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Trimethylolpropane trioleate as eco-friendly lubricant additive

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ABSTRACT

Approximately 17.9% of fuel energy is used to overcome engine friction in passenger cars with engine frictional losses further broken down into losses along hydrodynamic (40%), elastohydrodynamic – due to pure sliding motion (40%), mixed (10%) and boundary (10%) lubrication regimes. Therefore, to assess the tribological influence of TMP trioleate as an eco-friendly additive to a low viscosity Polyalphaolefin (PAO) at different lubrication regimes, the present study adopted a Stribeck-type analysis. Through this study, the viscosity index of PAO was found to increase significantly when blended with 5-vol% TMP trioleate. Tribologically, across the tested conditions at different sliding velocities and applied normal loads, it was determined that this blend could potentially reduce friction power and wear scar diameter by up to 6.09% and 39.65%, respectively, when compared with the neat PAO. Such an improvement was demonstrated to also synergistically enhance the friction modifier effect of this blend at the mixed lubrication regime, delaying the onset of boundary lubrication regime when the contact is lubricated by this mixture.
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1. Introduction

Vegetable oils are not commonly adopted as a lubricant, especially for a closed system of lubrication (e.g. engine lubrication system) due to its poor thermo-oxidative stability. Chemical modification is often conducted on vegetable oils to overcome it. Oxidative and thermal stability of vegetable oil can be improved by eliminating the hydrogen molecule on the beta carbon position of the molecules [1], which could be executed via transesterification process of vegetable oil in producing fatty acid methyl esters (FAME). Knothe and Steidley described that the excellent lubricity of FAME is attributed by their polarity imparting oxygen atom, allowing for the molecules to adsorb to metal surfaces in forming sufficiently thick protective film [2]. Such a characteristic can similarly enhance the friction modifier effect of the lubricant. Even though FAME is intended as an alternative to petro-diesel fuel in compression ignition engines, numerous studies have been conducted to explore the potential of FAME as biodegradable lubri-

cants [3–6]. However, the main drawback of FAME when being considered as a lubricant is its relatively low viscosity, which often results in undesirable load-carrying capacity.

To maintain the lubricity of FAME, a second transesterification process could be introduced in converting FAME into polyol esters. Apart from being biodegradable, polyol esters have excellent thermal stabilities [7–10], making them suitable for operation over a broad range of temperatures. Trimethylolpropane (TMP), which is more commonly accessible as compared to other polyol groups (such as neopentyl glycol and pentaerythritol), is often used for the synthesis of these esters [11]. One typically investigated TMP ester comes in the form of TMP trioleate ($C_{24}H_{28}O_5$), which is derived from the fully monounsaturated oleic acid. This TMP ester is widely used for industrial applications, such as hydraulic fluids, two-stroke engine oils and metalworking oils [7,12–15].

TMP trioleate has been demonstrated to possess high biodegradability levels [12,16]. It also has a thermal stability in the range of 213–230 °C [8,12] (measured using thermogravimetric analysis), comAOarable with the operating temperature requirements for engine lubricants (between 230 °C and 260 °C). From a tribological point of view, the viscosity index (VI) of TMP trioleate is measured to be in the range of 190 [12,15,17], which is higher

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than most commercially available engine lubricants. Apart from TMP trioleate, numerous types of vegetable oil have been utilised to derive their respective TMP ester-based biodegradable lubricants [18–22]. To date, biodegradable lubricants, such as polyol esters, are commonly used in open lubrication systems, where the used lubricant is directly lost to the environment during operation [10]. Even with the increasing need for environmentally friendly lubricants, the biodegradable lubricant is still not widely adopted. This is mainly because of the higher costs (estimated to be 2 to 5 times more expensive than existing lubricants) incurred in synthesising these oleochemical lubricants [23].

Apart from being considered as base oil, polyol ester-based fluids could also be used for production as additives [24,25]. Thus, this ester-based fluid not only could present itself as a potential base fluid but also as a potential lubricant additive. As an example, Rico et al. investigated the tribological influence of natural and synthetic esters when mixed with Polyalphaolefin (PAO) base oil [26] using a four-ball tester. It is to note that PAO base oil consists of saturated oligomers derived through catalytic oligomerisation of alpha-olefins [27]. They observed that such esters present themselves as potential candidates as wear reducers in low polarity base oils, such as PAO and mineral oils, due to their polarity as compared to hydrocarbon-based lubricants. Through their study, they concluded that synthetic esters (e.g. TMP-based esters) could function better under boundary lubrication regime as compared to natural esters (e.g. vegetable oil). However, the study only reported the wear characteristics with little to none emphasis of the frictional performance of the investigated tribological conjunction.

When being tested at extreme pressure conditions using a four-ball tester and a high frequency reciprocating rig (HFRR), Zulkifli et al. observed that the wear preventive lubrication characteristics of a typical lubricant could be improved by adding up to 3-vol% of palm oil-based TMP ester [28]. They explained that such a positive tribological trait is a result of sufficient surface-active elements in the form of fatty acid TMP ester covering the surface asperities in preventing direct surface-to-surface contact. On the other hand, along fluid film lubrication regime (measured using HFRR), they reported that reduced frictional losses could be achieved by adding up to 7-vol% of palm oil-based TMP ester to the tested lubricant. The finding has also been similarly reported by Yunus et al. [29] in which they observed a lower amount of wear when using palm oil-based TMP ester as compared to typical hydraulic fluid. In a separate study, Zulkifli et al. further studied on the extreme pressure lubrication of palm oil-based TMP ester blended with paraffin oil [30]. They demonstrated that adding up to 5-vol% of palm oil-based TMP ester could lead to improved extreme pressure characteristics for the tested paraffin oil, resulting in lower surface roughness when compared with the ones obtained from neat paraffin oil.

The reported studies on TMP trioleate to date focus on wear characteristic with only coefficient of friction values provided at limited sliding velocity and applied normal load ranges. Such minimal information is insufficient to thoroughly assess its frictional performance across different regimes of lubrication. Not denying the importance of wear, frictional performance of TMP trioleate at different operating regimes of lubrication is equally imperative, particularly for engine lubrication systems, where the operating range typically covers a broad spectrum of lubrication regimes [21]. For a passenger car, approximately 17.9% of fuel energy is used to overcome engine friction [31] with the engine frictional losses further broken down into losses along hydrodynamic (40%), elastohydrodynamic – sliding motion (40%), mixed (10%) and boundary (10%) lubrication regimes [31].

To fundamentally assess the impact of a lubricant and its additive across different regimes of lubrication, a Stribeck-type analysis should be conducted. Through the Stribeck curve, as given in Fig. 1, the influence of the studied additive towards the frictional charac-
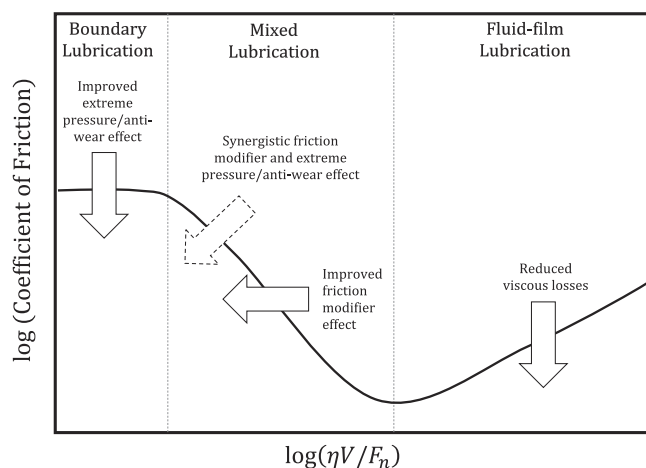

Fig. 1. Regimes of lubrication based on Stribeck curve as a function of Hersey number.

teristics of the selected base oil could then be evaluated accordingly. For example, a delay in the onset of boundary lubrication regime (shifting of the Stribeck curve towards the right hand side along the Hersey number) could indicate improved friction modifier effect. On the other hand, a reduction in friction along the boundary lubrication regime could indicate the potential of the additive in enhancing either the extreme-pressure or the anti-wear effect of the lubricant blend. It is, thus, possible to ascertain either the synergisticism or the antagonisticism of the additive concentration across different lubrication regime.

The present study aims to extend the work on TMP trioleate by the authors [32] to consider its potential as an eco-friendly additive for engine lubricant systems. The aim is achieved by determining the tribological influence of TMP trioleate when added in small concentrations to a low viscosity synthetic low viscosity PAO base oil at varying applied normal loads and sliding velocities using a pin-on-disk tribometer, sufficient for a Stribeck-type analysis. The analysis is also expected to allow for a more comprehensive fundamental elucidation of the role of TMP trioleate as a potential lubricant additive to a low viscosity synthetic base oil across a wide range of lubrication operating regimes.

2. Experimental approach

The experimental approach adopted in the present study included measurements of 1) rheological properties; 2) frictional performances and 3) wear characteristics of tribological conjunctions lubricated with a low viscosity PAO base oil blended with TMP trioleate up to concentrations of 10-vol%. For each of the test lubricants, one (1) litre of the sample was prepared. The TMP trioleate (CAS No. 57675–44-2) used to prepare the test lubricants was provided by Wilmar Oleochemicals. Durasyn 164X PAO was selected as the low viscosity base oil. This PAO base oil is for high-performance applications, such as transmission fluids and engine oils. The blends of PAO base oil and TMP trioleate were stirred at 2000 rpm for 30 min to ensure homogeneous blending before being left for 24 h to observe for any separation. It is to note that no separation layer was observed for all the prepared samples.

2.1. Rheological properties

Rheological properties, namely density and kinematic viscosity, for the test lubricants, were measured at temperatures between 25 °C and 100 °C before and after the friction testing. In the present study, a Brookfield rotational viscometer was used to measure the

dynamic viscosity of the test lubricants. The test lubricants were heated up to the desired temperatures using an oil bath. Then, to convert the measured dynamic viscosity to kinematic viscosity, the density of the test lubricants was measured using a density meter at the corresponding temperatures. These properties were then being applied to determine the lubricant viscosity-pressure coefficient, α, which was used to calculate the minimum lubricant film thickness (to be discussed in the following section). In the present study, the viscosity-pressure coefficient, α was calculated according to the free-volume theory proposed by Wu et al. [33]. For mineral oil and synthetic hydrocarbon-based lubricants, α at temperature, T, is given as:

$$\alpha = (0.1593 + 0.2189 \log \eta_0) \times m' \qquad (1)$$

where $\log (\log (\eta_0/1000 + 0.7)) = -m' \log(T + 273) + N'$. On the other hand, the term m' is the slope while the term N' is the interception of the logarithmic linear relationship between lubricant dynamic viscosity and temperature. It is to note that η_0 refers to the bulk lubricant dynamic viscosity at the corresponding measured temperature, T. Then, the viscosity index (VI) for the tested lubricant blends were calculated based on ASTM-D2270.
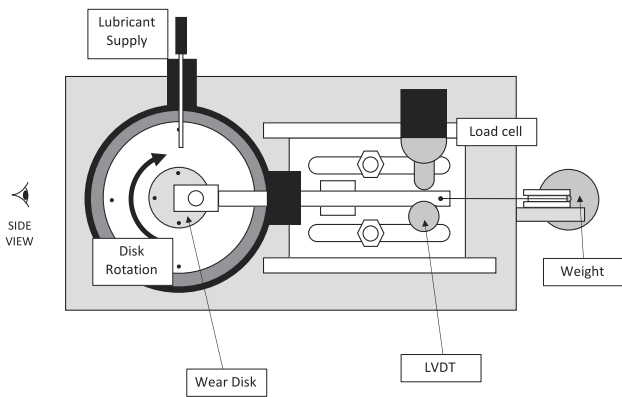
(a) Top view
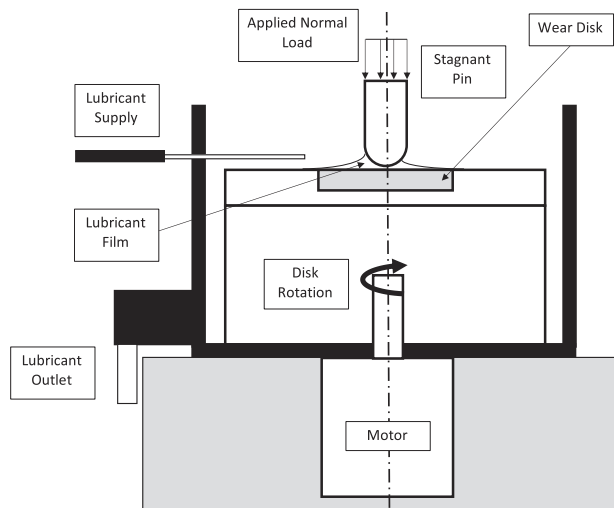
(b) Side view

Fig. 2. Schematic diagram of tribometer configured for a pin-on-disk setup.

2.2. Frictional performance testing

Frictional performance for the test lubricants was measured using an ASTM-G99 compliant tribometer, configured for a pin-on-disk setup given in Fig. 2. This allows for the lubricant characteristics to be assessed under a pure sliding condition. In this study, a cast iron sliding pin was rotated against a wear disk fabricated from JIS-SKD11 tool steel at room temperature condition. The friction tests were repeated three times for each of the tested lubricants. The elemental composition for these materials was determined using the Energy-dispersive X-ray spectroscopy (EDX) and given in Table 1. The modulus of elasticity and Poisson's ratio for the sliding pin and the wear disk are given as $E_1 = 110$ GPa, $v_1 = 0.21$ and $E_2 = 210$ GPa, $v_2 = 0.27$, respectively.

During the friction measurements, the sliding pin was subjected to a load between 10 N and 50 N while the wear disk was rotated between 20 rpm and 2000 rpm. The selected applied normal loads were determined to give maximum Hertzian contact pressure values in the range of 0.767 GPa and 1.311 GPa. A wear track radius of 20 mm was set for all the friction measurements, giving wear disk sliding velocities in the range of 0.042 m/s and 4.2 m/s. In the present study, the friction test was conducted starting from 20 rpm up to 2000 rpm, beginning with 10 N up to 50 N at an increasing interval of 10 N. Such configuration allows for a more comprehensive evaluation of the frictional performance based on a broader range of lubrication operating regimes. For each of the test configurations, a sliding time of three (3) minutes was adopted, giving rise to a cumulative total sliding distance for each of the test lubricants of 25,827 m. It is to note that the lubricant was supplied continuously to ensure a fully flooded inlet conjunction.

To fundamentally elucidate the measured frictional properties with respect to the operating regimes of lubrication, the minimum lubricant film thickness was estimated using the equation derived by Hamrock and Dowson [34]. The minimum lubricant film thickness for a circular contact is given as:

$$\frac{h_{min}}{R} = 3.63 U^{0.68} G^{0.49} W^{-0.073} (1 - e^{-0.68}) \qquad (2)$$

where $E' = 2[(1 - v_1^2)/E_1 + (1 - v_2^2)/E_2]^{-1}$, $G = \alpha E'$, $U = u\eta_0/E'R$ and $W = w/E'R^2$. The applied normal load and sliding velocity are represented by the terms w and u, respectively. On the other hand, the term R, in this study, refers to the cast iron sliding pin end cap curvature radius (5 mm).

2.3. Wear characterisation

Apart from determining the frictional performance of the test lubricants, wear characterisation for sliding pins and wear disks was also conducted before and after the friction testing. Wear scar diameters of the sliding pins were measured using an optical microscope while the surface roughness of the sliding pins and

Table 1
Atomic percentage (%) of elemental composition for cast iron (sliding pin) and JIS SKD-11 tool steel (wear disk) used in the present study with the remaining composition being iron (Fe)

Element type	Cast iron (Sliding pin)	JIS SKD-11 tool steel (Wear disk)
Carbon (C)	3.51	1.5
Silicon (Si)	3.2	0.3
Manganese (Mn)	0.4	–
Phosphorus (P)	0.018	–
Sulphur (S)	0.01	–
Cromium (Cr)	–	12
Molybdenum (Mo)	–	0.7
Vanadium (V)	–	0.4

wear disks were determined using the non-contact mode Atomic Force Microscopy (AFM). For a scan area of 20 μm × 20 μm, the surface roughness parameters for the sliding pins and the wear discs before the friction tests were measured and summarised in Table 2. To further establish any form of tribological impact incurred by the test lubricants during the friction tests, elemental concentrations on the wear disk along the wear track were also quantified using EDX. It is to note that surface roughness and EDX measurements were taken on average based on three (3) separate locations along the wear track on the wear disk.

3. Results and discussions

Fig. 3 presents the density and the kinematic viscosity of neat PAO and neat TMP trioleate measured at temperatures between 25 °C and 100 °C. Generally, it can be observed that neat TMP trioleate is much more viscous as compared to the studied neat PAO base oil across the tested temperature range. At hydrodynamic lubrication regime, the more viscous TMP trioleate is generally expected to generate better load carrying capacity but at the expense of generating higher viscous shear losses as compared to the neat PAO ($\tau \propto \eta$). When adopted for automotive engines, this would also impose higher pumping and hydraulic viscous losses [35,31]. Nowadays, to save energy from viscous losses, lubricants for machine elements are preferred to be of viscosity as low as possible. Consequently, the adoption of neat TMP trioleate as the base oil might be less preferred as compared to the selected neat PAO. This criterion for lubricant selection is even more critical for applications, such as engine in-cylinder lubrication, where viscous losses are estimated to amount up to 40% of the total frictional losses along the piston ring-liner conjunction [31].
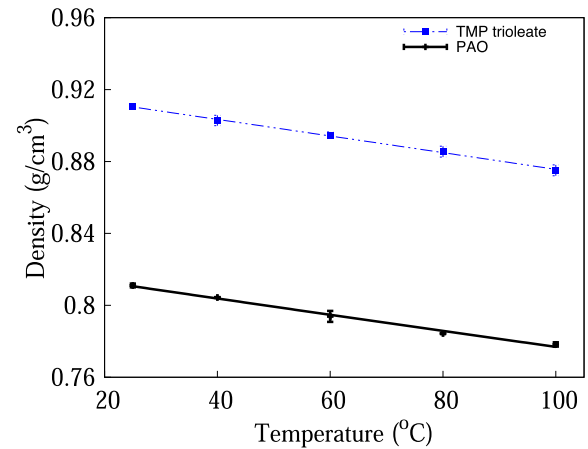
Thus, instead of exploring the potential use as the base oil for engine lubricant, which is often reported in literature, the present study aims to identify the tribological role that TMP trioleate could play as an eco-friendly additive to the low viscosity synthetic PAO base oil across a wide range of lubrication regimes under pure sliding conditions. As a first approximation, Fig. 4 gives the measured density and kinematic viscosity for PAO when blended with TMP trioleate at concentrations from 2.5-vol% up to 10-vol%. Across the measured temperature range, the density of PAO when added with 2.5-vol% TMP trioleate can be seen to vary only marginally as compared to the base oil of PAO. However, when the amount of TMP trioleate is further increased, the density of the mixture is observed to elevate. Such a trend is also similarly observed for the measured kinematic viscosity of the tested lubricant mixtures. In the present study, the concentration of TMP trioleate to PAO is added up to 10-vol% only because beyond this, the viscosity of the mixture has been measured to increase more than 10% at room temperature condition. Under this circumstances, the pumping and hydraulic viscous losses in an engine at cold start would have also increased by the same margin [35], making it less desirable when adopted as an engine lubricant.

Using the measured rheological properties above, Table 3 summarises the viscosity index (VI) values for the tested lubricants and the estimated viscosity-pressure coefficient, α, calculated using Eq. (1). It is shown that the VI values for the lubricant blends increase
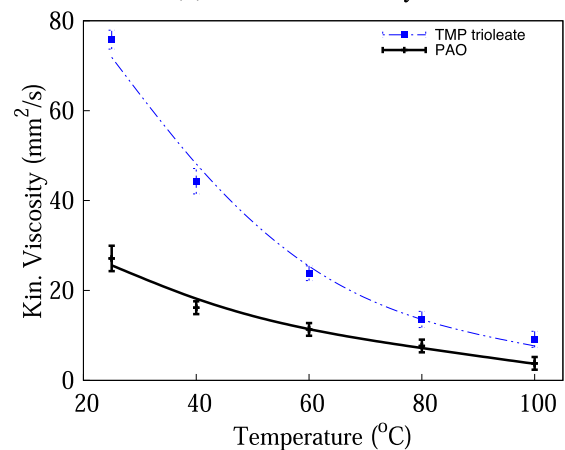

(a) Lubricant density

(b) Lubricant kinematic viscosity

Fig. 3. Measured density and kinematic viscosity for PAO and TMP trioleate at different temperatures.

as compared to the neat PAO up until 5-vol% of added TMP trioleate. However, with further increase in TMP trioleate concentration, the VI is seen to decrease. Higher VI values mean a lesser change in viscosity is expected of the lubricant at higher operating temperatures. In this case, this indicates that TMP trioleate does possess the ability to improve the VI of PAO (more than two folds) when added up to 5-vol% concentrations. As a result, such a lubricant blend can be presumed to be capable of better maintaining its load-carrying capacity across a wide range of operating lubricant temperatures, potentially delaying the inception of boundary friction. Such a positive trend bodes well with applications, such as engine in-cylinder lubrication system, where applied normal loads, sliding velocities and operating temperatures vary significantly during operation. It is to note that the increase in VI for lubricant base oil, when added with TMP ester-based fluid, is also similarly observed by Zulkifli et al. [28].

On the other hand, the viscosity-pressure coefficient, α is used to quantify the change of lubricant viscosity at extremely high pressures (in the range of GPa), especially along elastohydrodynamic lubrication regimes [36]. Fig. 5 further plots the change of viscosity-pressure coefficient, α with the dynamic viscosity for PAO blended with varying concentrations of TMP trioleate. The calculated trend for α varies linearly with the change in dynamic viscosity, which in turn reduces with increasing temperatures (see Fig. 3 and 4). Such a trend along with the range of measured values (for neat PAO) are similarly reported by LaFountain et al. [36]. On
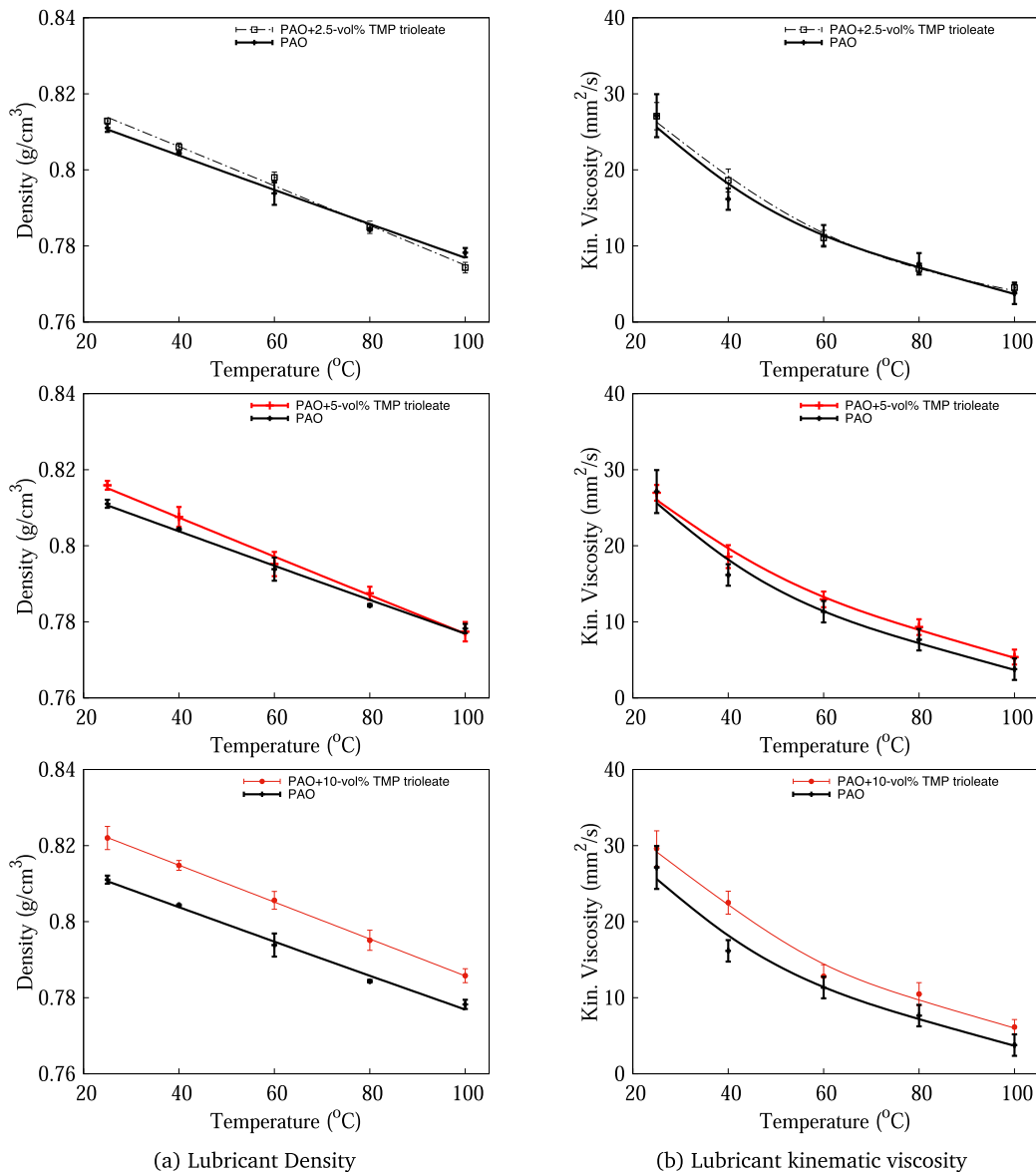
Table 2
Measured surface roughness parameters for sliding pin and wear disks using AFM (scan area of 20 μm × 20 μm) before friction tests.

Surface Roughness parameter	Sliding pin	Wear Disk
Average roughness, R_a	0.0871 μm	0.0896 μm
Root mean square (RMS) roughness, R_q	0.117 μm	0.1147 μm
Average maximum height of profile, R_z	0.2990 μm	0.3068 μm

(a) Lubricant Density

(b) Lubricant kinematic viscosity

Fig. 4. Measured density and kinematic viscosity for PAO blended with various volumetric percentages of TMP trioleate at different temperatures.

Table 3
Viscosity index (VI) and Viscosity-pressure coefficient (α) for tested lubricants.

Lubricant Type	Viscosity Index (VI) [–]	Viscosity-pressure coeff @ 25 °C (α) [GPa^{-1}]
PAO	125	16.56
PAO + 2.5-vol% TMP trioleate	166	15.75
PAO + 5-vol% TMP trioleate	255	13.02
PAO + 10-vol% TMP trioleate	247	12.67
TMP trioleate	194	17.04

top of this, it has also been shown that the viscosity-pressure coefficient decreases when TMP trioleate is added to PAO up to 10-vol %. Assuming that the lubricant viscosity and contact conditions (e.g. applied normal load, sliding velocity) remain constants, higher viscosity-pressure coefficient values would be preferred because this is expected to encourage thicker lubricant film formation [26], especially at elastohydrodynamic lubrication regime. Thus, the mixtures of PAO added with TMP trioleate with reduced viscosity-pressure coefficients are anticipated to form a less thick
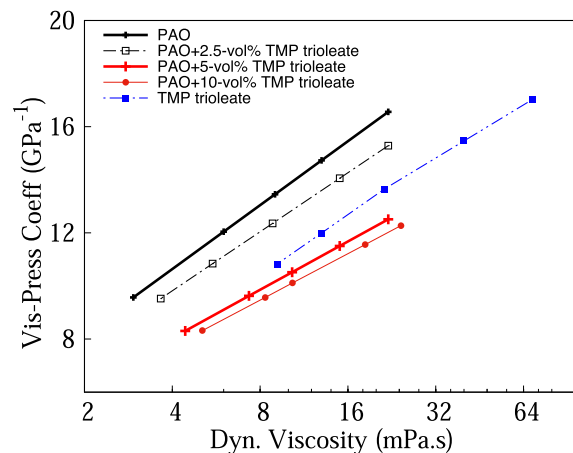

Fig. 5. Viscosity-pressure coefficient variation with dynamic viscosity for PAO blended with various volumetric percentages of TMP trioleate at temperatures between 25 °C and 100 °C.

film, which could be tribologically undesirable as compared to the neat PAO.

Rheological properties, similar to the parameters mentioned above, are predominantly identified by the lubricant industry as the performance benchmark for commercial engine lubricants. However, sole-reliance on such features in lubricant selection is often insufficient. Thus, the present study further conducted frictional measurements using a tribometer at varying sliding operating conditions. Fig. 6(a) first illustrates the estimated minimum lubricant film thickness, calculated using Eq. (2), for neat PAO and neat TMP trioleate. By comparison across the tested tribological configurations, the estimated minimum film thickness for the contact lubricated with neat TMP trioleate is found to be relatively thicker as compared to the one lubricated by neat PAO. Aside from having a slightly larger viscosity-pressure coefficient (see Table 3), such a characteristic could also be attributed to the fact that neat TMP trioleate is significantly more viscous than neat PAO (see Fig. 3). Consequently, this results in a larger load-carrying capacity.

Fig. 6(b), on the other hand, illustrates the measured coefficient of friction (CoF) values of neat PAO and neat TMP trioleate at varying applied normal loads and sliding velocities. It can be observed that both tested lubricants exhibited a Stribeck-like trend when plotted against the ratio of sliding velocity (V) and applied normal load (W). Above $0.008 < V/W < 0.04$ (assumed to be mixed lubrication regime based on the measured CoF), even with larger estimated film thickness, the CoF for neat TMP trioleate is measured to be larger, which manifests in a less desirable friction modifier

(a) Estimated minimum film thickness

(b) Coefficient of friction

Fig. 6. Tribological properties of a pin-on-disk contact conjunction lubricated with PAO and TMP trioleate.

effect, as compared to the neat PAO. Such a counter intuitive trend can be attributed to the larger viscous friction component generated by the more viscous TMP trioleate at the mixed lubrication regime. On the contrary, at $V/W < 0.008$ (taken to be boundary lubrication regime based on the measured CoF), the contact lubricated with neat TMP trioleate is shown instead to generate CoF values that are up to 11.94% lower than that of neat PAO. Such a trend can be explained to be attributed to the polarity of TMP trioleate molecules in forming a more effective boundary film as compared to neat PAO to further separate the opposing surfaces apart, thus, reducing boundary interactions along surface asperities. Otherwise, such a trend could also be correlated to an improved extreme-pressure effect along the measured Stribeck curve, reflecting also on the less drastic transition from mixed to boundary lubrication for TMP trioleate. This assumption, rather than considering enhanced anti-wear effect (typically involves chemical adsorption of molecules under high load and high shear conditions) as given in Fig. 1, is based on the fact that fatty acid molecules are better known for their physical adsorption ability due to their polarity in forming thick boundary lubricant films [2].

At this point, individually, the measured rheological and frictional properties for both neat TMP trioleate and neat PAO have been demonstrated to have their own tribological advantages and disadvantages. In the present study, to further investigate the effect of blending of both fluids, the estimated minimum film thicknesses for PAO added with TMP trioleate at different concentrations are determined. The Stribeck separation parameter, λ ($= h_{min}/\sigma$) is adopted to distinguish between the frictional properties at different operating regimes of lubrication. The term σ refers to the composite surface roughness, computed using:

$$\sigma = \sqrt{R_{a-pin}^2 + R_{a-disk}^2} \qquad (3)$$

Typically, surface roughness values used for the separation parameter are based on the ones measured on untested samples. However, when sliding occurs, sharp peaks at opposing surfaces will be flattened, leading to varying surface roughness being experienced by the confined contact during the sliding process. Hence, as a first approximation, the present study used the surface roughness parameters measured after the completion of the experimental procedure. The measured roughness properties will be discussed later in this section.

Fig. 7(a) shows the separation factor, λ for the tested PAO mixtures as a function of the ratio between sliding velocity and applied normal load (V/W). For 10-vol% of added TMP trioleate, no difference in terms of the separation factor can be observed when being compared with neat PAO. However, the separation factor for both PAO mixtures blended with 2.5-vol% and 5-vol% TMP trioleate is shown to be larger than the one from neat PAO as the ratio of V/W increases. The larger separation factors observed indicate an increased probability of fluid film lubrication occurring, which potentially could generate lower friction forces. As an example, PAO mixtures blended with 2.5-vol% and 5-vol% TMP trioleate can be seen to transit to fluid film lubrication ($\lambda > 3$) at V/W between 0.15 and 0.16 m/N.s while neat PAO transits at a larger ratio of 0.2 m/N.s.

The CoF values for PAO blended with varying concentrations of TMP trioleate is illustrated in Fig. 7(b). At V/W ratio larger than 0.2 m/N.s (under fluid film lubrication regime, where $\lambda > 3$), the CoF values for PAO mixtures across all TMP trioleate concentrations are found to be lower than that of neat PAO. For PAO mixtures with 2.5-vol% and 5-vol% TMP trioleate concentrations, the CoF values are lower by 4.83% and 5.94%, respectively, as compared to the neat PAO. In view of the fairly similar viscosity values, such an improvement could otherwise be associated to the more substantial separation factor, λ as compared to the neat PAO, which poten-
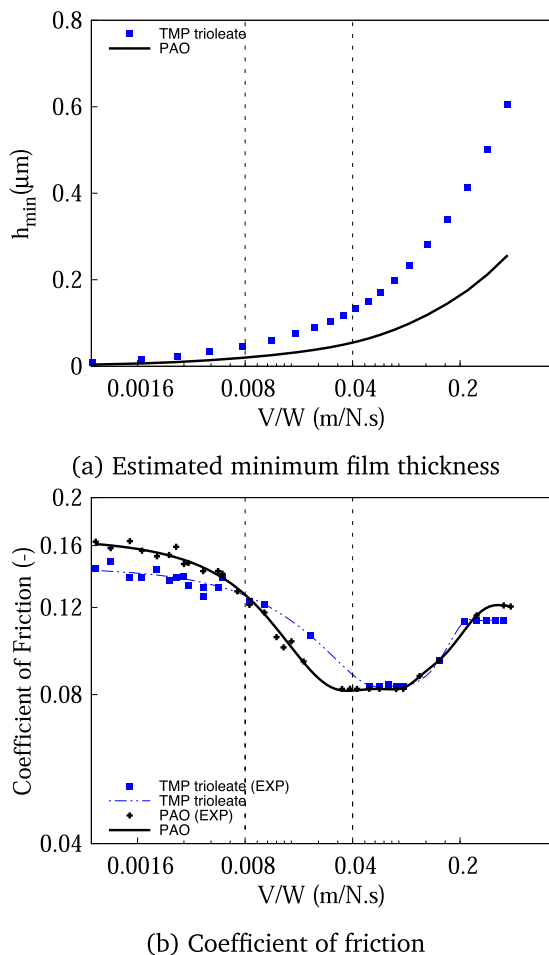
(a) Separation factor, λ
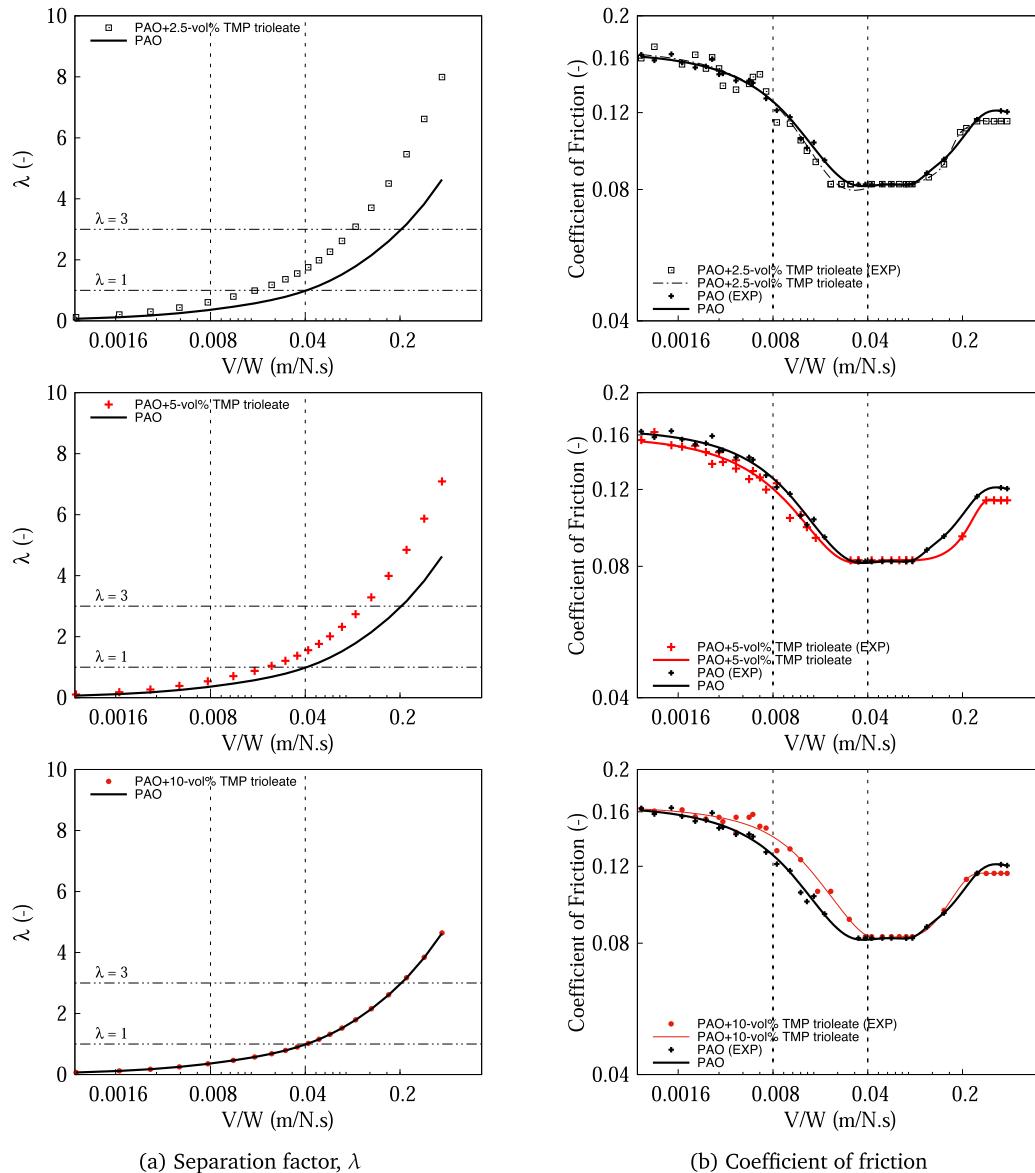
(b) Coefficient of friction

Fig. 7. Tribological properties of a pin-on-disk contact conjunction lubricated with PAO blended with various volumetric percentages of TMP trioleate.

tially increases the probability of the contact in experiencing fluid film lubrication. However, for the mixture with 10-vol% added TMP trioleate, even though the separation factor is similar to the neat PAO, lower CoF values (as much as 4.02% reduction) is still being measured. This could possibly be down to the larger load carrying capacity generated by this more viscous mixture, which predominantly influences shear properties at fluid film lubrication regime.

At V/W between 0.008 m/N.s and 0.04 m/N.s, for 2.5-vol% TMP trioleate concentration, a slightly smaller set of CoF values is observed, indicating marginal improved friction modifier effect. However, no obvious change in the onset of boundary lubrication is observed as compared to the neat PAO. Ironically, with higher concentrations of TMP trioleate up to 10-vol%, the CoF values from mixed lubrication regime until the onset of boundary lubrication regime ($1 < \lambda < 3$ and $0.008 < V/W < 0.04$) are found to be less desirable as compared to the neat PAO, unveiling a much-reduced friction modifier effect. Contradictorily, the CoF values at boundary lubrication regime for these mixtures do not change much in comparison with the neat PAO, showing no signs of frictional reduction.

For PAO mixture with 5-vol% TMP trioleate concentrations, a set of lower CoF values (by 5.97%) is measured at the mixed lubrication regime ($1 < \lambda < 3$ and $0.008 < V/W < 0.04$), revealing an improved friction modifier effect. More importantly, such an enhanced effect has also been observed to be synergistic towards the extreme pressure effect for this lubricant blend, resulting in lower CoF values under boundary lubrication regime ($\lambda < 1$ and $V/W < 0.008$). The CoF trend exhibited by this PAO mixture is shown to be lower by as much as 4.43% as compared to the neat PAO. At this regime, the mechanism underlying boundary friction is no longer dominated by the bulk lubricant properties. Instead, it is influenced by the effectiveness of the boundary-adsorbed film formation. Thus, the reduced CoF measured could be attributed to the polarity of the added 5-vol% TMP trioleate molecules, leading to the formation of sufficiently thick boundary film at the rubbing surfaces. Consequently, this contributes to the presumed improved extreme-pressure effect at this operating regime of lubrication. see Table Table 5.

Under an engine operation, specifically within the piston ring-liner conjunction, the contact is known to operate within a wide

Table 5
Friction power change for PAO blended with various volumetric percentages of TMP trioleate in relative comparison with neat PAO across measured friction force.

| Lubricant Type	Total Friction Power Change
PAO	–
PAO + 2.5-vol% TMP trioleate	↓ 1.08%
PAO + 5-vol% TMP trioleate	↓ 6.09%
PAO + 10-vol% TMP trioleate	↑ 1.75%
TMP trioleate	↓ 0.46%

spectrum of lubrication regimes [37]. Therefore, friction power assessment would be beneficial in better evaluating the frictional performance of the tested lubricants as a potential engine lubricant. Table 4 shows the friction power change for PAO blended with different concentrations of TMP trioleate at various regions of measured friction forces in relative to the neat PAO. The tabulated friction power is calculated by determining the area under the CoF against V/W curves measured in Fig. 6 and 7. Through this information, as an example, if the lowest friction power is desired, then neat TMP triolete would be the ideal choice (reduced friction power of 6.34%). However, for a contact operating within the range of $0.008 < V/W < 0.04$, PAO added with 2.5-vol% of TMP triolete would be desirable (the most friction power reduction at 2.35% for this region). Overall, for an optimised friction power, PAO mixture with 5-vol% would then be the preferred choice, which generates an overall friction power reduction of 6.09% across the measured sliding velocity and load conditions (as given in Table 4).

Aside from frictional properties, wear scar diameter on the sliding pin when lubricated by the tested lubricants is also given in Fig. 8(a). The wear scar diameter is measured after all the test configurations (varying applied normal loads and sliding velocities) have been completed. It can be observed that the sliding pin wear scar diameter is the smallest for PAO mixture added with 5-vol% TMP trioleate, which is calculated to be approximately 39.65% lower when compared with the one measured for neat PAO. Such a trend correlates well with the better boundary frictional properties (enhanced extreme-pressure effect) observed for PAO added with 5-vol% TMP triolete in Fig. 7 when compared with the neat PAO. On the contrary, further adding TMP trioleate to PAO, up to 10-vol%, resulted in an adverse tribological impact in which a more significant wear scar diameter is measured. The measured increased wear scar diameter is also in line with the less desirable friction force properties measured at the mixed lubrication regime of the contact lubricated with this PAO blend. These findings indicate that an optimum concentration of additive (i.e. TMP trioleate) exists, where a more desirable tribological performance is generated. Such a trend is a result of the synergistic competitive interaction between boundary adsorbing molecules in forming a coherent boundary film [38,39].

Fig. 8(b) and (c) presents the measured roughness parameters, R_a, R_q and R_z for the sliding pin (along the wear scar) and also the wear disks (along the wear track) when lubricated by the tested PAO blends, respectively. It is to note that these measured

Table 4
Friction power change for PAO blended with various volumetric percentages of TMP trioleate in relative comparison with neat PAO at different regions of measured friction forces.
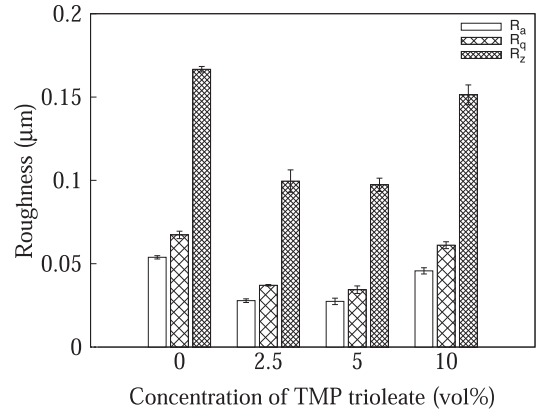
Lubricant Type	V/W ⩽0.008	0.008 < V/W < 0.04	V/W ⩾0.04
PAO	–	–	–
PAO + 2.5-vol% TMP trioleate	↑ 0.86%	↓ 2.35%	↓ 1.04%
PAO + 5-vol% TMP trioleate	↓ 4.46%	↓ 1.57%	↓ 6.50%
PAO + 10-vol% TMP trioleate	↑ 5.98%	↑ 12.70%	↑ 0.75%
TMP trioleate	↓ 6.34%	↑ 13.38%	↓ 1.40%
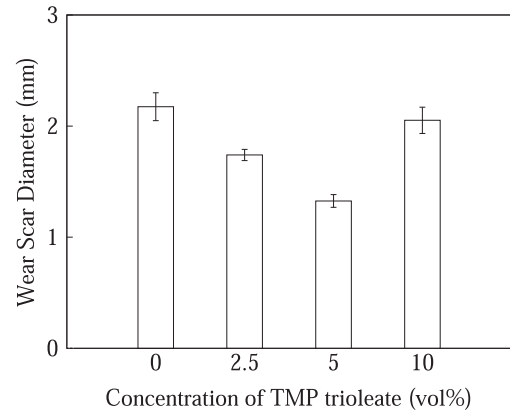
(a) Wear scar diameter on sliding pin
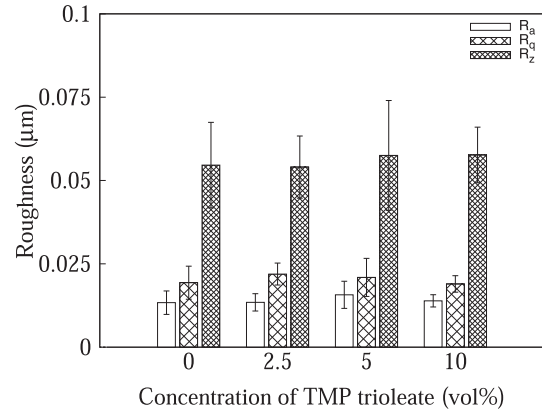
(b) Surface roughness on sliding pin

(c) Surface roughness along wear track on wear disk

Fig. 8. Measured wear properties of sliding pin and wear disks when lubricated with PAO blended with various volumetric percentages of TMP trioleate.

R_a values for the pin-disk conjunction are used to determine the separation factor, λ presented in Fig. 7. From this figure, the roughness parameters for surfaces lubricated by all the tested lubricants can be observed to be much smoother than the values measured before the friction tests (given in Table 2). The smoother surface roughness properties of contacts lubricated with TMP trioleate have been reported in the literature to be a result of the "polishing" effect [28,40]. The effect is attributed to the surface reactions between TMP trioleate and the metal surface, resulting in smaller roughness because of polish wear. In general, the surface roughness values for the sliding pin are shown to not vary much due to the fairly significant amount of wear observed in Fig. 8(a). On

the contrary, it can be seen that the wear disk lubricated by PAO added with 2.5 and 5-vol% of TMP trioleate exhibited somewhat similar surface roughness characteristics, which generated a smoother wear track surface as compared to the neat PAO and the mixture added with 10-vol% TMP trioleate. It can, thus, be concluded that TMP trioleate concentration above 5-vol% could result in a rougher surface along the wear track of the wear disk, in line with the antagonistic frictional effect demonstrated in Fig. 7.

Fig. 9 illustrates the elemental concentrations along the wear track of the wear disks when lubricated by the test lubricants. Interestingly, the highest amount of Fe and the lowest amount of C are concurrently measured for PAO with 2.5 and 5-vol% concentrations of TMP trioleate. The higher Fe amount could be attributed to the "polishing" action in the presence of TMP trioleate, resulting in the removal of oxide layers from the wear disk during sliding, thus, exposes the nascent iron surface. The removal of oxide layers is reflected with the slightly lesser amount of O concentration when compared with the sample lubricated by neat PAO. On the other hand, for C, typically, it has been one of the common practices to eliminate this element for any EDX quantitative analysis based on the assumption that contaminants could either possibly exists on the sample or even the test apparatus [41]. However, in the present study, since the EDX measurements are done under a controlled and vacuum environment, it could only be concluded that the concentration observed could be a result of contaminants existing on the wear disks. Thus, on top of removing oxide layers, it

could also be surmised that the lower amount of C concentration is a result of the more effective "polishing" action in removing contaminants on wear disks lubricated by PAO added with 2.5 and 5-vol% of TMP trioleate.

4. Conclusions

Using a Stribeck-type analysis, the present study determines the tribological impact of TMP trioleate as an eco-friendly additive in a low viscoisty synthetic PAO base oil at various operating regimes of lubrication. Blending TMP trioleate with PAO at concentrations up to 5-vol% have been shown to increase not only the viscosity but also the VI of the mixture by more than two folds as compared to neat PAO. The reverse can be observed for the viscosity-pressure coefficient, which is observed to reduce with higher TMP trioleate concentrations being added to PAO, potentially forming a less thick film that is not tribologically desirable. On the contrary, it has been instead concluded that PAO added with 5-vol% of TMP trioleate concentrations exhibits a more desirable frictional performance, where the presumed synergistic extreme-pressure and friction modifier effect observed has led to lower CoF values than neat PAO at mixed (by 5.97%) and boundary (by 4.43%) lubrication regimes. From an energy analysis point of view, optimum friction power reduction is achieved when the contact is lubricated by PAO with 5-vol% TMP trioleate, giving a fric-
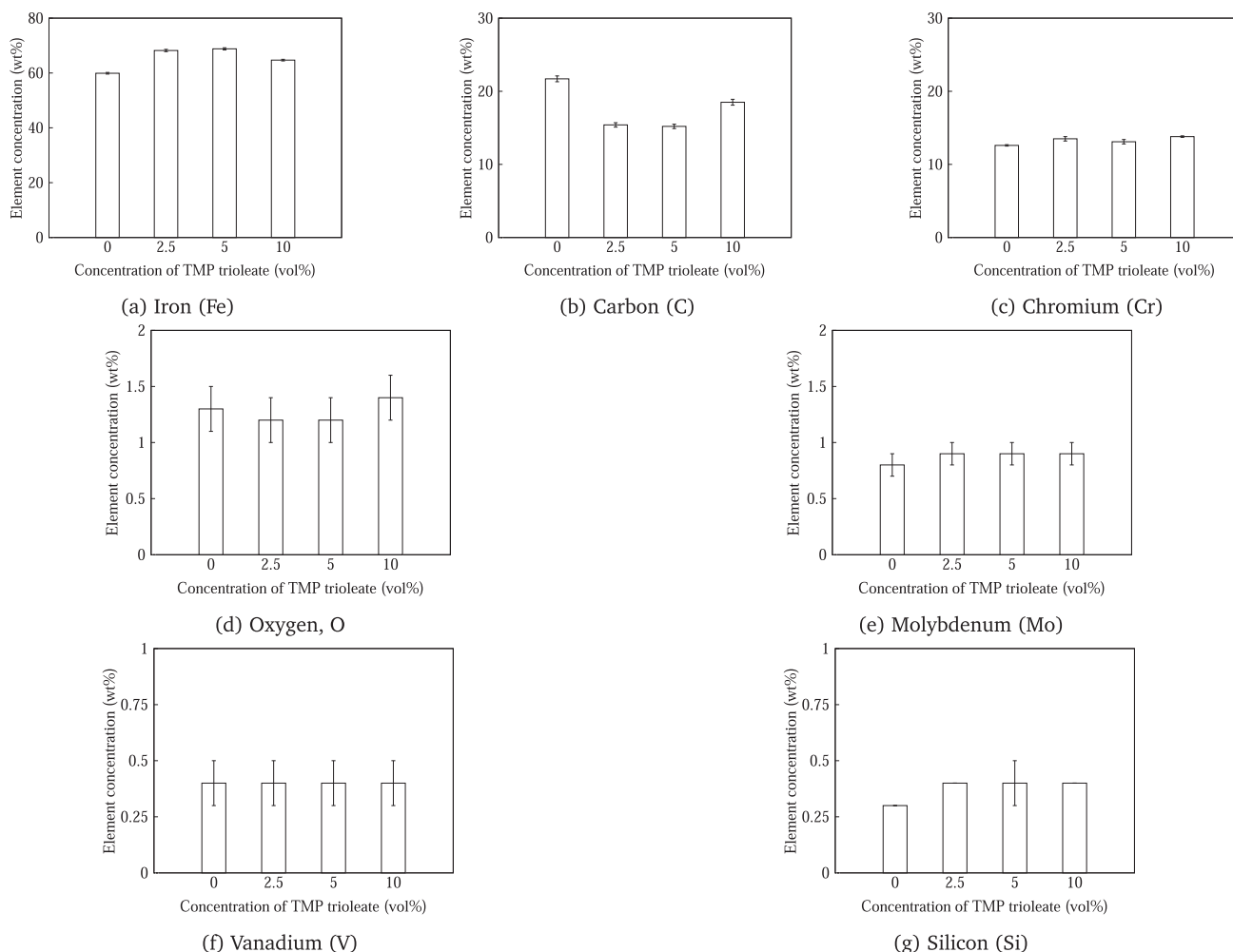

Fig. 9. Elemental concentrations obtained on wear track along the wear disk using Energy-dispersive X-ray spectroscopy (EDX) when lubricated with PAO blended with various volumetric percentages of TMP trioleate.

tion power drop of 6.09% across the measured sliding velocity and applied normal load range. Building on this positive tribological trait, the wear scar diameter for the sliding pin lubricated by this PAO mixture is also determined to be smaller by 39.65% in comparison with the one from neat PAO.

It can, thus, be surmised that the selection of lubricants solely based on rheological parameters, such as the viscosity-pressure coefficient, could be insufficient. The present study demonstrated that tribological properties, especially when boundary interaction is of essence at mixed and boundary lubrication regimes, is dependent on the concentration of the additives (i.e. TMP trioleate). The presence of different molecules (base oil and additive) at different concentrations and polarity could lead to either a synergistic or antagonistic competitive adsorption phenomena. The present study also shows that there exists an optimum molecular mix (i.e. 5-vol% TMP trioleate) to form a coherent boundary film, which can lead to a synergistic tribological effect. Thus, the proposed approach is expected to allow for a more effective elucidation of the tribological performance for lubricant blends, which could potentially lead to a more optimised design of application-specific lubricant formulation across a wide range of lubrication regimes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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