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Asperity level frictional interactions of cylinder bore materials and lubricant composition

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Abstract

Parasitic frictional losses in internal combustion engines of race vehicles adversely affect their performance. A significant proportion of these losses occur within the piston-cylinder system. This paper presents a study of the compatibility of cylinder bore surface materials with typical lubricant base constituent stock (Poly Alpha Olefin (PAO) and Polyolester (POE)) as well as a fully formulated lubricant. Nanoscale boundary friction is measured using lateral force microscopy. The effect of material properties, nanoscale roughness and lubricant species upon underlying mechanisms of generated friction is presented. Advanced cylinder materials and coatings and lubricant molecular species used for high performance engines are investigated, an integrated approach not hitherto reported in literature.

Keywords: Atomic force microscope; Lateral Force Microscopy; Lubricant-Surface combination; Friction

Nomenclature

A	Hertzian (apparent) contact area
A_a	Asperity contact area
C_F	Calibration factor
E^*	Effective (equivalent) Young's modulus of elasticity
F_f	Friction
h	Standardised surface separation
L	Applied normal load
R	Radius of AFM probe tip
Z_o	Equilibrium atomic spacing

Greek Letters

α	Fraction of real contact area
ε	Fractional energy loss
η	Areal density of asperities
σ	RMS roughness
σ_s	Summit standard deviation

β	Average asperity tip radius of curvature
γ	Surface energy
τ	Interfacial shear stress
τ_a	Asperity interfacial shear strength
τ_v	Viscous shear on confined fluid

Abbreviations

AFM	Atomic Force Microscope
LFM	Lateral Force Microscopy
RMS	Root Mean Square
TMR	Trace Minus Retrace

1- Introduction

For motorsport applications, where engine operating conditions are often reasonably predictable and in some cases entirely controllable, focus can be placed upon the enhanced performance through reduced friction of in-cylinder components. Reduction of gradual wear is a secondary concern as competition engines are often rebuilt based on a mileage or a measured unit time interval, which in some instances can be less than 200 miles or 10 hrs running under race conditions. During such operations, frequent inspection of any indicators of wear can be made and some remedial actions undertaken.

To highlight the importance of reducing friction in the piston-cylinder subsystem, it is necessary to consider the magnitude of the accrued losses. A typical spark ignition engine has an inefficiency, which may be as high as 60-70%. Of the underlying losses a large proportion are thermal, but as much as 33% can be attributed to engine friction. Almost half of these losses can be attributed to the frictional losses related to the piston assembly, 7-8% of which occurs at the interface between piston compression rings and the cylinder liner.

With the development of lightweight and durable aluminium alloys, the cast-iron cylinder blocks (with no requirement for liners or inserts) have been largely replaced. However, these new lightweight castings require either spray coatings or pressed-in inserts to prevent excessive cylinder bore wear and friction. As a result, designers have turned their attention to an array of selected spray coatings, electro-plates or liners which replicate or outperform cast-iron tribologically.

Engine and component level testing [1-4] has been shown to be an excellent methodology to benchmark alternative lubricant-surface combinations. In recent years, the development of nanoscale experimental techniques, such as surface force apparatus techniques and atomic force microscopy (AFM) have led to an improved fundamental understanding of asperity level interactions and confined fluid behaviour. The fluid cell atomic force microscopy has become an important tool for the investigation of the growth and frictional properties of surfaces, self-assembled monolayers

and tribofilms [5-12]. Pidduck and Smith [5] and Leighton et al [9] showed that AFM can be used to investigate generated tribofilms, generated through use of tribometry. A range of lubricant formulations containing ZDDP were investigated on EN31 hardened Steel surface [5]. Miklozic and Spikes [6] conducted tests for various lubricant formulations, including the dispersants; MoDTC and ZDDP with both tribometers and AFM. Tests are conducted on a single Steel type substrate (i.e. AISI 52100), demonstrating the variation in surface film formation and frictional properties of the two additives under investigation. The same approach was reported by Leighton et al [9] for a base oil and formulated lubricants with different viscosity modifiers. Also Bhushan et al [7] investigated friction and wear resistance of ionic lubricants for MEMS Devices. Again, they showed that varying the lubricants' composition altered the performance with a single material type (in that case Silicon). Campen et al [8] investigated the formation of various fatty acids using lateral force microscopy on Mica surfaces. The study demonstrated fluid cell atomic force microscopy to be a suitable method for investigating and elucidating the tribological behaviour of surfaces and boundary films. These investigations have significantly advanced the understanding of thin confined fluid film lubrication behaviour. Styles et al [11] used lateral force microscopy to determine the boundary shear characteristics of various cylinder liner surface types under dry conditions, whilst Bewsher et al [12] used pieces of real cylinder liners subjected to long-term dynamometric testing together with sample lubricants in fluid cell lateral force microscopy. Most investigations have predominantly focused on varying the lubricant additives, whilst using the same surface specimen.

This paper investigates asperity-level interactions and lubricant-surface synergies using fluid cell lateral force microscopy. Five sample surfaces with different coatings, commonly used for automotive cylinder liners, particularly for high performance engines, are investigated in the presence of Poly Alpha Olefin (PAO), Polyolester (POE), and a mixture of both with a fully formulated lubricant.

2- Materials and method of measurement

Lateral force microscopy (LFM) was conducted using a Bruker Dimension 3100 Atomic Force Microscope, controlled by Digital Instruments Nano Scope 614r1 software. The hardware is mounted on an anti-vibration platform in a laboratory with a controlled atmosphere of 20° C ($\pm 0.5^{\circ}\text{C}$) and Relative Humidity (RH) of 50% ($\pm 5\%$) with a barometric pressure of 101.345 kPa. Non-conductive Silicon Nitride DNP-10 tips (cantilever D) with a tip radius of 20 ± 1 nm and a cantilever arm stiffness of 0.06 N/m are used for all the LFM tests. Each test constitutes 256-line scans over an area of $1\mu\text{m}^2$ with the tip sliding speed of $1\mu\text{m/s}$. The normal tip load was increased between successive tests, with the same lubricant-surface combination, from 10nN to 50nN in increments of 2.5nN. The mean contact pressures are found using the classical Hertzian contact theory for concentrated point contacts, for the upper and lower bounds of the applied load corresponding

pressures shown in Table 1. The values for the elastic moduli for each contacting surface are reported by Umer et al [13].

Table 1: Tip Contact Pressures

Pressure	NiSiC2	DLC	FeMo	TiO2	PEO
(10 nN) GPa	2.6	3.6	3.2	3.4	2.3
(50 nN) GPa	4.4	6.2	5.4	5.8	3.9

Before each measurement a blind calibration procedure is used [10,11] with a TGF 11 monocrystalline silicon grating. Friction was measured using the trace-minus-retrace (TMR) method, where:

$$C_F = \frac{TMR[V]}{L[nN] \times 0.19} \quad (1)$$

Friction is then obtained as:

$$F_f[nN] = \frac{TMR[V]}{C_F} \quad (2)$$

Asperity level frictional performance of a combination of 5 surface types with 4 formulated lubricants, which are used for automotive cylinder bore surfaces, is studied here. For this purpose an atomic force microscope in LFM is used.

Tables 2 and 3 provide the specifications of sample surfaces, substrate materials and any applied coatings. The listed coatings comprise a wide range of commonly used surfaces for advanced cylinder bores or liner inserts. These include Nickel Silicon Carbide (Ni-SiC2), Diamond Like Carbon (DLC), Ferro Molybdenum (FeMo), Titanium Dioxide (TiO2) and Aluminium Oxide (PEO). These coatings are applied to bespoke flat specimen of dimensions 100x50x8mm (Table 3).

Any variations in surface topography of various samples is minimised as far as possible. The DLC coated sample is used as the topographic baseline (datum), whilst the other surfaces were lapped using a 9µm polycrystalline diamond polishing paste to attain a comparable surface finish to the DLC sample. The microscale roughness parameters are listed in Tables 2 and 5. The measurements were made using an Alicona focus variation microscope using a 100x magnification objective.

Table 2: Surface Coatings

Sample	Ni-SiC2 Nickel Silicon Carbide	DLC Diamond Like Carbon Coating	FeMo Ferro Molybdenum	TiO2 Titanium Oxide	PEO Aluminium Oxide
Coating	Electroplated nickel with co-deposited silicon particulate	Thin film vacuum deposited diamond like carbon	High energy thermally sprayed iron and molybdenum	High energy thermally sprayed titanium dioxide	High energy 'plasma' anodised
Surface finish as deposited Sq [nm]:	N/A	44	N/A	N/A	N/A
Surface finish as lapped Sq [nm]:	38	N/A	108	84	29
Thickness as finished [μm]	70	2	400	400	10

Table 3: Substrate Materials

Sample	Ni-SiC2 Nickel Silicon Carbide	DLC Diamond Like Carbon Coating	FeMo Ferro Molybdenum	TiO2 Titanium Oxide	PEO Aluminium Oxide
Classification	BS970: 1991 817M40T	BS970: 1991 817M40T	BS970: 1991 817M40T	BS970: 1991 817M40T	AA 4032 T6
Processed	Alloy steel quenched and tempered	Alloy steel quenched and tempered	Alloy steel quenched and tempered	Alloy steel quenched and tempered	Aluminium alloy solution treated and artificially aged

Four different lubricants are used for the current investigation (Table 4). The first two are synthetic non-polar Poly Alpha Olefin and a Polyolester, both of which are typical base stock components used in commercial automotive engine oils. In addition, a fully formulated lubricant, containing Poly Alpha Olefin, Polyolester, a viscosity modifier and an additive package is used. The fully formulated

oil contains a Molybdenum-based inorganic friction modifier and an anti-wear additive containing Zinc. The mixture is created with a ratio of 50:1 Poly Alpha Olefin to Polyolester. These base stocks were mixed at 65°C for 6 hours.

Table 4: Lubricants

Serial Number	Description	Kinematic viscosity (40 and 100 C°) cSt	Additional information
PAO	Low viscosity synthetic base PAO	31.0 and 5.8	Viscosity Index 138
PEO	Synthetic base Polyolester	19.0 and 4.3	Viscosity Index 136
FF	Fully formulated commercial 0W40 oil	70.8 and 12.9	Viscosity Index 186
PAO/POE	Blend of PAO and Ester lubricants	30.7 and 5.8	Blended to 50:1 by wt. ratio

The AFM tip radius was measured using a TGT1 silicon wafer with a calibrated surface geometry. The tip was scanned over 20 peaks, with the deconvolution of the measured data, yielding the tip radius.

Initially, the frictional performance of each surface was investigated without the presence of a lubricant (nominally dry LFM). Each sample surface was subsequently divided into four equal sections along its length, with each partitioned area tested in the presence of PAO, PEO, PAO/POE and the Fully Formulated lubricant respectively (fluid cell LFM). This partitioning is carried out in order to prevent any cross-contamination at the various lubricant-sample interfaces. The sample surfaces were thoroughly cleaned prior to each test with petroleum ether (40-60). The calibration procedure is carried out for all wet conditions for topography and friction in all the four sections of all the specimens. Each test (lubricant-surface combination) is repeated three times at different locations within the apportioned regions. A fluid cell is used to keep any lubricant meniscus action away from the vicinity of the tip-sample contact, thus mitigating any potential capillary adhesion, affecting the measurements.

3- Contact mechanics

The conjunction of the AFM tip - to - a sample surface is subjected to mixed regime of lubrication under suitable conditions [14]. Therefore, the generated friction is expected to be due to the combined result of direct interfacial interaction of contacting surfaces (boundary friction) and friction of a thin fluid film (viscous friction). In ultra-thin film conjunction of LFM, the boundary friction is caused by the shear strength of the interface between the surfaces (τ_a) and viscous shear

stress(τ_v) of any formed fluid film [14]. Contact friction can be determined through specifying the proportion of the two shear stresses. This can be determined by the ratio of the real contact area (α) characterised by the direct contact of the contiguous real rough surfaces and the apparent area of contact, A . Thus [14-16]:

$$F = A[\tau_a\alpha + \tau_v(1 - \alpha)] \quad (3)$$

where:

$$\alpha = \frac{A_a}{A} \quad (4)$$

The Bowden and Tabor's model [15], described above, has been used by Tambe and Bhushan [13], and Gohar and Rahnejat [16] to effectively predict the generated friction in nanoscale contacts, including at the conjunction of an AFM tip and a sample. It has been shown that the apparent contact area, A , created between an atomic force microscope tip and a sample can be reasonably represented by the classical continuum contact mechanics theory [17-19]. Contact adhesion is largely mitigated in the presence of a lubricant in fluid cell LFM. Therefore, it is reasonable to determine the apparent area of contact using the classical Hertzian contact mechanics [16, 20, 21]:

$$A = \pi \left(\frac{3LR}{4E^*} \right)^{3/2} \quad (5)$$

where, the reduced equivalent radius of the contacting pair: the AFM tip against a semi-infinite elastic half-space (a sample surface) is:

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \quad (6)$$

And the equivalent (composite) modulus of elasticity of the elastic half-space becomes:

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad (7)$$

The composite elastic modulus, E^* , for the materials used in this study are taken from AFM measurements reported by Umer et al [19]. To determine the real contact area, A_a , the model proposed by Greenwood and Williamson [22] is used. In this model real contact area and the asperity load carrying capacity are given as:

$$A_a = \pi\eta\sigma_s\beta Ae^{-h} \quad (8)$$

$$L = A \left(\frac{\sigma_s}{\beta} \right)^{\frac{1}{2}} E^* \pi^{\frac{1}{2}} \eta \sigma_s \beta e^{-h} \quad (9)$$

where, the roughness parameter $\eta\sigma_s\beta$ comprises the asperity peak areal density, the standard deviation of summit heights and the average asperity peak radius.

Combining equations (5), (8) and (9), the fraction of the real contact area, can be determined as:

$$\alpha = \frac{A_a}{A} = \frac{8\sqrt{3}}{9\sqrt{\pi}} \sqrt{\frac{\beta}{\sigma_s}} \frac{\sqrt{E^*}}{R^{\frac{3}{2}}\sqrt{L}} \quad (10)$$

Isolating the surface roughness and material property parameters in equation (10), it can be observed that the real contact area fraction between the AFM tip and the surface is a function of surface elastic modulus, the standard deviation of summit heights and average radius of curvature as:

$$\alpha \propto \sqrt{\frac{\beta}{\sigma_s}} \frac{\sqrt{E^*}}{R^{\frac{3}{2}}} \quad (11)$$

Homola et al [23] showed that the interfacial shear strength of the contact in the absence of a lubricant can be approximated by the cobblestone model as:

$$\tau_a = \varepsilon \left(\frac{2\gamma}{Z_o} \right) \quad (12)$$

where, Z_o is the equilibrium atomic spacing, indicating the lateral distance moved through dislocation in order to initiate any sliding motion. By combining the surface-specific terms in equation (11) with equation (12), the boundary friction component in Bowden and Tabor's relationship (equation (3)) would be proportional to the surface-dependent parameters, as well as surface energy as another surface-dependent parameter, thus:

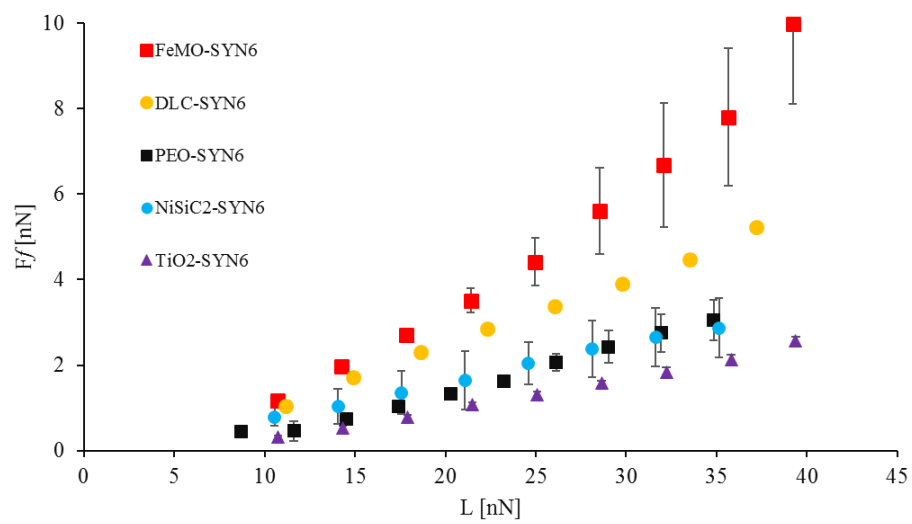
$$\tau_a \alpha \propto \sqrt{\frac{\beta}{\sigma_s}} \frac{\sqrt{E^*}}{R^{\frac{3}{2}}} \gamma \quad (13)$$

The surface-specific equilibrium atomic spacing parameter, Z_o , is not included in the proportionality relationship (13) as a reliable method to measure its value is not available to the authors.

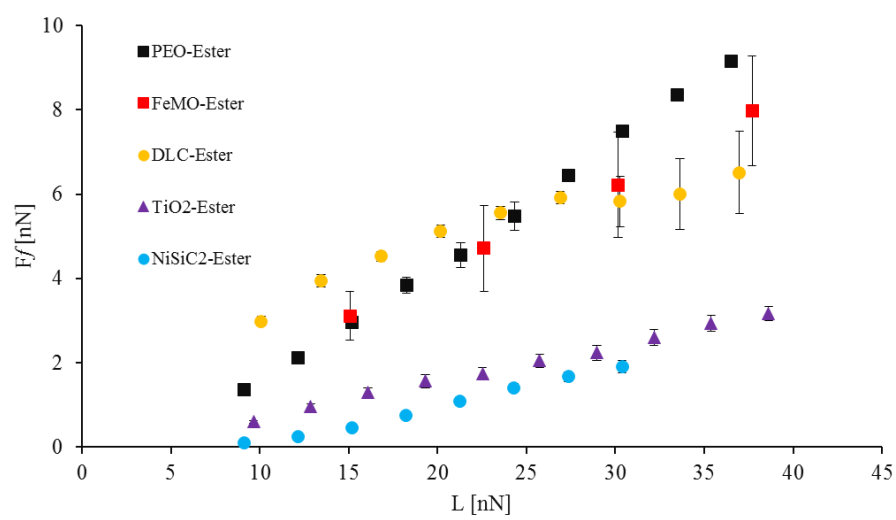
4- Results and discussion

Friction is obtained using LFM on the 5 sample surfaces commonly used for automotive cylinder bores, particularly for high performance applications and in the presence of 4 lubricant types; two of which are constituent components of the lubricant base stock (i.e. PAO and POE), another is a mixture of the two (i.e. PAO and POE), and finally a fully formulated lubricant: 0W40 (FF).

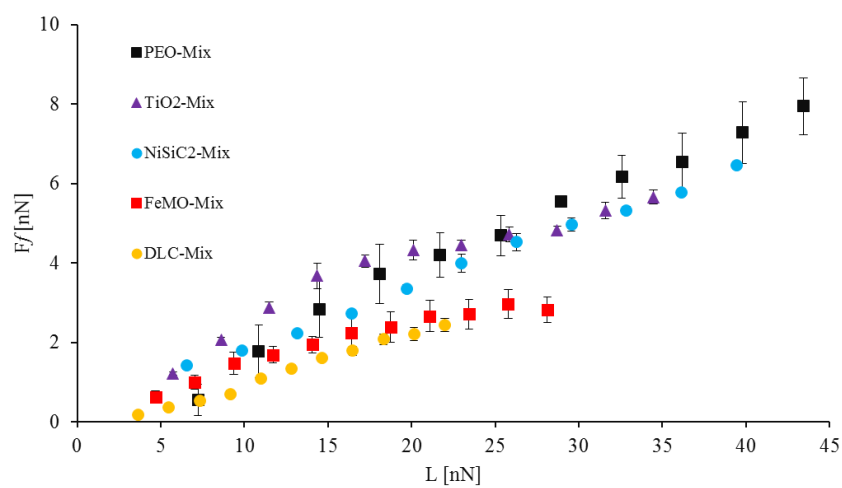
Figure 1 shows the measured friction for each lubricant in combination with the various sample surfaces.



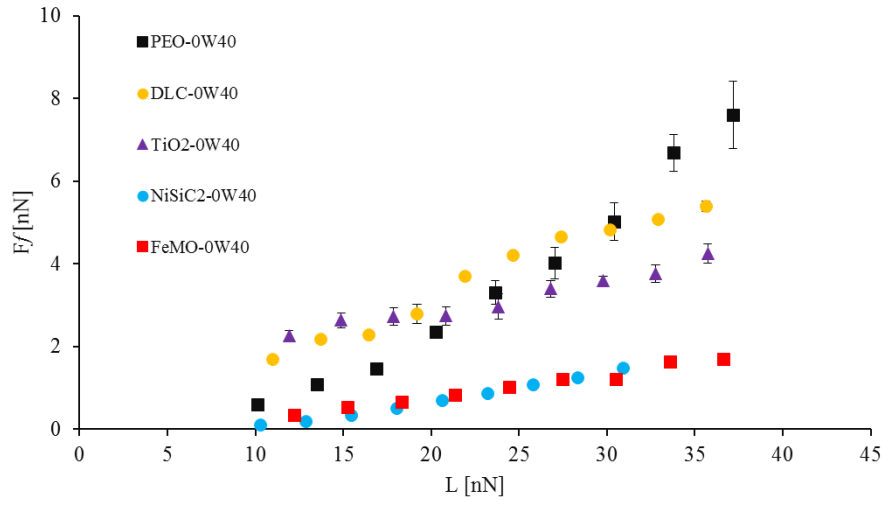
(a)



(b)



(c)



(d)

Figure 1: Variation of friction with normal load for different surface coatings in the presence of (a) PAO, (b) POE, (c) PAO and POE mix, and (d) fully formulated oil

Figure 1a is for the case of the Poly-Alpha Olefin fluid. The results show the influence of surface type upon frictional behaviour when wetted with the PAO. This finding is repeated in the case of all lubricant variants. In all cases, there is a near linear relationship between the load and the measured interfacial friction. The slope is analogous to the coefficient of friction by definition. Therefore, a higher slope constitutes greater friction. It is shown that Titanium Dioxide coating, when paired with PAO, produces the lowest coefficient of friction.

Figure 1b displays the interfacial friction of sample surfaces wetted by the POE fluid. Again, as with the surfaces wetted with the PAO oil (figure 1a), there is a clear distinction in frictional behaviour of the tested surfaces. The interfacial friction for the FeMo, TiO₂ and DLC surfaces does not appear to be directly proportional to the applied load (as is the case in figure 1a). Such a result suggests slip at the lubricant-surface boundaries as also shown by Fillot et al [24]. The same deviation from linearity is also noted in the presence of a mixture of the PAO and POE fluids for the FeMO, DLC, TiO₂ and PEO samples (figure 1c). The relative frictional performance of the sample surfaces shows that neither constituent fluid mixtures (PAO or POE) dominate the characteristic responses in figures 1a or 1b. There appears to be some synergistic or antagonistic interactions, which are commonplace with such lubricant species.

Figure 1d shows the interfacial frictional behaviour when each surface is wetted with a fully formulated commercial lubricant. As it would be expected the two most common piston liner materials/coatings for high performance applications; FeMO and NiSiC₂ show the lowest coefficient of friction. Fully formulated lubricants, containing surface-active species such as friction modifiers allow NiSiC₂ and Ferro Molybdenum Oxide to attain lower coefficients of friction. From similar experiments in literature, employing similar contact types and conditions (Gosvami [25]) at elevated

temperatures and higher shear, a large number of sliding cycles are required in order to generate a tribofilm. Due to the relatively low temperature in the current tests and a limited number of sliding cycles there is low chance of tribofilm formation of any significant thickness.

A comparison of the measured coefficients of friction thus far with independently (separately) measured surface parameters is shown in figure 2. The surface parameter selected is provided in equation (13) and is referred to as the boundary friction propensity parameter. The trend in the coefficient of friction variation with this parameter gives an indication of the influence of intervening a lubricant layer upon the mechanics of contact of all the sample surfaces. The surface roughness parameters required for this analysis are measured using AFM (table 4) and post-processed to remove any long wavelength surface forms. The results for the surface energy, asperity radius of curvature and RMS roughness are listed in table 5.

Table 5: AFM Surface Roughness Measurements

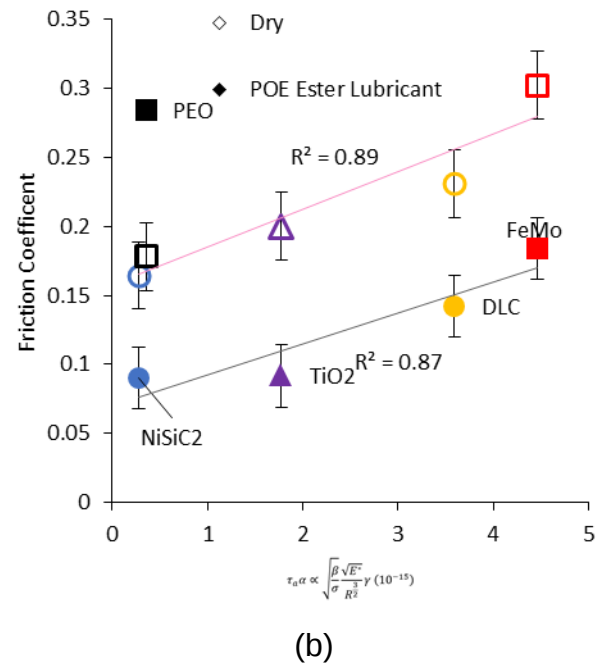
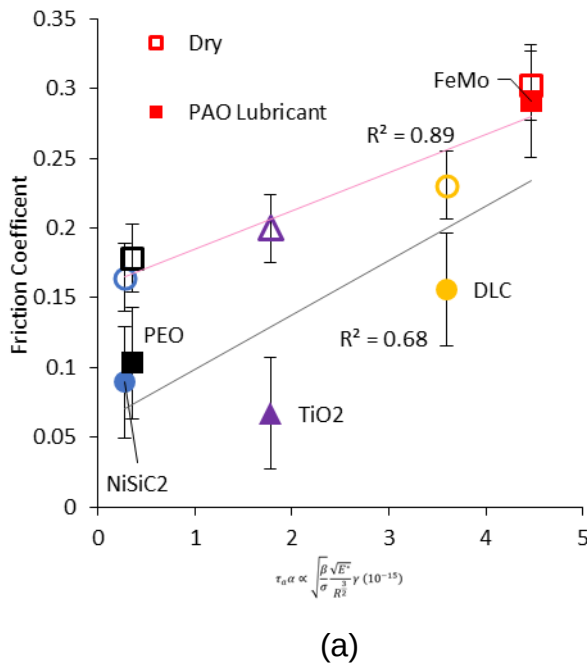
Sample	Asperity Radius of Curvature (β) (nm)	RMS Roughness (σ) (nm)	Surface energy (γ)
Ni-SiC2 Nickel Silicon Carbide	11.6	1.7	0.002
DLC Diamond Like Carbon Coating	42.0	2.1	0.30
FeMo Ferro Molybdenum	6.4	2.9	0.026
TiO2 Titanium Oxide	22.2	2.6	0.016
PEO Aluminium Oxide	11.4	2.0	0.003

The data presented in Table 5 are those measured at a length scale limited by the machines used to measure them. The length scales over which the measurements are taken are close to, but not completely appropriate, for the theory described in the analytical section. For this reason, only the relative performance of the surface types is investigated rather than attempting to quantify individual frictional components. This is appropriate if one assumes that the surface parameters in table 4 would have the same value relative to one another at the length scale appropriate for the analytical model. In addition, it should be noted that the RMS roughness σ is used to replace the summit height standard deviation σ_s in equation(13) in current study. Such an approximation is deemed reasonable for the limited analysis that follows as it has been shown by Tomanik et al [26] that for a range of surfaces the RMS roughness varies linearly with the peak height standard deviation.

Figure 2a shows that the surfaces with a larger value of boundary friction propensity parameter; (see equation (13)), demonstrate a minor reduction in the coefficient of friction through introduction of PAO. This means that PAO, when used in isolation as a lubricant, neither reduces the coefficient of friction by effectively separating the surfaces (i.e., reducing α) or by lowering the shear strength of the adsorbed film on the surface (i.e., reducing τ_s). For the surfaces, where the boundary friction propensity parameter is low, a significant reduction in the coefficient of friction is observed. This is

thought to be primarily due to the displacement of the condensed water layer present on any sample surface by the PAO lubricant. Condensed water films are present on nominally dry surfaces in measurements conducted in a humid environment. The confined water films have been reported to have very high apparent viscosities during confinement [27]. Furthermore, Tambe and Bhushan [24] have shown that the formation of meniscus bridges can influence frictional behaviour of AFM tip-sample conjunction. Therefore, it is proposed that the introduction of the PAO lubricant reduces the shear stress (τ_v), promoting a reduction in friction generated by the sheared fluid in patches of the contact intervened by the presence of a thin fluid film.

In Figure 2b the introduction of the POE reduces the coefficient of friction by a similar amount for all the surfaces except for the case of PEO. The reason for a consistent drop in the coefficient of friction for all surface variants is due to a change in the value of (α) as defined by equation (3). This is due to the Ester forming a fluid film, promoting an increased gap between the surfaces. The reason for the increased friction of the PEO surface with the introduction of the Ester cannot be explained through the current analysis.



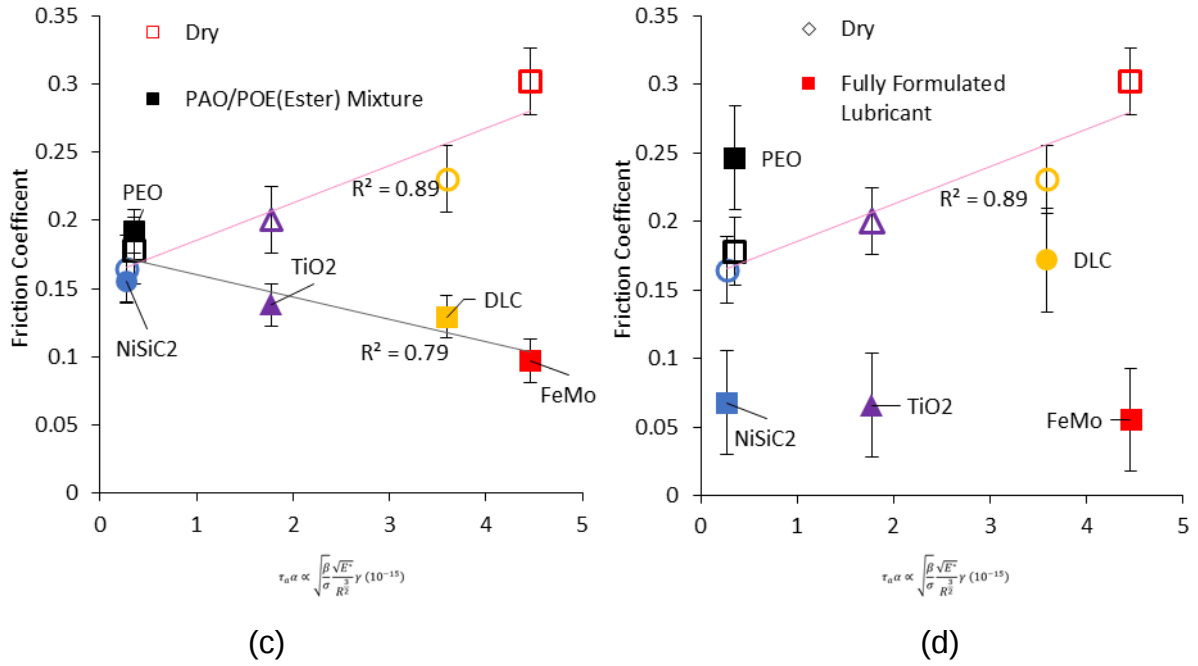


Figure 2: Friction coefficient versus propensity of boundary friction parameter for surfaces lubricated with (a) PAO, (b) POE, (c) PAO/POE mixture, and (d) fully formulated oil compared with corresponding dry surface performance

Figure 2c shows the effect of introducing a mixture of PAO and POE (Ester) to the AFM tip-sample conjunction. The results show that the coefficient of friction is significantly reduced for contacts with a high propensity to boundary friction parameter. This indicates that the specified mixed fluid decreases the incidence of boundary friction through either reducing τ_s by the formation of a low shear strength layer on the surface, or by reducing (α) through increased contact separation. For low values of the boundary friction propensity parameter, the benefit accrued through contact separating ability of the Ester and PAO in isolation (enhanced load carrying capacity) is not maintained by their combined mixture. This highlights the complex behaviour of even simple lubricant-surface systems.

The results for the fully formulated lubricant, shown in figure 2d, do not indicate any particular trend with respect to the boundary friction parameter. A similar low coefficient of friction is achieved for each sample surfaces which contains a transition metal (i.e., NiSiC2, FeMo and TiO2). There is evidence in literature that commonly used inorganic friction modifiers form low friction tribofilms on surfaces containing transition metals [28-30].

5- Conclusion

This paper shows the interfacial response depends upon both the fluid in confinement and the properties of the confining surface materials. At the level of asperities, the influence of nanoscale roughness, surface modulus of elasticity and real contact area can be used to determine the dominant frictional behaviour for Esters, PAO and a mixture of the two. The Ester (POE) is shown

to increase separation of the surfaces (increased load carrying capacity). Consequently, the coefficient of friction is reduced due to a decreased level of boundary interactions. The PAO is shown to reduce the viscous shear in the contact. The Fully Formulated oil is largely independent of the topographical and material mechanical parameters, with improved frictional performance for all the surfaces containing transition metals (i.e. NiSiC₂, FeMo and TiO₂).

The study has shown that lubricant composition can be tailored to meet the requirement of friction reduction for a chosen cylinder bore/liner material for a variety of engine applications. However, it has also been shown that due to the plethora of synergistic or antagonistic interactions between the lubricant species and the surfaces the simplest of lubricant-surface combinations require detailed combined integrated measurements and contact mechanics analysis.

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