



Addition of graphene oxide (GO) nanoparticles in trimethylolpropane ester (TMPe) bio-lubricant: Impact on tribological characteristics of friction and wear

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KEYWORDS	ABSTRACT
Trimethylolpropane ester Bio-lubricant Graphene oxide Nanoparticle Tribology	Growing awareness of sustainability and green technology legislation has driven research towards green lubricants. Mineral-based lubricants, widely used despite their toxicity and non-biodegradability, are depleting natural resources. Bio-lubricants, derived from plants, offer high biodegradability and minimal environmental impact, with virtually limitless resources. This study explores trimethylolpropane ester (TMPe) as a bio-lubricant, with graphene oxide (GO) as a nanoparticle additive at 0.05, 0.1, and 0.5wt%. Tribological performance was assessed using a four-ball tribo-tester following ASTM 4172B. Addition of GO reduced the coefficient of friction (COF), with the 0.5wt% GO-TMPe showing the highest COF reduction (21%). However, the wear resistance of the 0.1wt% GO-TMPe was 6.3% higher than pure TMPe, mitigating adhesive wear and yielding smoother surfaces.

1.0 INTRODUCTION

The lubricant industry is undergoing a significant transformation driven by a growing emphasis on sustainability and environmental responsibility. There has been increased interest in bio-based lubricants, which offer a green and sustainable alternative to traditional petroleum-based lubricants (Mohanraj and Radhika, 2021). Derived from renewable sources like plant oils (e.g., soybean, rapeseed), animal fats (although less common due to sustainability concerns), and

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even microbial organisms, bio-based lubricants can significantly reduce the lubricant industry's environmental impact (Campos et al., 2023). Many studies have been conducted on using plant oil as a bio-lubricant, and they have demonstrated promising improvements in reducing friction and wear (Paiman et al., 2024; Zulhanafi et al., 2023; Appiah et al., 2022; Yadav et al., 2021; Negi et al., 2021; Syahrullail et al., 2011). However, susceptibility to oxidative degradation is a major challenge regarding bio-based lubricants (Narayana et al., 2022; Syahrullail et al., 2005). This process occurs when the lubricant reacts with oxygen, particularly at high temperatures and under demanding operating conditions like heavy loads and high shear forces. Oxidation leads to the breakdown of the lubricant's molecular structure, compromising its lubricating properties. Such degradation leads to increased friction and wear on mechanical components, ultimately leading to equipment failure and downtime (Shah et al., 2021). Esterification has emerged as a key strategy that addresses this challenge by enhancing the oxidative stability of bio-based lubricants. Esterification is a chemical reaction where organic acids and alcohols react to form esters. These esters exhibit superior oxidative stability compared to the original feedstock, making them more resistant to oxidative breakdown (Karmakar et al., 2021). Improved stability offers better performance in high-temperature and high-stress environments, allowing bio-based lubricants to function effectively in applications where traditional lubricants might degrade rapidly (Zulhanafi and Syahrullail, 2019; Golshokouh et al., 2013).

In essence, esterification plays a vital role in bridging the performance gap between bio-based and petroleum-based lubricants. It strengthens the bio-based lubricant's ability to withstand harsh operating conditions, paving the way for broader adoption sustainably (Zulhanafi et al., 2021).

1.1 Trimethylolpropane Ester (TMPE) As Bio-Lubricant

Transesterification is an efficient method to improve the thermal properties and oxidative stability of lubricants. Trimethylolpropane esters (TMPE) produced from methyl esters of palm and palm kernel oils exhibit a strong potential when used as base oils for lubricants (Yadav et al., 2018). Transesterification eliminates the hydrogen molecule at the beta-carbon position of the palm oil substrate, enhancing the oxidative and thermal stability of the TMPE (Zulkifli et al., 2013a). The benefits of palm oil-based TMPE are also described by Gulzar et al. (2018), where the authors stated that the lubricant exhibits a high viscosity index and superior thermo-oxidative stability. Meanwhile, Opia et al. (2023) listed other advantages, such as a stable flash point, increased viscosity, adequate density, and a freezing point suitable for use as engine oil.

Researchers Yunus et al. (2020) reported that TMPE are mainly incorporated in synthetic lubricants and are also used for compressor oil and crankcase lubricants. They also remarked on the tribological properties, suggesting that TMPE have a load-carrying capability and tribological performance comparable to a fully formulated mineral lubricant. Another study by Zulkifli et al. (2013b) detailed the palm oil-based TMPE preparation process. Figure 1 illustrates the palm oil-based TMPE synthesis reaction.

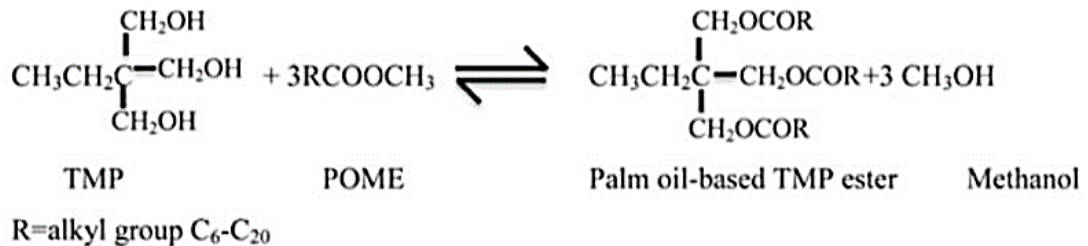


Figure 1: The synthesis of the TMPE.

1.2 Graphene Oxide (GO) As Nanoparticle Additive

Graphene oxide (GO) is a popular graphene derivative first synthesized in the 19th century. It comprises a single carbon monolayer with randomly distributed aromatic (sp² carbon atoms) and oxygenated aliphatic (sp³ carbon atoms) regions comprising carbonyl (=O), carboxyl (-COOH), epoxy (-O-) and hydroxyl (OH) functional groups (Sabri et al., 2024). These functional groups provide GO with hydrophilic properties (Penkov, 2020). Researchers Smith et al. (2019) indicated that the superior properties of GO can be attributed to the oxygenated groups when compared to graphene. These properties include higher solubility and broader application in nanocomposite materials due to higher surface functionalization. Figure 2 illustrates the difference in the chemical structures of graphene and its derivative GO.

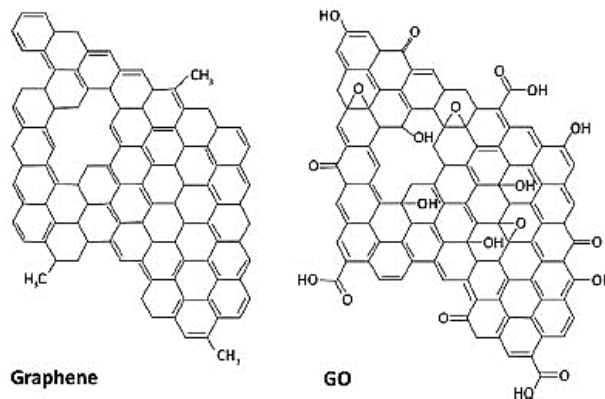


Figure 2: The chemical structures of graphene and GO (Penkov, 2020).

GO may possess a single or multi-layered structure like other two-dimensional (2D) carbon-based materials. However, GO containing more than 11 layers is known as graphite oxide (Opia et al., 2021; Jirickova et al., 2022; Azizan et al., 2024). GO can be synthesized by the oxidation of graphite into graphite oxide, followed by exfoliation. It should be noted that the GO synthesis process significantly influences its properties, which impact the type and amount of oxygen-containing groups present in GO. The oxidation level of GO can be regulated based on the method, reaction conditions, and the graphite precursor used. Graphene boasts many superior qualities, like thermal and chemical stability, gas impermeability, exceptional thinness, and high strength (Kumar et al., 2022). Additionally, the authors listed several other properties, such as high

fracture toughness, high hardness, and eco-friendliness. Graphene is considered a green lubricant additive because of the absence of nitrogen, sulfur, phosphorus, heavy metal elements, and toxic particles. Regarding tribological application, excellent chemical inertness, supreme strength, and strong shear characteristics are some beneficial aspects of graphene (Berman et al., 2014). Hence, it has been used as a lubricant in solid and colloid liquid forms. Researchers Chouhan et al. (2020) are aligned with the observations and stated that the weak Van der Waals forces between graphene lamellae reduce the material's shearing resistance, consequently lowering friction.

Liu et al. (2020) explained several unique friction-reducing and anti-wear properties of graphene. They noted that graphene is sought after due to its outstanding mechanical strength and strong wear resistance. Besides, high thermal conductivity allows for easier dissipation of the heat generated during the sliding motion. Additionally, graphene's impermeability protects the tribo-pairs by preventing oxidation and corrosion that often triggers more surface damage. Lee et al. (2010) tested graphene strength. The study used free-standing graphene membranes that were analyzed using a diamond atomic force microscope (AFM). It enabled the authors to measure their breaking strength. The defect-free graphene sheet had a 1 TPa Young's modulus, making it the strongest material ever tested.

Surface defects typically occur during GO synthesis, leading to inferior mechanical properties compared to defect-free monolayered graphene. Thus, GO blends have been produced to attain properties close to that of pristine graphene (Smith et al., 2019). The properties depend on the number of surface groups and remaining defects after oxidation and other treatment processes. Suk et al. (2010) reported that monolayer GO (mGO) manufactured via the modified Hummer's method had Young's modulus of around 207.6 GPa. Although this was comparably lower than that of pristine graphene, the GO strength is still remarkably high.

1.3 Graphene Oxide (GO) Incorporated in Bio-Lubricant

Many studies have been conducted to investigate the performance of GO with bio-based lubricants. Graphene oxide (GO) is a proven beneficial additive that improves the tribological performance of bio-based lubricants. Bhaumik et al. (2021) investigated the tribological performance of a new customized cashew nut and castor oil-based biodegradable gearbox lubricant that was blended with various percentages of reduced graphene oxide (rGO) nanoplatelets. They revealed that the blended oil's tribological characteristics were 61.7% better than that of mineral-based oil. Xie et al. (2020) evaluated the tribological performance of graphene by adding multi-layer graphene into natural wax extracted from the non-medicinal parts of *Codonopsis Pilosula*. They used a ball-on-disc tribo-tester and found that adding multi-layer graphene improved load-carrying capacity and high-temperature lubricity. Xue et al. (2022) investigated the performance of GO when incorporated with water lubrication and concluded that graphene-based material with water lubrication improved lubricant efficacy owing to excellent mechanical properties and water dispersibility. Hasnul et al. (2021) fluorinated graphene nanoparticles and incorporated them in a water-based lubricant. They found that fluorinated graphene oxide (fGO) exhibited superior dispersibility in water and tremendous abrasive wear resistance. He et al. (2018) combined GO and alumina hybrid in a water-based lubricant and found that both additives reduced the coefficient of friction (COF) by 64% compared to GO alone. Min et al. (2019) studied the synergistic behavior of graphene and ionic liquid additives in bio-lubricants and revealed that the combination reduced friction by up to 33%. In contrast, the ionic liquid and graphene alone reduced friction by 13% and 7%, respectively. Similarly, Huang et al. (2019) found that a combination of graphene and ionic liquid significantly improved tribological properties

compared to neat ionic liquid. Furthermore, they revealed that the ionic liquid with a moderate concentration of chemically modified GO resulted in good wear and friction performance.

It is known that higher nanoparticle concentration leads to agglomeration issues. As such, Wang et al. (2019) examined ultralow GO concentrations as additives in bio-lubricants using hexadecane-based oil (16C) as a lubricant and blended with an ultralow GO concentration using the phase transfer method. They found that graphene nanosheet adsorption on the contact surface was the key to low friction and wear. Many studies suggest that GO nanoparticle additives can improve the tribological performance of lubricants. The present study used TMPe as a bio-lubricant and a GO nanoparticle additive and investigated the tribological properties, such as COF, wear scar diameter (WSD), surface roughness (S_a), and physical wear of TMPe blended with various GO concentrations.

2.0 EXPERIMENTAL PROCEDURE

In this study, GO was added to the TMPe in various ratios: 0.05, 0.1, and 0.5wt%; these ratios were based on a previous study (Duan et al., 2023). A four-ball tribo-tester was used to evaluate the tribological performance of the lubricants. The analysis involved COF, WSD, physical wear observation, S_a , and surface topography (ST). The tribological performances of blended TMPe were compared to that of pure TMPe as benchmark oil.

2.1 Properties of Lubricant And Nanoparticle Additive

Trimethylolpropane ester (TMPe) was used as the base lubricant, with graphene oxide (GO) serving as the nanoparticle additive. The physical properties are presented in Tables 1 and 2.

Table 1: The physical properties of the TMPe.

Physical state and appearance	Liquid
Colour	Yellow to amber
pH	5-8
Boiling point	> 250°C
Flash point	> 200°C
Auto-ignition temperature	> 300°C

Table 2: The physical properties of the GO from Adnano Technologies.

Physical state and appearance	Liquid
Colour	Yellow to amber
pH	5-8
Boiling point	> 250°C
Flash point	> 200°C
Auto-ignition temperature	> 300°C

2.2 Mixing the Nanoparticle

Each lubricant mixture was processed using an IKA T25 homogenizer at 13000 rpm for about 45 minutes (Azman et al., 2024; Azman et al., 2018) Lubricant samples were used immediately after mixing to avoid nanoparticle settling and ensure that the best tribological performance was obtained. For each subsequent test, the mixtures were mixed for a few more minutes to ensure that settlements were dispersed

2.3 Tribological Testing

A four-ball tribo-tester was used to evaluate the COF of all the lubricant samples. The test rig was specifically designed to evaluate the performance of oils and greases. It was equipped with a simple oil rig loaded with steel balls and lubricants. A lever arm was used to apply loads to the oil rig. Additionally, the oil rig was connected to a thermocouple for temperature control. An electric panel was connected to the machine to record all experimental data about frictional torque (T), temperature, and applied load (W). Figure 3 illustrates the four-ball tribo-tester and the oil test rig.



Figure 3: The four-ball tribo-tester and the oil rig.

2.3.1 Materials

12.7mm-diameter chrome-alloy steel balls that met AISI E-52100 standards, with extra polish (EP) grade 25 and a hardness of 64–66 HRC (Rockwell Hardness C) were used. Before each experiment was conducted, the balls were cleaned with acetone to remove debris and wiped dry with a fresh, lint-free cloth.

2.3.2 Coefficient of Friction (COF)

The COF was obtained directly from the four-ball tribo-tester. During the initial phase, T increased rapidly and reached a steady-state condition after a while. The data were collected only when the machine had been run in steady-state conditions. The COF was calculated by using Equation (1):

$$COF = \frac{T\sqrt{6}}{3Wr} \quad (1)$$

where, T is the frictional torque, W is the applied load, and r is 3.67 mm, which is the distance from the center of the contact surfaces on the lower balls to the axis of rotation.

2.3.3 Wear Scar Diameter (WSD)

The WSDs of the steel balls were measured using the optical charge-coupled device (CCD) of a high-resolution microscope. i-Solution Lite was used to capture the wear image before the measurement could be obtained. Each ball was cleaned using acetone to remove excess lubricant. The WSDs of the three bottom balls were measured. A higher WSD indicated higher wear severity. A high-definition microscope was used to observe physical wear scars (WS), inspect the quality of the wear surface, and deduce wear type. The overall condition of the WSs was observed using a 10× magnification lens, and specific areas were further inspected using a higher magnification (20×).

2.3.4 Surface Roughness (S_a) and Topography (ST)

The Sensofar S neox 3D optical microscope was utilized to measure the S_a of the steel balls' WS and quantify it in terms of the average S_a and the summation of the maximum peak height and valley depth (S_z). The WS was not damaged during or after the analysis because 3D optical microscopes use lasers to measure roughness. Surface topography (ST) analysis was also performed with a 3D optical microscope, which helped visualize the surface texture of the WS area, which was generated by drawing a line perpendicular to the sliding direction.

2.3.5 Experimental Conditions

The experiment followed the ASTM D4172 standard, and the experimental conditions are tabulated in Table 3. Triplicates of each sample were produced and examined to ensure the reliability of the results.

Table 3: Experimental condition.

Properties	Value
Temperature	75°C
Load	392 N
Rotational speed	1200 rpm
Duration	60 minutes

3.0 RESULTS AND DISCUSSION

3.1 Coefficient of Friction (COF)

Figure 4 shows the COF over time for the pure TMPE and the 0.05, 0.1, and 0.5wt% GO-TMPE. Figure 4(a) shows the COF trend for the whole hour while Figure 4(b) shows the COF in the final 600 seconds of the tribological test, where a steady state had been achieved and data fluctuations were relatively lower.

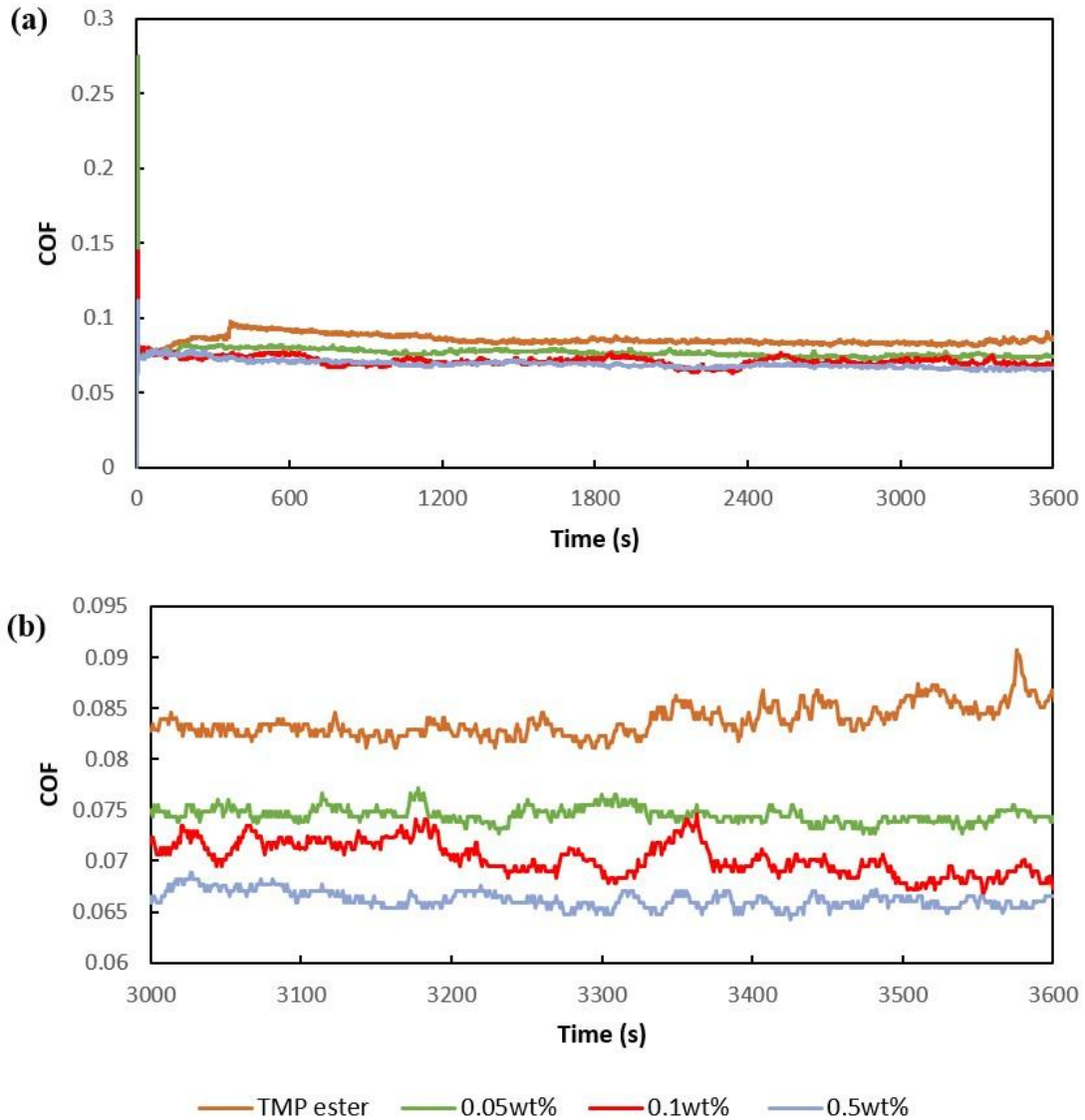


Figure 4: A graph of the COFs of the pure TMPe and the 0.05, 0.1, and 0.5wt% GO-TMPe (a) over the hour-long test and (b) in the final 600 seconds.

The GO-TMPe exhibit similar COF trends over time regardless of GO concentration. A very sharp instantaneous friction peak occurred when the experiment started, immediately followed by a steady frictional state that stayed relatively constant throughout the rest of the test. The 0.05wt% GO-TMPe had the highest COF, followed by the 0.1 and 0.5wt% GO-TMPe. It differs quite a bit from the pure TMPe, which had a more gradual increase in COF, which peaked before gradually lowering to a steady state. The unusually high COF at the beginning of the test may be due to the presence of GO nanoparticle clusters. Nanoparticles may accumulate at the contact

area, causing insufficient lubricant supply and starvation at the contact zone (Guo et al., 2020; Sani et al., 2017).

The steady-state region of the 0.1wt% GO-TMPe fluctuated more, as evidenced by a slight dip in COF at the 600-1000th second and the 2000-2400th second. Similar observations were also noted in the final 600 seconds, where variations in the COFs of the GO-TMPe were more apparent than those of the 0.05 and 0.5wt% GO-TMPe

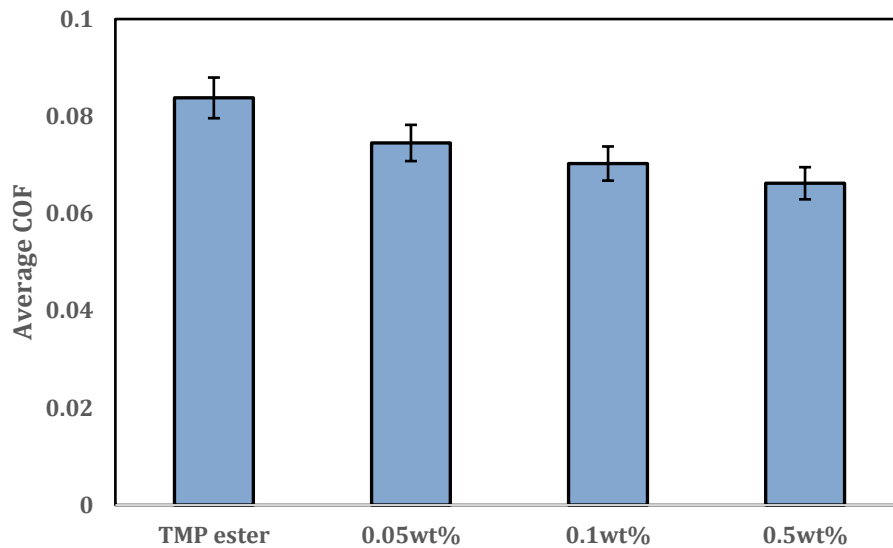


Figure 5: A bar graph of the average COFs of the pure TMPe and the 0.05, 0.1, and 0.5wt% GO-TMPe.

Figure 5 exhibits bar graphs representing the average steady-state COFs of the three GO concentrations and pure TMPe. The average COF indicated significantly enhanced frictional performance when GO was added. It was true for all GO-TMPe concentrations, as evidenced by COF reductions. This was due to the low interlaminar shear stress between the GO sheets. Previous studies have found that GO nanoparticles possess a wrinkled textured surface with layered sheet morphology. When GO nanosheets are added to the base oil, they are adsorbed onto the lubricated surfaces and form a tribo-film that prevents the surface asperities from contacting each other (Wang et al., 2019). The low interlaminar shearing of GO sheets then assists in lowering the COF. Similarly, Zhang et al. (2018) noted that the weak Van der Waals forces between the GO sheets are easily broken by shear force during sliding, allowing the adsorption film to effectively reduce the shear strength between the interacting pairs, minimizing friction.

Incremental COF reductions were observed as the GO concentration increased. The COF reduction corresponding to 0.05, 0.1, and 0.5wt% GO incorporation compared to pure TMPe was 11.1%, 16.1%, and 21.0%, respectively. Rising GO concentration allowed more GO to get adsorbed onto the surface, further decreasing the probability of metal-to-metal contact. Another possible justification is an increase in the lubricant's viscosity index when the nanoparticles were added. Farhana et al. (2015) reported an increase in lubricant viscosity and density when higher nanoparticle concentrations were added, and these observations were attributed to the higher

possibility of nanoparticle agglomeration. Another possibility is the rise in the viscosity index when higher nanoparticle concentrations were added (Al-Tabbakh et al., 2022, Roselina et al., 2020). It suggests the lowered impact of temperature on the lubricant's viscosity, allowing the oil to retain its viscosity as the temperature varies, which is a desirable attribute. The rise in viscosity with increasing nanoparticle incorporation is also reported by Zin et al. (2016). In the study, the authors quoted that for hydrodynamic lubrication, the increase in viscosity is beneficial in regard to the load-carrying capability, while during boundary lubrication, the condition can help reduce friction power loss. However, it should be noted that extreme viscosity modification may result in detrimental frictional properties instead.

3.2 Wear Scar Diameter (WSD)

The bar graph in Figure 6 presents the average WSDs post-lubrication with TMPe containing 0.05-0.5wt% GO. The WSD trend differed from that of the COFs'. The anti-wear performance of the 0.05 and 0.5wt% GO-TMPe were worse than that of the pure TMPe, where their WSDs were 2.5 and 0.75% larger than that of the pure TMPe, respectively. However, the 0.1wt% GO-TMPe's anti-wear performance was better than that of the pure TMPe, as its WSD was 6.33% smaller than that of the pure TMPe.

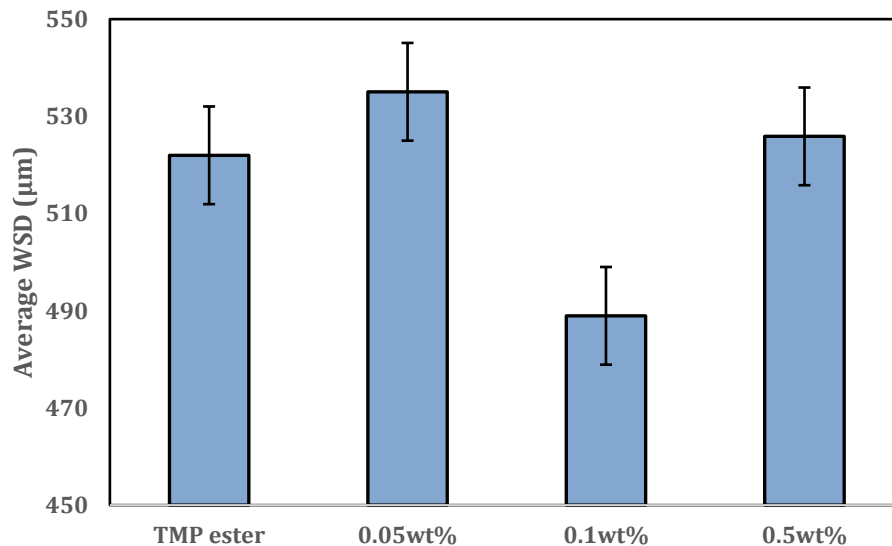


Figure 6: A bar graph of the average WSDs of the pure TMPe and the 0.05, 0.1, and 0.5wt% GO-TMPe.

It can be noted that the proper GO addition allows it to smoothly enter the frictional contact area and lower the shear strength at the interface during sliding motion. This phenomenon reduces the direct contact between the rough asperities of the interacting surfaces, suppressing material wear. Ismail et al. (2020) noted that when an optimum nanoparticle quantity is incorporated into the lubricant, the contact surfaces can be completely covered and attached to the nano-additives. Reduced surface exposure leads to lower surface wear activity.

Although the addition of an appropriate amount of GO could increase the anti-wear performance of a lubricant, other concentrations may lead to inferior wear properties, as shown by the higher WSDs formed when 0.05wt% and 0.5wt% of GO were added. Zin et al. (2016) stated that suboptimal concentrations had nanoparticle quantities that failed to protect the metal surfaces from wear. On the other hand, when the optimum concentration was exceeded, the nanoparticles agglomerated, lowering suspension stability and causing the large aggregates to scratch the surfaces during loading, leading to larger WSDs. Similarly, Ismail et al. (2020) reported nanoparticle agglomeration at higher concentrations and a tendency to restack when the optimum concentration is exceeded. Some aggregates became abrasive particles, leading to increased scrapings on the metal surfaces. Therefore, it can be deduced that frictional properties improve at higher GO concentrations owing to more adsorption onto the metallic friction pairs; however, the agglomerated nano-additives act as abrasive particles, damaging the surface and reducing its anti-wear capability.

3.3 Physical Wear Observation

Figure 7 shows the WSs of the 0.05, 0.1, and 0.5wt% GO-TMPE. The scratch lines on the 0.05wt% GO-TMPE were mostly light, indicating shallow grooves. However, multiple large-sized pits were observed at the WS, which indicated severe adhesive wear. Additionally, delamination was observed at the bottom edge of the scar, which indicates adhesive wear. The large pits may explain the sample's higher COF at the early stage of the four-ball test (Figure 7a). Although the other GO-TMPE exhibited similar trends, the maximum COF of the 0.05wt% GO-TMPE was significantly higher than that of the 0.1 and 0.5wt% GO-TMPE. The peak COFs generated by the three GO-TMPE were 0.27, 0.14, and 0.11, respectively. Therefore, the maximum COF of the 0.05wt% GO-TMPE was two and 2.5 times higher than that of the 0.1 and 0.5wt% GO-TMPE, respectively. The exceedingly high friction generated by the 0.05wt% GO-TMPE was due to the significant energy required to remove the material from the surface of the metal when the pits formed.

In the case of the 0.1wt% GO-TMPE, a pit can also be seen in the scar, where a part of the steel material was removed from the surface. However, it is smaller and not as severe as that in 0.05wt% GO-TMPE. On the other hand, the parallel grooves that indicate abrasive wear were much deeper than the previous lower concentration, as shown by the grooves with darker regions. It indicates that the produced nanoparticles may cluster together to become larger abrasive particles that leave deeper scratches on the metal surface. Another observation is that some parts of the WSD were shiny and were unaffected by friction, producing a more irregular WS pattern than others. The 0.5wt% GO-TMPE exhibited better wear as its outer surface was comparatively less ragged. Additionally, no sign of adhesive wear was observed. The rough edges of the scar seen in all three GO-TMPE may be due to the wear caused by particles that detached from the metal ball hitting the surface, entering in and out of the contact zone. Moreover, rough edges are also attributed to the GO nanoparticles that themselves act as surface abrasives.

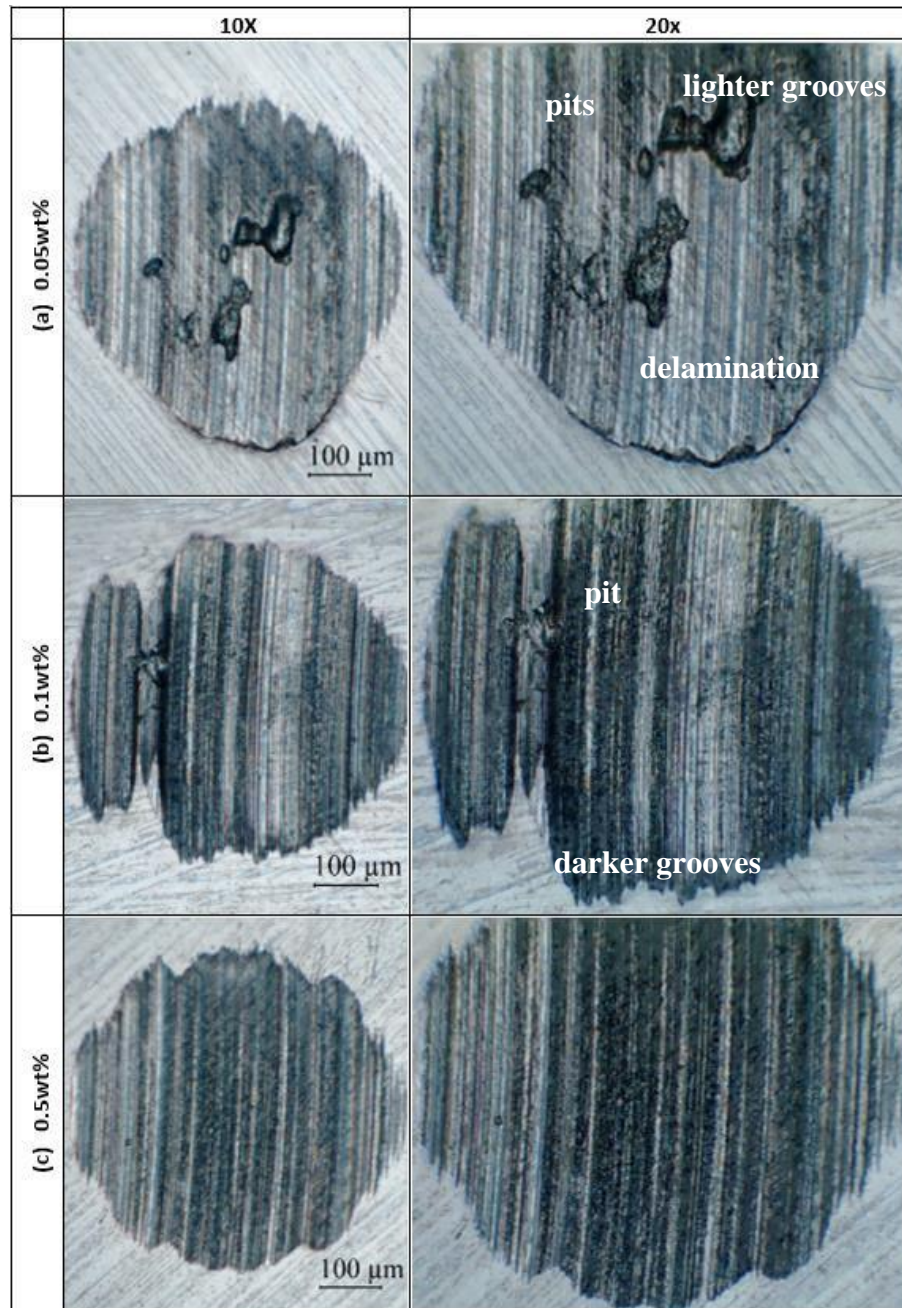


Figure 7: The wear scar on balls lubricated with (a) 0.05, (b) 0.1, and (c) 0.5wt% GO-TMPE.

3.4 Surface Roughness And Topography

Figure 8 depicts the S_a and S_z of the 0.05, 0.1, and 0.5wt% GO-TMPE and pure TMPE used as a benchmark. It can be noted that the surface asperities of the steel balls lubricated with the 0.05 and 0.1wt% GO-TMPE were significantly rougher than the ball lubricated with pure TMPE. Compared to pure TMPE, the two GO concentrations caused S_a to rise by 82.7% and 73.3%, respectively. On the other hand, the 0.5wt% GO-TMPE sample showed comparably similar average roughness, with the S_a being only 3.27% lower than the benchmark. The trend in the S_z was similar to S_a , where the 0.05% and 0.1wt% GO-TMPE' S_z was significantly higher than that of pure TMPE, while the 0.5wt% GO-TMPE's S_z was slightly lower than the benchmark. However, it can be observed that the S_a of the 0.05wt% GO-TMPE exceeded that of the 0.1wt% GO-TMPE, while the observation was the opposite for S_z .

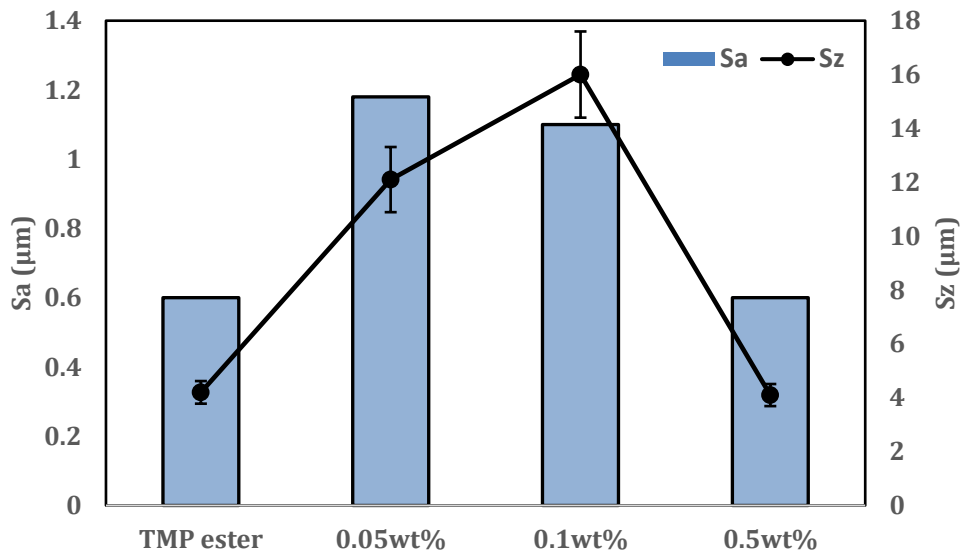


Figure 8: A graph of the S_a and S_z of the pure TMPE and the 0.05, 0.1, and 0.5wt% GO-TMPE.

Figures 9 and 10 present the surface topography (ST) of the steel ball lubricated with the TMPE incorporated with the three GO concentrations. This ST corresponds to the WS cross-section marked by the straight line spanning across the image. In the 0.05wt% GO TMPE case, the surface does not exhibit extreme variations in surface asperities except on the parts containing the pits, such as the black region labeled as A on the scar image. This pit signifies the formation of a deep valley, as shown by the sudden dip in the surface topography (ST) line. The presence of pits contributes to high S_a and S_z (Figure 8).

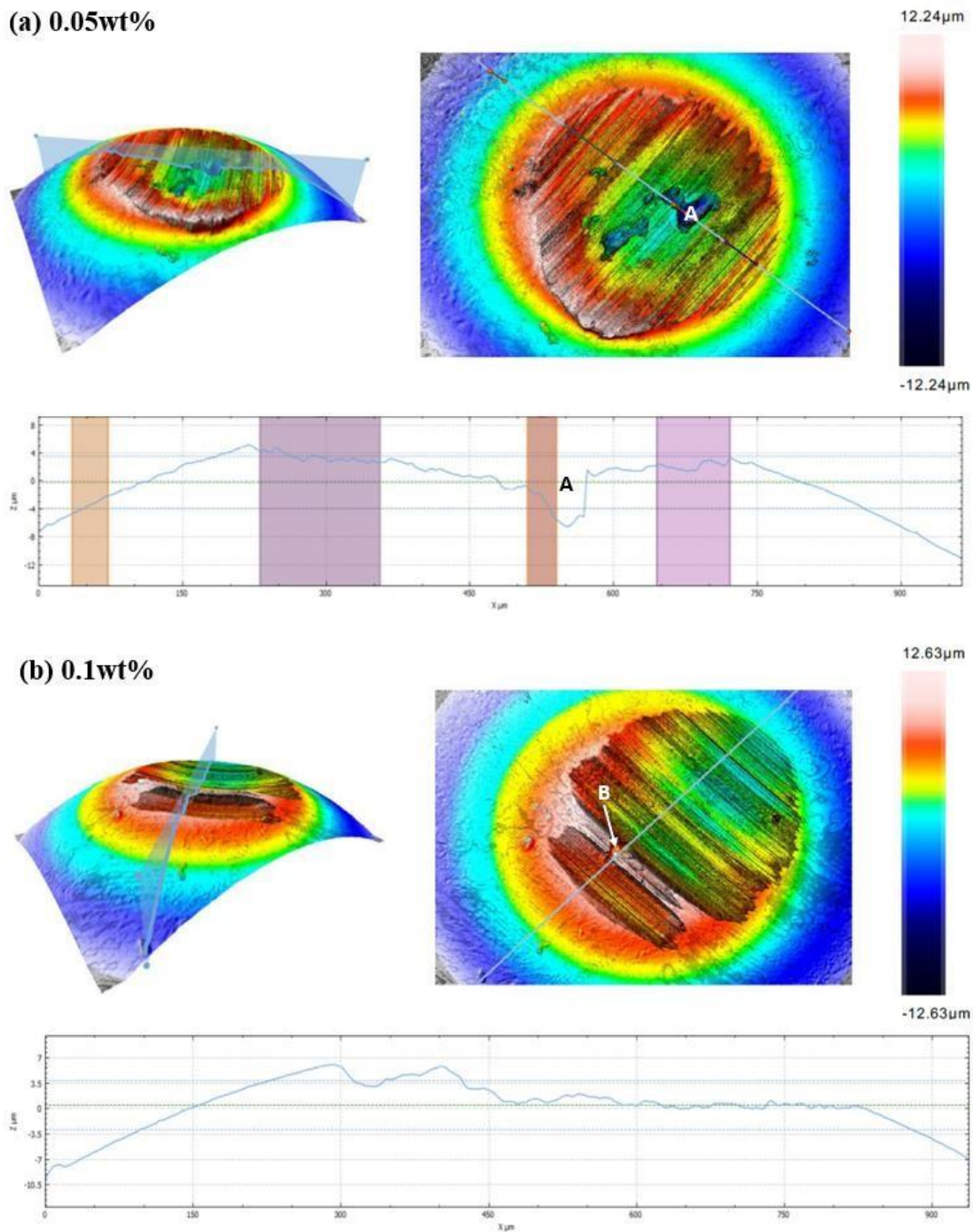


Figure 9: The surface topography (ST) of the steel balls lubricated with pure TMPe and (a) 0.05 and (b) 0.1wt% GO-TMPE.

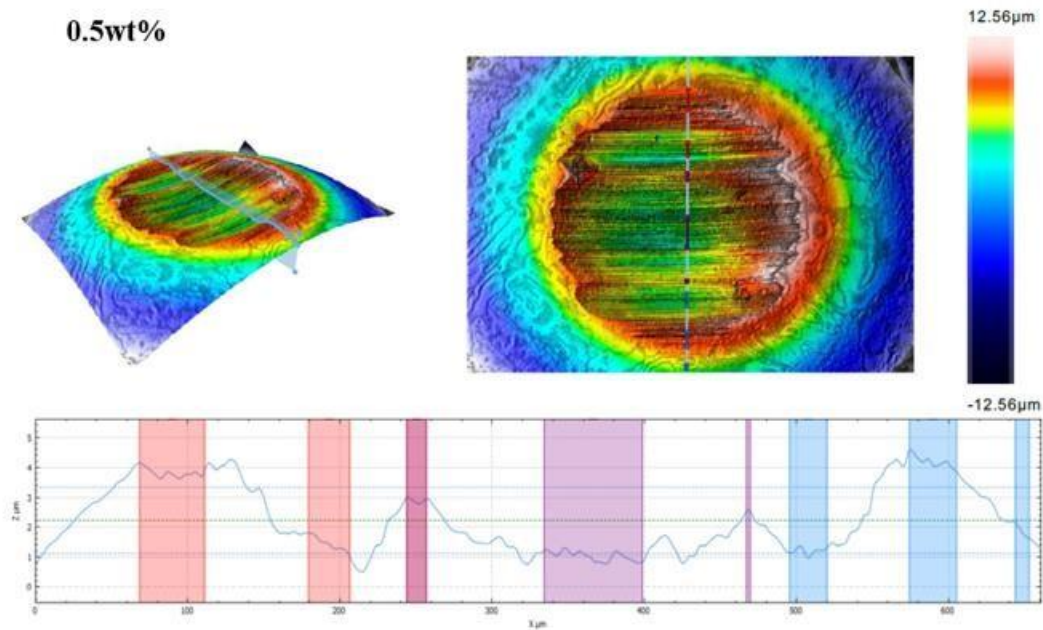


Figure 10: The surface topography (ST) of steel balls lubricated with pure TMPe and 0.5wt% GO-TMPe.

The ball lubricated with the 0.1wt% GO-TMPe exhibits a much smoother overall surface texture compared to the previous concentration. It corresponds to a lower S_a as opposed to the 0.05wt% GO-TMPe sample. Although a pit denoted B can be observed at the WS of the 0.1wt% GO-TMPe, the absence of a drastic change in surface topography (ST) indicates that the pit valley was not as deep as the one in 0.05wt% GO-TMPe. However, the 0.1wt% GO-TMPe had a higher S_z , indicating that the summation of maximum peak height and valley depth for the stated concentration was larger compared to lubricants with lower GO concentrations. It could be attributed to some GO nanoparticles being tribo-sintered onto the surface, causing an increase in peak height and leading to a higher S_z . However, the pit found in the WS of the 0.1wt% GO-TMPe was not as deep as that of 0.05wt% GO-TMPe. This observation is more clearly shown by the black stripe in Figure 11. It can be seen that the surface height peaked in the region marked by the black strip. It indicates that nanoparticles may have been tribo-sintered onto the surface, leading to an increase in surface peak.

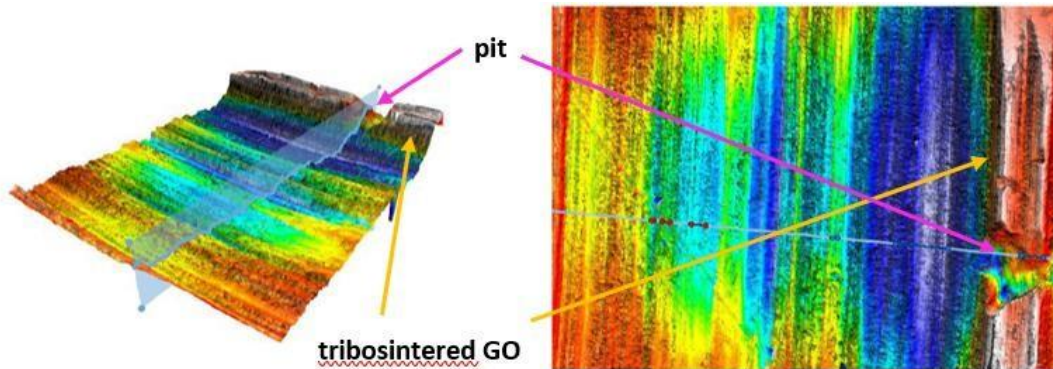


Figure 11: The surface topography (ST) of steel balls lubricated with the 0.1wt% GO-TMPE.

The surface topography (ST) graph of the steel balls lubricated with the 0.5wt% GO-TMPE appears to have more apparent fluctuations than the other GO-TMPE. However, the range between the maximum and minimum z in the ST graph (Figure 10) represents that the height asperities are smaller than the other two lower GO-TMPE. Therefore, the surface of the 0.5wt% GO-TMPE is smoother than the 0.05 and 0.1wt% GO-TMPE, aligning with the previous result of a lower S_a obtained for the 0.5wt% GO-TMPE. The smoothness of the steel ball surface may be attributed to the surface polishing effect. A higher GO concentration may cause some nanoparticle aggregation. These particles may act as abrasives that plough and remove the surface asperities, leading to a smoother interface.

CONCLUSIONS

The evaluation and comprehensive discussion of the addition of GO to TMPE yielded the following conclusions:

- a. The addition of GO nanoparticles reduces the COF. The higher the GO concentration, the lower the COF. The COF of the 0.5wt% GO-TMPE was 21% lower than that of the pure TMPE.
- b. However, a higher GO concentration does not promise good wear resistance. The 0.1wt% GO-TMPE was the best concentration for reducing WSD. Higher concentrations of nanoparticles tend to agglomerate, which lowers the stability of the suspension and causes the large aggregates to scratch the surface during loading, thereby, leading to larger WSDs.
- c. An insufficient amount of GO results in adhesive wear. The 0.5wt% GO-TMPE was the best for this purpose as it yielded a smoother surface and mitigated adhesive wear. Although its WSD was larger than that of the 0.1wt% GO-TMPE, the differences in the heights of the peaks and valleys of the asperities were lower, leading to a smoother surface.

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REFERENCES

- Al-Tabbakh, B. A. A., Jaed, D. M., Qubian, N. A., & Kareem, S. (2022). Preparation of CuO Nanoparticles for Improving Base Oil Properties. *Journal of Petroleum Research and Studies*, 12(1), 191-205.
- Appiah, G., Tulashie, S. K., Akpari, E. E. A., Rene, E. R., & Doodoo, D. (2022). Biolubricant production via esterification and transesterification processes: Current updates and perspectives. *International Journal of Energy Research*, 46(4), 3860-3890.
- Azizan, M. A. H., Fadhli, N. H. E. M., Kamarudin, M. A., Idrus, M. F., & Sulaiman, M. H. (2024). Investigations into friction, film thickness and heat generation of water-based lubricants containing nanoparticles, surfactant and dispersant in hydrodynamic journal bearing. *Jurnal Tribologi*, 40, 199-211.
- Azman, N. F., Samion, S., Paiman, Z., & Hamid, M. K. A. (2024). Tribological performance and mechanism of graphite, hBN and MoS₂ as nano-additives in palm kernel oil-based lubricants: A comparative study. *Journal of Molecular Liquids*, 410, 125616.
- Azman, N. F., Samion, S., & Sot, M. N. H. M. (2018). Investigation of tribological properties of CuO/palm oil nanolubricant using pin-on-disc tribotester. *Green materials*, 6(1), 30-37.
- Berman, D., Erdemir, A., & Sumant, A. V. (2014). Graphene: a new emerging lubricant. *Materials today*, 17(1), 31-42.
- Bhaumik, S., Kamaraj, M., & Paleu, V. (2021). Tribological analyses of a new optimized gearbox biodegradable lubricant blended with reduced graphene oxide nanoparticles. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 235(5), 901-915.
- Campos Flexa Ribeiro Filho, P. R., Rocha do Nascimento, M., Otaviano da Silva, S. S., Tavares de Luna, F. M., Rodríguez-Castellón, E., & Loureiro Cavalcante Jr, C. (2023). Synthesis and frictional characteristics of bio-based lubricants obtained from fatty acids of castor oil. *Lubricants*, 11(2), 57.
- Chouhan, A., Mungse, H. P., & Khatri, O. P. (2020). Surface chemistry of graphene and graphene oxide: A versatile route for their dispersion and tribological applications. *Advances in Colloid and Interface Science*, 283, 102215.
- Duan, L., Li, J., & Duan, H. (2023). Nanomaterials for lubricating oil application: A review. *Friction*, 11(5), 647-684.
- Farhanah, A. N., & Syahrullail, S. (2015). Tribological behaviour of zinc dialkyl-dithiophosphate (ZDDP) as a lubricant additive in RBD palm stearin. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 11(1), 19-26.
- Golshokouh, I., Golshokouh, M., Ani, F. N., Kianpour, E., & Syahrullail, S. (2013). Investigation of physical properties of jatropha oil in different temperature as lubricant oil. *Life Science Journal*, 10(8), 110-119.
- Gulzar, M., Mahmood, K., Zahid, R., Alabdulkarem, A., Masjuki, H. H., Kalam, M. A., ... & Malik, M. S. S. (2018). The effect of particle size on the dispersion and wear protection ability of MoS₂ particles in polyalphaolefin and trimethylolpropane ester. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 232(8), 987-998
- Guo, J., Peng, R., Du, H., Shen, Y., Li, Y., Li, J., & Dong, G. (2020). The application of nano-MoS₂ quantum dots as liquid lubricant additive for tribological behavior improvement. *Nanomaterials*, 10(2), 200.

- Hasnul, M. H., Mohd Zulkifli, N. W., Hassan, M., Zulkifli, S. A., Mohd Yusoff, M. N. A., & Zakaria, M. Z. (2021). Synergistic behavior of graphene and ionic liquid as bio-based lubricant additive. *Lubricants*, 9(5), 46.
- He, T., Dai, Q., Huang, W., & Wang, X. (2018). Colloidal suspension of graphene oxide in ionic liquid as lubricant. *Applied Physics A*, 124, 1-7.
- Huang, S., He, A., Yun, J. H., Xu, X., Jiang, Z., Jiao, S., & Huang, H. (2019). Synergistic tribological performance of a water based lubricant using graphene oxide and alumina hybrid nanoparticles as additives. *Tribology International*, 135, 170-180.
- Ismail, N. A., Zulkifli, N. W. M., Chowdhury, Z. Z., & Johan, M. R. (2020). Grafting of straight alkyl chain improved the hydrophobicity and tribological performance of graphene oxide in oil as lubricant. *Journal of Molecular Liquids*, 319, 114276.
- Jiříčková, A., Jankovský, O., Sofer, Z., & Sedmidubský, D. (2022). Synthesis and applications of graphene oxide. *Materials*, 15(3), 920.
- Karmakar, G., Dey, K., Ghosh, P., Sharma, B. K., & Erhan, S. Z. (2021). A short review on polymeric biomaterials as additives for lubricants. *Polymers*, 13(8), 1333.
- Kumar, D. S., Garg, H. C., & Kumar, G. (2022). Tribological analysis of blended vegetable oils containing CuO nanoparticles as an additive. *Materials Today: Proceedings*, 51, 1259-1265.
- Lee, C., Li, Q., Kalb, W., Liu, X. Z., Berger, H., Carpick, R. W., & Hone, J. (2010). Frictional characteristics of atomically thin sheets. *science*, 328(5974), 76-80.
- Liu, Y., Ge, X., & Li, J. (2020). Graphene lubrication. *Applied materials today*, 20, 100662.
- Min, C., He, Z., Song, H., Liang, H., Liu, D., Dong, C., & Jia, W. (2019). Fluorinated graphene oxide nanosheet: A highly efficient water-based lubricated additive. *Tribology International*, 140, 105867.
- Mohanraj, T., & Radhika, N. (2021). *Biolubricants*. In *Tribology and Sustainability* (pp. 143-161). CRC Press.
- Narayana Sarma, R., & Vinu, R. (2022). Current status and future prospects of biolubricants: properties and applications. *Lubricants*, 10(4), 70.
- Negi, P., Singh, Y., & Tiwari, K. (2021). A review on the production and characterization methods of bio-based lubricants. *Materials Today: Proceedings*, 46, 10503-10506.
- Opia, A. C., Abdollah, M. F. B., Hamid, M. K. A., & Veza, I. (2023). A review on bio-lubricants as an alternative green product: tribological performance, mechanism, challenges and future opportunities. *Tribology Online*, 18(2), 18-33.
- Opia, A. C., Hamid, M. K. A., Syahrullail, S., Johnson, C. A., Rahim, A. B., & Abdulrahman, M. B. (2021). Nano-particles additives as a promising trend in tribology: A review on their fundamentals and mechanisms on friction and wear reduction. *Evergreen* 8 (4), 777-798.
- Paiman, Z., Samion, S., Yazid, M. N. A. W. M., & Rasep, Z. (2024). Tribological Performances of Trimethylolpropane (TMP) Blended with Graphene Oxide Using Four-Ball Tribotester. *Tribology Online*, 19(1), 1-10.
- Penkov, O. V. (2020). *Tribology of graphene: simulation methods, preparation methods, and their applications*. Elsevier.
- Roselina, N. N., Mohamad, N. S., & Kasolang, S. (2020). Evaluation of TiO₂ nanoparticles as viscosity modifier in palm oil bio-lubricant. In *IOP Conference Series: Materials Science and Engineering* (Vol. 834, No. 1, p. 012032). IOP Publishing.
- Sabri, A. M., Talib, N., Sani, A. S. A., Zamri, Z., Kamdani, K., Kunar, S., & Abdullah, H. (2024). Enhancing the physical and tribological characteristics of modified jatropha oil via the incorporation of hybrid nanoparticle additives. *Jurnal Tribologi*, 41, 49-67.

- Sani, A., Sahab, A., Abd Rahim, E., Talib, N., Kamdani, K., & Rahim, M. Z. (2017). Performance Evaluation of Palm-Olein TMP Ester Containing Hexagonal Boron Nitride and an Oil Miscible Ionic Liquid as Bio-Based Metalworking Fluids. *Journal of Mechanical Engineering (JMEchE)*, (1), 223-234.
- Shah, R., Woydt, M., & Zhang, S. (2021). The economic and environmental significance of sustainable lubricants. *Lubricants*, 9(2), 21.
- Smith, A. T., LaChance, A. M., Zeng, S., Liu, B., & Sun, L. (2019). Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites. *Nano Materials Science*, 1(1), 31-47.
- Suk, J. W., Piner, R. D., An, J., & Ruoff, R. S. (2010). Mechanical properties of monolayer graphene oxide. *ACS nano*, 4(11), 6557-6564.
- Syahrullail, S., Azwadi, C. S. N., & Ing, T. C. (2011). The metal flow evaluation of billet extruded with RBD palm stearin. *International Review of Mechanical Engineering*, 5(1), 21-27.
- Syahrullail, S., Nakanishi, K., & Kamitani, S. (2005). Investigation of the effects of frictional constraint with application of palm olein oil lubricant and paraffin mineral oil lubricant on plastic deformation by plane strain extrusion. *Japanese journal of tribology*, 50(6), 727-738.
- Wang, W., Zhang, G., & Xie, G. (2019). Ultralow concentration of graphene oxide nanosheets as oil-based lubricant additives. *Applied surface science*, 498, 143683.
- Xie, M., Cheng, J., Huo, C., & Zhao, G. (2020). Improving the lubricity of a bio-lubricating grease with the multilayer graphene additive. *Tribology International*, 150, 106386.
- Xue, S., Li, H., Guo, Y., Zhang, B., Li, J., & Zeng, X. (2022). Water lubrication of graphene oxide-based materials. *Friction*, 10(7), 977-1004.
- Yadav, A., Singh, Y., & Negi, P. (2021). A review on the characterization of bio based lubricants from vegetable oils and role of nanoparticles as additives. *Materials Today: Proceedings*, 46, 10513-10517
- Yadav, G., Tiwari, S., & Jain, M. L. (2018). Tribological analysis of extreme pressure and anti-wear properties of engine lubricating oil using four ball tester. *Materials Today: Proceedings*, 5(1), 248-253
- Yunus, R., Rasheed, H. S., & Zulkifli, N. W. M. (2020). Wear and friction behavior of semi synthetic engine oil blended with palm oil/TMP ester and nano glass powder additive. *Jurnal Tribologi*, 26, 16-36
- Zhang, G., Xu, Y., Xiang, X., Zheng, G., Zeng, X., Li, Z., ... & Zhang, Y. (2018). Tribological performances of highly dispersed graphene oxide derivatives in vegetable oil. *Tribology International*, 126, 39-48.
- Zin, V., Barison, S., Agresti, F., Colla, L., Pagura, C., & Fabrizio, M. (2016). Improved tribological and thermal properties of lubricants by graphene based nano-additives. *RSC advances*, 6(64), 59477-59486.
- Zulhanafi, P., Syahrullail, S., & Faizin, Z. N. (2023). Tribological performance of trimethylolpropane ester bio-lubricant enhanced by graphene oxide nanoparticles and oleic acid as a surfactant. *Tribology International*, 183, 108398.
- Zulhanafi, P., & Syahrullail, S. (2019). The tribological performances of Super Olein as fluid lubricant using four-ball tribotester. *Tribology International*, 130, 85-93.
- Zulhanafi, P., Syahrullail, S., Abdul Hamid, M. K., & Chong, W. W. F. (2021). The effect of saturated and unsaturated fatty acid composition in bio-based lubricant to the tribological performances using four-ball tribotester. *Journal of Oil Palm Research*, 33(4), 653-667.

- Zulkifli, N. W. M., Kalam, M. A., Masjuki, H. H., & Yunus, R. (2013a). Experimental analysis of tribological properties of biolubricant with nanoparticle additive. *Procedia Engineering*, 68, 152-157.
- Zulkifli, N. W. M., Kalam, M. A., Masjuki, H. H., Shahabuddin, M., & Yunus, R. (2013b). Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant. *Energy*, 54, 167-173.