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TRIBOLOGICAL EVALUATION OF PALM OIL-BASED TRIMETHYLOLPROPANE (TMP) LUBRICANT ENHANCED WITH GRAPHENE OXIDE FOR ENGINE OIL APPLICATIONS

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Abstract: Palm oil's long molecular fatty acid chains make it a promising candidate for lubricants due to its potential to reduce wear and friction. However, its thin fluid film may sometimes fail to protect contact surfaces. To solve this, an effective additive is required. This study used trimethylolpropane (TMP) as the base lubricant and graphene oxide (GO) as a nano-based additive. The combination's performance was evaluated using a Four-ball tribotester, measuring friction coefficient, wear scar, and surface roughness under various conditions, and compared with synthetic and mineral oils. While the TMP +0.5wt% mixture had a slightly higher friction coefficient than pure TMP, it outperformed both mineral and synthetic oils in friction reduction. Additionally, the TMP+0.5wt% formulation showed significant improvements in surface roughness and wear scar diameter, indicating enhanced surface protection and wear resistance with the inclusion of graphene oxide.

Keywords: graphene oxide, nanoparticle additive, bio lubricant, trimethylolpropane (TMP).

1. INTRODUCTION

Many different types of industry have made extensive use of lubricants, including the manufacturing and automotive industries [1]. The primary function of these lubricants is to lower friction by creating a coating of lubricant between two surfaces contact each other. Importantly, tribological contact is responsible for around a quarter of the world's overall energy consumption [2]. Twenty percent of that goes towards reducing friction, and three percent goes towards revising procedures caused by wear and wear-related problems. In light of the probable future shortage of mineral oil supplies, it is crucial to solve this issue by creating sustainable lubricants that can help us move away from products made of minerals and towards more environmentally friendly, biodegradable alternatives. One potential bio-lubricant candidate is palm oil, which has many desirable qualities such as being biodegradable, having high viscosity indices, being low volatility, and having high flash points [3].

Because they have a stronger attraction to metal surfaces, biobased lubricants have better lubricity, according to previous research [4-7]. As a result, the thin film strength is significantly higher than that of mineral oil. As reported by Tulashie and Kotoka [8] that bio-lubricants derived from coconut oil and palm kernel oil have a higher viscosity than other bio-lubricants. In a study that looked at the wear properties of TMP ester blends with lubricating oil that were based on palm oil, researchers discovered that adding 7% TMP may cut the friction coefficient in half. Palm oil and other bio-based lubricants have several advantages over mineral oil, but they also have some disadvantages, most notably in the area of engine components and corrosion [6]. Importantly, synthetic-grade motor oil, such as SAE20W40, is less corrosive than chemically treated vegetable oil, as reported Arumugam et al. [9].

Lubricants offer many benefits but also have drawbacks such as low flash temperature, poor degradability, and limited oxidative stability. To address these issues, additives like graphene are added due to its remarkable properties such as hardness, electrical and thermal conductivity, elasticity, flexibility, and light weight. Positive results were shown by Pal et al. [10], where adding graphene nanoparticles to vegetable oil-based cutting fluid reduced the friction coefficient by 57.1% compared to

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pure minimum quantity lubrication (MQL). Similarly, Wu et al. [11] found that adding 0.075 mass% graphene to base oil reduced friction by 27% and increased wear resistance of Si3N4 ceramic and GCr15 steel by 43%. Li et al. [12] reported that a moderate concentration of graphene nanoparticles yields the lowest friction coefficient, a finding supported by Mao et al. [13], who identified the optimal graphene concentration at around 0.1 mass%. Rashmi et al. [14] found that using nanoplatelets of graphene (NGO) in TMP increased viscosity by 168%, leading to a 7% reduction in friction and a 16.2% improvement in wear resistance.

Trimethylolpropane (TMP) derived from palm oil was used in this study's tests, which were combined with 0.5 mass percent graphene oxide (GO). Pure palm oil TMP, fully synthetic engine oil, and mineral-based oil were used to evaluate and compare the performance of TMP+0.5wt%. Important tribological measures such as wear scar diameter, friction coefficient, surface roughness, and wear characteristics were the focus of the evaluation.

2. MATERIAL AND METHODS

2.1. Apparatus

The fourball tribotester is a device used to measure the coefficient of friction (COF) and anti-wear (AW) capabilities of lubricating oil and additives. The normal load, rotating speed, and temperature of the machine were all established in compliance with ASTM D4712 (See Table 1) guidelines.

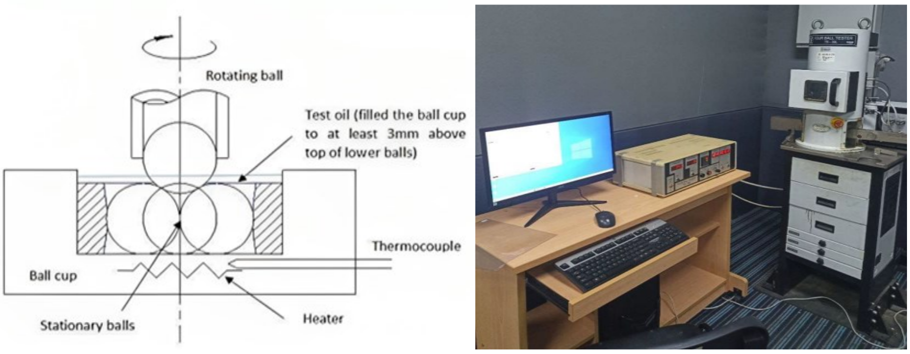


Figure 1. Schematic of the fourball arrangement and sample lubricant.

Table 1. Set parameters of ASTM D4712 standard

Parameters	Details
Standard	ASTM D4172
Load (N)	392
Speed (rpm)	1200, 1300, 1400, 1500, 1600
Duration (min)	60
Quantity (ml)	10
Temp (°C)	75

2.2. Sample Preparation

Four different types of sample lubricants have been established for this experimental work. Using a homogeniser, the primary lubricant TMP+0.5wt% GO has been prepared. An IKA T25 homogeniser is used to blend it, and it runs at 1300 rpm for approximately 45 minutes. Base TMP and this formulation will be contrasted. Graphene oxide is purchased from Adnano Technologies Private Limited, which has a molecular weight of 12.01 g/mole. According to study by Xie et al. [15], 0.5wt% of GO has been selected as the test concentration in this experiment because it is effective in reducing friction and protecting against wear. The TMP ester, fully synthetic engine oil with viscosity grade 5W-40, and mineral engine oil with viscosity grade 10W-30 will be compared to this main composition. Table 2 lists this lubricant's characteristics.

Table 2. The rheological properties of all sample lubricant.

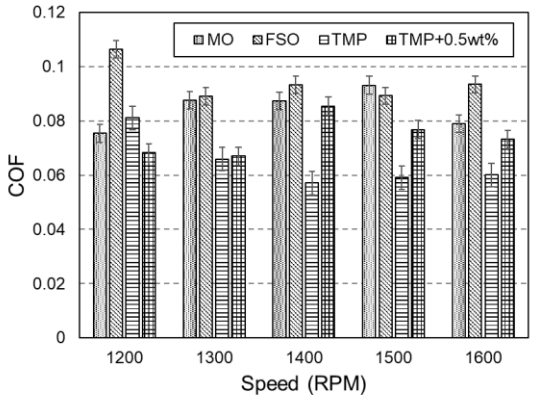
Parameter	TMP Ester	MO	FSO	TMP + 0.5%wt	Standard
Specific density at 25°C (g/cm^3)	0.926	0.875	0.854	0.902	ASTM D1298-85(90)
Dynamic viscosity at 40°C (mPa.s)	40.63	20.021	22.868	-	ASTM D7042
Kinematic viscosity at 40°C (mm^2/s)	45.0	105.4	79.1	12.35	ASTM D445-94
Kinematic viscosity at 100°C (mm^2/s)	16.54	14.5	13.1	9.15	ASTM D445-94
Viscosity index (VI)	383	141	167	>200	ASTM D2270

3. RESULTS AND DISCUSSION

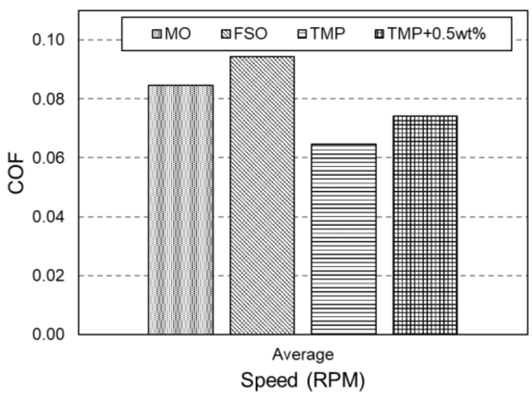
3.1. Coefficient of friction (COF)

Figure 3(a) shows the coefficient of friction against different speeds. This picture clearly illustrates the relationship between COF and speed for a variety of lubricants, including fully synthetic and commercialised mineral oil, TMP, and TMP+0.5wt%. According to the findings, the average friction coefficient is practically constant across all speeds. When the speed is increased, there is no obvious change. The coefficient of friction varies from one type of lubricant to another. Nevertheless, as shown in Figure 3(b), when the average value of the friction coefficient is taken into account, notable variations become apparent.

Mineral engine oil (MO), at about 0.082, and fully synthetic engine oil (FSO), at about 0.0984, have the highest friction coefficient values. It may be concluded that when compared to the lubricant based on palm oil (TMP), both MO and FSO exhibit higher friction coefficients. Numerous variables could be responsible for this phenomenon. The viscosity of the lubricant may fluctuate as a result of temperature and shear rate variations. This might potentially diminish the film thickness between moving surfaces and increase wear and friction. Besides that, friction modifiers and anti-wear compounds are two examples of additives whose effectiveness in decreasing friction may be accelerated by the high-speed operation. Apart from that, the lubricant or its additives may experience thermal deterioration due to the increased mechanical and thermal stresses at higher speeds, which would impair their functionality and raise friction. The ability of the lubricant to reduce friction may also be impacted by the development of thicker boundary layers between moving surfaces at high speeds and possible changes in tribological regimes, such as from hydrodynamic to mixed or boundary lubrication.



(a)



(b)

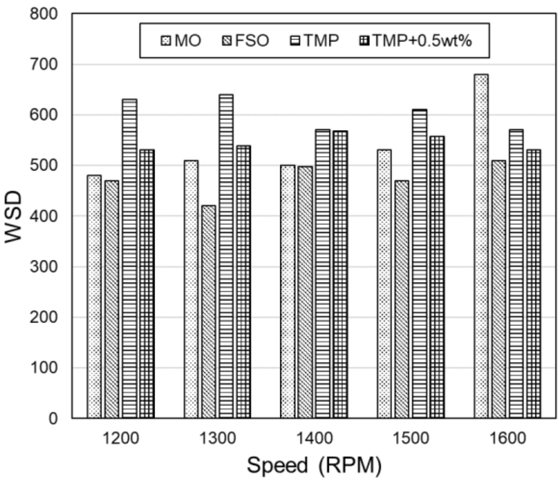
Figure 3. (a) Coefficient of friction for all sample and (b) Average coefficient of friction for all sample.

Compared to MO and FSO, the TMP-based lubricant demonstrates superior performance due to its lower friction coefficient. This is attributed to the long molecular fatty acid chains, which form a protective layer on metallic surfaces, enhancing the thickness of the adsorbed film and providing good anti-friction properties [16]. TMP's structure, with three hydroxyl groups and tight molecular bonds, contributes to its excellent oxidative and thermal stability. Its long polar fatty acid chains allow for both chemisorption and physisorption, with chemisorption forming a strong chemical bond to the metal surface and physisorption providing additional stability through van der Waals forces. These adsorbed chains act as boundary lubricants, creating a barrier that prevents direct metal-to-metal contact, reducing friction under high pressure and shear conditions.

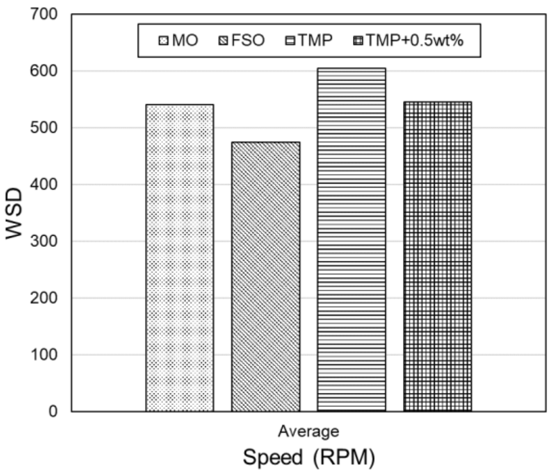
It was found that TMP+0.5wt% (TMP with graphene oxide) has a friction coefficient approximately 5.69% higher than pure TMP, due to the increased concentration of graphene oxide. Higher graphene levels lead to aggregation, which causes abrasive wear as the particles can't fit into surface troughs [17,18]. Additionally, excessive graphene reduces the lubricant's fluidity, resulting in a thinner film at friction boundaries, impairing its effectiveness. Similar findings by Gupta et al. [19] show that too much graphene leads to stacking and aggregation, increasing surface wear and friction. This is further supported by Gupta et al. [20], who observed that excessive nano-additives form physical barriers that disrupt interfacial sliding and affect shear mobility between graphene layers. Therefore, selecting the right graphene concentration is crucial for reducing wear and friction.

3.1. Wear Scar Diameter (WSD)

The wear scar diameter (WSD) of each lubricant at different operation speeds is shown in Figure 4(a). It was noted that none of the lubricants had a clear pattern. The wear scar diameter shows an up-and-down pattern for every type of lubricant. However, at an increased rate of 1600 rpm, Mineral Engine Oil (MO) showed a sharp increase. Several variables can be related to the observed increase in wear scar diameter in mineral oil (MO) compositions, even with the addition of anti-wear additives. The efficacy of these additives in creating a strong protective layer may be compromised if they are incompatible with the particular operating circumstances or the makeup of metal surfaces. Furthermore, the depletion of anti-wear compounds over time might result from thermal and oxidative stress, reducing their ability to alleviate wear [21].



(a)



(b)

Figure 4. (a) Wear scar diameter (in µm) for all sample and (b) Average wear scar diameter (in µm) for all sample.

The presence of impurities and abrasives in the operating environment poses a challenge, as the lubricant may struggle to suspend or remove these particles, reducing the mineral oil's anti-wear effectiveness and increasing wear scar diameter. Despite additives, this issue persists. TMP, however, shows a steady Wear Scar Diameter (WSD) trend at all speeds due to its unique molecular structure with branching hydroxyl groups, which form a strong, chemically stable layer on metal surfaces, reducing wear and preventing metal-to-metal contact. TMP's high chemical affinity for metal surfaces ensures effective lubrication even under high pressure. Its resistance to oxidation, thermal degradation, and shear stability enhances long-term performance, providing efficient lubrication across a wide temperature range. TMP's natural lubricity also reduces the need for external anti-wear additives, maintaining low WSD over time. As shown in Figure 4(a), TMP exhibits a steady WSD trend but, on average, has a larger WSD compared to other lubricants.

The average values reveal a significant variation in Wear Scar Diameter (WSD) between the lubricating oils, as shown in Figure 4(b). FSO exhibited a lower WSD compared to other lubricants. Despite initially having lower friction coefficients, both pure TMP and TMP+0.5wt% showed higher WSDs than FSO and MO. TMP displayed the highest WSD at 615.19 µm in Figure 6, while FSO had the lowest at 491.59

μm. This difference is attributed to FSO's effective anti-wear formulation, which creates a boundary layer that reduces friction and lowers WSD. Similar findings were reported by Zulkifli et al. [22], who observed that a fully formulated lubricant had a lower WSD than TMP ester.

3.3. Wear Observation

Using a high-definition microscope, the physical wear appearances of the steel ball lubricated by each lubricant were recorded, as shown in Figure 5. Wear scar analysis of MO and FSO at 100× magnification at sliding speeds of 1200 and 1600 rpm reveals deep grooves and uneven scar shapes, indicating abrasive and adhesive wear, which are common in the steel ball's wear scars. In contrast, Figure 5 also shows that the TMP and TMP+0.5wt% formulations produced smoother and more consistent sliding patterns. However, a noticeable dent is observed in the wear scar of TMP+0.5wt% at 1600 rpm, likely due to graphene oxide aggregation, which is forced against the contact interface by high sliding force during friction testing. Despite this, other areas of the surface remain smooth. Overall, the TMP-based lubricant exhibits a smoother and more consistent wear pattern compared to FSO and MO. The smooth surface of TMP + 0.5wt% is partly due to the presence of its long fatty acid chains, while SO and MO show decreased tribological performance, evidenced by the deep grooves.

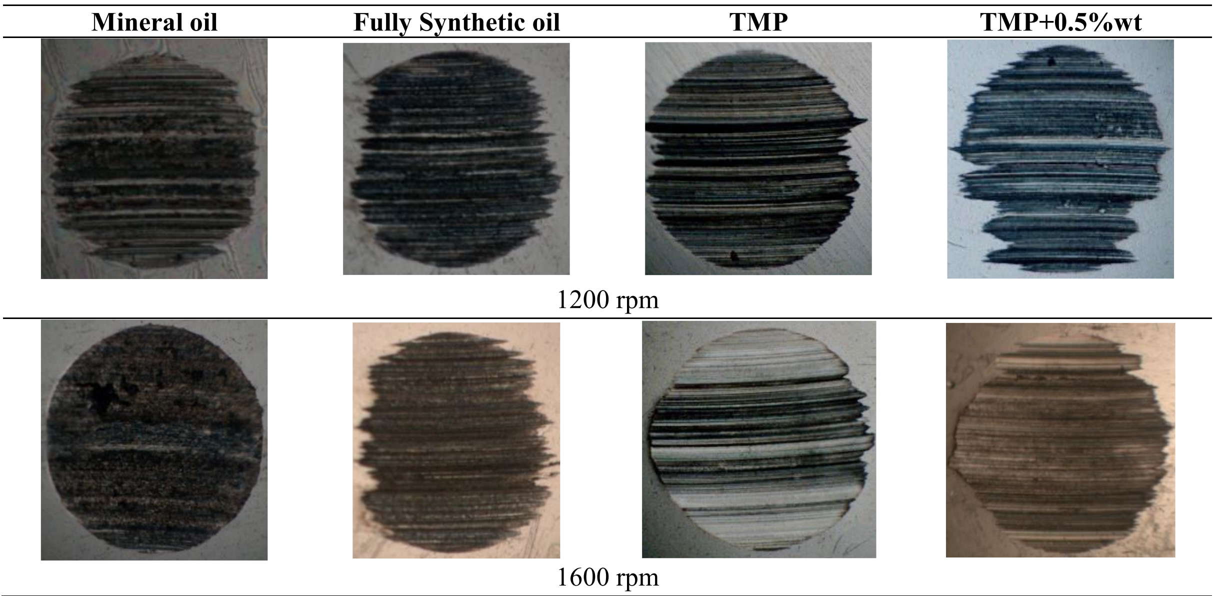


Figure 5. Wear observation for all sample at 100×.

CONCLUSIONS

The tribological behavior of TMP + 0.5wt% was compared to pure TMP, FSO, and MO under different operating conditions. The results showed that both TMP + 0.5wt% and pure TMP had lower coefficients of friction (COF) than FSO and MO. However, adding graphene oxide to the TMP base caused a slight increase in COF due to the agglomeration effect from the significant concentration of graphene. Despite this, graphene oxide's two-dimensional structure and high surface area helped increase Wear Scar Diameter (WSD) in the TMP-based stock by improving coverage and protection of contact surfaces, resulting in reduced wear. Additionally, even with a larger WSD, TMP and TMP + 0.5wt% produced a smoother surface than FSO and MO, which can be attributed to the reduction of adhesive wear, surface smoothing mechanisms, and the protective effect of graphene oxide against deeper wear.

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