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In-Situ Reflection-XANES study of ZDDP and MoDTC lubricant films formed on Steel and Diamond Like Carbon (DLC) surfaces

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Abstract

Chemical characterisation of boundary lubricated interfaces is essential for developing mechanistic models that describe lubricant additive interactions with the surface and their effect on tribological performance. In this study the potential for using the synchrotron-based reflection mode X-ray absorption spectroscopy (XAS) technique for *in-situ* chemical characterisation of lubricant films has been studied. Thermal films formed from Zinc Dialkyl Dithio Phosphate (ZDDP) and Molybdenum Dialkyl Dithio Carbamate (MoDTC) lubricant additives have been formed and analysed *in-situ* using the X-ray Absorption Near Edge Structure (XANES) spectroscopy technique. The surface sensitivity of this approach was improved by doing the analysis in reflection mode, enabling analysis of only top layer (up to around 10 nm) of the solid surface. In addition, *in-lubro* analysis of pre-formed tribofilms from the same additives was done using non-vacuum conditions. The results are discussed in conjunction with XANES and X-ray Photoelectron Spectroscopy (XPS) analysis of similar additives published in the literature. The results obtained are consistent with the existing ZDDP and MoDTC literature and provide some new insight into intermediate species not reported before. The advantages and disadvantages of the developed XANES methodology for *in-situ* surface chemical analysis of lubricated conditions are discussed.

Keywords: Lubricant additives; Tribofilm; XANES; MoDTC; ZDDP

1. Introduction

Effective lubrication is essential for many mechanical systems, ranging from reliable functioning of human artificial joint implants to energy efficiency of internal combustion engines and reliable functioning of offshore wind turbine gearboxes. Ultimately, lubrication has a significant impact on a number of industries such as healthcare technologies, transport, energy production and industrial manufacturing [1]. The lubrication process is based on the ability to separate two moving surfaces either by a fluid layer (hydrodynamic lubrication) or, as is the case in highly loaded contacts, with a low shear and durable lubricant film (boundary lubrication). The film then helps to reduce material wear and energy losses due to friction. At high speeds and low contact pressures, the fluid mechanics described by the Navier-Stokes equation ensure the formation of a liquid viscous film [2], which physically separates the surface and reduces friction and wear. However, at low speeds and high contact pressures the fluid film cannot be maintained and effective lubrication is greatly influenced by the lubricant chemistry, i.e. the chemical additives in the lubricant. In these conditions, the material will interact, physically and chemically, with the lubricant and additives contained within it to form tribofilms. In the so called boundary lubrication regime, tribofilms are crucial for management of wear and control of friction. Understanding the surface and interface phenomena in conditions when a liquid lubricant film cannot be formed and where the system performance relies on thin tribofilms is essential for the development and optimization of effective lubricant chemistries, materials and tribological systems. Studies of the nature of the tribofilms formed in lubricated contacts in boundary lubrication have been reported for several decades; much focus has been on the physical nature of the film (roughness, thickness and hardness) and the chemical nature, particularly of elements such as Zn, S and P.

Various techniques have been applied to study the tribofilms. Although a significant progress has been obtained in understanding tribochemistry through characterising end-of-test chemical properties of tribofilms, the real time chemical composition of these films has not yet conclusively been evidenced experimentally. The reason for this is mainly the difficulty in accessing the tribofilms while in contact and also the nanometre thicknesses [3] which make real-time chemical and physical analysis of tribofilm formation and removal extremely challenging.

Two of the key surface active lubricant additives used in current engine oils are zinc dialkyl dithiophosphate (ZDDP) as antiwear additive and molybdenum dialkyl dithiocarbamate (MoDTC) as friction modifier. In case of tribofilms formed from the ZDDP additive on steel components, the vast research work indicates that the film is thin (few hundred of nanometres), patchy in nature and chemically a long-chain zinc poly(thio)phosphate film, superimposed on a thicker short-chain mixed Fe/Zn polyphosphate film [4, 5]. Embedded ZnO and ZnS nanocrystallites are also seen to be components of the ZDDP tribofilms. Molecular dynamics modelling has been used recently to simulate the proposed mechanism of iron oxide digestion by the zinc polyphosphate glass as the key mechanism for wear reduction [6]. In case of tribofilms formed from ZDDP+MoDTC additives on steel components, it is generally accepted that the film has a two phase composition: Zn/Mo phosphate glass and a carbon-rich amorphous phase with MoS_2 sheets embedded in the phosphate glass [7-12].

Considering the nature of surface films formed from these additives, surface analytical techniques have shown to be essential in researching the lubricated interface phenomena that lead to the ZDDP/MoDTC tribofilm formation. In the majority of tribofilm research, the formation of tribofilms is simulated in samples generated from bench top tribometers which are then analysed using techniques such as Scanning Electron Microscopy (SEM/EDX)**,** Auger Electron Spectroscopy (AES), Secondary Ion

Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS), soft X-ray XANES, Fourier Transform Infrared (FTIR), Atomic Force Microscopy (AFM) and optical interferometry based techniques such as the spacer layer interferometry method (SLIM). Of great importance are shown to be the vacuum-based techniques such as X-ray/Auger Electron Spectroscopy (XPS, AES), soft X-ray XANES and Time of Flight Secondary Ion Mass Spectroscopy (ToF SIMS). This is mainly because of the surface sensitivity of these techniques, only providing information on the tribofilm without interference from the substrate. However, the need for vacuum environment means that the chemical characterisation of tribofilms can only be done post-test and after careful sample cleaning to remove the lubricant, limiting the ability to experimentally study the kinetics of thermal and tribofilm formation. In recent years, new surface techniques have been developed to enable *in-contact* (study within the rubbing contact itself), *in-situ* (within the rubbing test apparatus without removing supernatant lubricant) and *in-lubro* (sample removed from the tribometer but still uncleaned and covered with the original test lubricant) chemical and physical characterisation of rubbed surfaces [5].

The primary objective of *in-situ* interface analysis is to obtain the physical and chemical characteristics of the films formed in lubricant/surface interface, avoiding any potential sample alteration due to the cleaning process. There has been some progress in obtaining the kinetics of tribofilm formation from physical point of view (tribofilm thickness) by using techniques such as contact resistance, conductance and interferometry [3]. At this stage, the technique which has shown the greatest potential for accurately measuring the tribofilm thickness *in-lubro*, and hence obtaining information on kinetics of tribofilm thickness, is the Spacer Layer Imaging (SLIM) method [13]. For chemical analysis, vibrational spectroscopies are of great importance for *in-situ* surface analysis (reviewed recently in [14]). *Post-test* Raman analysis of tribofilms formed from fully formulated engine oils have shown formation of orthophosphates at 962 cm^{-1}, Fe_2O_3 at 677 cm^{-1}, $CaCO_3$ at 1090 cm^{-1} and hydrocarbon at ~ 2930 cm^{-1} [15] and MoS_2 and MoO_3 from MoDTC containing oil at 405 cm^{-1} and 951 cm^{-1}, respectively [16], indicating the potential of this technique for analysing tribofilms formed when using typical engine oil additives.

Raman spectroscopy has already been used to analyse the effect of hydrostatic pressure on lubricant chemical structure, using the Diamond Anvil Cell (DAC) [17, 18]. Other studies involving *in-contact* chemical analysis have involved optical methods and FTIR [19, 20]. The drawback of using infrared microreflection absorption spectroscopy is the large depth of the material analysed making it unsuitable for analysing tribofilms in the range of 200 nm thick. The use of an Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) tribometer has increased the surface sensitivity of the FTIR [21]. Recent studies using the ATR-FTIR have given valuable information on the kinetics of triphenyl phosphorothionate (TPPT) thermal film [22] and tribofilm [23] as well as information on the behavior of *n*-alkene molecules during friction process [24].

Another potential technique to be used for *in-situ* and *in-lubro* chemical analysis of tribological surfaces is the synchrotron based X-ray absorption spectroscopy (XAS). One advantage of the XAS is that it can be used to study the electronic transitions from atomic core levels to unoccupied molecular states below and above the vacuum level in the absorbing atom [25], enabling surface chemical analysis under realistic pressures and temperatures [26]. Using monochromatic X-ray photons at a synchrotron, it is possible to tune the photon energy to probe the element of interest. In XAS analysis, the detection technique, either electrons (total electron yield) or photons (fluorescence yield), provides information on the chemical structure at different sample depths. In order to identify the chemical nature of tribofilm species, the obtained spectra are compared with the spectra of different model compounds with known chemistry [12, 25, 27-33]. To enable non-vacuum environment analysis, hard X-rays are required. Use of hard X-rays prohibits the analysis of some key low molecular weight elements constituents of novel lubricant additives as well as analysis of P and S L-absorption edges, but considering that analysis is done in ambient conditions it can potentially provide useful information on the lubricant film formation process by analysing higher molecular weight species of the film. To obtain the depth sensitivity required to analyse thin lubricant layers it is important to maximize the beam intensity in the thin layer [34, 35]. An alternative lubricant film analysis methodology is via reflection mode. This is the approach taken in this study and will be discussed in detail in the following section.

For any *in-situ* and *in-lubro* chemical analysis of lubricants films it is important to (i) run the analysis in ambient non-vacuum conditions, enabling analysis of lubricated samples and (ii) have good surface sensitivity needed for analysing thin lubricant films. The main aim of the current study was to develop the synchrotron based XAS methodology for this purpose. By using the XAS technique a wide range of elements can be analysed a non-vacuum environment. In order to assess the ability of the developed technique for real-time lubricant film chemical analysis, surface films formed from the above reviewed ZDDP and MoDTC lubricant additives are formed and analysed using the reflection mode XANES methodology. Surface films formed on both ferrous and diamond-like carbon (DLC) surfaces have been analysed and discussed in relation to published results obtained using other techniques.

2. Experimental Details

2.1 XAS system for *in-situ* study

The XAS analysis were performed using a microfocus beamline (I18) at the Diamond Light Source (Harwell Science and Innovation Campus, UK) [36]. This beamline operates with a range of energy from 2-20.8 keV enabling scanning the K-edges of the elements from P through to Mo and the L-edges from Mo to Pu. More details on the optical scheme of I18 can be found in [36]. The X-rays generated from the synchrotron source were scanned in energy regions of P, S, Zn, Mo K-edges and Mo L-edges. Considering that X-rays penetrate the material being analysed, the surface sensitivity can be increased by changing the experimental geometry and/or the detection mode [34, 37]. In the current study, the surface sensitivity was increased by setting the experimental geometry so reflection mode XANES under glancing angle conditions could be performed. In this setup, the X-ray beam will undergo total external reflection, restricting the penetration depth to a range of 1- 10 nm [34, 38] on the surface hence providing the surface sensitivity needed to analyse lubricant films adsorbed on the surface.

Figure 1 shows schematically the experimental set-up for the reflection mode XANES spectroscopy experiment. A horizontal sample holder containing the sample is placed on the Precision Rotation Stage enabling high resolution sample rotation around the perpendicular axis. The sample positioning was enabled by the 7-axis Newport – Microcontrole sample stage. The stage allows the positioning of the sample to 100 nm resolution by moving along the three vertical axes of a tripod and two normal horizontal axes. Samples were analysed with a vertical beam size of 200 μm for S and P elements (100 μm high for Zn and Mo elements) and 10 μm wide, giving a beam footprint on the sample of 45-60 mm long and 10 μm wide. Experiments were performed at 100˚C at atmospheric pressure. Analysis could be done in air for Zn and Mo K-edges. However, air is not transparent to X-rays with energies below 3 keV. Thus, the more challenging part of this experiment was obtaining the spectra of lower atomic number (Z) elements P and S. These two elements are key constituents of the ZDDP and MoDTC tribofilms, hence being able to obtain their chemical structure in a non-vacuum environment is a significant step towards developing the methodology for *in-situ* lubricant film chemical characterization. This is possible by collecting the reflection XANES spectra at the P K-edge, S K-edge (Mo L-edge) using a four element Si drifts detector (SII-Nanotechnology) in a He filled bag.

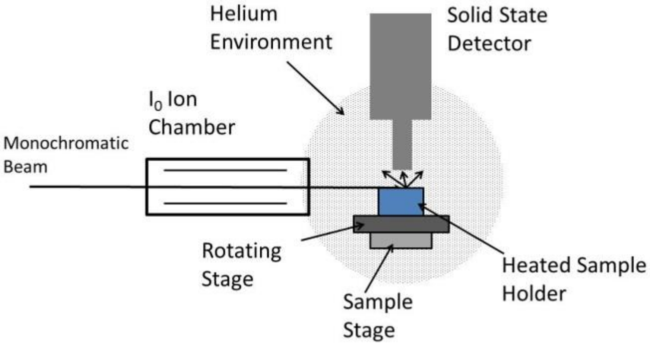


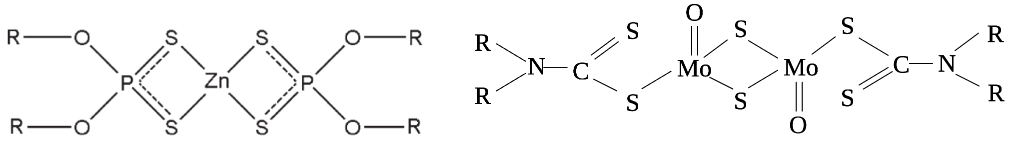
Figure 1. Schematic representation of the experimental methodology applied for analysing lower Z elements in lubricant thermal films and tribofilms

The near edge absorption spectra contain fine structure that reveals the electronic and geometrical environment of the absorbing atom. The absorption edge energy could vary by as much as ± 10 eV because of modifications of the local electronic structure linked to the environment and oxidation state of the absorbing element [39]. In this study, XANES spectra were collected and compared with known standards to identify phases by a fingerprint technique. Spectral normalisation and analysis were done using the programme Athena [40].

2.2 Materials/lubricants

The material used was AISI52100 steel (C 0.95-1.05, Cr 1.30-1.65, Si 0.15-0.35, Mn 0.25-0.45, P <0.027 and S <0.025, all in weight per cent) and hydrogenated Diamond Like Carbon (DLC) coated samples. Samples were plates of dimensions 6 mm x 60 mm x 3 mm with a mirror-like surface finish. The DLC (15% hydrogen) coating was deposited on the plate sample using a hybrid unbalanced magnetron sputter ion platting/PECVD deposition system. Full details on the coating deposition process as well as tribological performance of this coating using similar lubricants to the current study can be found in [41].

Model lubricants used in this project contain two surface active additives, ZDDP and MoDTC. Figure 2 shows their representative molecular structure [4, 42, 43]. The base oil used was a blend of polyalphaolefin synthetic oil (PAO6) with 10 wt% dodecanionic acid di-iso-octyl ester added to improve the additive solubility in the PAO. Two model lubricants were tested: ZDDP and ZDDP+MoDTC lubricants. They were produced by blending the base oil with 0.8 wt% ZDDP and 0.8 wt% MoDTC additives.



a) b)

Figure 2. Molecular structure of a) ZDDP and b) MoDTC additives

2.3 Tribology test conditions

The tribological tests were done using a pin-on-reciprocating plate tribometer. In these tests, both lubricated components were immersed in the lubricant tested. Tests were performed at 100˚C lubricant temperature, 730 MPa contact pressure, 1 Hz frequency and 40 mm long stroke, resulting in maximum sliding speed of 0.125 m/s in the middle of the wear scar. Contact pressure and the lubricant temperature are chosen to simulate the running conditions of the cam/follower in the internal combustion valve train system. The duration of each tribological test was four hours. The wear scar generated on the plate surface was around 500 μm wide and 40 mm long. The full details on the tribological test procedure and tribometer used can be found in [11]. These samples were then removed from the tribometer and while still covered with the test lubricant were chemically characterised using the X-ray Absorption Spectroscopy methodology explained in Section 2.1 (*in-lubro* analysis). In comparison with ZDDP lubricant friction results, ZDDP+MoDTC lubricant gave around 50% friction reduction (friction coefficient 0.05) when tested on steel and around 20% friction reduction when tested on DLC (friction coefficient 0.08). Since the focus of this study is not the tribological performance, no further information for friction and wear obtained has been given.

The lubricant thermal films were formed and analysed *in-situ*. During these experiments, the sample was covered with a thin layer (few tens of micrometres) of lubricant and heated at 100^{0}C for at least six hours. During this time, the XANES spectra were collected continuously. Each spectrum took around 30 minutes to collect. Table 1 gives a summary of the XANES experiments and analysis done in this study.

Table 1. Summary of the XANES experiments and analysis

XANES	Thermal film	Tribofilm
Analysis mode	*In-situ*[1]	*In-lubro*[2]
Chemical elements analysed in air	K-edge: Zn, Mo	K-edge: Zn, Mo
Chemical elements analysed in He environment	K-edge: P, S L-edge: Mo	K-edge: P, S L-edge: Mo
1) Sample analysed within the test apparatus, without removing the supernatant lubricant 2) Sample removed from the tribometer but still uncleaned and covered with the test lubricant.		

3. Results

3.1 Lubricant thermal films on steel

Figure 3 shows the P K-edge spectra obtained from ZDDP thermal film, providing information on the chemical nature of P species which form from ZDDP thermal decomposition. Also shown in this figure are spectra for concentrated ZDDP additive (in liquid form dispersed on a steel sample) and Zn phosphate powder at room temperature. In agreement with the previous XANES work of ZDDP additive done in a vacuum environment [44, 45], the P K-edge peak observed for the concentrated ZDDP additive is at 2150 eV and for the Zn phosphate is at 2152.3 eV. Comparing the spectrum of concentrated ZDDP additive on steel with the spectra obtained after heating the lubricated sample, it can be observed that there is no chemical shift of the P K-edge peak indicating that the layer of the ZDDP adsorbed on the surface is only un-reacted ZDDP additive. These results support the findings from the only other published research work on *in-situ* analysis of ZDDP thermal films obtained with ATR-FTIR analysis [46]. The nature of P species formed on the surface by heating the ZDDP-containing lubricants is shown to change only at temperatures higher than 150^0C [46, 47]. Not observing any change of P K-edge structure at 100^{0}C indicates that there is no additive decomposition at this temperature, however analysis of P L-edge could provide more conclusive information on this.

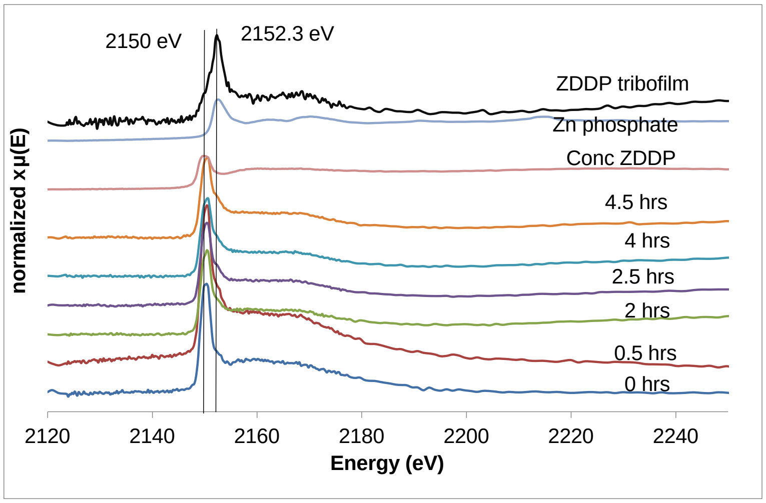


Figure 3. P K-edge absorption spectra from ZDDP thermal film formed on steel at 100°C. The time shown represents the time the sample was heated at test temperature before the spectra was acquired

Figure 4 shows the S K-edge absorption spectra obtained from *in-situ* formed ZDDP thermal films and the spectrum from analysis of concentrated ZDDP additive. The spectrum obtained from *in-lubro* analysis of a pre-formed ZDDP tribofilm is added for analysis purpose. To the knowledge of authors, this is the first chemical composition study of *in-situ* and real-time thermal film ZDDP-derived S species in a non-vacuum environment. Three peaks could be observed in the S K-edge spectra of ZDDP thermal films formed on steel: 2471.9 eV (unreacted ZDDP), 2473 eV (sulphoxides [47]) and 2481. 6 eV (sulphates [47]). Comparing the key features of these spectra it can be observed that a peak at 2473 eV starts to appear after around 1.5 hours heating at 100˚C. This result indicates that with heating the ZDDP-containing lubricant, other S species will start to form in the sample surface. These results are in line with the XPS analysis of ZDDP thermal films at a temperature comparable to the current study [48, 49], indicating ZDDP additive decomposition. Analysis of P L-edge spectra could provide more detailed information of P film structure in ZDDP thermal films.

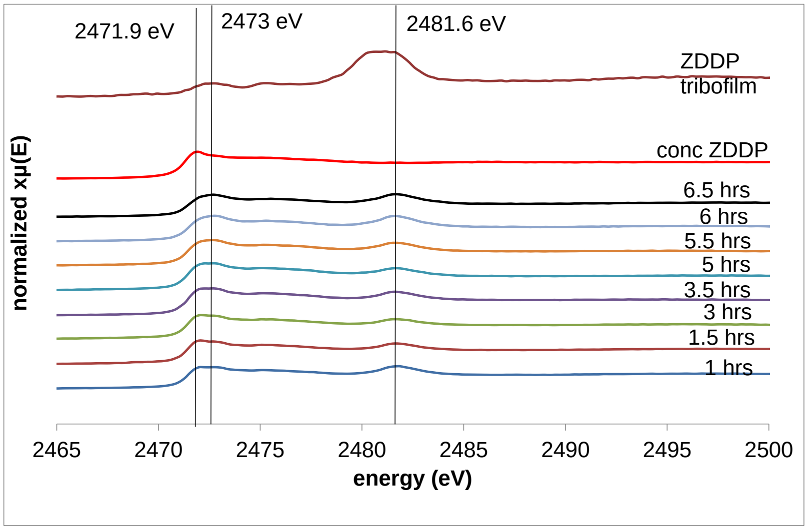


Figure 4. S K-edge absorption spectra from ZDDP thermal films formed on steel at 100°C. The time shown represents the time the sample was heated at test temperature before the spectra was acquired

Similar results were also seen when testing thermal films formed on steel from ZDDP+MoDTC additive (Figure 5 and Figure 6). There was no change in the P species formed on the steel surface by heating the ZDDP+MoDTC-containing lubricant (Figure 5). The position of the main P K-edge peak at 2150 eV did not change on heating the sample at 100^{0}C for 6 hours, indicating mainly un-decomposed ZDDP additive adsorbed on the surface.

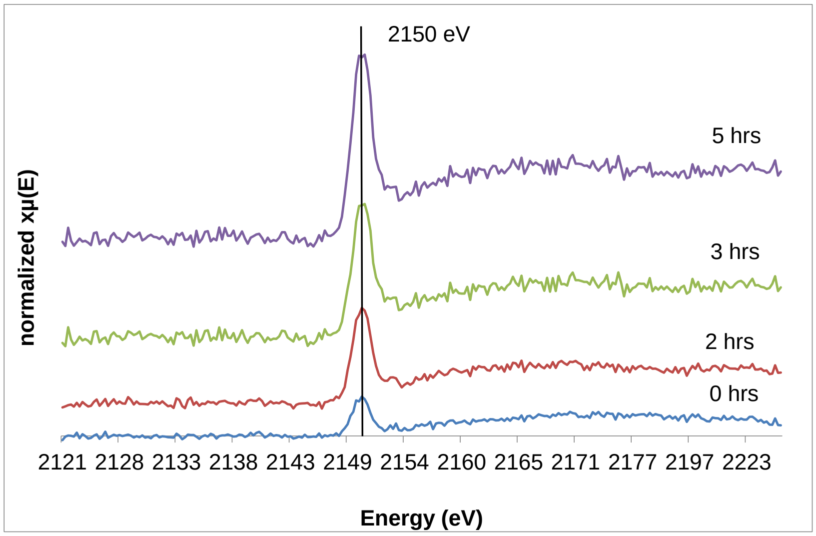


Figure 5. P K-edge absorption spectra from ZDDP+MoDTC thermal film formed on steel at 100°C

The role of MoDTC additive in the lubricant is to form $MoS_{2,}$ which with its layer lattice structure, can then reduce friction [50-52]. The absorption edge for MoS_2 is reported to be around at 2470.2 eV [10, 53]. The S K-edge spectra of ZDDP+MoDTC thermal films (Figure 6) show that MoS_2 is not formed. This is also confirmed by the analysis of the Mo K-edge spectra obtained from the same lubricant films shown in Figure 7. What is seen is that the sample heating causes the appearance of a new peak at 20007 eV (circled peak in Figure 7), indicating the formation of MoO_3 on the surface [54]. Both, results on S and Mo species are in full agreement with the analyses of similar thermal films using XPS technique [11]. To obtain kinetic information with techniques such as XPS requires analysing samples obtained from tests at varying time intervals. The advantage of this new technique is primarily the ability to access information *in-situ* as the sample is heated.

While the XPS analyses are end-of-test results obtained ex-situ in vacuum after sample cleaning, the methodology developed in this study clearly shows the potential of obtaining the chemistry of surface films *in-situ*.

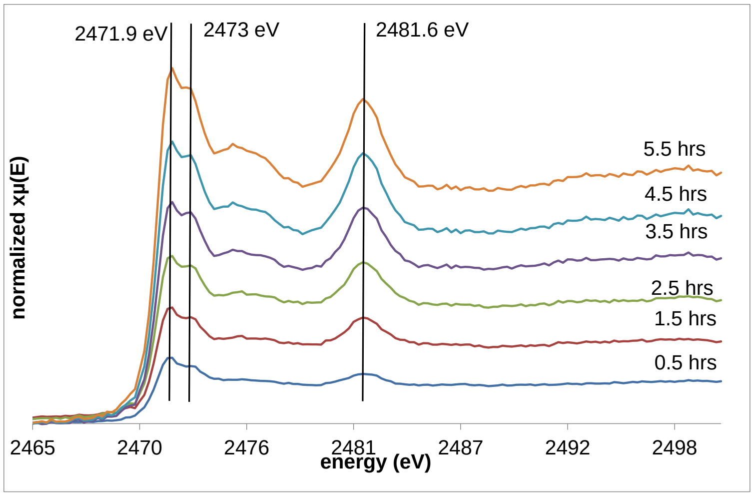


Figure 6. S K-edge absorption spectra from ZDDP+MoDTC thermal film formed on steel at 100°C

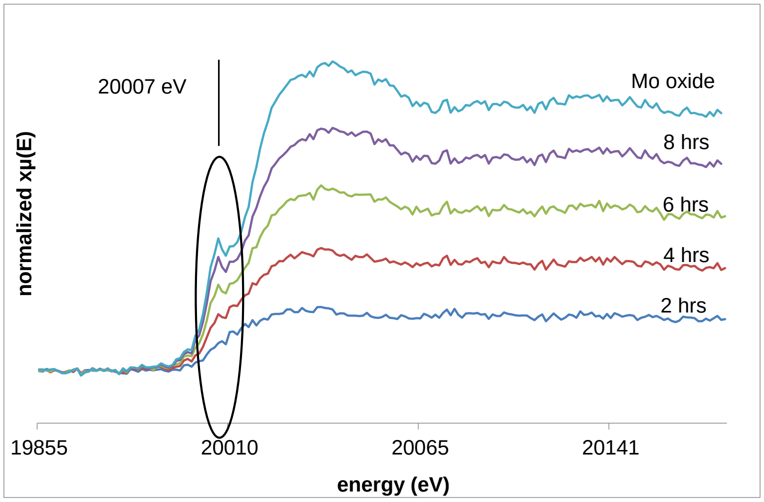


Figure 7. Mo K-edge absorption spectra from ZDDP+MoDTC thermal film formed on steel at 100°C

3.2 Lubricant thermal films on DLC

Tests with the ZDDP+MoDTC lubricant were also performed using the DLC coating as a substrate. Previous research has shown that thiols can be oxidized by iron oxide. The objective of the current experiment was to see if the nature of substrate affects the formation of lubricant thermal films. Figure 8 shows the P K-edge spectra obtained *in-situ* from the lubricated surface when heated at 100˚C for different time periods. In contrast to the results shown for steel samples, the XANES spectra indicate a change of phosphate species with lubricant heating. Figure 8 shows that even after 1 hour heating at 100˚C, a peak starts to appear at 2152.2 eV indicating formation of some kind of phosphates. The intensity of this peak was seen to increase with the duration of this test. In the case of S species (Figure 9), a broader peak at around 2472 eV was seen to form with time, indicating formation of another S-containing species on the surface, in conjunction with the S species from un-reacted ZDDP. Heating also caused an increase of oxidized S peak at 2481.6 eV (Figure 9).

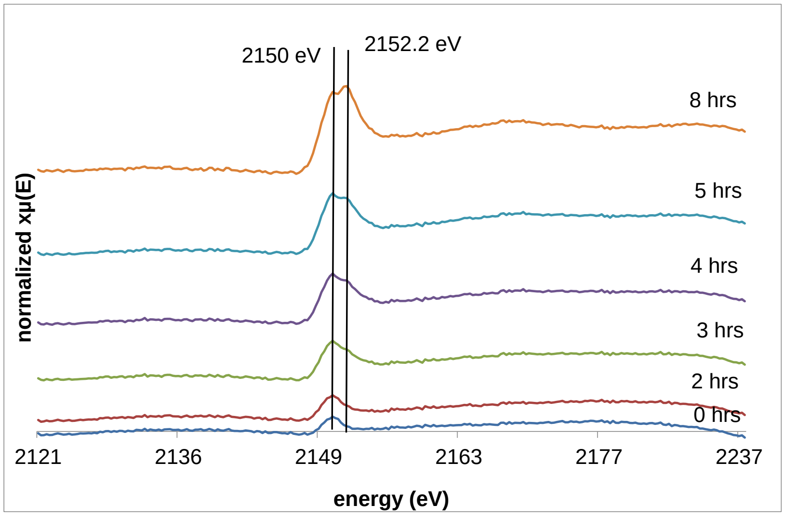


Figure 8. P K-edge absorption spectra from ZDDP+MoDTC thermal films formed on DLC at 100°C. The time shown represents the time the sample was heated at test temperature before the spectra was acquired

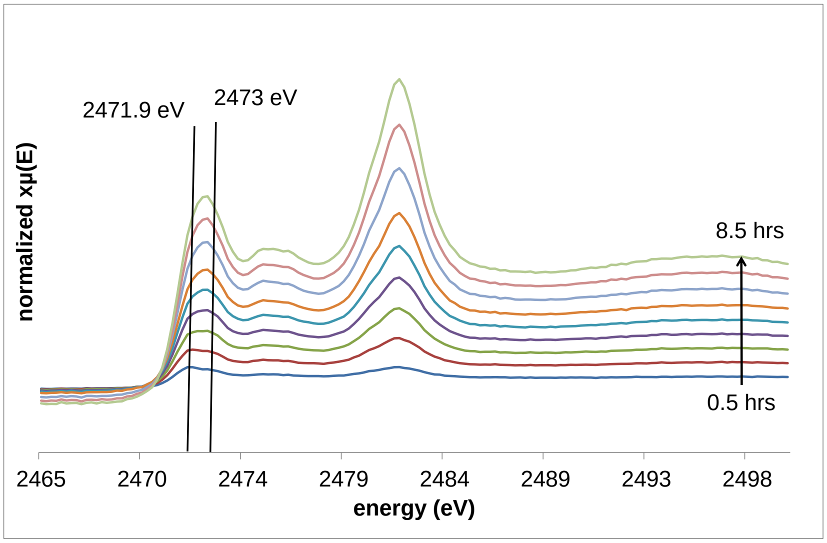


Figure 9. S K-edge absorption spectra from ZDDP+MoDTC thermal films formed on DLC at 100°C. The time shown represents the time the sample was heated at test temperature before the spectra was acquired

The other observation from the *in-situ* analysis of thermal films formed on DLC is lack of formation of both MoS_2 and MoO_3 from the MoDTC additive on DLC. Figure 10 compares the Mo K-edge spectra obtained from thermal films formed on DLC and steel. The peak at 20007.3 eV which corresponds to MoO_3 was not seen to form on ZDDP+MoDTC thermal films formed on DLC.

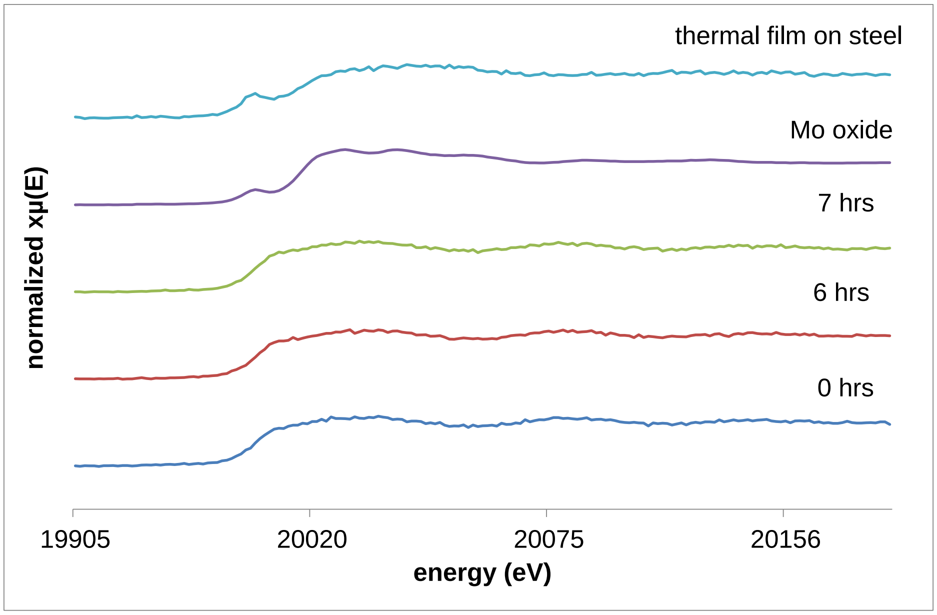


Figure 10. Mo K-edge absorption spectra from ZDDP+MoDTC thermal films formed on DLC, Mo oxide powder and ZDDP+MoDTC thermal film formed on steel. The time shown represents the time the sample was heated at test temperature before the spectra was acquired

3.3 *In-lubro* analysis of lubricant tribofilms formed on steel and DLC

In addition to the analysis of *in-situ* thermal films, *in-lubro* analyses of pre-formed lubricant tribofilms were done. These samples were removed from the tribometer, following the tribological test, and analysed uncleaned and covered with the test lubricant. The spectra obtained were compared with the spectra of standard chemistries of concentrated ZDDP additive, Zn phosphate and MoS_2 powder. Figure 11 shows the S K-edge XANES spectra (obtained in He environment) of ZDDP and ZDDP+MoDTC tribofilms and model compounds. The concentrated ZDDP spectrum shows an S K-absorption edge at 2471.9 eV which is consistent with what is observed in literature [53, 55, 56] when similar films were analysed *in vacuum environment*. Tribofilm spectra showed a peak consistent with the concentrated additive spectrum. This is not surprising since the samples were not cleaned with any solvent prior to this analysis. The other two distinctive peaks observed in both tribofilms are peaks at 2474.5 eV and 2480.3

eV, indicating formation of sulphite and sulphate on the wear scar [53]. Looking at the ZDDP+MoDTC tribofilm spectrum, formation of the MoS_2 and MoO_3 in the lubricant film can be clearly shown by the Mo L-edge absorption peaks observed at 2523.6 and 2526 eV. The broad peak detected in the region between 2465 and 2473 eV indicates that different sulphides are formed in the ZDDP+MoDTC tribofilm (absorption edges for FeS_2, ZnS and MoS_2 are reported to be at 2471.3, 2472.9 and 2470.2 eV, respectively [53, 55, 56].

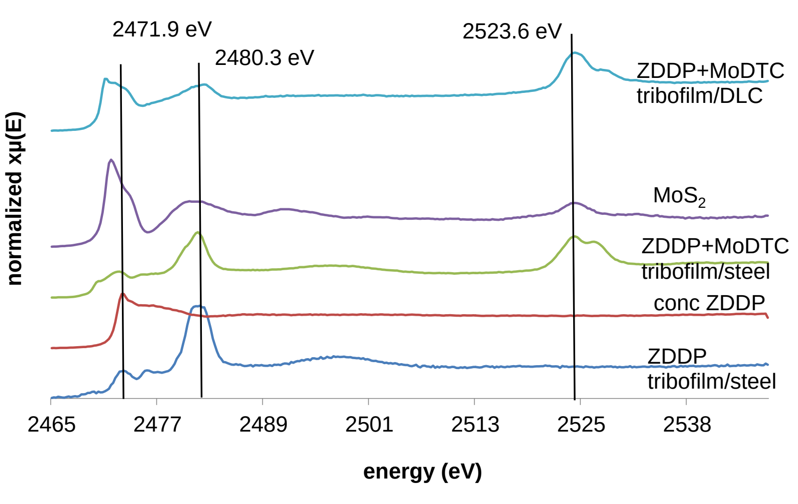


Figure 11. Sulphur K-edge XANES spectra of ZDDP and ZDDP+MoDTC tribofilms formed on steel and DLC, MoS_2 powder and concentrated ZDDP additive

Analysis of Zn and P species formed in the tribofilm can give more information about the chemical structure of ZDDP tribofilms. Figure 12 shows the Zn K-edge spectra obtained from ZDDP+MoDTC tribofilm, ZDDP+MoDTC thermal film, Zn phosphate and ZnO powders. The main absorption edge observed in the tribofilm aligns well with the peak obtained when analysing the concentrated ZDDP. Formation of ZnO and/or Zn phosphate cannot be proved by using the fingerprint method, detailed curve fitting is required to clearly indicate the formation of these species.

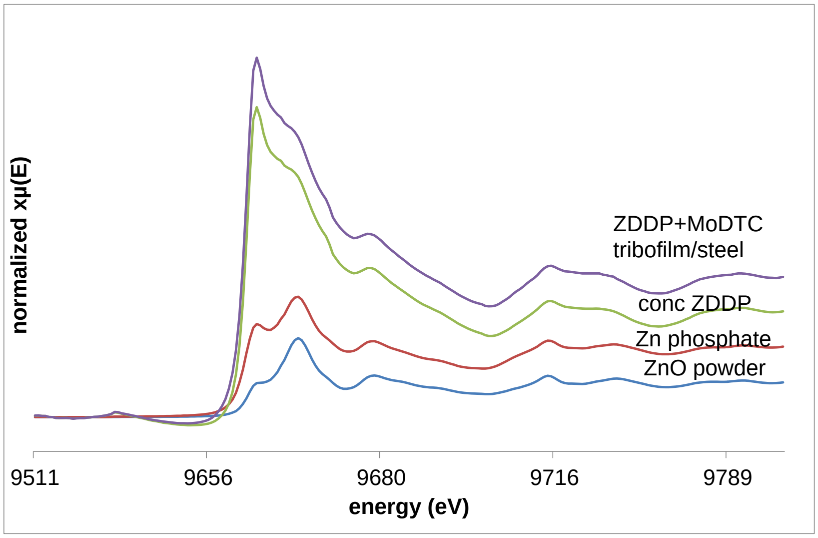


Figure 12. Zinc K-edge XANES spectra of ZDDP and ZDDP+MoDTC tribofilms formed on steel and model compounds

Figure 13 shows the P K-edge spectra obtained from ZDDP and ZDDP+MoDTC tribofilms formed on both steel and DLC, as well as the spectrum obtained from analysing the Zn phosphate powder. The main peak was observed at 2152.5 eV, shifted by ~2.5 eV from the peak observed for unreacted ZDDP (see Figure 3). This shift is in agreement with the previous XANES studies done on ZDDP tribofilms [47, 56]. Previous XANES studies on phosphates with different cations [57] show that P K-edge appear to be the same whether the cation is Fe or Zn.

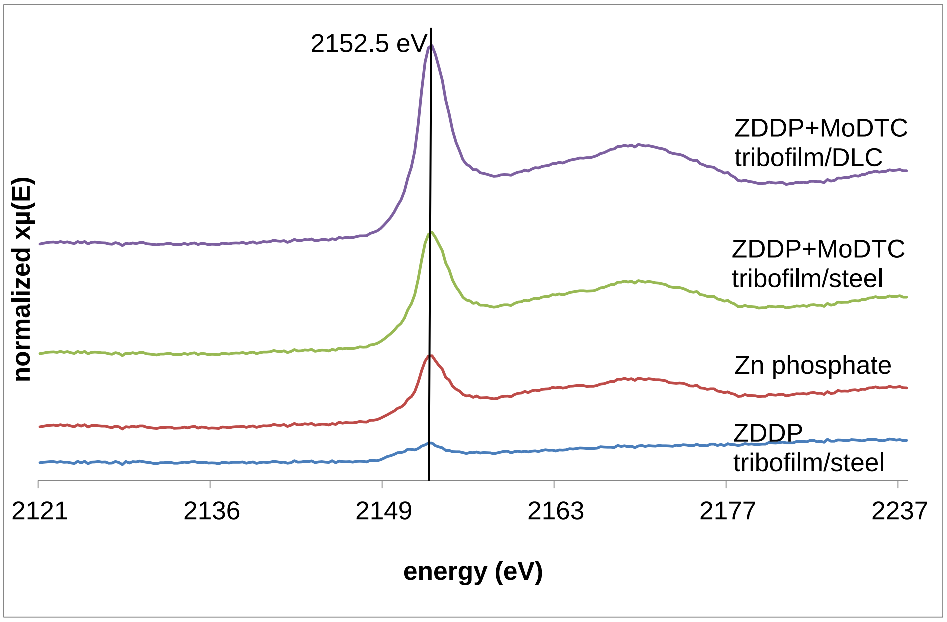


Figure 13. P K-edge XANES spectra of ZDDP and ZDDP+MoDTC tribofilms formed on steel compared to model compounds

4. Discussion

4.1 ZDDP and ZDDP+MoDTC thermal film formation on steel and DLC

Post-test analysis of ZDDP lubricated steel surfaces at 100^0C using soft energy XANES did not show any change to the P K-edge spectra with heating time [25]. This was also confirmed by the *in-situ* study of a similar system using the ATR-FTIR [46]. Current results shown in Figure 3 and Figure 5 support the above finding for ZDDP thermal films formed on steel. However, results of P K-edge spectra obtained from *in-situ* analysis of *DLC lubricated surfaces* (Figure 8) show that only after 1 hour heating at 100^0C a second peak at 2152.2 eV starts to appear. Comparison with the Zn phosphate spectrum indicates formation of Zn phosphate on the DLC surface as a result of just heating the lubricated sample.

Analysing the S species in surface films can give information on the oxidation state of S species formed on the surface from the ZDDP additive. Until now, chemical characterisation of ZDDP thermal films has been done only post-test using techniques such as soft X-ray XANES [47]. Figure 4, Figure 6 and Figure 9 show the *in-situ* chemistry of S films formed on both steel and DLC by heating the ZDDP-containing lubricant, not reported before. Reduced S species (such as sulphide, disulphide, thiol and thiophene) are characterised by peaks at 2472.8 – 2473.8 eV region [58, 59]. Detection of the S K-edge peak at 2473 eV in ZDDP thermal films indicates the formation of sulphide/thiols on the film, which is in line with the suggested mechanisms of ZDDP thermal film formation on steel (reviewed in [5]). However, the advantage of the methodology developed here is that formation of these species on the surface can now be studied *in-situ*.

Looking at the species that could form from MoDTC additive, no MoS_2 (expected peak at 2470.2 eV [53]) was seen to form on steel or DLC coating. This is in agreement with XPS analysis of similar films formed on steel [11, 52], however an interesting observation is the formation of MoO_3 on steel but not on DLC surface. Figure 14 summarises schematically the chemical nature of the ZDDP+MoDTC thermal films on steel and DLC as a function of heating time.

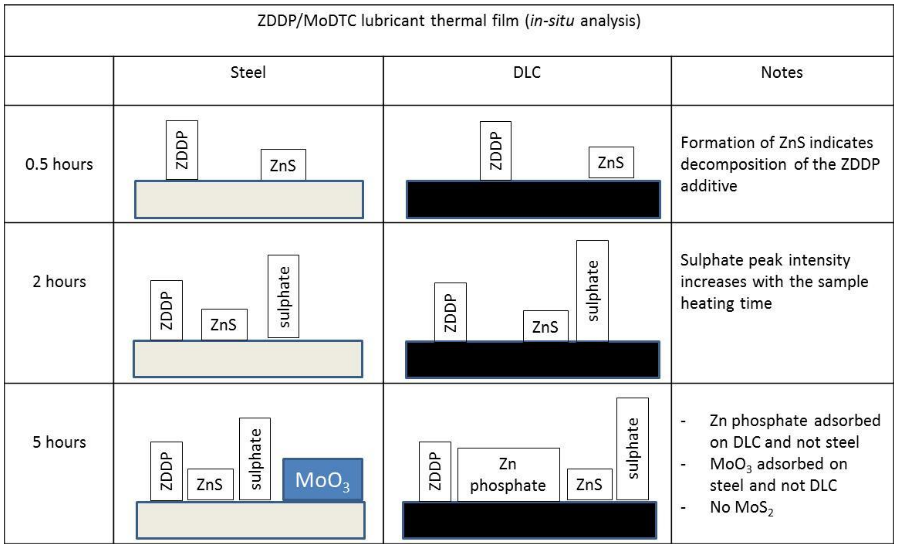


Figure 14. Schematic representation of the ZDDP+MoDTC thermal films formed on steel and DLC coating

Bulk lubricant experiments have shown that ZDDP decomposes at temperatures between 130^{0}C and 230^{0}C, depending on the alkyl group of the additive [5]. This is done via a O/S exchange in the ZDDP molecule [60]. However, numerous studies show that ZDDP thermal films form on steel at much lower temperatures than the additive decomposition temperature [25, 52, 61, 62], indicating a catalytic effect of the steel surface. The results obtained from *in-situ* experiments in the current paper show the 1) formation of sulphide and sulphate species on steel and DLC surface, 2) formation of Zn phosphate on the DLC surface and 3) formation of Mo oxide on the steel surface. DLC coating and steel will have different wettability properties that will affect the specific chemical reactions by the adsorbed species and the surface, defining the chemical nature of thermal films.

4.2 ZDDP and ZDDP+MoDTC tribofilm chemical composition obtained by XANES

The purpose of analysing pre-formed tribofilms (*in-lubro* analysis) was to evaluate the results obtained by the XANES methodology developed in this study in comparison with the results published in literature. The S K-edge spectra (Figure 11) show that, apart from formation of sulphides, sulphates are also formed from the ZDDP additive. Formation of sulphates in ZDDP tribofilms has not been reported in the literature, ZDDP tribofilms are shown to contain mainly reduced form of sulphur. To check if detection of sulphates in the ZDDP tribofilm is related to the sample cleaning procedure, the same tribofilms were analysed after the cleaning the sample with heptane and the results show that sulphate peak is still present. Formation of sulphates could potentially be related to the testing being done at high air relative humidity [63]. Detailed analysis of S K-edge and Mo L-edge spectra show the formation of MoS_2 in the ZDDP+MoDTC tribofilm, explaining the low friction coefficient obtained in the tribological test. The Zn K-edge spectra indicate formation of ZnO in the tribofilm. ZnO is a constituent part of the phosphate glass [64], its detection is in line with the results obtained by analysing similar films using vacuum-based techniques such as XPS [5]. Formation of phosphates is also documented by the P K-edge spectra shown in Figure 13, but finger-print comparison of the main peak cannot indicate the phosphate structure.

Based on the results shown, the developed methodology is capable to identify P species by obtaining only P K-edge spectra. The P K-edge peak does not appear to be very useful to assess the cation nature in the phosphate molecule as well as the chain length of the phosphate formed [57], useful for characterising the ZDDP tribofilm. This can be done with the P L-edge XANES analysis. Analysis of P L-edge spectra can determine the phosphate chain length as well as the nature of cation in the phosphate molecule [25, 27, 33, 57]. However, considering that the P L-edge absorption peak appears at around 135 eV, it cannot be obtained in non-vacuum conditions. Nevertheless, the XANES methodology developed in this study can clearly indicate the formation of phosphates by analysing the P K-edge as well as Zn K-edge absorption spectra.

The environmental legislation requires the use of additives which are of organic nature, so called NOCH (additives containing only nitrogen, oxygen, carbon and hydrogen) additives. Analysis of these elements with XANES spectroscopy cannot be done using hard X-ray, hence the developed methodology in this study will not help with characterising tribofilms formed from these additives. Another drawback of this technique is the lateral resolution. The geometry of the analysis results in a large beam footprint in the X-ray direction, limiting the ability of analysing chemical structure spatially on the wear scar. In any case, P and S-containing additives are still an important part of lubricants and are expected to be for the foreseeable future and any progress in understanding the formation kinetics of these tribofilms will have significant impact in optimising their use.

5. Conclusions

The potential of reflection mode XANES methodology for *in-situ* lubricant thermal and *in-lubro* tribofilm analyses has been investigated. Initially, detailed explanation of the technique developed has been given, indicating its advantages and disadvantages relevant to our purpose. Following the development work, chemical characterisation of thermal lubricant films and pre-formed tribofilms has been performed to evaluate the potential of this methodology. The key conclusions following the analysis of the thermal films and tribofilms are:

- S, P, Zn and Mo species formed in lubricant films can be characterised *in-situ* and *in-lubro* by using the reflection mode XANES technique.
- Heating the lubricated steel and DLC samples affects the chemical reaction between the adsorbed species and the surface, resulting in different chemical composition of the ZDDP+MoDTC thermal film formed on steel or DLC.
- There is a greater effect of temperature on S species than P species formed on ZDDP thermal films.
- The P K-edge spectra are not very useful to show the chemical structure of phosphates formed.
- Both S K-edge and Mo L-edge spectra can identify clearly the Mo species such as MoO_3 and MoS_2.

Future work will focus on the development of tribometer which will enable *in-situ* XAS analysis of films formed by rubbing two surfaces. Ability to identify the surface chemistry in non-vacuum conditions enables detailed studies on the parameters which affect formation and removal of tribofilm species such as phosphates, MoS_2, ZnS, MoO_3 and sulphates, giving experimental information on the lubricant film chemistry change as a function of testing conditions.

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