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The effect of clearance between tappet insert and camlobe on the tribological and tribochemical performance of cam/follower surfaces

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Abstract

This paper examines the effect of tappet insert clearance on the tribological and tribochemical performance of the camlobe/follower tribopair when lubricated in a fully-formulated oil containing 1 wt% of Molybdenum Dialkyl Dithiocarbamate (MoDTC). Tests were performed on a Single Cam Rig (SCR), taken from 1.25l FORD Zetec (SE) engine. White Light Interferometry and Talysurf contact profilometry were used to characterise the wear scar on the tappet inserts and camlobes respectively. In addition, Scanning Electron Microscopy (SEM) was used on both (i.e. camlobes and tappet inserts) for wear mechanisms assessment as well as to assess the durability of coatings used on tappet inserts. Energy-Dispersive X-ray (EDX) and Raman spectroscopy analyses were also used to understand the tribochemical interactions between oil additives and the cam/follower interface. Results show that the chemistry of the tribofilm derived on camlobes and tappet inserts vary as a function of tappet insert clearance and cam profile. Also, regardless of the type of coating, the smaller clearance of tappet inserts exhibited higher friction and wear. Therefore, based on this work, the use of the thicker tappet insert would be inadvisable as this possibly can cause higher fuel consumption and inefficient performance of the intake/exhaust valves of the engine.

Keywords: Tappet Insert Clearance, Valvetrain, MoDTC, ZDDP.

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1. Introduction

Engine developers and lubricant formulators are continuously challenged to reduce fuel consumption and emissions of automotive engines. In an internal combustion engine, the mechanical energy consumption on the four basic components (namely the piston assembly, valvetrain, engine bearings and pumping system) has been reported previously [1]. The valvetrain has the third largest energy loss and it experiences the greatest contact pressure among these four tribological systems. The wear of valvetrain components is generally accepted to limit the performance and life of automotive engines. A potential reason for this is that the valvetrain (especially the cam/follower components) is subjected to sliding/rolling motion, different lubrication regimes, and high

acceleration speeds causing increased inertia forces and high stresses on the structure. Therefore, many researchers have focused their work on studying the cam/follower interface in order to improve engine efficiency and durability which in return leads to improved fuel economy and reduced emissions.

The valvetrain tribological performance is practically important now with an increasing trend of using lower viscosity engine oils and novel engine technologies such as start/stop technology. Several monitoring techniques have been used to examine the wear of cam/follower contact. Historically, surface layer activation (SLA) technique has been adapted to measure the wear effectively in real time [2-5]. Ipek *et al.* [6] measured the wear as thickness loss by using a level meter (LM) under sliding conditions. Others used electrostatic sensors focused on the cams [7] or used a radionuclide technique [8-11]. Purmer *et al.* [12] used two electronic transducers, one to measure the cam lift, the other to measure the angle. It was observed that the wear changes in each location on the camlobe (i.e. there is a direct correlation between the wear rate and the geometry of the camlobe). Liu *et al.* [13] studied the relationship between camlobe wear and tribofilm chemical composition using seven angular locations on the camlobe ($\pm 14^\circ$, $\pm 10^\circ$, and cam nose 0° degree). It was shown that tribofilms were different at each location. Various chain lengths of polyphosphate glass were found on all camlobe tribofilms, where long chain polyphosphate tribofilms have provided better antiwear characteristics than short chain polyphosphate tribofilms.

The clearance between the follower and the camlobe plays a considerable role in engine efficiency; incorrect clearance can negatively affect the tribological and tribochemical responses of the system. The incorrect tappet insert clearance can be defined as the clearance between the cam/follower tribopair which could be very small or very large. Small/large tappet insert clearance can cause inefficient performance of the engine valves (i.e. the valves may stay open or may not fully open/close). This would lead to valve leak (i.e. the leak can occur during compression and working stroke) and thus the power of engine would be declined [14]. Also, small/large tappet insert clearance can cause vibrations for the valvetrain which in turn would lead to increase wear and possible failure of the cam/follower system. Therefore, the clearance between the cam/follower tribopair is an important parameter that should be strictly taken into consideration during the design of an engine (direct acting tappet in particular) or in the process of maintenance (i.e. adjusting process for valve clearance). Selection of the thickness of the tappet insert will depend on the following factors; friction, wear, lubrication, noise, vibration and harshness (NVH). It is also worth mentioning that engine manufacturers would consider further factors (such as the configuration/design of valvetrain, tappet insert thickness, valve lift, cam lift, etc.) before selecting the correct/appropriate clearance. Tappet insert with variable clearance will affect the valve lift and as such the flow of air/exhaust in the combustion chambers of the engine. As a result, the engine power will be affected. However,

cam/follower clearance will also affect wear, friction and NVH, possibly even leading to failure and inefficient performance of the intake/exhaust valves of the engine. Hence, it is important for engine manufacturers to understand the effect of the cam/follower clearance on friction, wear and tribochemical responses. Therefore, in this study, the first objective was to observe the friction and wear behaviour of the camlobes/tappet inserts with different tappet thickness values and types of surface coating. The second objective was to map the tribochemical films across the camlobes as well as the tappet inserts, with the tappet coating and clearance being the parameters of focus.

2. Experimental Details

2.1. Single Cam Rig (SCR)

A Single Cam Rig (SCR), taken from 1.25l FORD Zetec (SE) engine, was used to run the experiments, as shown in Fig. 1. The rig has been developed and calibrated by MacDonald *et al.* [15]. Further, the experimental details have already been presented in [16]. Basically, the rig was used in a non-fired mode (i.e. a 2.2 kW ABB motor was used to drive the camshaft). A heating system was installed to maintain the required test temperature (in a 5 l reservoir) with a sensitivity of ± 0.10 °C. Experiments were carried out using steel tappet inserts (coated with MnPO_4 and DLC coatings) rubbing against cast iron camshafts. The Mn-phosphate coating (MnPO_4) had a thickness of 0.5-2.0 μm . In addition, the DLC coating contained 15 at. % hydrogen (a-C: 15H) and had a thickness of 1.5-5.5 μm . The DLC coating was deposited on the steel tappet insert (by Oerlikon Balzers Ltd., UK.) using Plasma Assisted Chemical Vapour Deposition (PACVD) process. From PACVD, a gas contained the elements of DLC coating (a-C: 15H) was supplied into the vacuum chamber and a discharge powered by an AC voltage was ignited. As a result, free carbon and hydrogen atoms (ions and radicals) were created and then reacted chemically with the substrate surface. This in return led to form the DLC coating on the steel tappet insert. The surface roughness of cast iron camlobe is in the range of 0.1 – 0.2 μm (R_a). In addition, the surface roughness values were 0.25 μm (R_a) and 0.02 μm (R_a) for the MnPO_4 and DLC coating respectively. The tappet insert is made of 16MnCr5 steel (with thin film surface coating of Mn-Phosphate) with a hardness of 60 – 70 HRC (typically harder than the camshaft). The hardness of the camshaft was in the range of 50 – 55 HRC. Also, the hardness of DLC coating was in the range of 15 – 25 GPa.

For the engine used in this work, different tappet insert thicknesses ranging from 2 mm to 3.3 mm can be employed. However, only three thicknesses of tappet inserts were chosen for this study, 2.275, 2.575 and 2.75 mm, which were commercially available and in line with the methodology of this work. The clearances of the three tappet insert thicknesses were measured and mentioned later in this section. For MnPO_4 tappet inserts, two oil temperatures (100 °C and 130 °C) were applied. For DLC

tappet inserts, however, the test was only carried out at 100 °C due to limited availability of sensors used in tappet rotation measurement; further details are available in reference [16].

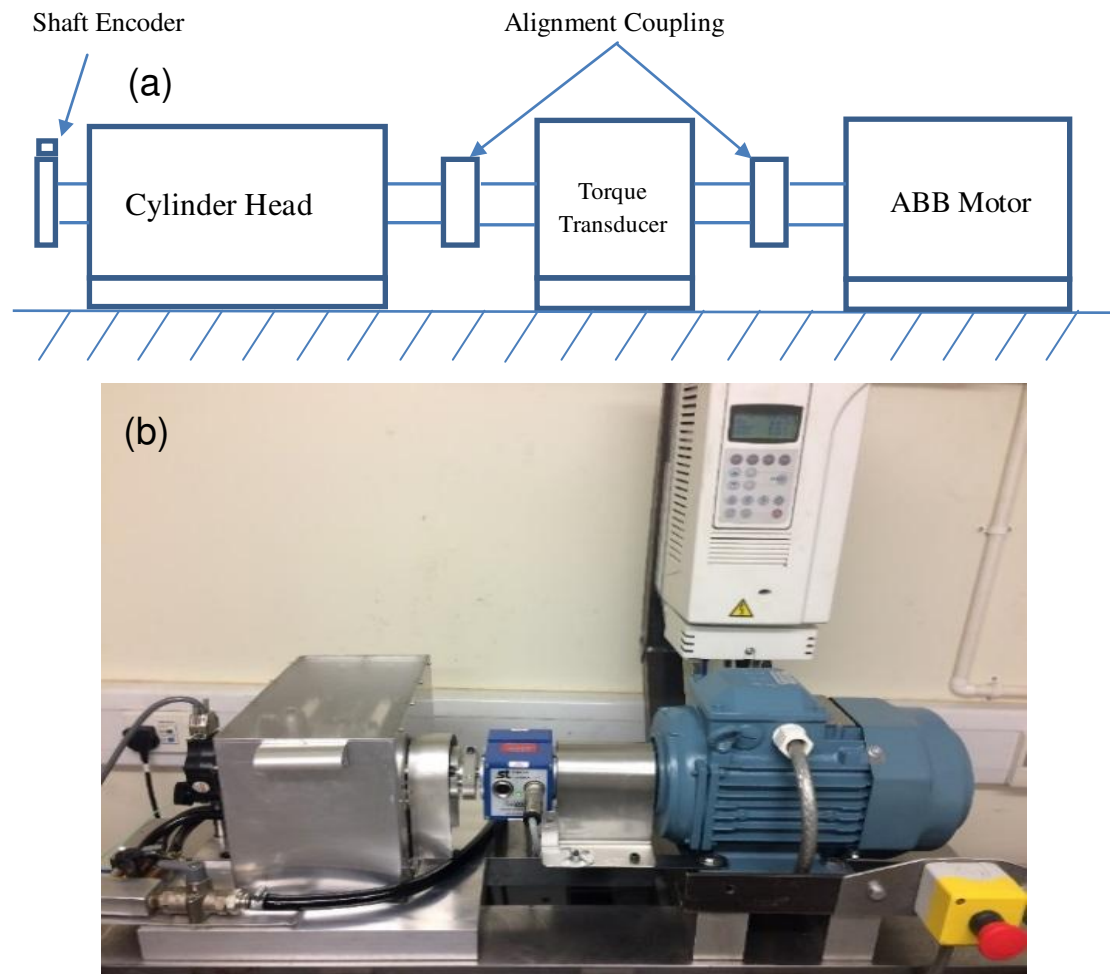


Fig. 1. The motored single cam rig: (a) 2D-schematic diagram (b) photograph of the rig

Molybdenum Dialkyl Dithiocarbamate (MoDTC) additive has been extensively used in engine oils as a friction modifier since the 1960s. MoDTC produces MoS_2 friction sheets which result in low friction under boundary lubrication [17-19]. This additive was also reported to form MoO_3 compounds in the tribofilm [18, 20]. More recently, iron (II) molybdate (FeMoO_4) has been found to be a product of MoDTC decomposition [17, 19, 21]. Zinc DialkyIDithioPhosphate (ZDDP), a well-known antiwear additive, was found to promote the formation of MoS_2 sheets when used together with MoDTC and lower friction and wear were obtained as a result [22]. Recently, the interaction between MoDTC and Diamond-Like Carbon (DLC) coatings has attracted a lot of interest. DLC coatings generally offer a reduction in friction with MoDTC additive [23, 24]. However, MoDTC additive has been reported to be detrimental to the wear of some DLCs [25-28]. In this work, one lubricant was used, a Group III (SAE 5W-30) fully formulated oil containing additives such as ZDDP,

MoDTC, detergent, dispersant, antioxidant, viscosity index improver as well as cold flow improver. The concentration in this oil for both ZDDP and MoDTC additives is 1 wt% each. The lubricant contains 1065 ppm of P and 1000 ppm of Mo. The dynamic viscosity of the lubricant was (7.66×10^{-3} Pas) at 100 °C and (3.87×10^{-3} Pas) at 130 °C.

Each test in this study run 80 hrs; this duration is shared between six cycles, where each cycle lasts 12.5 hrs. The test cycle used in this study is shown in Table 1. The single cam rig was set to run for a longer duration at low speeds (300 - 600 rpm), which is under predominantly boundary lubrication regime. However, based on the results obtained from the previous work [15], it was suggested to increase the test duration (i.e. to be longer than [15]), as increasing the test duration is believed to be essential for wear and durability evaluation.

To evaluate the lubrication regime at the cam/follower interface, Dowson and Higginson equation for line contact was used [29]. For both coatings (i.e. $MnPO_4$ and DLC) and based on the speed range tested, the oil film thickness lies in the range of 0.05-0.21 μm . In addition, the calculated Lambda ratio (λ) was 0.21 at 300 rpm and around 3.12 at 2100 rpm (i.e. boundary/mixed regime).

Table 1. Single cam rig experiment cycle

	Camshaft speed (rpm)	Time (hrs)
Running-in	500	2.5
	1000	2.5
	300	3
Steady state	600	2.5
	1000	2.5
	1200	1.5
	1500	1.5
	1800	1
	2100	28.5 (min)
	1350	0.5 (min)
	900	0.5 (min)
	300	0.5 (min)

The tappet insert with smaller clearance was discussed and understood to provide a longer contact area between the camlobe and the follower [16]. This could potentially lead to a higher friction torque for the thicker tappet insert. Further, based on Hooke's Law, $F=kx$ (where F: is the spring force, k: is the spring constant and x: is the deformation of the spring), the tappet insert with smaller clearance will result in relatively larger spring displacement and hence larger force (see Fig. 2). Therefore, if higher pressure would not lead to an enhanced decomposition of MoDTC friction modifier, a higher

friction torque would be expected for the thicker tappet insert. The valve lift can be related to the cam lift and the clearance between camlobe and follower using Equation 1:

$$\text{Valve lift} = \text{cam lift} - \text{clearance} \quad \text{Equation 1}$$

The cam lift of the setup used in this work was 6.88 mm. The clearance between the followers and base circle of the camlobes depends on the tappet insert thickness. Thus, the clearance was measured (as a function of tappet insert thickness) and reported around 0.11 mm for 2.75 mm tappet thickness, 0.28 mm for 2.575 mm tappet thickness and 0.58 mm for 2.275 mm tappet thickness. As a result, from Equation 1, different valve lift values were calculated and reported, as shown in Fig.2. In other words, the valve lift values for 2.275 mm, 2.575 mm and 2.75 mm tappet thicknesses were reported around 6.3 mm, 6.6 mm and 6.77 mm respectively. It is also worth mentioning that the contact load for the spring and camlobe combinations is cyclic (constant) and is not expected to change for a particular rpm range. However, the thickness would potentially change the instantaneous point of contact which in turn affects the slide-roll ratio and the tappet rotation, consequently affecting tribological performance.

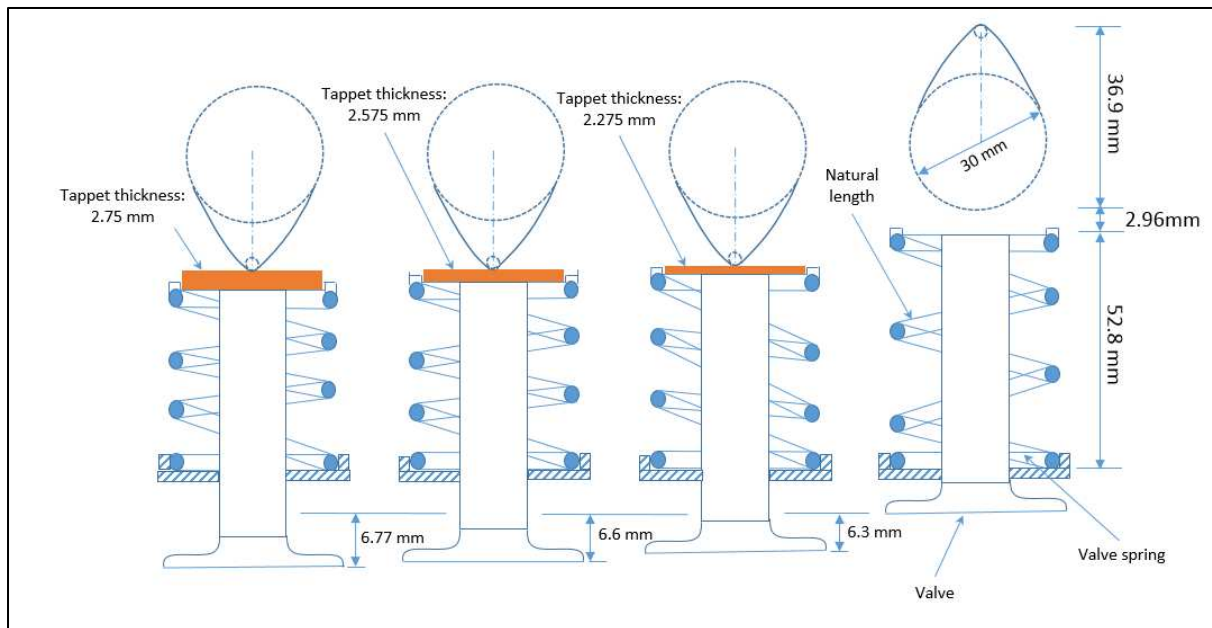


Fig. 2. Effect of clearance on valve spring

2.2. Wear Measurement

White Light Interferometry (NPFLEX) was used before and after each test in order to characterize the wear of the tappet inserts. Before using the White Light Interferometer (WLI), all tappet inserts were cleaned in acetone in an ultrasonic bath for at least 15 minutes. The tribofilm was removed from

the wear track by using a droplet of ethylenediaminetetraacetic acid (EDTA). This process was necessary to avoid any inaccurate wear measurements, as the presence of ZDDP tribofilm on the wear scar of the tappet insert can cause misleading to wear measurements when WLT (NPFLEX) is used because of their transparent characteristics [30]. Different traces were taken and the average was used as the wear scar for the tappet insert. A typical wear scar of tappet insert is presented in Fig. 3.

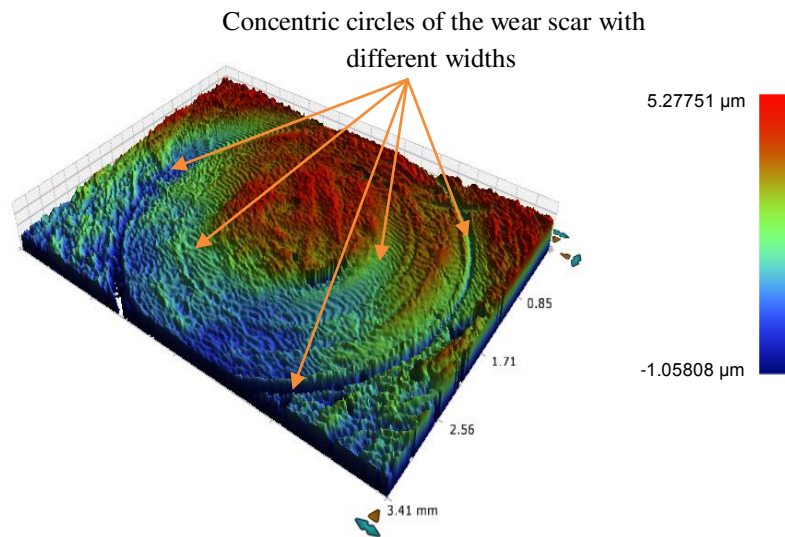


Fig. 3. Typical wear scar of MnPO_4 tappet insert

In an attempt to link the wear of the camlobes with standard engine tests, wear examination took place at seven locations on the cam profile ($\pm 14^\circ$, $\pm 10^\circ$, $\pm 4^\circ$ and cam nose- 0°), in accordance with ASTM D6891 standard (sequence IVA). This method has been recently used in [13, 15]. For the seven selected locations, the contact pressure, lubricant entrainment velocity and load per unit length were evaluated by the authors of this work [31] in order to correlate these values to the wear mechanisms (see Fig. 4 and Table 2). This was done to understand the nature of tribofilms formed across the cam profile which typically, has varying pressure, film thickness, slide roll ratio and lubricant entrainment velocities.

Talysurf contact was used to measure the wear on camlobes at these seven locations. The cam nose (0°) was considered as the reference and other locations were indexed with respect to this location. However, all locations were measured with angular digital dial and protractor which was affixed on the camlobes with an accuracy of $\pm 0.5^\circ$. At all locations, several traces were taken and the average was used as the wear scar for the camlobe. A typical cam nose profile pre-test and post-test are presented in Fig. 5.

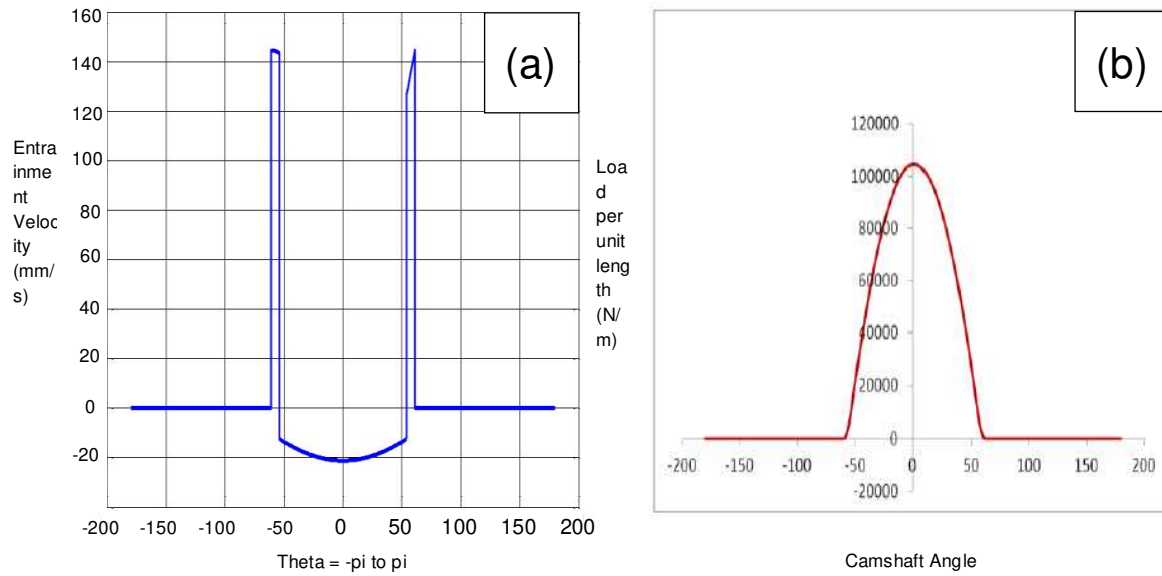
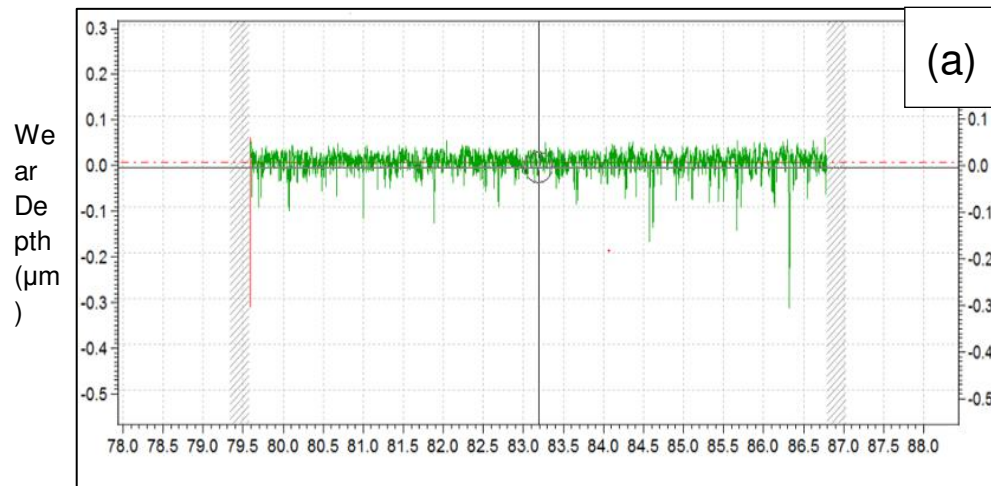


Fig. 4. Calculations for: (a) lubricant entrainment velocity and (b) load per unit length versus camshaft angle [31]

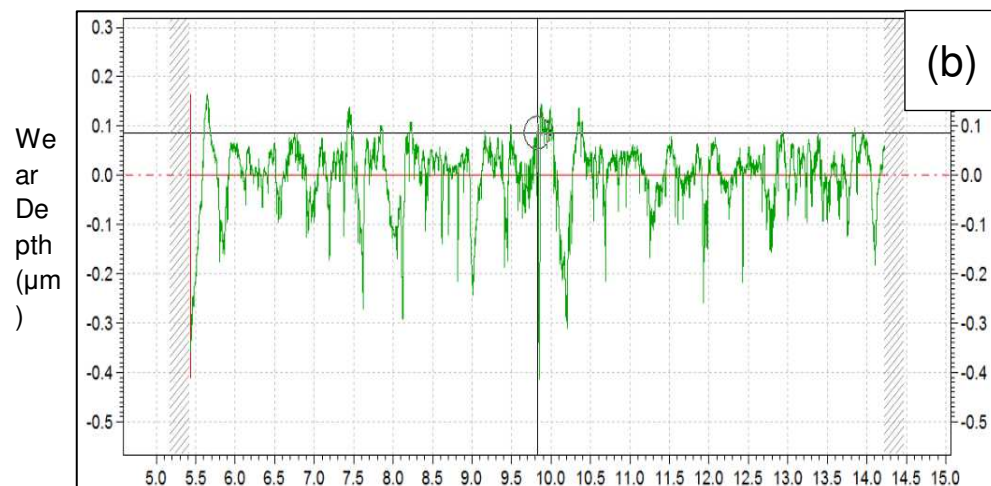
Table 2. Contact pressure across camlobe

Angle	Pressure
0° (cam nose)	0.76 GPa
±4°	0.70 GPa
±10°	0.62 GPa
±14°	0.59 GPa
180 ° (base circle)	0 GPa

[31]



Measurement across the cam nose (mm)



Measurement across the cam nose (mm)

Fig. 5. Cam nose profile (a) pre-test (b) post-test

2.3. Surface Analysis

A Zeiss EVO MA15 variable pressure SEM was used to examine the worn camlobe/tappet insert surfaces and to investigate the durability of the coatings employed. An Oxford instrumented EDX (probes to 1 μm depth) was connected to the SEM to provide the elemental composition of the coated tappet inserts. Energy-Dispersive X-ray (EDX) analyses of the tappet inserts were obtained from inside and outside the wear tracks. For camlobes, the element composition was observed at different regions of the camlobe but mostly at the cam nose. For both tribopairs, it was essential to examine an unworn surface for comparison. Thus, SEM/EDX analyses were performed before and after the test.

Raman spectroscopy has been commonly used to examine the structure/composition of the tribofilms formed on a surface. In this study, a Renishaw inVia Raman spectroscopy (488 nm

wavelength and 10% power filter) was used to observe the structural modifications inside and outside the wear track of the coated tappet inserts. For camlobes, the structural modifications of the tribofilms were also observed at the seven specified locations using ASTM D6891 standard. This is however an attempt to map the tribochemical films across the camlobes and correlating this to the wear. It is worth mentioning that the spectra at $\pm 4^\circ$ and $\pm 10^\circ$ were essentially seen to have the same trend as the spectra at the cam nose (0°). Therefore, in this work, Raman spectra are reported at three locations only (-14° , 0° , $+14^\circ$). Likewise, for camlobes and followers, Raman analyses were also used before and after the test to provide a better insight into the potential structural modifications during the test.

2.4. Repeatability of Friction Torque Data

The single cam rig has proved to have good repeatability and high ability to determine the frictional response of different coatings and fully formulated lubricants [15]. A high sensitivity torque transducer (RWT 421) was connected to the camshaft using flexible coupling to obtain speed and torque measurements. The calibration of the torque transducer has frequently been made by the manufacturer. However, an additional calibration was done by the authors of this work [31]. Representative friction data over 80 hrs test duration are shown in Fig. 6. The obtained friction data were stable and comparable for the whole test duration. Therefore, the average friction torque was calculated based on all cycles (i.e. six test cycles). It is worth mentioning that this behaviour was seen for all coatings and speeds tested in this work. Nevertheless, all tests were performed twice at the same operating conditions with repeatable results.

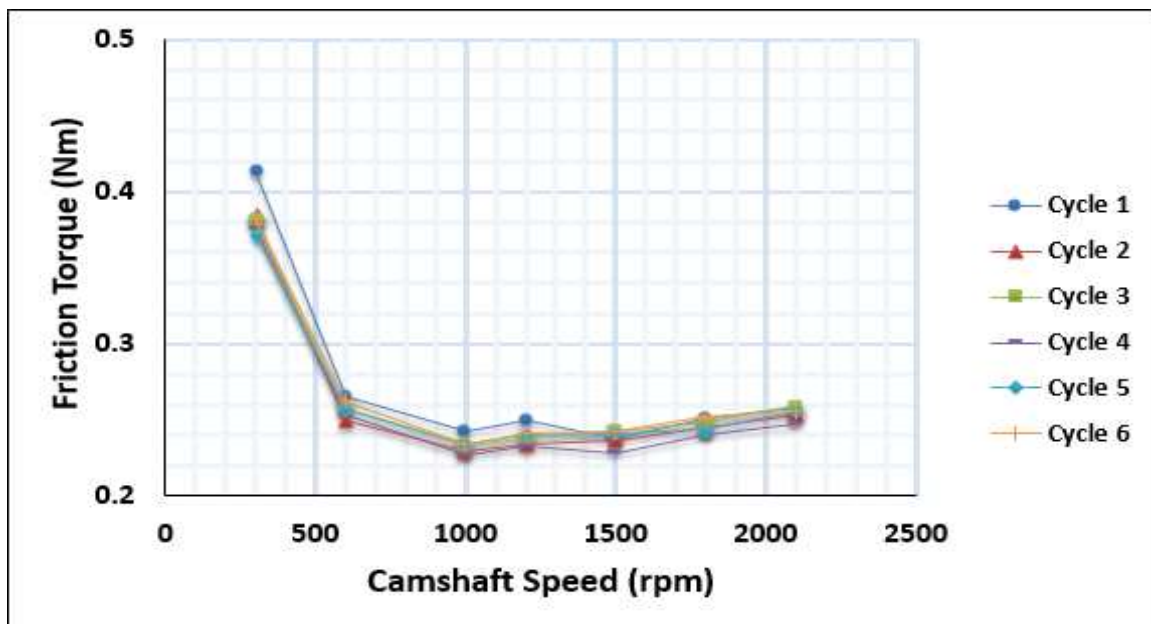


Fig. 6. Repeatability of friction torque data for MnPO_4 insert (2.75mm tappet thickness) over 80 hrs test duration at 100°C

3. Results and Discussion

3.1. Friction Torque and Wear for $MnPO_4$ Coated Tappet Inserts

$MnPO_4$ coating is commonly used in cam/follower inserts for adhesive wear prevention (i.e. $MnPO_4$ coatings give good oil wettability, absorbance and oil retention characteristics) [10, 32]. The average friction torque for $MnPO_4$ tappets as a function of the effect of tappet thickness and camshaft speed is shown in Fig. 7.

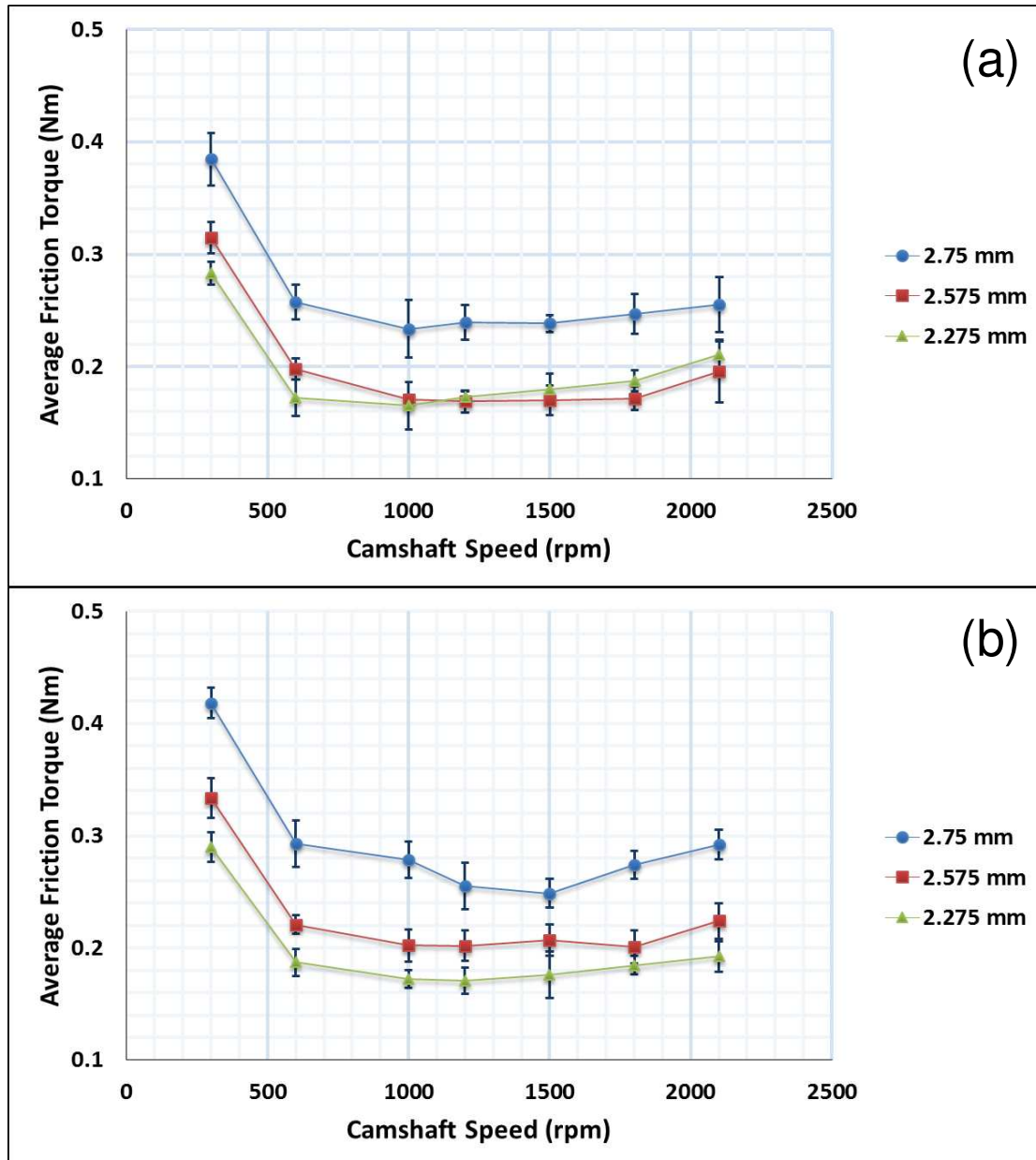


Fig. 7. Average friction torque versus camshaft speed for $MnPO_4$ inserts at different thicknesses (a) at 100 °C, (b) at 130 °C

As expected, the average friction torque generally reduced with increasing camshaft speed due to increased lubricant entrainment velocity into the cam/follower interface region. Similar results were reported previously [8, 10, 15, 33]. For both temperatures, a high friction torque was observed at 300 rpm (lowest speed) due to the contact being in the boundary lubrication regime, where more asperity-asperity interactions occur with the friction determined by the chemical and physical actions of thin films of molecular proportions [34]. The mixed lubrication regime is mainly represented at higher speeds where the lubricant film does not provide full separation (i.e. the load of contact is shared between the asperities and the elastohydrodynamic lubrication film) [35, 36].

From Fig. 7, the smaller clearance of tappet inserts generally gave a higher friction torque, suggesting a high asperity interaction at the cam/follower interface along with less reactivity to lubricant additives. More recently, the authors of this work have reported that tappet rotation is affected by changing the clearance of the tappet inserts [16]. However, regardless of tappet rotation, the tappet insert with smaller clearance offered high friction torque. The thicker tappet insert experiences the lowest minimum film thickness and, as such justifies the high friction torque obtained. Figure 7 also shows that an increase in the average friction torque was observed with increasing lubricant temperature which is in agreement with previous works [15, 37, 38]. This is due to decreased oil viscosity (resulting in a lower oil film thickness) under high temperatures leading to more asperity interactions. Wear tracks on the tappet insert surface correspond to the rotation of the tappet and the interaction points during the cam cycle. The MnPO_4 tappet inserts with the smallest clearance showed the highest wear depth, as shown in Fig. 8.

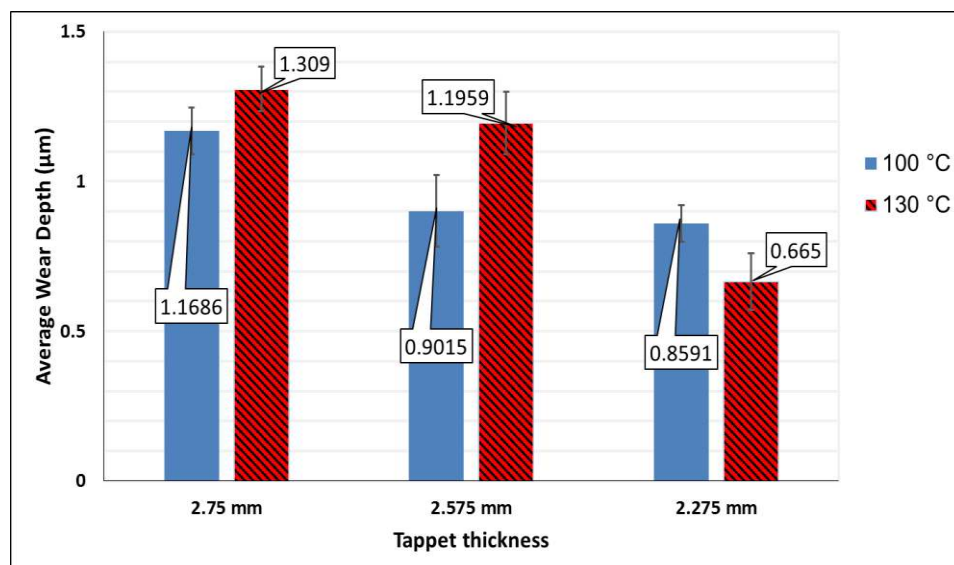


Fig. 8. Average wear depth versus tappet thickness for MnPO_4 inserts at 100 °C and 130 °C

This suggests a higher interaction between the cam/follower tribopair with decreasing tappet clearance. Accordingly, tappet inserts with a thickness of 2.275 mm have shown the lowest wear

among the three thicknesses. However, noisy running was observed for the tappet inserts with the largest clearance, which could potentially result in higher wear of the valvetrain for longer test durations. In general, the greatest wear depth was observed at the centre of the insert due to the contacts with the cam nose, flank, shoulder and ramp regions. At the edge of the insert, however, there was no significant wear on the surface. As expected, and in line with previous findings [15, 39], the follower surface indicated concentric circles of the wear scar with different widths. A potential reason for these concentric circles is the effect of tappet rotation which offers circumferential rubbing action to take place on the surface of inserts. At higher temperature, the wear rate was mostly increased due to the effect of high temperature on the lubricant viscosity.

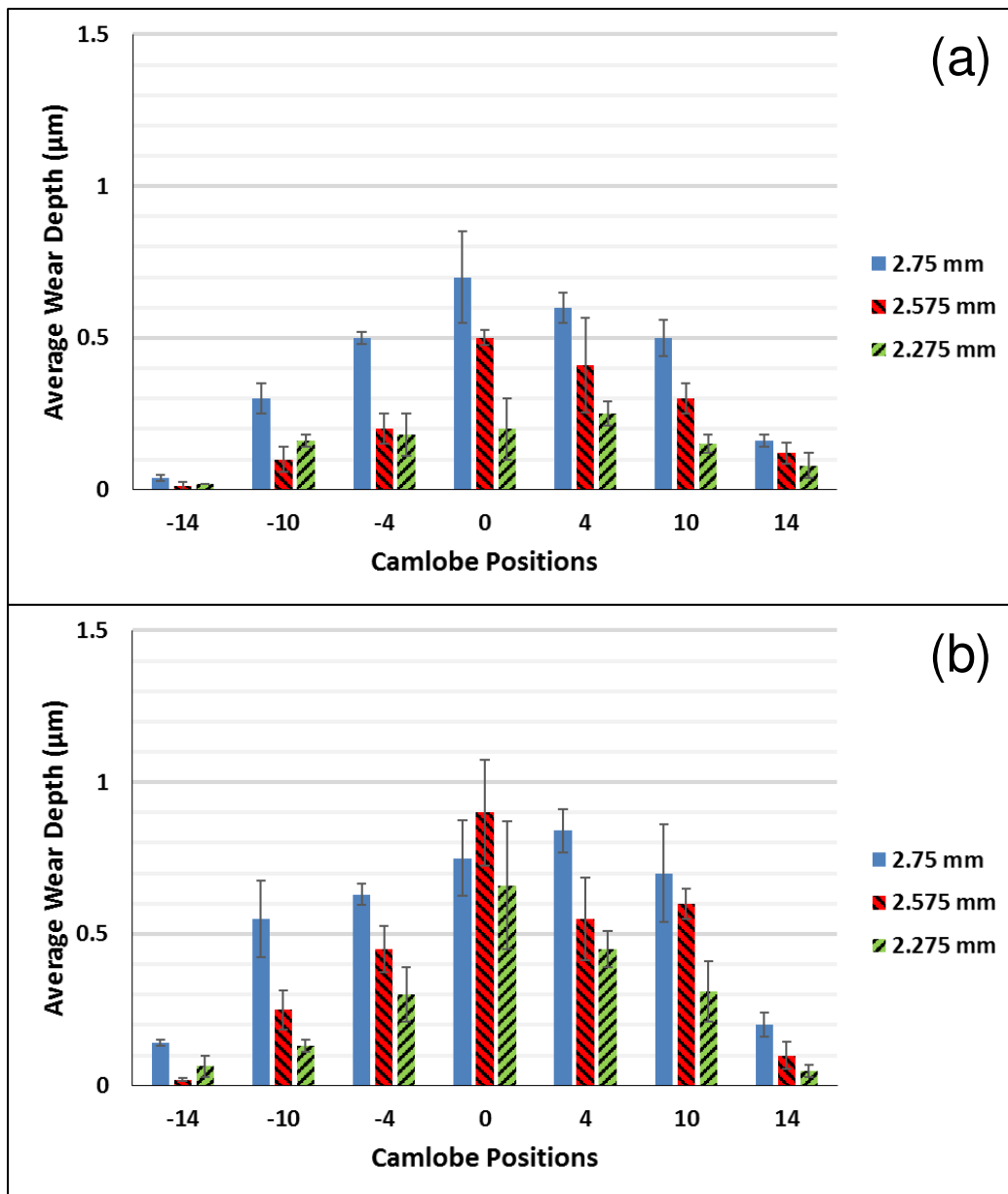


Fig. 9. Average wear depth across the camlobe when interacting with MnPO₄ follower: (a) at 100 °C, (b) at 130 °C

In line with standard engine tests, wear of the CI camlobes was measured from seven locations around the cam. However, as the cam half period (i.e. action angle) is at 56° , different traces were also taken (not shown here) in the region between 14° and 56° (both sides). As expected, the wear on this region was not considerable as compared to the wear on the selected seven locations. Average wear depth across the camlobe (rubbing against MnPO_4 inserts) at 100°C and 130°C is shown in Fig. 9.

For both temperatures, the small clearance of tappet inserts generally showed the high wear depth on the camlobe surface. The cam nose is found to be a region of significant wear, especially toward the edges (i.e. sharp edges and worn tip) [40]. This is called edge loading which occurs due to high load/pressure on the nose (i.e. harsh conditions). For all thicknesses, a significant increase of wear was observed at two locations (cam nose and 4°), mainly due to the adverse effect of boundary lubrication and sliding action. Similar results showed that the camlobe wear was the highest near the camlobe nose [41]. In addition, camlobes mostly showed higher wear at the positive section ($+14^\circ$, $+10^\circ$, $+4^\circ$) than the negative section and this behaviour is basically due to the action of opening the valves [31]. A significant deformation of the CI camlobe surface occurred during the opening of the valve, probably due to greater energy/work which is expended during valve opening actions. Similar findings were reported previously [15, 41]. At higher temperature, the wear rate was generally increased which indicates that the durability (wear) of the MnPO_4 coating is reduced at high temperature, most probably due to lower oil viscosity.

3.2. Friction Torque and Wear for DLC Coated Tappet Inserts

DLC coatings have shown to reduce friction and improve the durability of engine components [42]. Particularly, DLC tappet inserts have offered extreme-low friction in boundary lubrication regime even in unlubricated conditions [43, 44]. Kano [45] found that DLC coatings have super low friction properties; 45% reduction in friction was observed when using DLC coatings as compared with common phosphate coatings. Therefore, the effect of DLC coating on the average friction torque was also tested in this study. For DLC coated tappet inserts, the average friction torque as a function of tappet thickness and camshaft speed is shown in Fig. 10. Although the average friction torque of DLC tappet inserts (as a function of tappet thickness) seems to be within the standard deviation, similar findings to those noticed on MnPO_4 tappets were observed regarding the effect of tappet clearance on friction performance (i.e. the tappet insert with smaller clearance generally showed higher friction torque). This is best described in [16] where the percentage of the cycle increases as the tappet clearance decreases. Also, the average friction torque when using DLC coating was decreased compared to inserts coated with MnPO_4 . This was expected due to the high roughness of MnPO_4 tappet insert (which is a commercial standard production surface coating for inserts). The

higher roughness of MnPO_4 coating gave rise to asperity interactions and thereby led to high wear and friction [32]. Nevertheless, coating properties, as well as the interactions between the coating, the counter-body and the lubricant are crucial to the friction/wear and tribochemical performance. Thus, the observed friction reduction could also be attributed to the performance of DLC coatings in the attendance of MoDTC, where DLC coatings offer friction reduction by forming MoDTC derived MoS_2 sheets on DLC surfaces [23, 24, 44].

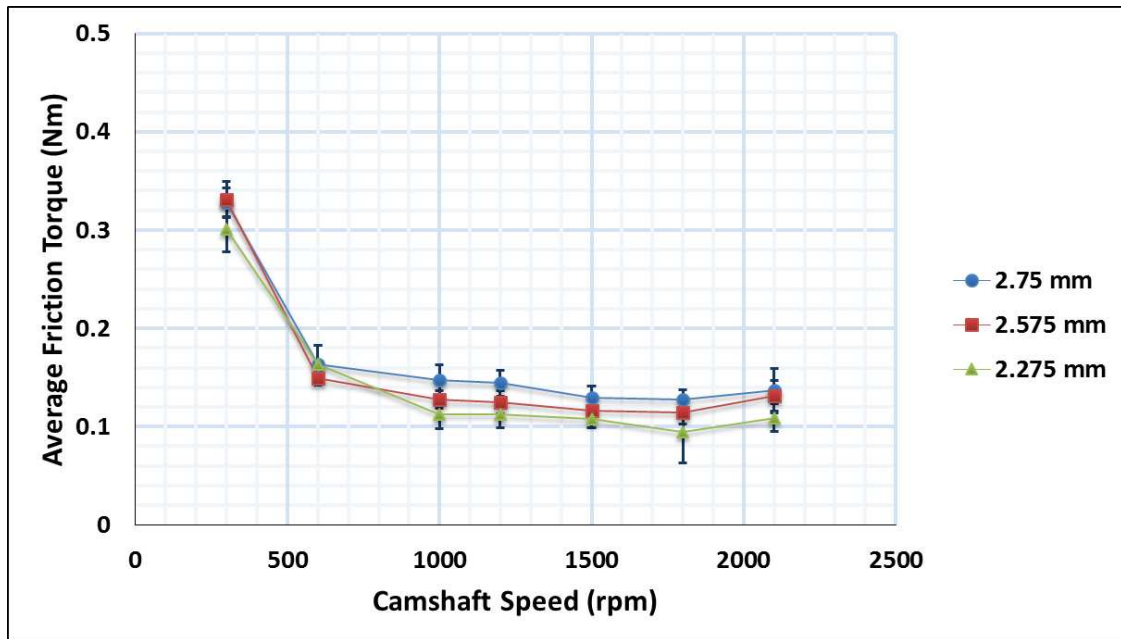


Fig. 10. Average friction torque versus camshaft speed for DLC inserts at 100 °C

For DLC coated tappet inserts, the average wear depth versus tappet thickness is shown in Fig. 11. It can be seen that the smallest clearance also showed the highest wear depth. Thus, it is fair to conclude that the wear performance of tappet inserts is also more controlled by the tappet thickness rather than the type of coating. Further, the wear depth of the DLC insert was relatively lower than the wear depth of the MnPO_4 insert. This is however in contrast with the literature [18, 25-27, 46, 47], where DLC coating was worn quicker in the presence of MoDTC when rubbed against a ferrous counterpart. This discrepancy could be explained by the lubricant used in this study. As the lubricant contains 1%wt of ZDDP, this probably hinders the MoDTC potency in giving high wear to DLC coating in the DLC/ferrous combinations [18]. In addition to the properties of DLC coating (a-C-15H), the differences in surface roughness between coatings were also believed to play a vital role on wear performance (i.e. DLC coating experienced low wear rate due to its low roughness). Likewise, the DLC coating was reported by the authors [16] to offer a high rotation of inserts, this also in return would help to reduce wear of the DLC inserts by promoting lubricant retention in the contact.

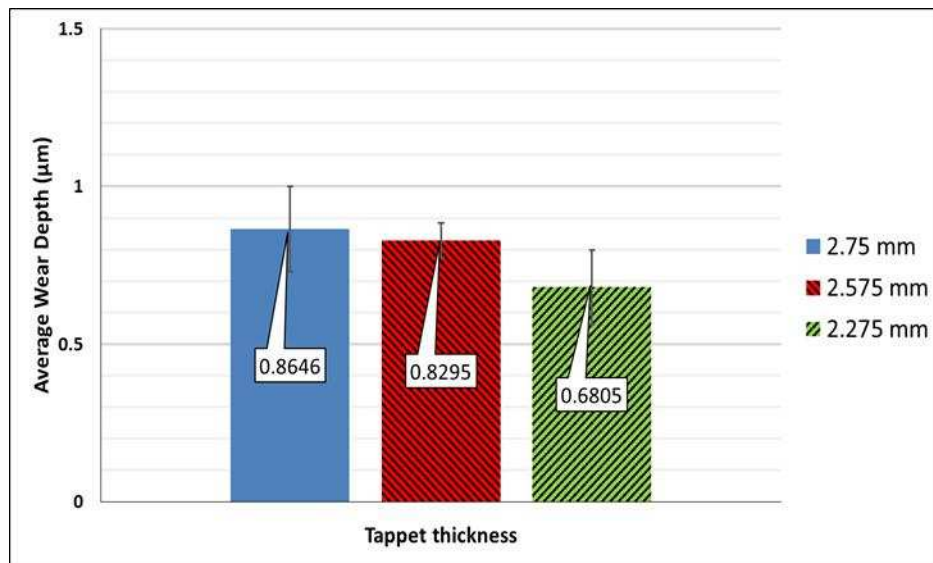


Fig. 11. Average wear depth versus tappet thickness for DLC inserts at 100 °C

The average wear depth across the camlobe (rubbing against DLC inserts) is shown in Fig. 12. A similar trend was observed under the effect of tappet clearance (i.e. the small clearance of tappet inserts relatively showed high wear rate). It is interesting to note that regardless of the type of counterpart, the wear rate is comparable for all camlobe positions. In other words, wear of the camlobe is not affected by the type of tappet insert. This is similar to findings by MacDonald *et al.* [31]. Nevertheless, the wear depth of the CI camlobe rubbed against a DLC insert was generally higher than the wear depth of the CI camlobe rubbed against a MnPO_4 insert. This is mainly due to the differences in hardness and surface roughness between coatings. Also, it is believed to be related to the tribochemistry of the interface which will be discussed in detail in the following section.

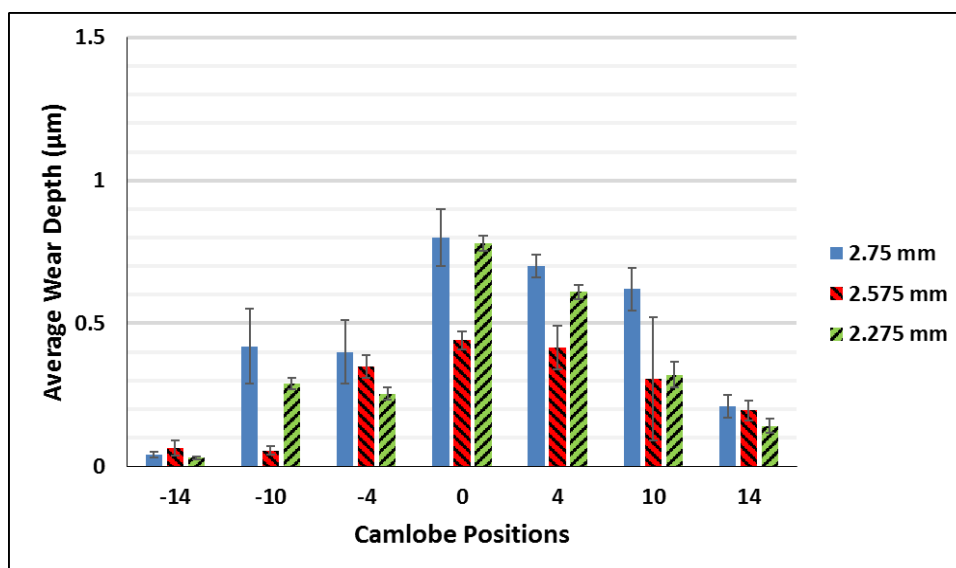


Fig. 12. Average wear depth across the camlobe when interacting with DLC follower at 100 °C

3.3. Tribochemistry of Cam/Follower Interface

3.3.1. Mapping the Tribofilm Formation using SEM-EDX

From Fig. 13 and Fig. 14, SEM micrographs revealed that interactions took place between oil additives, the camlobe surface and the coating insert surface. Unlike the camlobes, the wear scar of the inserts for both coatings (i.e. MnPO_4 and DLC) was clearly identified by SEM. Figure 13 and 14 also show the effect of tappet insert clearance on the tribofilms formed on the cam/follower surfaces. For both coatings, the tappet insert with smaller clearance showed high interactions with the camlobe surface and the oil additive. EDX semi-quantification of CI camlobes and MnPO_4 coated steel inserts is presented in Table 3. In addition, the elemental composition of the CI camlobes and the DLC coated steel inserts is presented in Table 4. The CI camlobe in Fig. 13-a, showed the presence of phosphorus in both regions (i.e. region 1 and 2) on the cam nose. This can be derived either from the elements of the lubricant or the coating of the insert (i.e. due to rubbing action from the camlobe to the MnPO_4 insert). At region 1, little or no changes were observed in carbon, oxygen and iron concentrations as compared to a pre-test CI camlobe suggesting a minimal chemical reactions took place with the lubricant additives. Nevertheless, low levels of Mo, Zn and S were observed in both regions, implying a heterogeneous distribution of the lubricant derived films on the camlobe surface.

From Fig. 13-b and Table 3, the iron concentration inside the wear track (i.e. region 3) was high and the MnPO_4 coating appeared to be stripped off from the surface thereby exposing the 16MnCr5 steel substrate. This may be due to load/pressure variations, flash temperatures and reactivity/or interaction with the MoDTC additive on the substrate [31]. At region 4, the MnPO_4 coating is partially removed, revealing that the coating was not fully affected by the chemical reactions (thermally activated) outside the wear track. However, lubricant additive-derived elements of Mo, Zn, S, P and Ca were observed inside and outside the wear track with different concentrations, implying a heterogeneous distribution of tribofilm on MnPO_4 insert after 80 hrs of testing.

The CI camlobe in Fig. 14-a, showed scoring marks with high levels of carbon in both region 9 and region 10 as compared to a pre-test CI camlobe. These marks were not only seen on the cam nose but also on the cam flank (both sides). It is also important to note that there was no detection of Zn in these regions. In addition, in region 10, sulfur and phosphorus were not observed on the surface. This supports the wear results where the absence of the lubricant antiwear properties on the CI camlobe surface led to an abrasive wear process. Furthermore, high level of Molybdenum was observed on the CI camlobe rubbed against DLC shim (at region 9 and 10) when compared to the CI camlobe rubbed against MnPO_4 shim (region 1 and 2). The DLC insert in Fig. 14-b, showed low levels of carbon with high levels of iron in both regions (region 11 and 12) as compared to a pre-test DLC shim. This could be due to thinning of DLC coating resulting from wear. In addition, the high level of Mo, S and Zn

detected in the wear scar could be related to additive-derived elements leading to low friction and wear. This is also in line with the obtained friction and wear results.

From Fig. 14, the DLC inserts were supporting a polishing wear process (i.e. the wear produced a smooth burnished appearance on the surface) [39]. The polishing wear process which is caused by mild abrasive wear was observed by the White Light Interferometer, as shown in Fig. 15-a. It should be mentioned that this process was not observed on the DLC tappet insert with a thickness of 2.275 mm. For all MnPO_4 tappet inserts (see Fig. 14), however, the surface appears fairly rough (R_a is about $0.47 \mu\text{m}$ for the tappet insert with the largest clearance and $1.7 \mu\text{m}$ for the tappet insert with the smallest clearance) compared to MnPO_4 tappet insert before the test (R_a $0.25 \mu\text{m}$). The surface was consisting of ridges/grooves on the surface of the tappet insert. This is equally supporting an abrasive wear process for MnPO_4 tappet inserts (i.e. significant abrasive marks on MnPO_4 tappet inserts were observed by the White Light Interferometer, as shown in Fig. 15-b).

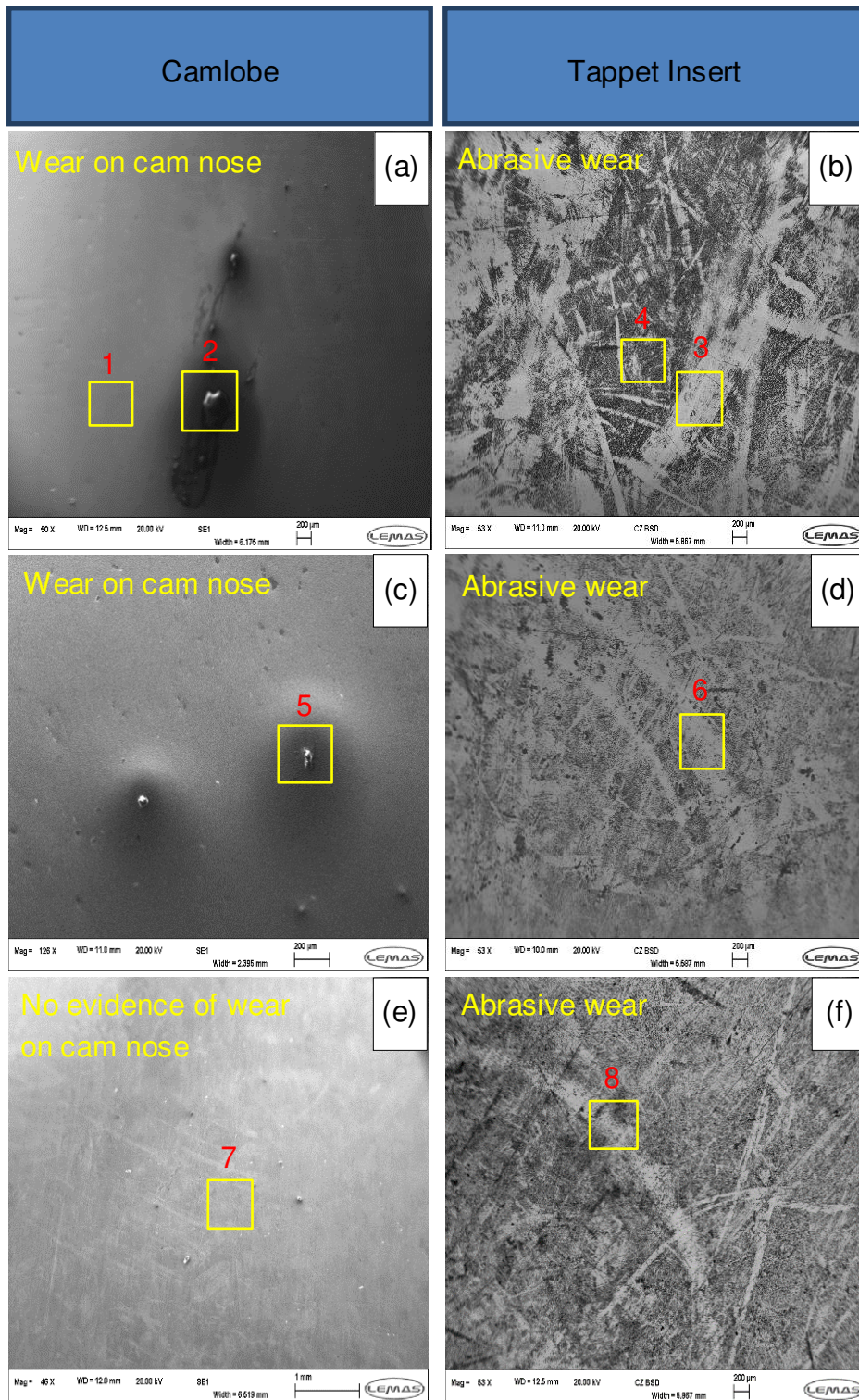


Fig. 13. Scanning electron micrograph (SEM) at 100 °C: (a) CI camlobe rubbed against (2.75 mm) MnPO₄ shim, (b) MnPO₄ shim with thickness 2.75 mm, (c) CI camlobe rubbed against (2.575 mm) MnPO₄ shim, (d) MnPO₄ shim with thickness 2.575 mm, (e) CI camlobe rubbed against (2.275 mm) MnPO₄ shim and (f) MnPO₄ shim with thickness 2.275 mm

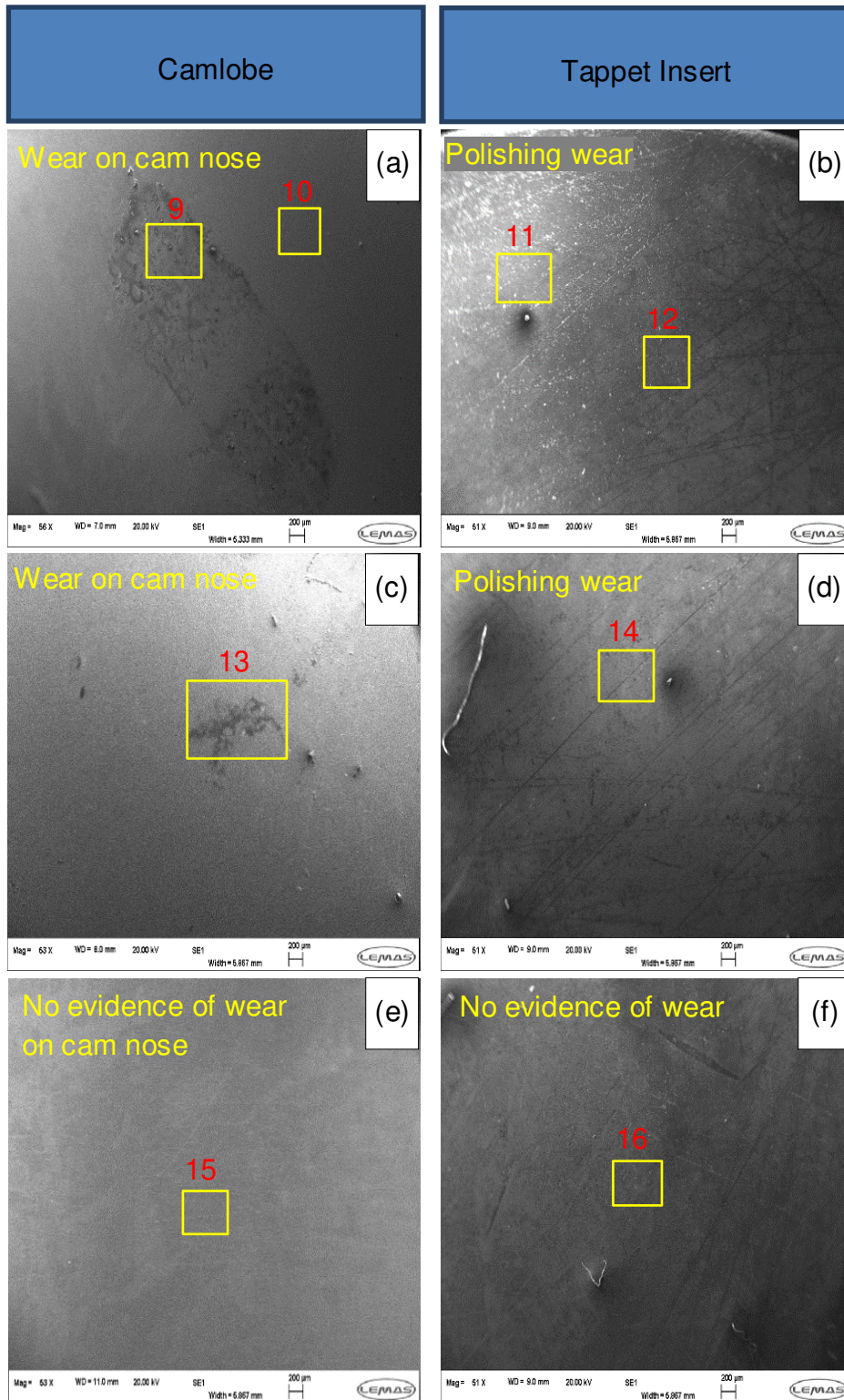


Fig. 14. Scanning electron micrograph (SEM) at 100 °C: (a) CI camlobe rubbed against (2.75 mm) DLC shim, (b) DLC shim with thickness 2.75 mm, (c) CI camlobe rubbed against (2.575 mm) DLC shim, (d) DLC shim with thickness 2.575 mm, (e) CI camlobe rubbed against (2.275 mm) DLC shim and (f) DLC shim with thickness 2.275 mm

Table 3. EDX semi-quantification of CI camlobes and MnPO₄ coated inserts at 100 °C

CI camlobe		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Before Test		0.60	8.57	-	-	-	0.96	-	87.84	1.06	0.97
After Test	Region 1	0.63	7.73	0.17	0.34	0.36	0.92	0.31	86.68	1.33	1.35
	Region 2	-	75.79	0.19	0.16	0.07	-	0.01	11.22	11.83	0.73
MnPO ₄ insert		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Before Test		0.68	6.36	15.46	-	-	14.24	-	21.96	39.61	1.69
After Test	Region 3	1.49	5.31	0.59	0.03	0.37	0.56	0.44	87.81	2.98	0.42
	Region 4	1.67	6.50	8.12	0.09	0.39	6.16	0.22	54.21	22.09	0.55
CI camlobe		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Region 5		0.46	32.21	0.27	0.57	0.37	0.80	1.17	58.61	3.97	1.57
Region 6		0.41	10.54	0.39	0.61	0.77	0.53	1.02	81.08	3.61	1.04
MnPO ₄ insert		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Region 7		1.59	6.19	5.33	0.08	-	0.37	1.17	80.35	4.64	0.28
Region 8		1.81	9.51	7.06	-	1.04	0.99	1.03	73.66	4.69	0.21

Table 4. EDX semi-quantification of CI camlobes and DLC coated inserts at 100 °C

CI camlobe		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Before Test		0.60	8.57	-	-	-	0.96	-	87.84	1.06	0.97
After Test	Region 9	0.39	44.07	0.43	0.26	-	0.66	1.04	38.80	12.08	2.27
	Region 10	0.55	26.63	-	-	-	0.74	1.75	66.24	3.33	0.76
DLC insert		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Before Test		28.15	71.45	-	-	-	-	-	0.20	-	0.20
After Test	Region 11	48.00	47.23	-	0.15	0.21	-	0.88	3.42	-	0.11
	Region 12	43.59	53.14	-	0.12	0.29	-	0.84	1.84	-	0.18
CI camlobe		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Region 13		0.70	26.37	0.06	0.16	-	0.88	0.91	67.06	3.16	0.70
Region 14		0.64	18.65	-	-	-	0.87	1.37	72.65	5.37	0.45
DLC insert		Element (wt %)									
		Cr	C	P	S	Zn	Mn	Mo	Fe	O	Others
Region 15		45.68	51.63	0.14	0.04	-	-	0.10	2.41	-	-
Region 16		30.14	65.89	-	-	-	-	0.76	1.78	-	1.43

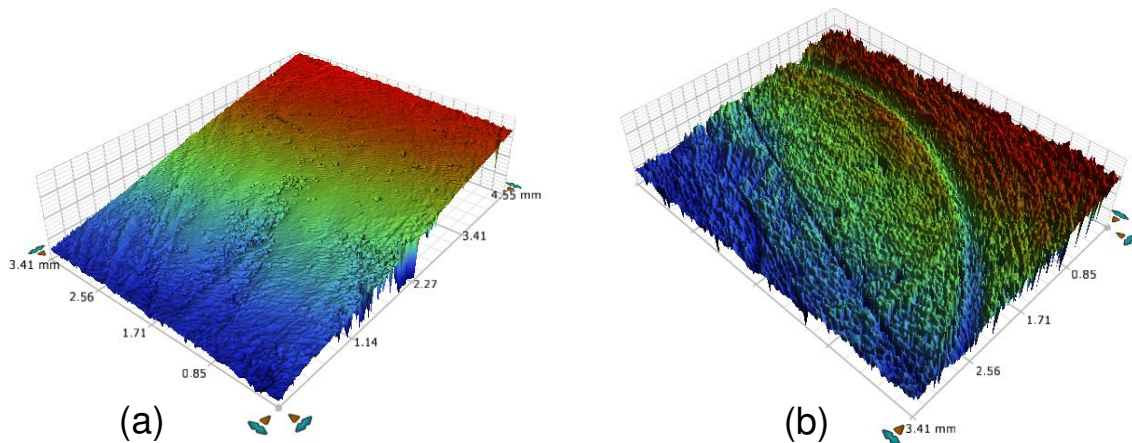


Fig. 15. Typical wear process on tappet inserts (a) polishing process (b) abrasive process

3.3.2. Mapping the Structural Modifications using Raman Spectroscopy

Raman peaks for typical lubricant tribofilms are reported at 383-410 cm^{-1} for MoS_2 , carbon (C) at 1366-1596 cm^{-1} , phosphate (PO_4^{3-}) at 949-970 cm^{-1} , haematite (Fe_2O_3) at 120-310 cm^{-1} and magnetite (Fe_3O_4) at 670-680 cm^{-1} [15, 19, 48-50]. The Raman spectra from CI camlobes (rubbed against MnPO_4 inserts with different thicknesses) are shown in Fig. 16.

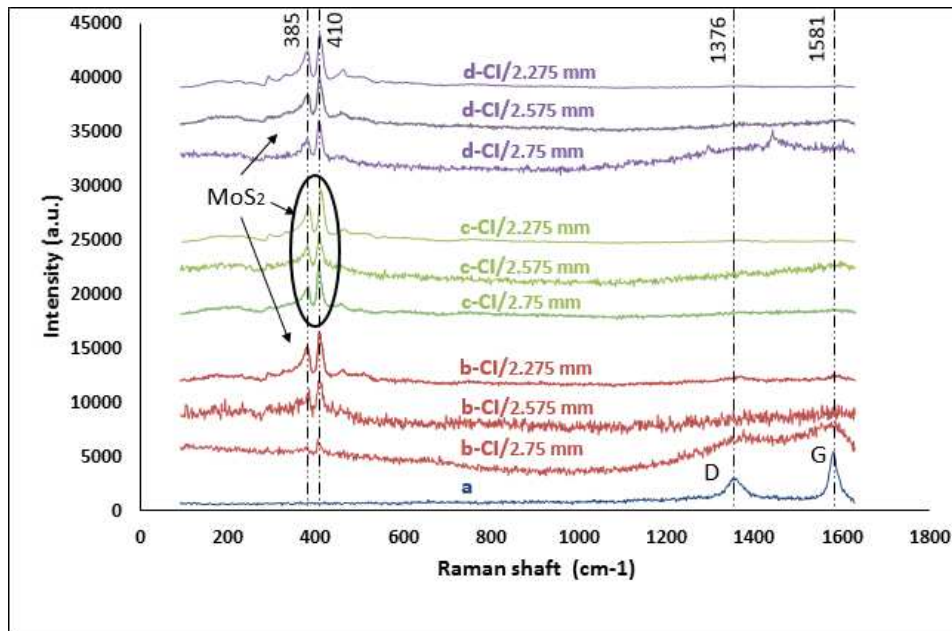


Fig. 16. Raman spectroscopy for the CI camlobes (rubbed against MnPO_4 inserts) at 100 °C: (a) before the test, (b) at cam nose, (c) +14° from cam nose, (d) -14° from cam nose

In general, similar Raman peaks were observed for all tappet thicknesses. These spectra indicate the presence of MoS_2 (385-410 cm^{-1}) in all regions (+14°, 0° cam nose, -14°) of the cam. At the cam nose, lower amount of MoS_2 was observed as tappet insert thickness increases, confirming low load

resistance of MoS₂ sheets with lower tappet insert clearance. Moreover, as graphite flakes are normally present in the microstructure of the cast iron, clear carbon peaks were detected on the camlobe before the test. The G and D peaks were around 1581 cm⁻¹ and 1367 cm⁻¹ respectively. The G peak represents the graphite and D peak represents the disorder in graphite [51].

Figure 17 shows the Raman spectra obtained from MnPO₄ inserts with different thicknesses. The Raman shift clearly indicated the presence of phosphate (956 cm⁻¹) outside the wear track for all thicknesses. However, for the thickness of 2.75 mm and 2.575 mm, no phosphate was observed inside the wear track, suggesting that the MnPO₄ coating is stripped off from the steel substrate. Peaks attributed to the formation of graphitic carbon were mainly observed outside the wear track, which confirms that there is a transfer of material from the camlobe to the MnPO₄ insert. It is, however, possible that the detected carbon could be from trapped oil (i.e. MnPO₄ is a porous coating and oil could be trapped between MnPO₄ crystals). For the thickness of 2.275 mm, carbon peaks were detected inside and outside the wear track. This could be related to the low wear rate seen on the tappet insert with largest clearance. Confirming EDX results, distinct MoS₂ peaks were observed for all thicknesses inside the wear track at 384 cm⁻¹ (E_{2g}¹ peak) and 411 cm⁻¹ (A_{1g} peak), whereas little or no MoS₂ peaks were observed outside the wear track, suggesting a higher amount of film formed inside the wear track. In addition, higher MoS₂ peak intensity was observed inside the wear track as tappet clearance decreases which could indicate more MoS₂ film formed inside the wear track. That could be related to higher pressure at the interface (for smaller tappet clearance) resulting in an enhanced MoDTC decomposition.

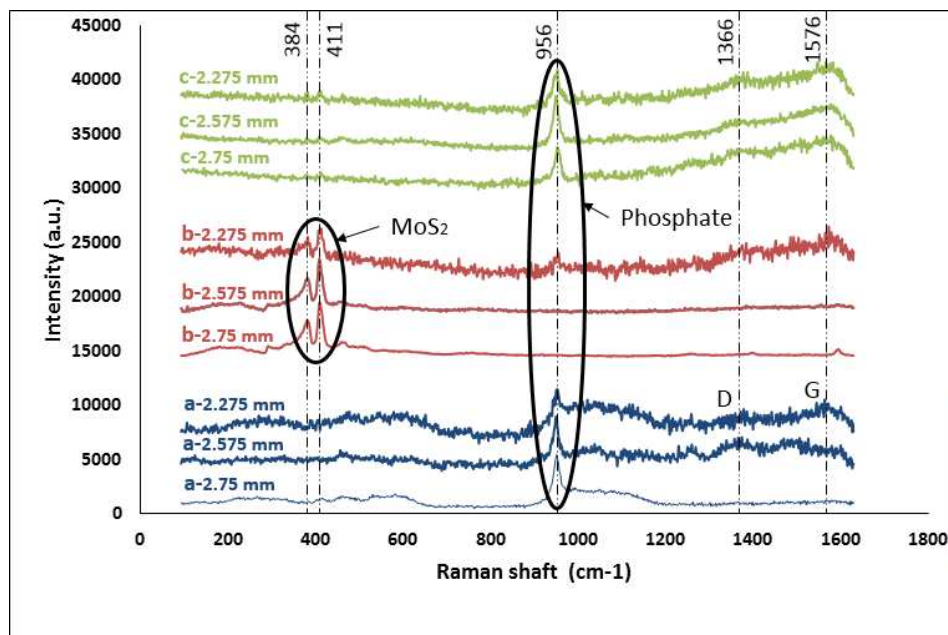


Fig. 17. Raman spectroscopy for the MnPO₄ inserts at 100 °C: (a) before the test, (b) inside wear track, (c) outside wear track

The results from Raman spectroscopy for the CI camlobes (rubbed against DLC inserts with different thicknesses) are shown in Fig. 18. In general, the spectra clearly indicate the presence of MoS_2 ($384\text{-}410\text{ cm}^{-1}$) and Fe_3O_4 (675 cm^{-1}) at all regions. Also, the additional peaks, 228 and 302 cm^{-1} were believed to be attributed to the formation of iron oxide (Fe_2O_3) [52]. Furthermore, carbon peaks at 1376 and 1581 cm^{-1} assigned to the formation of amorphous carbon were generally detected for all regions on the camlobe (i.e. cam nose and cam flank). Figure 19 shows the Raman spectra obtained from the DLC inserts with different thicknesses. The presence of MoS_2 ($384\text{-}410\text{ cm}^{-1}$) is mostly evident inside and outside the wear track. As can be seen from the figure, sharper MoS_2 peaks were detected inside wear track as compared to outside wear track. This indicates that the tribological contact promotes the formation of MoS_2 on the wear scar, in agreement with research done on benchtop tribometers. The broad peak in the range of $140\text{-}250\text{ cm}^{-1}$ inside wear track was attributed to stress-induced disorder in MoS_2 crystal structure [19]. As expected, regardless of tappet insert clearance, Raman peaks related to the presence of carbon were clearly observed inside and outside the wear track of the DLC inserts. On the other hand, it is worth mentioning that neither MoO_x peaks nor iron (II) molybdate (FeMoO_4) peaks were observed on any surfaces of camlobes and followers.

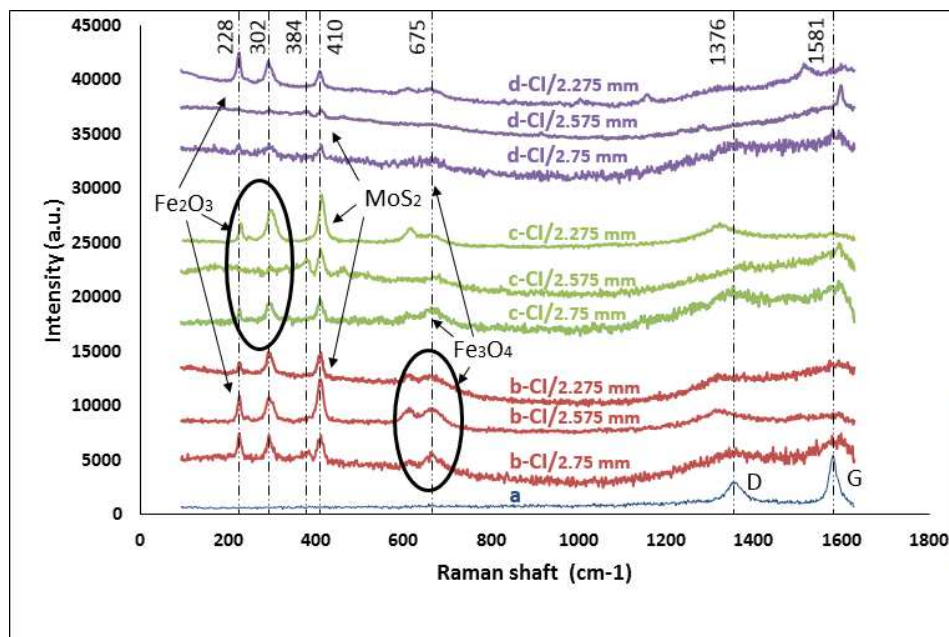


Fig. 18. Raman spectroscopy for the CI camlobes (rubbed against DLC inserts) at $100\text{ }^\circ\text{C}$: (a) before the test, (b) at cam nose, (c) $+14^\circ$ from cam nose, (d) -14° from cam nose

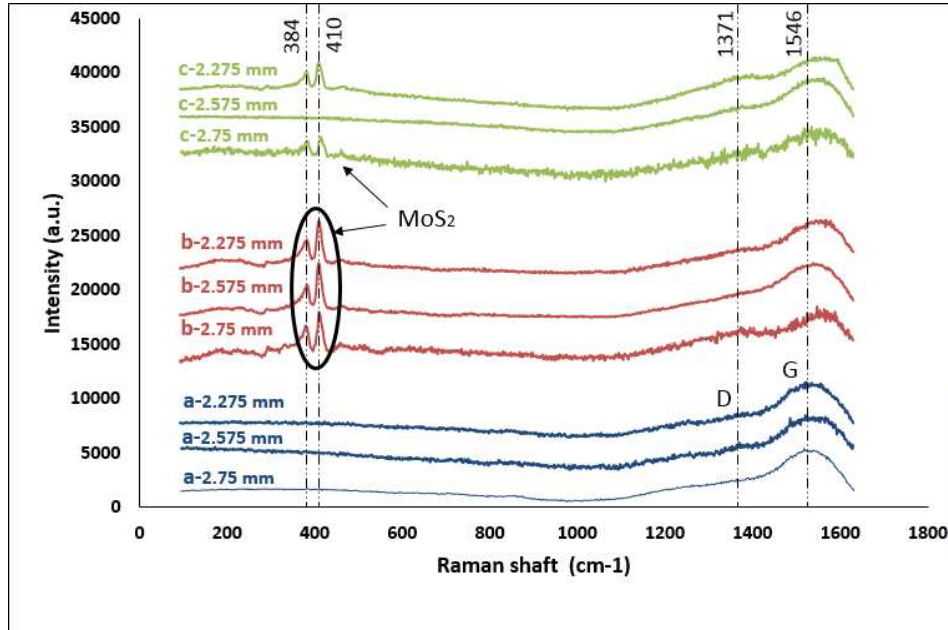


Fig. 19. Raman spectroscopy for the DLC inserts at 100 °C: (a) before the test, (b) inside wear track, (c) outside wear track

3.3.3. Understanding the Tribofilm Characteristics as a Function of Tappet Insert Clearance

Authors of this work have recently reported that tappet insert rotation is affected by changing the clearance of the tappet inserts [16]. In this work, the tribofilm derived on tappet inserts was also seen to be affected by changing the clearance of tappet insert. For example, from Fig. 13-f, inside the wear track (see region 8), the MnPO_4 with a thickness of 2.275 mm showed high levels of P, Zn and C and low levels of Fe as compared to the MnPO_4 tappet inserts with a thickness of 2.75 mm and 2.575 mm (i.e. region 3 and 6). That could explain the lowest wear obtained by the thinnest tappet inserts of 2.275 mm. The results were also supported by Raman, where MnPO_4 coating (with tappet thickness of 2.575 mm and 2.75 mm) was reported to be fully stripped off from the steel substrate. On the other hand, from Fig. 14-f (region 16), the DLC insert with a thickness of 2.275 mm, showed the highest levels of carbon with the lowest levels of iron as compared to the DLC tappet inserts with a thickness of 2.75 mm and 2.575 mm (i.e. region 11, 12 and 14). This also supports the wear results (i.e. the wear rate clearly reduced on the DLC insert with a thickness of 2.275 mm). It is important to note that detecting high levels of carbon with low levels of iron on the DLC insert obviously indicates that the DLC coating still exists and is not stripped off from the steel substrate. This in return helps to reduce wear on the surface.

The tribofilm derived on the camlobes was also reported to be varied when the camlobes rubbed against different tappet insert thicknesses. From Fig. 13-c and 13-e, the CI camlobe rubbing against the MnPO_4 insert with thicknesses of 2.575 mm and 2.275 mm, showed high levels of Mo, Zn, P and S in both regions (i.e. regions 5 and 7) as compared to the CI camlobe rubbing against MnPO_4 insert

with thickness of 2.75 mm (i.e. region 1 and 2). This reveals a heterogeneous distribution of the lubricant derived tribofilms on the camlobe surface when rubbing against the tappet inserts with the largest clearance. It should be mentioned that there was no evidence of wear on the cam nose and cam flank when CI camlobe rubbed against MnPO_4 with thickness of 2.275 mm. From Fig. 14-e, the CI camlobe rubbing against DLC insert with thickness of 2.275 mm, showed a smooth surface with low levels of carbon as compared to the CI camlobes rubbing against DLC inserts with a thickness of 2.75 mm and 2.575 mm (i.e. region 9, 10 and 13). This smooth surface was observed on both regions (i.e. the cam nose and the cam flank), with no evidence of wear on all regions of the camlobe. This could validate the lower friction and wear values obtained by CI camlobe rubbing against DLC insert with a thickness of 2.275 mm.

3.3.4. Understanding the Tribofilm Characteristics across Cam Profile

From this study, it was understood that the tribofilm derived across the camlobe (mainly at the seven specified locations) might vary due to the differences in contact pressure, load and lubricant entrainment velocity at the contact of the asperities. In particular, MoS_2 sheets were generally seen to be varied across the seven specified locations on the camlobe. From Fig. 16, MoS_2 peaks at the cam nose (for the CI camlobe rubbed against 2.75 mm MnPO_4) were not as pronounced as MoS_2 peaks detected on the cam flanks, suggesting that MoDTC-derived tribofilm was comparatively thin on the cam nose. That is why the cam nose was seen to have significant wear. Also, from Fig. 16, it can be seen that carbon peaks were only observed at the cam nose (for the CI camlobe rubbed against 2.75 mm MnPO_4) and the D and G peaks were not found in the spectrum taken from $+14^\circ$ and -14° positions inside the wear scar of the camlobe suggesting that the graphite flakes, which are normally present in the microstructure of the cast iron, did not participate in the formation of the transfer layer on these particular positions or the transfer layer from the counterpart (i.e. MnPO_4 insert) developed a thick deposition film on the cam flank (both sides), which in turn made the carbon/graphite flakes peaks from the cam flank undetectable. In the DLC/CI system, however, carbon peaks (i.e. distinct D and G peaks) in Fig. 18 were generally detected on both the cam nose and cam flank. This could be either due to the presence of a transfer layer (rich in carbon) from the DLC coating or the graphite flakes which are already presented in the microstructure of the camlobe before the test.

4. Conclusions

The main conclusions drawn from this study are:

- In both coatings, the tappet insert with smaller clearance resulted in higher friction and wear, suggesting a higher interaction between the cam and follower tribopair compared to a smaller tappet insert clearance.
- The tribofilm derived from camlobes and tappets was shown to vary as a function of tappet insert clearance and cam profile.
- Although less friction and wear was achieved using tappet inserts with a thickness of 2.275 mm, unstable running was observed. This possibly can cause an increase in the valvetrain wear for longer test durations.
- Tappet insert with a thickness of 2.575 mm (0.28 mm clearance) exhibited less friction and wear compared to 2.75 mm tappet insert thickness. Also, it showed lower vibrations, less noise and reduced wear for longer test durations, compared to 2.275 mm tappet insert thickness.
- Post-test DLC tappet inserts (with a thickness of 2.75 mm and 2.575 mm) indicate a polishing wear process while all MnPO₄ tappet inserts indicate an abrasive wear process.
- In terms of camlobes wear, the cam nose was considered to be a region of significant wear, especially toward the edges (i.e. sharp edges and worn tip). In addition, comparing the wear across the camlobe, the selected seven locations showed the highest wear while the wear of the other locations was not considerable.
- Tribochemical analysis showed that MoS₂ tribofilm was formed on non-ferrous surfaces (i.e. MnPO₄ and DLC surfaces).

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