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Wear of hydrogenated DLC in MoDTC-containing oils

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ABSTRACT

This paper describes a study of the effect on MoDTC-promoted a-C:H DLC wear of adding various surface-active additives used in engine lubricants, including ZDDP, an ashless EP additive, Ca detergents, dispersants, an OFM and a PAMA, to an MoDTC solution. Tribofilms formed on wear tracks on steel were analysed using SLIM, TEM, STEM-EDX, Raman spectroscopy and XPS. Relevant mechanisms by which these additives reduce the impact of MoDTC on DLC wear have also been suggested. DLC wear in PAO+Mo can be reduced by the presence of other surface-active additives in three ways. Firstly, asperity contact between DLC and steel can be mitigated by forming thick antiwear tribofilms. Secondly, other additives can increase the ratio of MoS_2:MoO_3, reducing the amount of wear-enhancing MoO_3 in the tribofilm. Thirdly, the amount of MoDTC tribofilm including MoO_3 can be reduced by the competitive adsorption of other surface-active additives. This study has practical implications for ways in which DLC surfaces can be protected by lubricant formulation.

1. Introduction

Diamond-like carbon (DLC) coatings on steel substrates have been widely applied in machine components to reduce friction; in crankcase engines components treated include rocker arms, valve lifters and piston rings. DLC is generally classified into four chemical types depending on the concentration of hydrogen and the carbon sp^3/sp^2 ratio [1] and these two characteristics strongly affect both the mechanical properties of DLCs and their surface reactivity with lubricant additives [2].

Another way to reduce friction in crankcase engines is to blend a friction modifier additive in the lubricant, and one important class of such additives are oil-soluble organomolybdenum compounds, in particular the molybdenum dialkyl-dithiocarbamates (MoDTCs). Research has shown that MoDTCs adsorb on rubbing surfaces and react under the severe conditions present at asperity contact to form tribofilms composed of molybdenum oxide (MoO_3) and molybdenum disulphide (MoS_2) [3]. MoS_2 has a layer-lattice structure with an inherently low shear strength, resulting in low friction coefficient and this can contribute significantly to increased engine efficiency [4]. Unfortunately, while MoDTCs can greatly reduce boundary friction, many studies have reported that MoDTC can cause high wear of DLC coatings, especially of the hydrogenated amorphous carbon (a-C:H) type. It is important to note that this high wear is seen only when DLC is rubbed against a steel counterface and is not observed when DLC is rubbed against DLC.

Although the precise mechanism of a-C:H DLC wear in MoDTC oil has not been unambiguously determined, several studies have suggested that this wear is related to the formation of MoO_3 from MoDTC in the DLC/steel tribocontact [2]. Masuko et al. [5] showed that DLC wear increased as surface $MoO_3/(MoO_3+MoS_2)$ ratio increased, while Shinyoshi et al. [6] proposed that MoO_3 on steel surfaces oxidized C–H and/or dangling bonds on DLC surfaces, resulting in a structural change of DLC from sp^3 to sp^2, *i.e.* graphitization. This graphitized carbon was then worn more easily by rubbing. This proposed mechanism has been supported by several other studies [7–9]. After carbon is worn from DLC, such carbon may transfer to the steel counterface and some studies suggest that this transferred carbon then reacts with MoDTC to form molybdenum carbide (MoC) species on steel surfaces [7,10,11]. Okubo et al. [11] proposed that this MoC species on steel wear tracks is much harder than a-C:H DLC, resulting in severe abrasive DLC wear. All these studies suggest that DLC wear in an MoDTC-containing oil may be considerably affected, directly or indirectly, by the extent to which MoO_3 is formed on the steel surface and interacts with the DLC counterface.

Some researchers have reported that the antiwear additive zinc dialkyldithiophosphate (ZDDP) can control the harmful effect of MoDTC on a-C:H DLC wear [11–14]. There are several possible origins of this response. ZDDP forms a thick phosphate tribofilm on rubbed surfaces and this should reduce asperity contact between DLC and steel, hence resulting in less DLC wear [11,13]. ZDDP also affects the MoDTC

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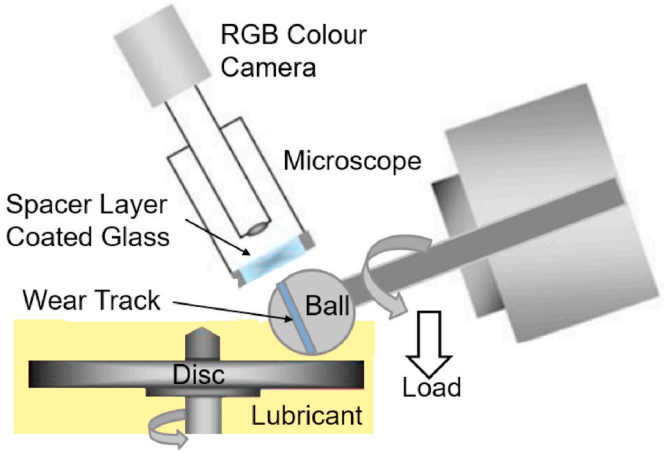


Fig. 1. A schematic illustration of the MTM ball-on-disc set-up.

decomposition reaction which may alleviate oxidation of Mo compounds to maximize formation of MoS_2 [13]. The availability of additional sulphur in ZDDP may also promote MoS_2 formation. However, the precise mechanism by which both the chemical properties of MoDTC tribofilms affect DLC wear and the way that ZDDP partially alleviates this wear are not fully proven. It should also be noted that the impact of other surface-active additives used in engine lubricants on MoDTC/DLC wear has not been studied to any significant extent.

Based on the above, this study aims to understand whether informed lubricant formulation can control the deleterious impact of MoDTC on a-C:H DLC wear and to determine the underlying mechanisms involved. In order to achieve this, the influence of various lubricant additives on wear of a DLC-coated component rubbed against a steel counterpart in MoDTC-containing oil has been investigated. Additives studied include a ZDDP, a phosphorus-based extreme pressure (EP) additive, Ca detergents, dispersants, an organic friction modifier (OFM) and a polymethacrylate (PAMA). The chemical properties of tribofilms generated were analysed by TEM, STEM-EDX, Raman spectroscopy and XPS. This study has practical implications for ways in which DLC surfaces can be protected by lubricant formulation.

2. Experimental details

2.1. MTM test rig

A mini traction machine (MTM) (PCS Instruments, UK) was employed to observe DLC wear and tribofilm growth during tests. The MTM is a ball on disc tribometer, the basics of which are shown schematically in Fig. 1. A ball is loaded against a disc which is immersed in the test lubricant. The ball and the disc are driven by separate electric motors, so that any slide-roll ratio can be reached. The load, rotational speeds and oil bath temperature are all computer-controlled by a program written by the user. Friction force is measured using a force transducer attached to the ball shaft and its value is recorded throughout the test. The MTM has an attachment to measure the tribofilm thickness using a spacer layer imaging method (SLIM) [15]. It is important to note that as well as ZDDP tribofilms, SLIM allows tribofilms formed from other lubricant additives, including as detergents and ashless antiwear additives, to be monitored [16,17].

2.2. Test lubricants

A single MoDTC (ADEKA Sakuralube) was studied at a concentration of 300 ppm of Mo in polyalphaolefin base oil (PAO). This is a slightly lower concentration than used in some modern engine oil formulations since MoDTC was not sufficiently soluble in PAO [18]. To ensure thin film and thus boundary lubrication conditions, this PAO (PAO 4) had a relatively low viscosity of 18.5 mm^2/s at 40 °C and 4.1 mm^2/s at 100 °C. A range of other additives commonly used in engine oils were blended individually with this MoDTC solution in PAO. These are all at their typically used concentrations except for the detergent that is often used at a somewhat higher concentration [18,19]. The oil formulations studied, together with their kinematic viscosities are listed in Table 1.

2.3. Test materials

AISI 52100 steel balls and a-C:H DLC-coated AISI 52100 discs were used. This hydrogenated DLC consists primarily of sp^2 with 30% sp^3, has a thickness of 2–4 μm and does not contain any metal dopants. Its commercial name is Dymon-iC, but it is denoted simply as DLC in this paper. The measured values of the surface roughness and hardness of the ball and disc are shown in Table 2. These are the average value of at least four measurements in different locations on each specimen, and of the range of measurements is shown. These values of surface roughness and hardness were measured using a Taylor Hobson Talysurf stylus profilometer and a Zwick Roell Z2.5 (ZHU 0.2) Vickers hardness tester, respectively.

Table 3 shows the chemical composition of the steel ball and DLC disc measured by a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS). An SEM, HITACHI S–3400 N, was used to capture high-resolution images of tribofilm surface topography and, for EDX, an Oxford X-ray System, INCA was used to analyse the chemical composition of materials. Since EDX is not a surface-sensitive method and analyses an approximate depth of penetration of about 1–1.5 μm, Cr from an interlayer beneath the DLC coating was detected on DLC discs. To assess the surface composition of DLC more accurately, the DLC specimens were also analysed using XPS, which generally has a penetration depth of less than about 10 nm. No metals were detected in the DLC surfaces by this XPS analyses.

Table 1
Test oil formulations.

Lubricant name	Additives concentration	Viscosity at 40 °C/100 °C, mm^2/s
PAO	–	18.5/4.1
PAO+Mo	Mo: 300 ppm	17.4/4.0
PAO+Mo+ZDDP(25) (ZDDP: secondary C6)	Mo: 300 ppm, P: 25 ppm	17.8/4.0
PAO+Mo+ZDDP(50) (ZDDP: secondary C6)	Mo: 300 ppm, P: 50 ppm	17.9/4.1
PAO+Mo+ZDDP(800) (ZDDP: secondary C6)	Mo: 300 ppm, P: 800 ppm	18.0/4.1
PAO+Mo+EP (EP: Alkylated triphenyl phosphorothionate)	Mo: 300 ppm, P: 800 ppm	18.1/4.2
PAO+Mo+Ca(OB) (Ca(OB): Overbased calcium salicylate)	Mo: 300 ppm, Ca: 1000 ppm, Base/Soap: 16.6/8.3 mmol/kg	18.3/4.1
PAO+Mo+Ca(Neu) (Ca(Neu): Neutral calcium salicylate)	Mo: 300 ppm, Ca: 1000 ppm, Base/Soap: 7.1/17.7 mmol/kg	18.7/4.2
PAO+Mo+Disp (Disp: Succinimide dispersant)	Mo: 300 ppm, N: 400 ppm	21.0/4.6
PAO+Mo+Disp(B) (Disp(B): Borated succinimide dispersant)	Mo: 300 ppm, N: 400 ppm, B: 400 ppm	19.4/4.3
PAO+Mo+OFM (OFM: Glycerol monooleate)	Mo: 300 ppm, OFM: 0.5 wt%	18.2/4.1
PAO+Mo+PAMA (PAMA: Comb type poly-alkylmethacrylate, 40 wt% solution in Gr. III base oil)	Mo: 300 ppm, PAMA: 4.0 wt%	18.4/4.4

Table 2
Measured properties of steel ball and DLC disc.

Material	Surface roughness Rq (nm)	Hardness (HV)
AISI 52100 steel ball	7 ± 2	830 ± 30
a-C:H DLC disc	11 ± 3	2450 ± 130

Table 3
Measured chemical composition of steel ball and DLC disc (atomic %).

Material	C	O	N	Fe	Cr	Mn	Si
AISI 52100 steel ball (SEM-EDX)	5.5	6.0		85.1	1.8	0.5	1.1
a-C:H DLC disc (SEM-EDX)	81.8				17.2	1.0	
a-C:H DLC disc (XPS)	93.7	5.0	1.3				

Table 4
MTM test conditions (boundary lubrication conditions).

Entrainment speed; $U = (U_{ball} + U_{disc})/2$	100 mm/s
Slide-roll-ratio; $SRR = 100*(U_{disc}–U_{ball})/U$	50%
Applied load (DLC on steel)	31 N; max. Hertz pressure = 0.95 GPa
Lubricant temperature	100 °C
Test duration	3 h
Initial lambda ratio	0.15

2.4. Test conditions and procedures

The MTM was used to investigate DLC wear and tribofilm formation under boundary lubrication at the test conditions listed in Table 4. By using a very low entrainment speed (mean velocity of the two surfaces with respect to the contact), MTM tests were controlled to an initial theoretical lambda ratio (ratio of EHD film thickness to composite surface roughness) of less than 0.2, thus providing boundary lubrication conditions. Load was set at a value that gave a maximum Hertz pressure of 0.95 GPa in the contact. After the tests, wear tracks on DLC discs were observed by an optical microscope, an optical white light interferometer (WLI, WYKO NT 9100) and Raman spectroscopy. The wear tracks on steel balls were observed by the optical microscope, transmission electron microscopy (TEM), scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDX), Raman spectroscopy, XPS and SEM-EDX. Most tribofilms formed on steel balls were quantified by SLIM, but tribofilms formed in PAO+Mo+OFM after 15, 30, 60 and 180 min were measured by a Talysurf profilometer since the tribofilm was too thick to measure by SLIM. For Talysurf measurements, the steel ball was removed from the MTM, and then gently rinsed with toluene to remove supernatant oil. After stylus profilometer measurement, the ball was returned to the rig, and the rubbing test restarted. The same lubricant sample remained in the test chamber for the whole 3 h test duration. All MTM tests were conducted twice to verify repeatability.

2.5. Surface analysis

TEM, STEM-EDX, XPS and SEM-EDX were carried out using the same methodologies as our previous study [20]. Spot size for XPS analysis was 150 μm. Before measurements, the specimens were gently rinsed by toluene to remove supernatant oil. This did not remove any measurable tribofilm. Raman spectroscopy was performed to examine the chemical composition of DLC discs and tribofilms on steels. This used a WITec Confocal Raman spectrometer alpha 300 equipped with multiple objectives and a charge-coupled device detector. A laser with 532 nm wavelength was employed and Raman spectra was collected from a 20 μm × 20 μm area. The D band and G band peaks attributed to carbon were fitted with Lorentzians and the area ratio of D peak to G peak (I_D/I_G) was estimated.

3. Results

3.1. DLC disc wear

Worn DLC disc surfaces after MTM tests were observed by optical micrography and WLI as shown in Fig. 2. It is important to note that the

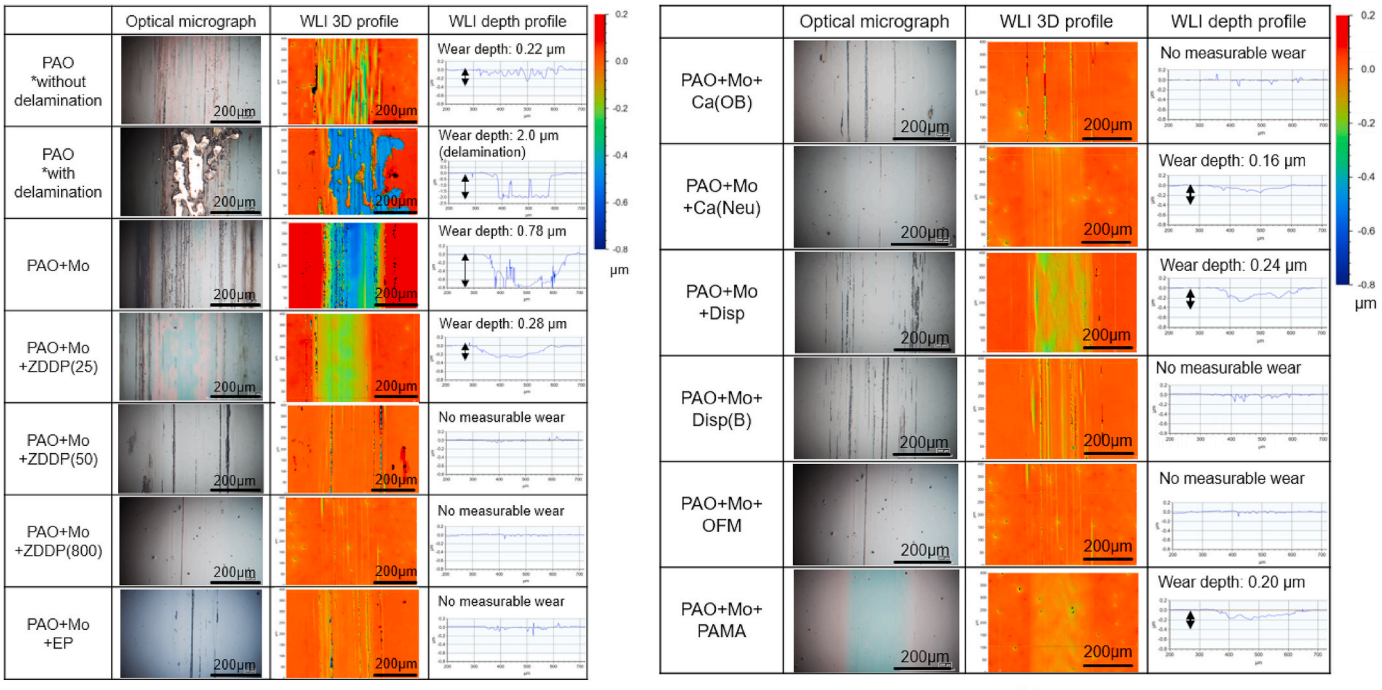


Fig. 2. Optical micrographs, WLI 3D profiles and depth profiles of wear tracks on DLC discs (Note that the colour scale is not applicable to the image with delamination obtained from PAO rubbing since its depth scale is much larger than others.).

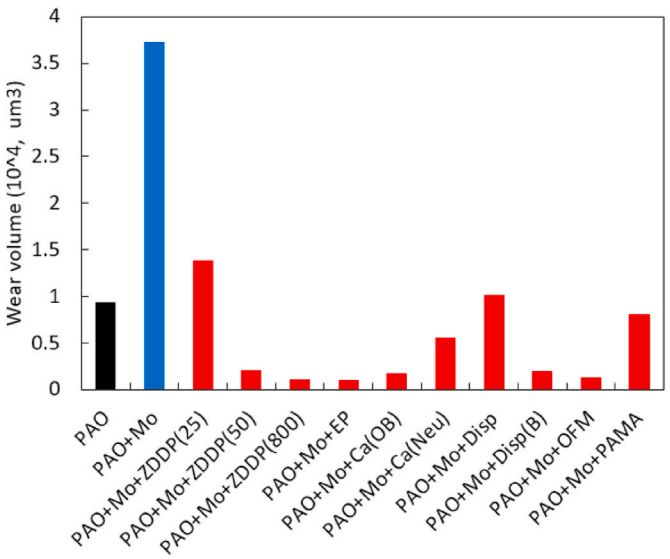


Fig. 3. Wear volume of DLC wear tracks measured using WLI (area: 400 μm × 600 μm in Fig. 2).

colour scale of WLI 3D profiles and the depth scale of WLI depth profiles correspond to -0.8 μm to 0.2 μm for most images, but that the scale in images obtained from PAO with delamination are -2.5 μm to1.0 μm. The wear volumes of DLC discs over the areas shown in Fig. 2 (400 μm × 600 μm) are summarized in Fig. 3. The wear volume from tests in PAO alone was obtained from the region without DLC delamination.

Rubbing the steel ball against DLC disc in PAO alone, without any additives, resulted in delamination of the DLC coating over approximately half of the track, with the remainder showing 0.22 μm depth and 0.9×10^3 μm^3 volume of predominantly abrasive wear. The worn surface was rougher than from other tests. By contrast, PAO+Mo oil generated a high level of quite even wear of 0.78 μm depth over the whole rubbed track, with 3.7×10^3 μm^3 wear volume. The addition of all surface-active additives alleviated this DLC wear to varying extents. ZDDP(25), Ca(Neu), Disp and PAMA partially reduced wear, with maximum depths of 0.28 μm, 0.16 μm, 0.24 μm and 0.20 μm, respectively, corresponding to less than 1.5×10^3 μm^3 of wear volume. ZDDP (50), ZDDP(800), EP, Ca(OB), Disp(B) and OFM gave less than 0.2×10^3 μm^3 of wear volume.

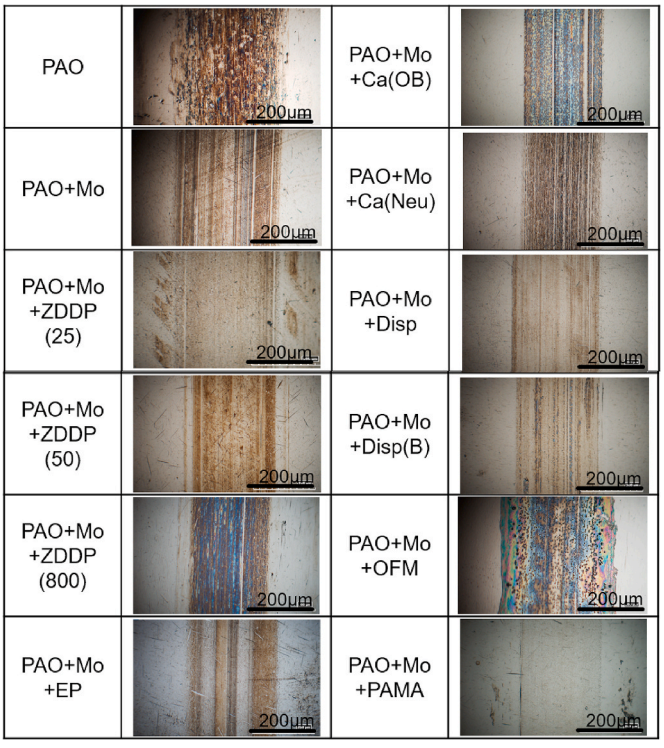


Fig. 4. Optical micrographs of the wear tracks on the steel balls after 3 h rubbing tests.

3.2. Tribofilm formation on steel balls

The wear tracks on the steel balls were observed using an optical microscope and in SLIM images in order to relate any tribofilms present to DLC wear. The film rubbed in PAO+Mo+OFM was quantified by stylus profilometry since it was too thick to measure using SLIM. Fig. 4 and Fig. 5 shows the optical micrographs and the evolution of film thickness during the tests. PAO alone formed dark coloured films on the wear track of 26 nm thickness at the end of the 3 h test. Given wear on the DLC disc and no additives in the lubricant, these dark coloured film may be attributed to carbon transferred from the DLC disc to the steel ball. PAO+Mo formed a lighter coloured film of 19 nm thickness. This film may consist of MoDTC tribofilm and/or transferred carbon from the DLC disc, since the latter experienced high wear in this oil. The addition of ZDDP(800), Ca(OB) and OFM resulted in thicker tribofilms than just PAO+Mo, respectively 39 nm, 40 nm and 410 nm. Interestingly,

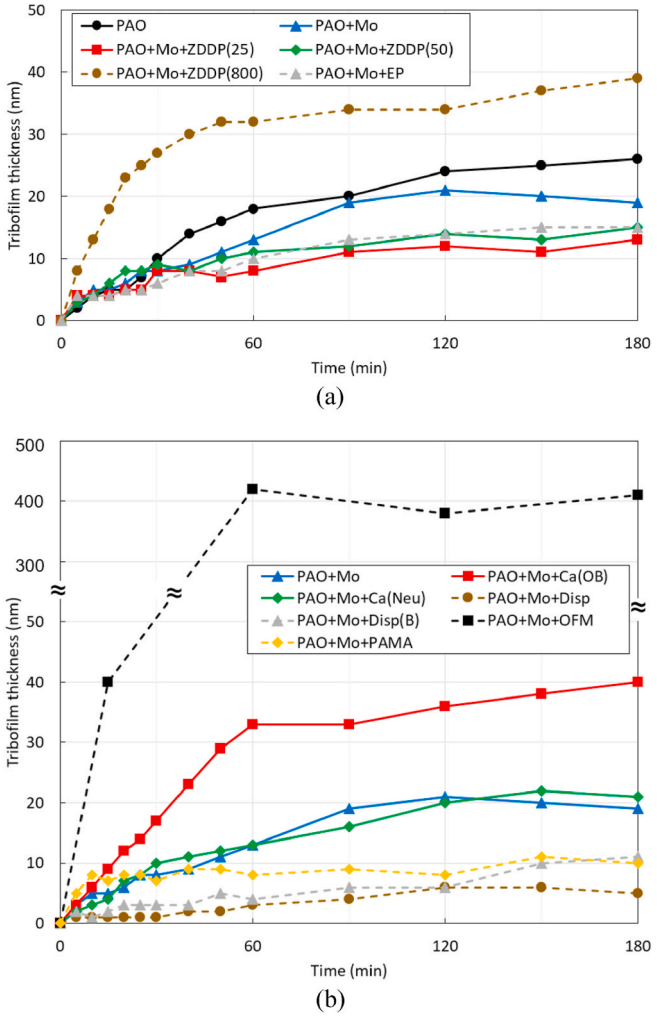


Fig. 5. The evolution of tribofilm thickness on the steel balls during the tests measured by using SLIM and, for PAO+Mo+OFM, using a stylus profilometer.

PAO+Mo+OFM formed a much thicker tribofilm than the other additives, covering the whole wear track. The addition of Ca(Neu) formed a tribofilm of *ca.* 20 nm, similar in thickness to that formed in PAO+Mo, whereas the oils with ZDDP(25), ZDDP(50), EP, Disp, Disp(B) and PAMA formed thinner tribofilms, approximately 10 nm, than PAO+Mo. These results suggest that films on the steel balls are composed of one or both of transferred carbon and tribofilms produced by adsorption or reaction of the various lubricant additives.

3.3. Friction behaviour

In order to understand the effect of friction on DLC wear, the evolution of friction coefficient during the MTM tests was measured as shown in Fig. 6. It should be noted that the sudden jumps obtained with all blends except PAO+Mo in the recorded friction coefficient traces in this figure are artefacts of the measurement method since they occur just after motion is paused for capture of a SLIM image.

For PAO alone, friction coefficient decreased from 0.08 to 0.07 at the beginning of test, and then increased after 10 min rubbing to reach 0.09–0.11 at the end of the test. Friction also showed relatively high fluctuations. The reduction of friction coefficient during the tests with a-C:H DLC/steel tribopair has been reported in dry condition [21,22] and in PAO alone [23], and in the latter the authors suggested that lowered friction coefficient resulted from carbon films transferred from DLC to a steel wear track. Given the apparent carbon films on the steel ball in Figs. 4 and 5, the reduction of friction coefficient in the first 10 min may result from this transferred carbon films as reported. After this, the DLC coating probably started to be severely delaminated with an increase of surface roughness, resulting in high friction coefficient [24,25].

PAO+Mo showed lower friction coefficient during the test than PAO alone, reaching 0.06 after 5 min, and then increased to 0.08. Note that no sudden friction jumps were observed for this blend since the test was carried out without halting the rig for SLIM measurement. The addition of ZDDP(800), Ca(OB), Ca(Neu), Disp to an MoDTC solution gave lower friction coefficient than PAO+Mo, that slightly increased towards the end of the tests to reach 0.07. By contrast, friction coefficient in the oils with ZDDP(25), ZDDP(50), EP, Disp(B), OFM and PAMA remained at a low level, 0.03–0.06 throughout the 3 h tests.

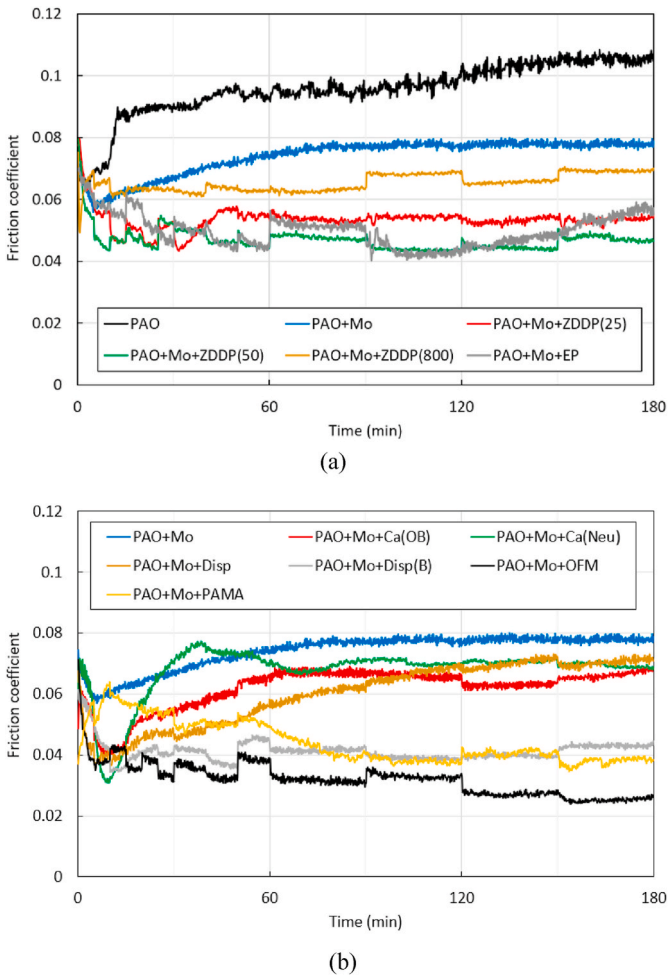


Fig. 6. The evolution of friction coefficient during the tests.

3.4. Elemental distribution of tribofilm on steel

The tribofilms formed on the steel balls rubbed against DLC in PAO+Mo at the end of 3 h tests were analysed using TEM and STEM-EDX in order to determine the morphology and elemental distribution in the film. Fig. 7 shows a TEM image, a STEM image and a STEM-EDX line profile along the yellow line in the STEM image. The TEM image shows tribofilm thickness is approximately 20 nm, which agrees with the thickness value measured by SLIM in Fig. 6. The EDX line profile shows that, while the tribofilm is mainly composed of Mo and S, smaller amount of C and O are present in all regions of the tribofilm. This result show that carbon is present within the MoDTC tribofilm rather than just being attached to the outermost surface.

3.5. Raman spectra of steel wear tracks

Worn surfaces on steel balls and the surface of a fresh DLC disc were analysed using Raman spectroscopy in order to examine the structure of transferred carbon on wear tracks on the steel ball. Abrasive type wear, high volume wear and mild volume wear were observed on DLC discs rubbed in PAO, PAO+Mo, and PAO+Mo+ZDDP(25) respectively. Also no measurable wear was observed in the oils with ZDDP(50) and ZDDP (800). Therefore, the films formed on steel balls rubbed in these 5 oils were analysed. Fig. 8 shows the resulting Raman spectra normalized to the maximum peak in spectral range 800 - 2200 cm^{-1}. The D and G peaks that are characteristic of carbon at 1300 - 1380 cm^{-1} and 1570 - 1600 cm^{-1} respectively are evident in the PAO, PAO+Mo and PAO+Mo+ZDDP(25) spectra, without any significant peak shifts. The D peak corresponds to disordered carbon or defective graphitic structure whereas the G peak corresponds to the graphitic layer and tangential vibration of the carbon atom [1]. An increase of ratio of these peaks, the I_D/I_G ratio, represents an increase of sp^2 structure of carbon, *i.e.* graphitization.

On the wear track rubbed in PAO alone, a similar I_D/I_G ratio of 1.10 compared to a fresh DLC disc ratio of 1.14, was observed. Given the optical image in Fig. 5, this suggests that carbon with a similar structure to fresh DLC disc was transferred to the steel ball rubbed in PAO. Understanding of I_D/I_G ratio of carbon film on steel transferred from a-C:H DLC is still controversial; Erdemir et al. [21] and Rabbani [22] found that carbon transferred from DLC to steel in dry contact had higher I_D/I_G than carbon in fresh DLC, suggesting that transferred carbon was graphitized. By contrast, Haque et al. [26] showed that an equivalent I_D/I_G ratio to DLC was observed in carbon film transferred onto a steel surface from DLC rubbed in PAO. In the current study, transferred carbon rubbed in PAO alone gave no significant change in I_D/I_G, as reported by Haque et al. [26]. Possibly, rubbing conditions and initial a-C:H DLC properties affect the properties of transferred carbon films on steel surfaces.

The addition of Mo and Mo+ZDDP(25) to PAO show lower I_D/I_G ratios (0.97 and 1.01 respectively) than that of a fresh DLC disc (1.14). This trend was observed in a previous study of a steel/a-C:H DLC tribopair in an MoDTC oil by Okubo et al. [11], and the authors suggested that a reduction of I_D/I_G ratio resulted from the formation of MoC species, which has a low I_D/I_G ratio, 0.45. Based on this suggestion, the low I_D/I_G ratio in this study may be tentatively attributed to MoC species on

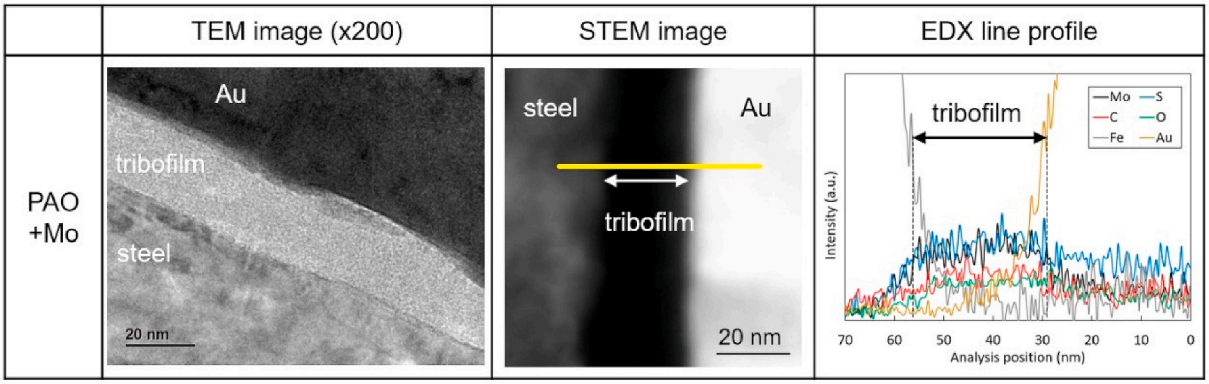


Fig. 7. TEM image, STEM-EDX image and element distribution of tribofilm on the steel ball rubbed in PAO+Mo after a 3 h test.

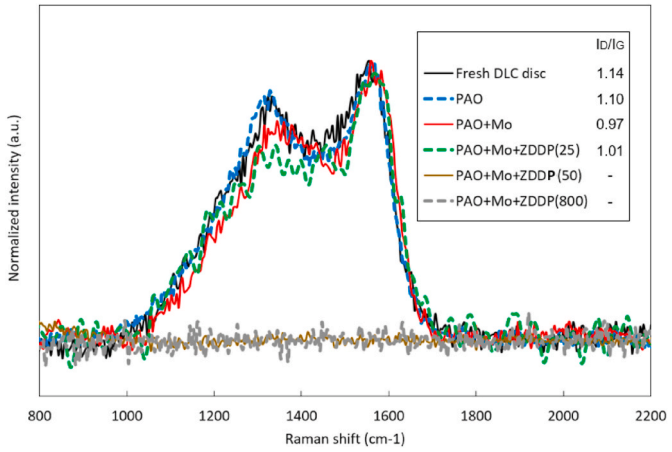


Fig. 8. Raman spectra from the wear tracks on the steel balls after 3 h tests and from the fresh DLC disc surface.

the steel balls rubbed in PAO+Mo and PAO+Mo+ZDDP(25). By comparison, the wear track rubbed in PAO+Mo+ZDDP(50) and PAO+Mo+ZDDP(800) does not give D and G peaks. This suggests that no carbon was transferred to the steel balls from the DLC discs and is consistent with the negligible DLC wear rubbed in this oil, as shown in Fig. 2.

3.6. XPS analysis of steel wear tracks

To understand the chemical environment of carbon and molybdenum in the tribofilms formed on the steel counterfaces, the wear tracks on the balls were analysed using XPS. C 1s and Mo 3d XPS spectra are shown in Fig. 9 and Fig. 10, respectively. All peaks were normalized by the highest peak. In Fig. 9, the C 1s spectra consist of the peaks of C–C at 284.8 eV, C–O at 286.6 ± 0.2 eV, C═O at 288.0 ± 0.2 eV and carbide at 283.1 ± 0.2 eV [27]. The peak area ratio of carbide/C–C is included in the figure. The wear tracks rubbed in PAO+Mo and PAO+Mo+ZDDP (25) show relatively higher intensity carbide peaks than the others, with carbide/C–C ratio of 0.068 and 0.048 respectively. By comparison, a quite small carbide peak is observed on the wear track rubbed in PAO. Thus, given the results of Raman spectra in Fig. 8, the carbide peaks

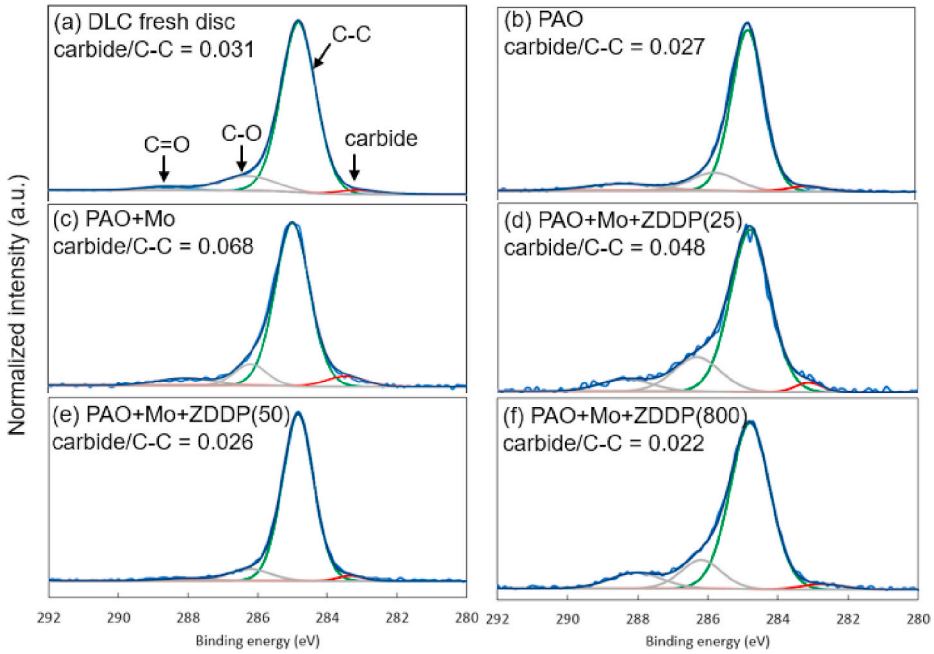


Fig. 9. C 1s XPS spectra of tribofilms on the wear tracks on the steel balls. (a) DLC fresh disc, (b) PAO, (c) PAO+Mo, (d) PAO+Mo+ZDDP(25), (e) PAO+Mo+ZDDP (50), (f) PAO+Mo+ZDDP(800).

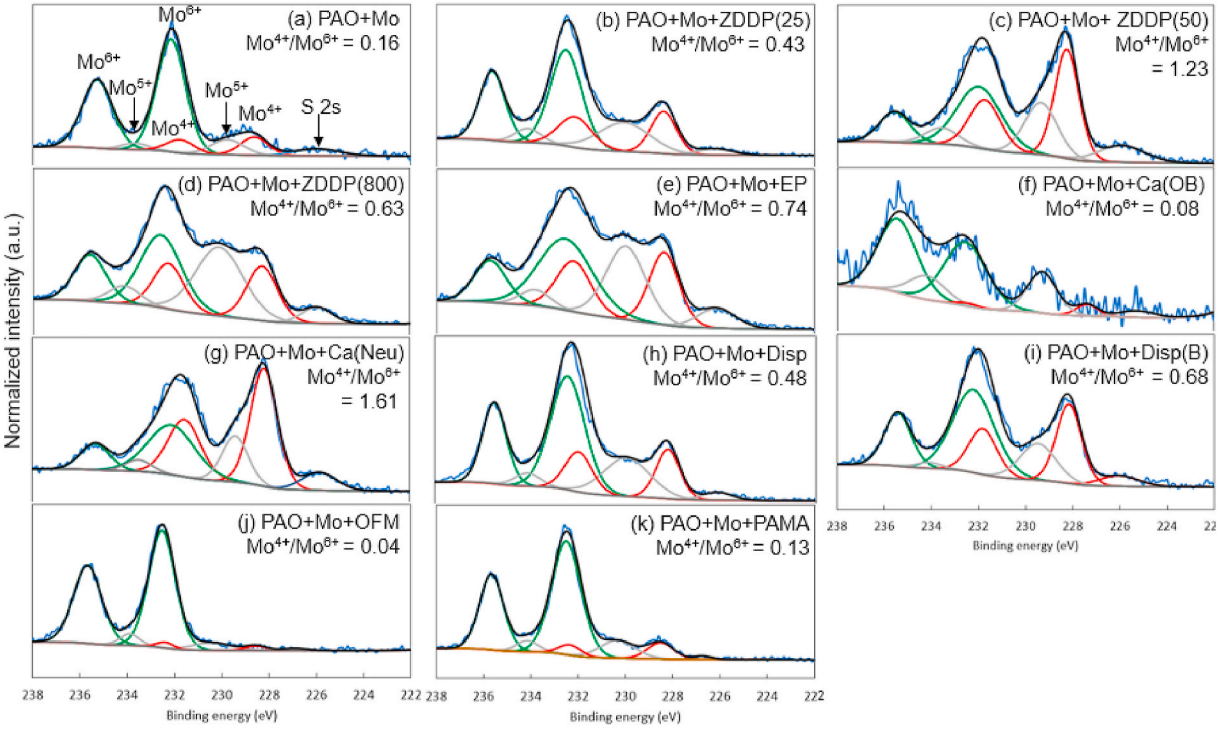


Fig. 10. Mo 3d XPS spectra of tribofilms on the wear tracks on the steel balls. (a) PAO, (b) PAO+Mo+ZDDP(25), (c) PAO+Mo+ZDDP(50), (d) PAO+Mo+ZDDP (800), (e) PAO+Mo+EP, (f) PAO+Mo+Ca(OB), (g) PAO+Mo+Ca(Neu), (h) PAO+Mo+Disp, (i) PAO+Mo+Disp(B), (j) PAO+Mo+OFM, (k) PAO+Mo+PAMA.

obtained from PAO+Mo and PAO+Mo+ZDDP(25) may be attributed to mainly Mo–C species, not Fe–C species.

As reported in many previous XPS analyses of MoDTC-derived tribofilms on steel rubbed against DLC [5,7,11,27], the Mo 3d spectra contain mainly the peaks of Mo^{4+} at 228.7 ± 0.4 eV and 232.2 ± 0.4 eV, Mo^{5+} at 230.0 ± 0.3 eV and 233.9 ± 0.3 eV, Mo^{6+} at 232.2 ± 0.2 eV and 235.4 ± 0.2 eV, and S 2s at 225.9 ± 0.3 eV Mo^0 and Mo^{2+}, attributed to Mo metal and Mo–C species, may exist in Mo 3d spectra, but unfortunately these peaks are difficult to distinguish from Mo^{4+}, Mo^{5+} and Mo^{6+} because of peak overlap and low intensity. Thus, Mo 3d spectra in Fig. 10 were fitted with, Mo^{4+}, Mo^{5+} and Mo^{6+}, attributed to MoS_2 and/or MoO_2, MoDTC, and MoO_3, respectively. Since MoS_2/MoO_3 ratio is believed to be an important property of MoDTC tribofilms [5], the peak area ratios of Mo^{4+}/Mo^{6+} are shown in Fig. 10. PAO+Mo gave a low Mo^{4+}/Mo^{6} of 0.16, which is similar to the values obtained from PAO+Mo+Ca(OB), PAO+Mo+OFM and PAO+Mo+PAMA. The addition of ZDDP(25) and Disp slightly increased Mo^{4+}/Mo^{6+} to 0.43 and 0.48 respectively. By comparison, the addition of ZDDP(50), ZDDP (800), EP, Ca(Neu) and Disp(B) increased Mo^{4+}/Mo^{6+} to over 0.6. This suggests that the addition of some additives changes the chemical properties of MoDTC tribofilms and increases Mo^{4+}/Mo^{6+}, while others do not.

4. Discussion

It is evident from the above results that, while wear of a-C:H DLC against a steel contact is promoted by MoDTC, such wear is mitigated to a greater or lesser extent by the addition of several commonly-used, surface-active engine oil additives to the MoDTC/base oil solution. Previous studies have suggested that addition of ZDDP to an MoDTC-containing oil forms a thick antiwear tribofilm, resulting in the prevention of asperity contact of DLC and steel surfaces and thus the reduction of DLC wear [11–14]. The results in this study provide some support for this suggestion as discussed below. However, based on the mechanism of DLC wear against steel, three possible reasons why DLC wear was reduced by the addition of surface-active additives to PAO+Mo can be suggested;

(i) formation of thick antiwear tribofilm
(ii) increase of MoS_2/MoO_3 ratio in the MoDTC tribofilm
(iii) reduction of MoDTC tribofilm formation

Each of these possibilities is discussed below with respect to the tribofilms observed with the various surface-active additives studied.

4.1. Formation of thick antiwear tribofilm

As reported, one of the most effective ways to protect DLC surfaces from wear is to form thick antiwear tribofilms to alleviate asperity contact between DLC and steel. In this study, as shown in Fig. 5, the addition of ZDDP(800), Ca(OB) and OFM formed thicker tribofilms than other additives. These also resulted in very little DLC wear. It is very well known that ZDDP forms surface-protective phosphate tribofilms on steel surfaces [28]. In this study, 800 ppm P concentration of ZDDP formed 39 nm tribofilm at the end of the test. This antiwear performance of ZDDP tribofilm on a-C:H DLC/steel tribopair agrees with previous studies [11–14].

Generally, overbased Ca detergents, that contain colloidal $CaCO_3$, form thick $CaCO_3$ tribofilms on rubbed surfaces, and these provide antiwear performance [29]. In the current study, 40 nm of tribofilm was formed from PAO+Mo+Ca(OB) at the end of the test; a similar thickness to that formed by PAO+Mo+ZDDP(800). Because it contains far less colloidal $CaCO_3$, Ca(Neu) forms a thinner tribofilm and gives more wear in PAO with MoDTC. By contrast, OFMs form physically and/or chemically adsorbed films, and do not generally form thick tribofilm. In this study, however, very thick tribofilms, of approximately 410 nm thickness were observed on the steel ball surfaces at the end of the test. In order to understand the composition of the tribofilm formed in PAO+Mo+OFM, this was analysed using SEM-EDX as summarized in Fig. 11, where it is compared with the tribofilm formed by PAO+Mo. Tribofilm formed in PAO+Mo+OFM was mainly composed of carbon with a higher carbon content than that formed in PAO+Mo, together

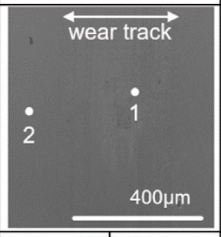
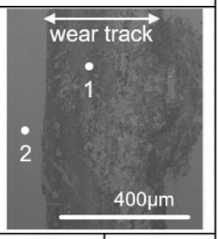
		PAO+Mo		PAO+Mo+OFM	
SEM image x150					
		point 1	point 2	point 1	point 2
chemical composition (atomic%)	Mo	2.1	None	1.0	None
	C	12.8	6.9	27.4	7.9
	O	10.4	8.9	16.5	9.4
	Fe	71.8	81.4	53.4	79.4
	Cr	1.7	1.3	1.1	1.9
	Mn	0.6	0.5	0.3	0.7
	Si	0.6	1.0	0.5	0.7

Fig. 11. Chemical composition of tribofilms formed in PAO+Mo and PAO+Mo+OFM using SEM-EDX.

with small amount of molybdenum. Given that there was no significant DLC wear in PAO+Mo+OFM in Fig. 2, this carbon was not transferred from the DLC disc. Thus, this carbon was formed from the lubricant component, probably mainly from OFM. A previous study showed that carbon-based tribofilms formed from PAO gave surface protection performance [30], thus, this thick carbon-containing film may protect surface in a similar fashion to the protection afforded by the tribofilms formed from the oils with ZDDP(800) and Ca(OB).

Although the mechanism of a-C:H DLC wear has not been clearly understood, Okubo et al. [11] suggested that MoC compounds formed through tribochemical reaction on the steel counterface have significantly higher hardness, *ca.* 25 GPa, than a-C:H DLC, *ca.* 10 GPa, and that this hard MoC causes severe abrasive wear of DLC surface. This severe abrasive wear may be reduced by forming thick tribofilms even if hard MoC compounds are also formed on steel surfaces. The presence of carbon and Mo–C species in tribofilms rubbed in PAO+Mo and PAO+Mo+Zn(25) was based on the analyses using STEM-EDX, Raman and XPS and little evidence of the presence of MoC species in tribofilms was observed. Alternatively, it has been proposed that the high wear of DLC promoted by MoDTC may originate from graphitization of the DLC that is easily abraded by the steel counterface [6–9]. In this case, the formation of a tribofilm on the steel counterface may limit this abrasion, or render the steel surface chemically inactive so that it does not, in combination with MoDTC, promote the graphitization.

4.2. Increase of MoS_2:MoO_3 ratio

Many of the additives studied reduced the DLC wear promoted by MoDTC but did not form thick tribofilms. This suggests that as well as protection by thick tribofilms, there may be other mechanisms by which additives can mitigate the severe DLC wear that occurs with MoDTC. Since MoO_3 is believed to be a culprit for promoting DLC wear by oxidizing or abrading DLC surfaces [5–9], reduction of the MoO_3 in MoDTC tribofilms is a possible way to reduce DLC wear. Grossiord et al. [3] and De Barros'Bouchet et al. [31] proposed a tribochemical reaction mechanism of formation of MoO_3 from MoDTC. They suggested that after adsorption, MoDTC is tribochemically decomposed to form MoS_2, $MoS_{2-x}O_x$ and MoO_x. While these compounds may be oxidized to form MoO_3, the latter can react with sulphur to form MoS_2. It is well studied that co-existent ZDDP provides sulphur to Mo compounds, promoting MoS_2 formation [31–33]. Thus, the prevention of oxidation and/or the promotion of sulphurization are both ways to increase the ratio of MoS_2:MoO_3 ratio in MoDTC tribofilms and thereby reduce DLC wear. In this study, while Mo^{4+} can in principle be attributed to both MoS_2 and MoO_2, MoS_2 is probably the main component as most studies discuss [5–7,31] since a higher intensity of S was observed than O in the MoDTC tribofilm in Fig. 5. Thus, the ratio of Mo^{4+} to Mo^{6+} can be regarded as representing the ratio of MoS_2 to MoO_3.

As shown in Fig. 10, the addition of ZDDP(50), EP, Ca(Neu) and Disp (B) all gave much higher Mo^{4+} to Mo^{6+}, and thus higher MoS_2 to MoO_3 ratios, than PAO+Mo and this correlates with their giving low DLC wear. ZDDP(50) and EP both contain sulphur, so they may be increasing the MoS_2:MoO_3 ratio by providing sulphur, but they are both also peroxide decomposers and so may also, or alternatively, be preventing oxidation of MoDTC breakdown products to MoO_3 [28]. From Figs. 3 and 10, it appears that the 25 ppm level of ZDDP in PAO+Mo+Zn(25) was too low to raise the MoS_2:MoO_3 ratio to a high enough value to prevent high DLC wear. Ca(Neu) and Disp(B) also both reduce DLC wear and raise the MoS_2:MoO_3 ratio but they do not contain any sulphur. In this case therefore, the likely mechanism by which they influence the MoS_2:MoO_3 ratio is by inhibiting oxidation to MoO_3. It has been reported that salicylates and borated additives can both prevent the oxidation of Mo compounds [34–37].

Although higher MoS_2:MoO_3 usually corresponded to lower friction coefficient, a direct correlation between friction behaviour and MoS_2:MoO_3, as reported in a previous study [5,26]. was not confirmed. This suggests that other factors that influence friction behaviour may also be active, such as a low friction carbon film transferred from DLC to steel [26].

4.3. Reduction of MoDTC tribofilm formation

Although the influence of other additives on reducing DLC wear in the presence of MoDTC can be explained by the above two mechanisms, a third likely mechanism should also be considered. This is simply competitive adsorption of these other additives on surfaces to suppress the rate at which MoDTC reacts on steel, thereby reducing its harmful effect on DLC wear. In this study, all the additives tested are capable of adsorbing on steel surfaces and may act in this fashion to some extent. Clearly, this might be beneficial in terms of reducing wear, but would be undesirable if MoDTC tribofilm formation, and thus its friction reduction was completely suppressed. It is possible that the modest reduction in DLC wear provided by PAMA results from inhibition of MoDTC reaction via adsorption since thick film and increase MoS_2:MoO_3 ratio were not observed. However, it is also possible that the PAMA adsorbs on the rolling/sliding ball on disc surfaces to form a thick separating film that prevents some asperity interaction and so limits wear via the mechanism outlined in section 4.3 [38]. PAMA has been shown to form thick viscous surface films that increase separation in dynamic conditions, but do not withstand static conditions, so boundary films generated from PAMA in rolling-sliding contacts might not be observed using SLIM.

This study shows that the addition of several types of surface-active additive can reduce DLC wear in an MoDTC oil to a greater or lesser extent, and indicates three possible mechanisms by which this may occur. Fig. 12 plots the wear volume against Mo^{4+}/Mo^{6+} ratio and, based on tribofilm thickness measurements and Raman analyses, maps the regions over which these mechanisms may be active. Thick tribofilms appear to suppress DLC wear very effectively without the need for increasing MoS_2:MoO_3 ratio, while increasing MoS_2:MoO_3 ratio without forming a thick tribofilm is also quite effective at suppressing wear. In practice, many surface-active additives exist together with MoDTC in engine lubricants and the extent to which these additives in combination suppress DLC wear in the presence of MoDTC remains to be determined. Also, modern requirements of high fuel economy and low emissions are resulting in considerable changes in the design of engine oils, as well, in

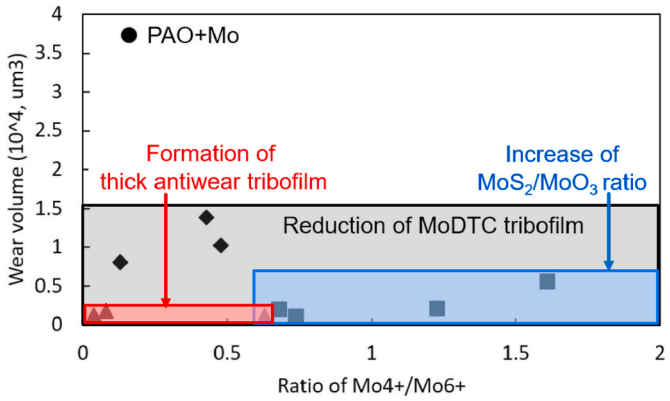


Fig. 12. The relationship between Mo^{4+}/Mo^{6+} and wear volume of DLC disc.

some cases, increasing Mo-base friction modifier concentrations, so it is important to understand and take account of the impact of other additives on DLC wear in the presence of MoDTC.

5. Conclusions

This study has used an MTM ball on disc tribometer, combined with SLIM and surface analysis based on TEM, STEM-EDX, Raman and XPS in order to understand the relevant mechanisms by which the addition of other surface-active additives improves a-C:H DLC wear of DLC against a steel contact rubbed in an MoDTC solution. The addition of all these additives reduces DLC wear to some extent, and in such a fashion that there appears to be more than one wear-reducing mechanisms. Key conclusions are as follows.

- While PAO+Mo resulted in severe wear of DLC surface, the addition of surface-active additives reduced this DLC wear. The addition of ZDDP (50), ZDDP(800), EP, Ca(OB), Ca(Neu), Disp(B) and OFM reduced DLC wear much more than Zn(25), Disp and PAMA.

- ZDDP(800), Ca(OB) and OFM, which gave negligible DLC wear, all formed thick tribofilms during rubbing. Despite not forming thick tribofilms, oils with ZDDP(50), EP, Ca(Neu) and Disp(B) also resulted in very little DLC wear.

- STEM-EDX analysis showed that the tribofilms fromed on the steel ball in PAO+Mo consisted of Mo, S, O and C. This carbon was distributed throughout the tribofilm, and it is likely to attribute to carbon transferred from DLC disc.

- I_D/I_G ratios of carbon transferred from DLC discs to on steel balls were analysed using Raman spectroscopy. PAO+Mo and PAO+Mo+ZDDP(25) gave smaller I_D/I_G than a fresh DLC disc, suggesting that transferred carbon existed as a different chemical structure which has low I_D/I_G. By comparison, measurable D peak and G peak were not observed on steel balls rubbed in PAO+Mo+ZDDP(50) and ZDDP(800), suggesting no transferred carbons on wear tracks.

- Mo^{4+}/Mo^{6+} measured using XPS was increased by the addition of most of the surface-active additives to PAO+Mo, with the exception of OFM and PAMA. The prevention of oxidation of Mo compounds may reduce DLC wear even when thick antiwear tribofilms are not formed on steel surfaces, especially in the oils with ZDDP(50), EP, Ca(Neu) and Disp(B).

- DLC wear in PAO+Mo can be reduced by the presence of other surface-active additives in three ways. Firstly, asperity contact between DLC and steel can be mitigated by forming thick antiwear tribofilms. Secondly, other additives can increase the ratio of MoS_2:MoO_3, reducing the amount of wear-enhancing MoO_3 in the tribofilm. Thirdly, the amount of MoDTC tribofilm including MoO_3 can be reduced by the competitive adsorption of other surface-active additives.

-By indicated the ways that the other additives commonly used in lubricants can control the severe wear of DLC caused by MoDTC, this study contributes to our ability to formulate advanced low friction, low wear lubricants.

CRediT authorship contribution statement

Mao Ueda: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization, Project administration. **Amir Kadiric:** Supervision, Writing – review & editing. **Hugh Spikes:** Supervision, Writing – review & editing.

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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