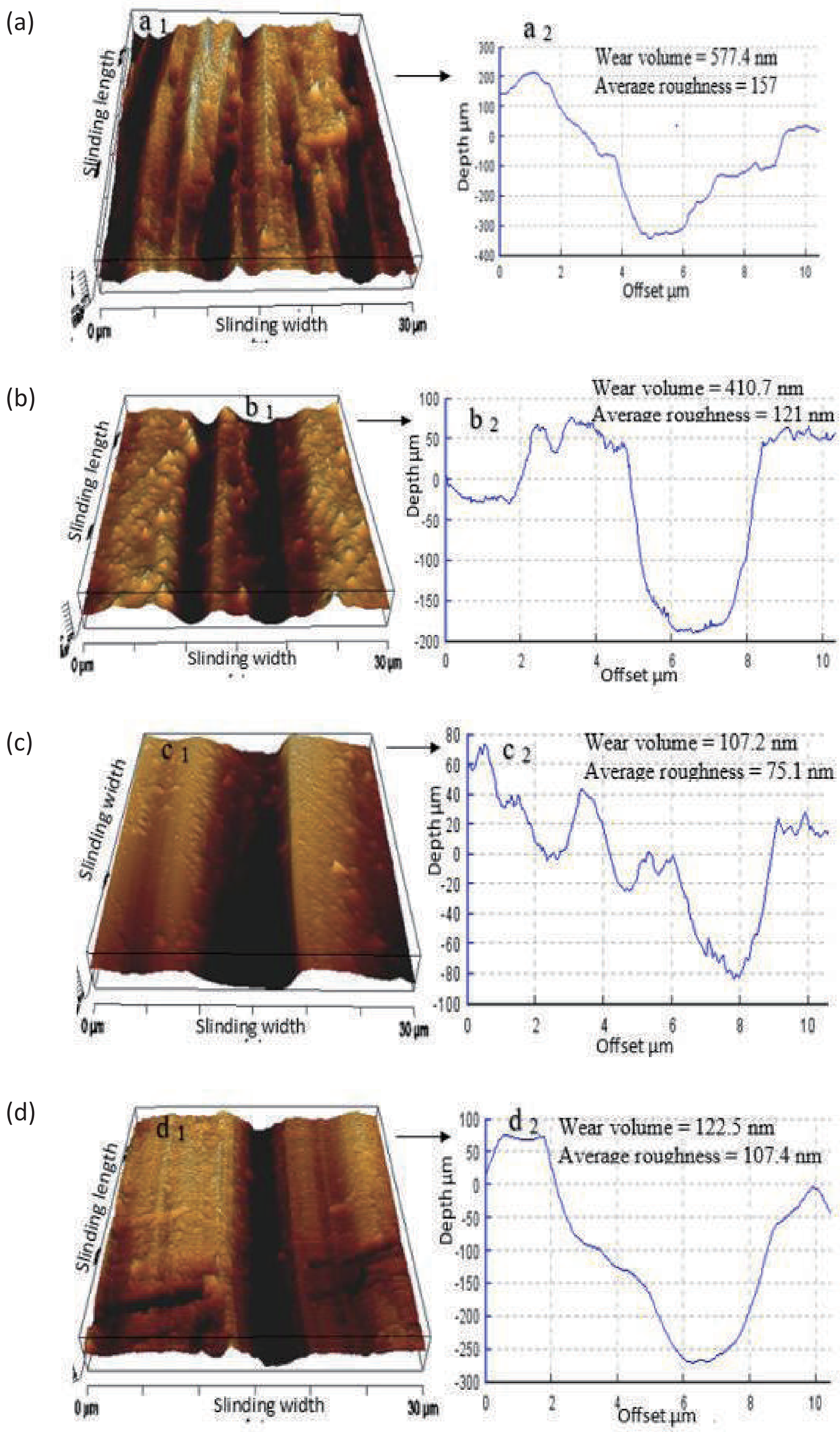


Fig. 10 3D topography images of various lubricated surfaces with profiles section of their wear tracks both wear volume and Ra after tests; (a) Base lubricant, (b) 60 ml base rap. oil + 2.5 mass% EC-CNT, (c) 120 ml base rap. oil + 2.5 mass% EC-CNTs, (d) 180 ml base rap. oil + 2.5 mass% EC-CNTs (120 N, 5 Hz 15 min)

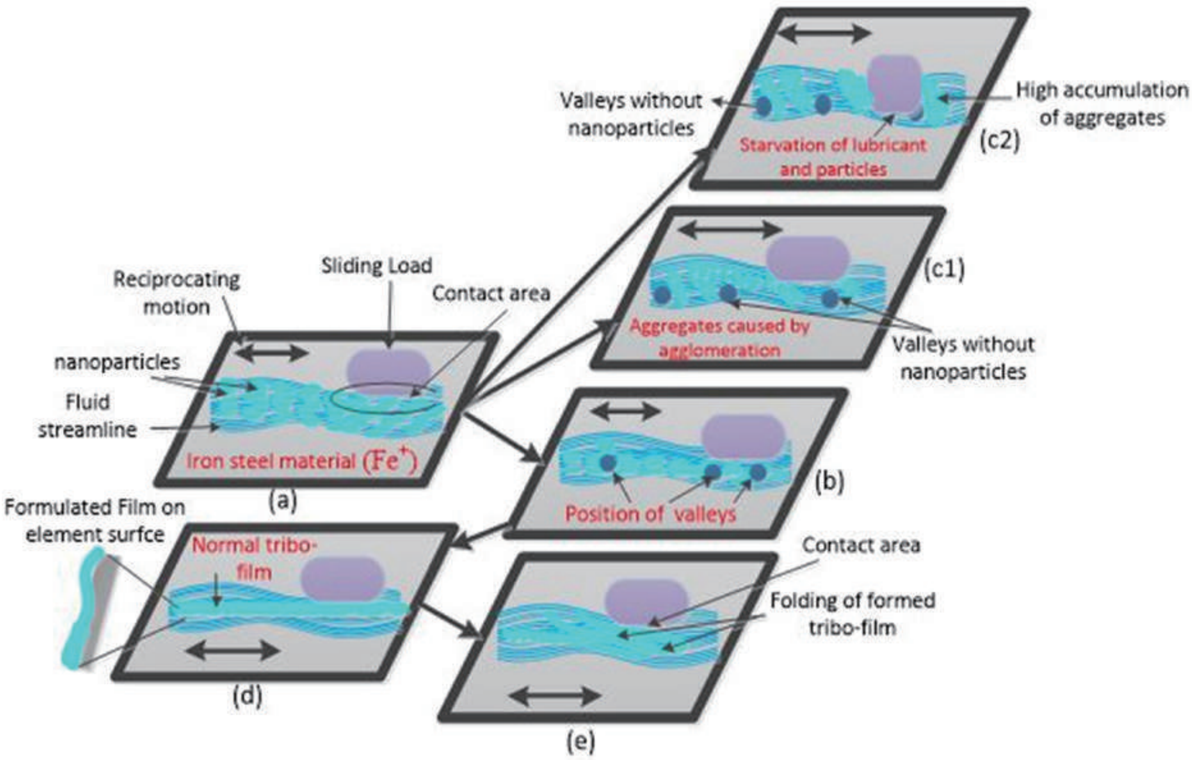


Fig. 11 Model mechanism of EC-CNT tribofilm of under sliding lubrication

CNT on base rapeseed oil (60 ml, 120 ml and 180 ml), base rapeseed oil and SEA 20W-40) shows that 2.5 mass% EC-CNT with 60 ml and 120 ml illustrated similar stability behavior with SEA 20W-40. COF decreases slowly and stabilizes form around 80 s till the end of the test. However, base rap. oil showed some increase on COF from around 80 s to 200 s and stabilizes till the end. As for 2.5 mass% EC-CNT with 180 ml, exhibited some rough operation, COF decreases with sudden increase before stabilizes. The sharp increase on the COF is suspected to be from break down on film molecules.

(4) Reduction in COF and wear are from the formation and behavior of tribo-film. As seen from the modelled mechanism of EC-CNT film, reduced friction through protective film and mending/healing mechanism. Nanoparticles of EC-CNT is highly amphipathic in nature as shown in FT-IR analysis, easily to stick on the steel surface. The sticky and film formation could be from frictional chemical reaction.

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