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# Transient processes of MoS<sub>2</sub> tribofilm formation under boundary lubrication

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## Abstract

A tribochemistry study that involves the application of Raman spectroscopy surface analysis has been undertaken to understand the time-dependent tribochemical reactions, for lubrication by Molybdenum dialkyl-dithiocarbamate (MoDTC) occurring in boundary lubricated conditions. Under the conditions of rubbing and high temperature, time-resolved Raman spectroscopy results show the intermediate steps that lead to the MoDTC additive to be tribochemically structured on the wear scar of the contacting surface. A MoS<sub>2</sub> tribofilm with a lattice layer structure is observed on the wear scar whenever the lowest friction was achieved. An apparent shift of the A<sub>1g</sub> and E<sub>2g</sub> Raman modes, indicating qualitative and quantitative information on the MoS<sub>2</sub> tribofilm formed, is observed to be related to low friction. Detailed analyses of Raman spectra obtained on wear scars at different test durations and temperatures indicate that both temperature and rubbing are needed for the formation of low friction MoS<sub>2</sub> tribofilm.

## 1. Introduction

Ever-increasing environmental governmental legislation demands the development of energy efficient automobile engines, with the desire to achieve less emissions but without compromising higher power outputs and improvements in performance. Lubricants along with their various additives have been known to enhance the performance of the modern engine and transmission technologies. Strict emission requirements have led to a greater interest in further understanding the tribological performance of these additives in automotive engine parts with the development of environmentally-friendly lubricant additives [1, 2].

Oil soluble organo-molybdenum compounds such as molybdenum dithiocarbamates (MoDTC) and Molybdenum dithiophosphates (MoDTP) are well-known friction modifier additives. Since the late 1970s, considerable research has been undertaken to investigate the mechanisms of these additives [3]. Various Molybdenum additives have been studied and analysed for their friction reducing capabilities [4]. In particular, Molybdenum dialkyl-dithiocarbamate (MoDTC) compounds containing both molybdenum and sulphur which are soluble in oil due to their hydrocarbon chain compounds are of interest [5, 6]. It is well documented under boundary lubrication conditions that this type of additive has been able to reduce friction to very low friction coefficient values of 0.04 to 0.075 [7, 8].

The tribological properties of this friction modifier have been attributed to the formation of the MoS<sub>2</sub> within the tribofilm. Various analytical techniques such as electron diffraction [9], X-ray methods [5, 10] and Raman spectroscopy [7, 8] detected the presence of the MoS<sub>2</sub> sheets on the rubbing surfaces. The MoS<sub>2</sub> tribofilm has a lattice-layered structure with low shear strength

which makes it possible for low friction between the tribology components [6, 11-14]. MoS<sub>2</sub> within the MoDTC tribofilm was reported to form on the rubbing surfaces in the presence of air and oxygen [6]. Graham et al. [7] concluded that the friction-reducing capability of the MoDTC tribofilm is highly dependent upon the temperature and MoDTC concentration. They confirmed the formation of the MoS<sub>2</sub> tribofilm on the wear scar with the use of Raman spectroscopy, and further concluded that friction is reduced when MoS<sub>2</sub> forms and only under true boundary lubrication conditions [15].

Martin et al [16] studied the effect of oxidative degeneration on the mechanism of friction reduction by MoDTC and showed significant decrease of friction reduction ability when about 80% of the additive content had been consumed by oxidation. It was suggested that the formation of MoS<sub>2</sub> sheets was delayed and/or inhibited due to the concentration of MoDTC being too low. It has also been stated that sulphur-containing additives such as Zinc dialkyldithiophosphates (ZDDP) are needed to promote MoS<sub>2</sub> formation [17-22] . Ligand exchange between the dialkyldithiocarbamate moiety and the dialkylthiophosphate in ZDDP influences the friction- modifying reaction of MoDTC. The antioxidants were required to prevent molybdenum additives from behaving as peroxide-decomposers and thereby being consumed and the antiwear additives promoting the formation of MoS<sub>2</sub> films by reducing the rate of their removal by wear [15].

Grossiord et al. [11], explains the tribofilm formation of MoS<sub>2</sub> with a two-step tribochemical reaction of MoDTC. Ultrahigh vacuum friction tests were conducted on MoDTC tribofilms, and analysed utilizing various surface techniques. Formation of the MoS<sub>2</sub> was proposed to be initiated by the degradation of the MoDTC molecule through electron transfer mechanism activated by the friction process. The initial step of MoS<sub>2</sub> formation was suggested via electron transfer at the Mo-S bond in MoDTC which lead to the formation of three free radicals. One of them corresponded to the core of the MoDTC and the other two to the chain end. The decomposition of the MoDTC core radical followed and MoS<sub>2</sub> and MoO<sub>2</sub> were formed, which could further oxidise in the presence of O<sub>2</sub>, and the chain end radical recombined to form thiuram disulphides [11].

While there is a good understanding of end-of-test MoDTC tribofilm composition, not much is known about the transient processes that lead to the formation of this tribofilm. The study presented here utilizes Raman spectroscopy to understand the development of the MoDTC tribofilm as a function of time. Raman spectroscopy provides the benefit of not requiring any sample preparation prior to the analysis and hence avoiding any contaminant effects. Raman spectroscopy is very sensitive to small chemical changes in molecular structure and therefore provides an appropriate analytical method for the study of tribofilm formation for the MoDTC lubricant under various conditions. Transmission Electron Microscopy (TEM) has also been used to support the results obtained by Raman.

## 2. Experimental methods and materials

### 2.1. High Speed Pin On Disk (HSPOD) experiment

Tribological experiments were conducted using a High Speed Pin on Disk tribometer to ensure the formation of the lubricant additive tribofilms and assess their friction performance. The tribometer is powered by a D.C brush motor, placed below the set-up of the rig to rotate the sample disk at the required speed. The tribometer consists of a fixed long arm perpendicular to the rotating disk with a load attachment on one end and equipped with its own calibration system. The tribometer consists of a counter weight at the opposite end of the load attachment to balance the distributed weight of the arm. The tribometer was instrumented to measure friction force via a transducer rod on the load arm which provides the friction force on the load cell. Before the initial experiment, the load cell was loaded under compression and calibrated with 12 load points, along with 6 observations at a given load. The calibration procedure produced a 96 % coefficient of determination, indicating a good fit for the data produced by the load cell.

The samples comprised of a steel disk and a ball bearing, clamped to a holder to be used instead of a pin. The steel disk was an AS series thrust washers made of spring steel AISI 1050 (60 – 64 HRC, 112 nm  $R_a$ ) and the ball bearing was AISI 52100 chrome steel ball bearings (60 - 67 HRC, 0.2 - 0.3  $\mu\text{m } R_a$ ). The sample disk had the dimension of 25 mm inner diameter/42 mm outer diameter with a thickness of 1 mm and the ball bearing had a 6.45 mm diameter. The experiments were conducted at room temperature ( $\sim 25^\circ\text{C}$ ) and  $100^\circ\text{C}$ , for the lubricants containing MoDTC for various time periods. The lubricant tested was a Polyalphaolefin 4 (PAO4) base oil containing 100 part per million (ppm) of Molybdenum as MoDTC additive. To ensure the disk and the ball were always submerged in the lubricant, 35 - 40 ml of lubricant was injected into the sample tray. The sample ball and disk were cleaned with acetone before each experiment to ensure that no contaminants would affect the experiment being conducted. The ball was loaded with a weight of 1.5 kg, producing an initial maximum Hertzian pressure of 1.9 GPa and the disk rotation was set at a speed of 500 rpm, producing a sliding speed of 0.88 m/s. To confirm the repeatability of tribological results, tests were repeated at least three times.

The lambda ratio was calculated to be 0.18 confirming that the test regime was firmly in boundary lubrication regime. The friction coefficients of the rotating disk on the pin were measured and calculated by the Labview based data acquisition system available on the attached PC. The friction force data collected were averaged for every second. These data were then used to calculate friction coefficient and plotted against time. All of the experimented samples were further analysed chemically with the aid of the Raman spectroscopy.

## 2.2. Raman spectroscopy surface analysis

Raman spectroscopy is a contact-free analytical technique for material characterization based on an inelastic scattering or Raman scattering of monochromatic light, usually from a laser source. The laser light interacts with molecular vibrations, photons or other excitations in the system, resulting in the Raman effect where the energy of the laser photons is shifted up or down in comparison with the original monochromatic frequency. This shift in the energy provides information about vibrational, rotational and other low frequency transitions in molecules [23]. In the current study, wear scars on both counterparts tested were chemically

analysed with the use of the Renishaw inVia Raman microscope. The Raman microscope was equipped with a laser of 488 nm wavelength (Modu-laser Stellar REN Argon laser) rated at a power of 30 mW. The samples were focused with a microscope objective lens of Olympus 50x and 50Lx (Long working distance) magnification lenses and the back scattered collection was also made through the same objective lens from a spot diameter size of 800 nm.

The Raman system was programmed with the Wire 3.4 software, which permitted the adjustment of various parameters such as laser power, type of scans, exposure time etc. for the Raman system before the analysis could be undertaken. A procedure to optimize the laser power was therefore undertaken to obtain good quality signal with the various Raman parameters, while ensuring no sample damage due to excessive heating. A measurement of the tribofilms was conducted to obtain laser power low enough to not burn the sample, but high enough to obtain good quality signal in the shortest time possible. Any change in the peak position, width and the intensity of the tribofilm, along with the observation of the spectrum background and the appearance of the carbon spectrum, was observed for indication of the sample damage. Raman analyses were therefore settled with a full laser power, an exposure time of 1 second and an accumulation of 10 scans for the best signal with no sample damage.

The Raman system is also provided with its own built-in calibration system, where the silicon sample was fitted inside the system and the lasers focused onto this sample. The corresponding Raman shift for the silicon of  $520\text{ cm}^{-1}$  was analysed with the lasers and any offset or change in the laser was calibrated accordingly. The calibrations for the lasers were performed every time the Raman system was in use and before any Raman analysis were undertaken.

HSPOD samples after the experiments were analysed with the Raman microscope with a method of in-lubro analysis. In-lubro analysis included the disk and the ball samples to be taken off from the test condition and, without rinsing with any solvent, wear scar analysed under the Raman microscope. Prior to the analysis, the disk sample was rotated for a minute to allow the centrifugal forces to remove any excessive oil from the sample surface.

To further indicate the formation and distribution of the  $\text{MoS}_2$  on the sample surface, a Raman map analysis was also carried out onto the surface. Due to high lateral resolution of the Raman microscope ( $1.1\text{ }\mu\text{m}$ ), a Raman map analysis was carried on the surface area of  $20\mu\text{m} \times 20\mu\text{m}$ . The analysis was undertaken with the same parameters to the single point analysis, and a similar mapping analysis was carried out on two to three different areas of the wear scar. The Raman map was obtained with the distribution of the normalized intensity variations of the  $\text{A}_{1g}$  Raman response of the tribofilm at room temperature and  $100^\circ\text{C}$ .

Characteristics of the Raman spectra that have been investigated include shifts in Raman peak values and full width at half maximum (FWHM) Raman bands, and normalised intensity variations. A linear curve fit was provided for all spectra with a Gaussian Lorentzian Product (Voigt profile function) in the Originlab software to provide a satisfactory fit to the Raman data. For Raman map data, a Matlab program was utilised to provide a linear background subtraction to provide normalised intensity variations along the analysed area.

### 2.3. Transmission Electron Microscopy (TEM)

Apart from Raman analysis, disk samples were also analysed using Transmission Electron Microscopy (TEM) to characterise the tribofilm. Sample disks from tests at high temperature (100°C) for 2 and a half minute and 1 hour tests were chosen to analyse the tribofilm at high and low friction values. Sample preparation for the TEM analysis involved application of the focused ion beam (FIB) to produce 15 x 2 µm is cut-offs from the bulk of the wear scar. FEI Nova 200 NanoLab high resolution Field Emission Gun Scanning Electron Microscope (FEGSEM) with precise Focused Ion Beam (FIB) - etch and deposition capabilities were utilised to deposit Platinum onto the surface, to protect the underlying surface. The chosen area was then treated with low-energy gallium ions for further thinning the sample area and to lift it out from the sample bulk and placed on a copper film suitable for high resolution TEM analysis. The TEM system utilised to analyse the sample wear scar surface was the FEI Tecnai TF20.

#### 2.4. Wear measurement

The wear scar diameter of the ball samples was obtained by using the Nikon Profile Projector. The wear scar was projected and magnified to measure the precise diameter across the x and y axis for each sample. An average of three readings was obtained across the wear scar and averaged to calculate the volume loss. The calculated volume loss was further divided by the sliding distance (m) and load (N) to produce the dimensional wear rate, which allows a comparison of the wear performance of the testing parameters.

### 3. Results

#### 3.1. Friction results

The tribological tests were conducted for time periods of 2 and a half minutes, 5 minutes, 10 minutes, 30 minutes and 1 hour. The tests were replicated at least three times. Figure 1 represents the end-of-test friction output averaged from the repeated tests with the corresponding standard deviation.

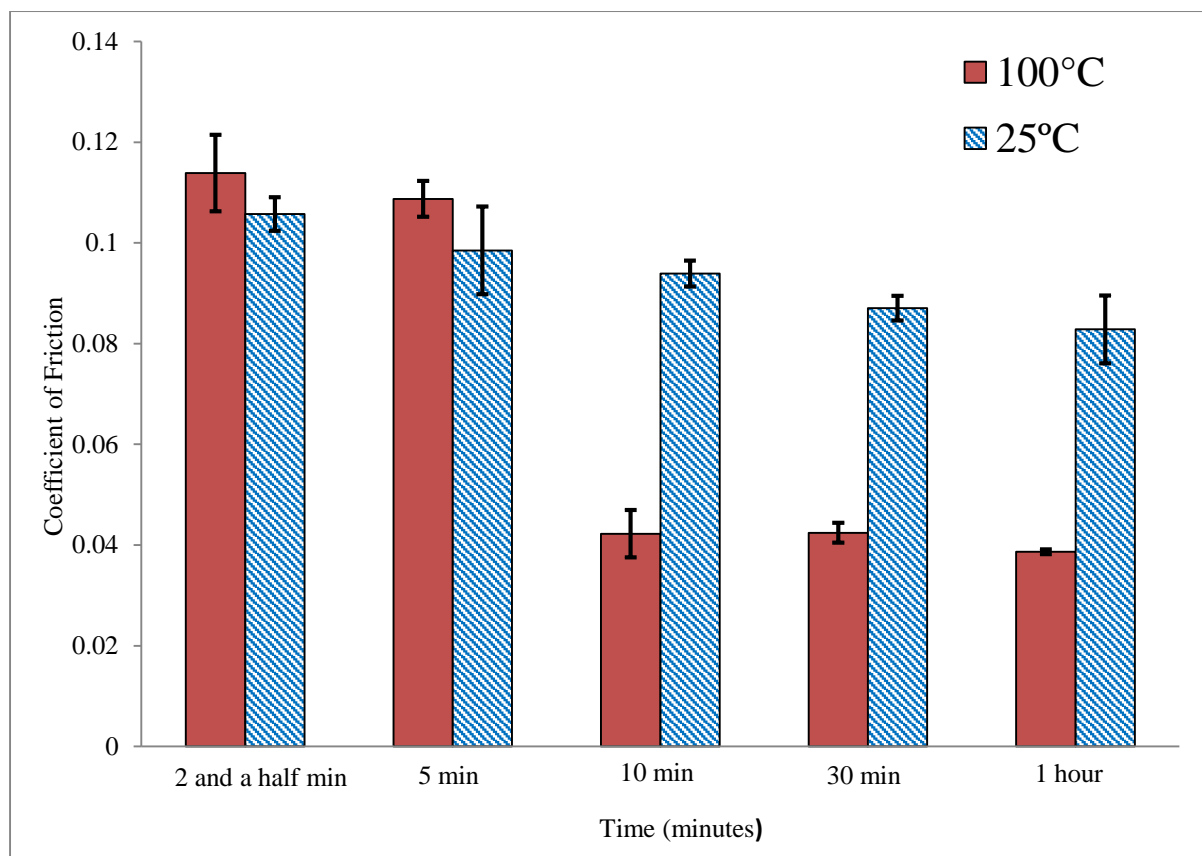


Figure 1. Mean friction coefficient and standard deviation for the end of each time period friction test.

Friction results over time for the tests at 25°C and 100°C are shown in Figure 2a) and b), respectively. Friction for base oil is included too. The MoDTC friction graph at 25°C shows no significant friction reduction, compared to the friction observed at the start of the test. At this temperature, after around 10-20 minutes time of the HSPOD experiment the friction coefficient of the MoDTC lubricant additive stabilises at a value of 0.08. Shorter time tests demonstrate that the friction coefficient starts at a higher value but with rubbing the friction decreases gradually and stabilises at 0.08.

Figure 2b shows the friction coefficient graph for the MoDTC additive at a higher lubricant temperature of 100°C. The higher temperature test with the MoDTC lubricant starts with a higher friction values in comparison to the room temperature (25°C) test. After around 10 minutes rubbing at these conditions, friction value shows a sharp decrease to 0.04, followed with a steady state friction for the rest of the test. The application of high temperature to the system therefore defines the friction reduction behaviour of the MoDTC lubricant additive. Under boundary lubrication, these molybdenum friction-reducing additives have been known to produce very low coefficient of friction values of 0.04 to 0.075 and the effect of temperature has been obvious [7, 8]. However, the tribochemical reaction pathway during the test is an area of interest. The ability of these additives to reduce friction from values above 0.1 to low friction coefficient of 0.04 is investigated using Raman spectroscopy.

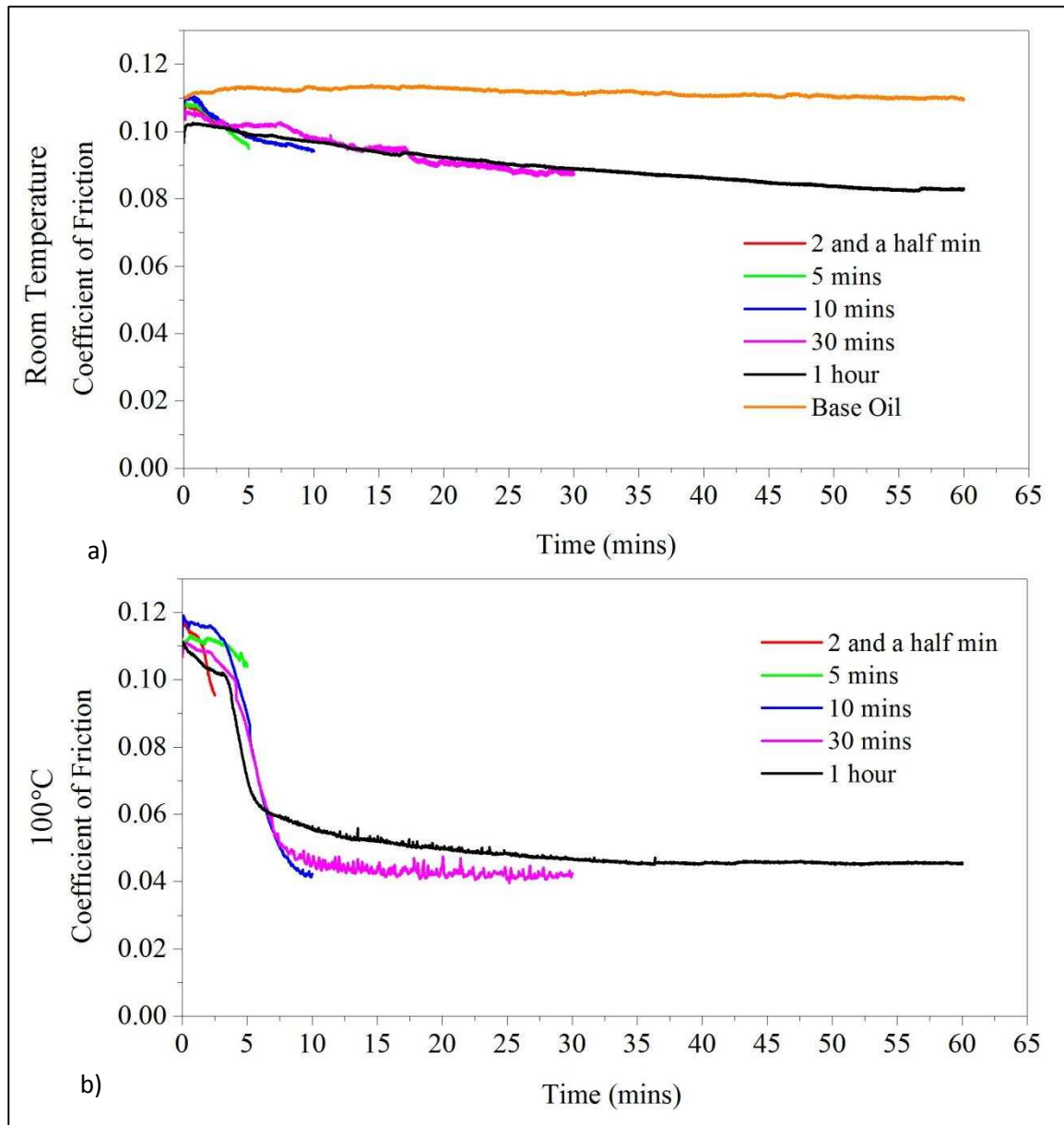


Figure 2. Friction coefficient of the MoDTC lubricant additive at (a) room temperature (25°C) and (b) at 100°C. PAO4 (base oil) friction coefficient at room temperature is also shown as a function of time.

### 3.2. Raman analysis of MoS<sub>2</sub>

Raman spectroscopy has been used to show the presence of a MoS<sub>2</sub>- containing tribofilm on the surface [24-26] and is highly suited for the molybdenum additive film, as both MoS<sub>2</sub> and MoO<sub>3</sub> are Raman active [27]. Figure 3 shows a typical MoS<sub>2</sub> Raman spectrum for a molybdenum (IV) sulphide powder (Sigma-Aldrich, <2 micron, 99%) sample.



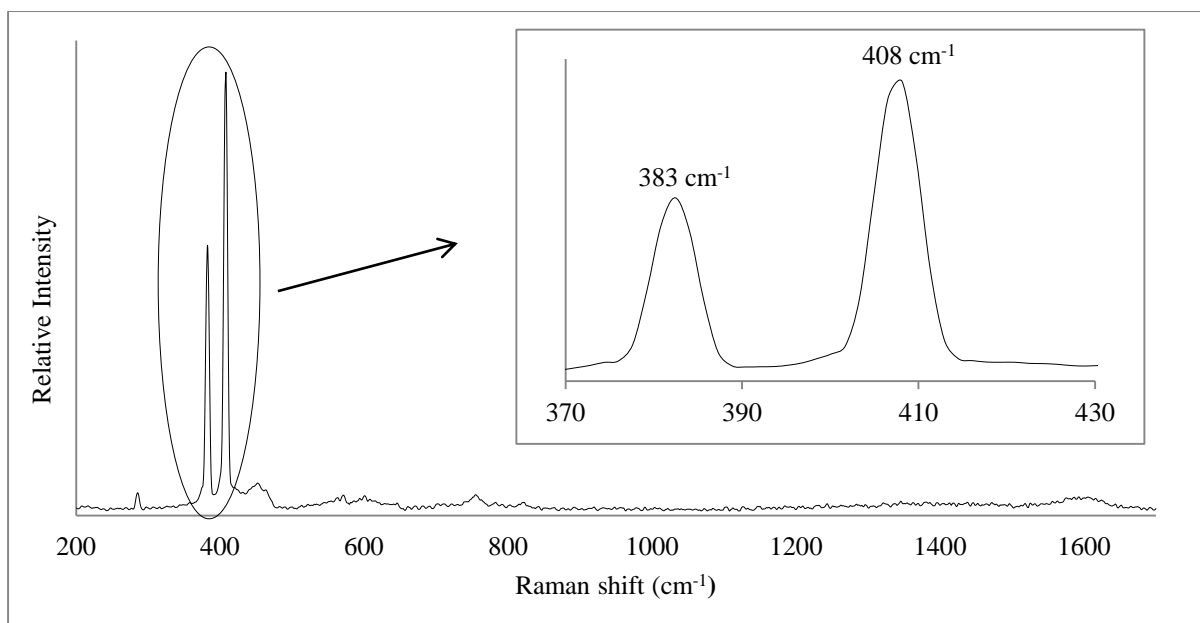


Figure 3. Raman spectrum of the Molybdenum (IV) sulphide powder (<2  $\mu\text{m}$  particle size, 99%)

Previous Raman studies have indicated the presence of four first-order Raman active modes that are present in most  $\text{MoS}_2$  Raman spectroscopic studies at  $286\text{ cm}^{-1}$ ,  $383\text{ cm}^{-1}$ ,  $408\text{ cm}^{-1}$  and  $32\text{ cm}^{-1}$ . The peaks at  $286\text{ cm}^{-1}$ ,  $383\text{ cm}^{-1}$  and  $408\text{ cm}^{-1}$  are a result of the vibrational mode within the sulphur-molybdenum-sulphur layer and the  $32\text{ cm}^{-1}$  is due to the vibration of the adjoining rigid layers [25, 27, 28]. Among the entire first order  $\text{MoS}_2$  Raman active modes, two modes at  $383$  and  $408\text{ cm}^{-1}$  show a well-defined peak for the structure of the  $\text{MoS}_2$ . The frequency mode of  $383\text{ cm}^{-1}$  (in plane  $E_{2g}$  mode) has been assigned to the motion of the Mo + S atoms in the x-y layered plane of the unit cell, which results from opposite vibration of two S atoms with respect to the Mo atom (Figure 4) [29]. The  $408\text{ cm}^{-1}$  frequency (out of plane  $A_{1g}$  mode) is assigned to the motion of the S atoms along the z axis of the unit cell in opposite direction (Figure 4) [29]. Raman active modes for the  $\text{MoS}_2$  therefore have characteristic peaks at approximately  $383$  and  $408\text{ cm}^{-1}$  (Figure 3), and for better identification the scanning frequencies are narrowed at a region of  $330 - 430\text{ cm}^{-1}$ . The FWHM value of the pure  $\text{MoS}_2$  sample is around  $5\text{ cm}^{-1}$ , exhibiting a high crystalline nature of the sample and a well-defined peak is observed.

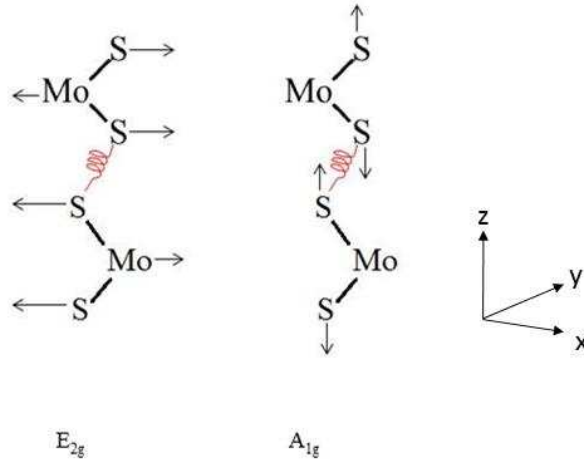


Figure 4. In plane phonon modes E<sub>2g</sub> and the out of plane phonon mode A<sub>1g</sub> of the MoS<sub>2</sub> molecule (Adapted from [28]).

Similarly the Raman bands for the MoO<sub>3</sub> are exhibited at 998, 821, 668, 474, 381, 367, 341, 294, 286, 248, 220 and 200 cm<sup>-1</sup> for different orders [30, 31]. The terminal Mo-O bonds are characterised by Raman bands occurring in the 920 – 1000 cm<sup>-1</sup> range and the bridging oxygen linking to two metal atoms presents a very characteristic and intense Raman line at about 820, 710 – 730 and 830 – 850 cm<sup>-1</sup>. The Raman band at 821 cm<sup>-1</sup> is regarded as the symmetry related vibrational mode and is very sharp and the most intense Raman band in the spectrum.

### 3.3. MoDTC tribofilm chemistry at different rubbing time

In-lubro Raman analysis was carried out on both steel disks and ball samples, not cleaned with any solvent prior to analysis. Raman active modes for the MoS<sub>2</sub> have characteristic peaks at 383 and 408 cm<sup>-1</sup> (Figure 3), and the characteristics of the Raman spectra therefore have been investigated with an analysis of the shifts in Raman peak values and full width at half maximum (FWHM) Raman bands, and normalized intensity variations.

#### 3.3.1. Raman analysis of HSPOD room temperature wear scar samples

A large number of analyses were carried out on various wear scar areas of the disk and the ball samples. In comparison to the friction coefficient of the base oil, a gradual friction decrease can be observed on Figure 2a) for the room temperature MoDTC test but not to the level attributed to MoS<sub>2</sub> formation [11, 15, 20]. Samples from different time periods at room temperature showed the two characteristic Raman responses for the particular Mo-S bond as shown in Figure 5. Figure 5 provides a comparison of the Raman peak position for various time periods samples. The typical Raman spectrum for the wear scar analysed shows a Raman response of the E<sub>2g</sub> and A<sub>1g</sub> peaks at 375 and 400 cm<sup>-1</sup>, respectively. This response was not observed on every area of the sample which indicates the uneven distribution of the tribofilm formation onto the surface. This is confirmed with the Raman mapping results shown later in this section. Under room temperature conditions for various Raman spectra, no apparent shift

of the Raman peak position was seen, indicating similar tribofilm structure is formed at all stages of the test.

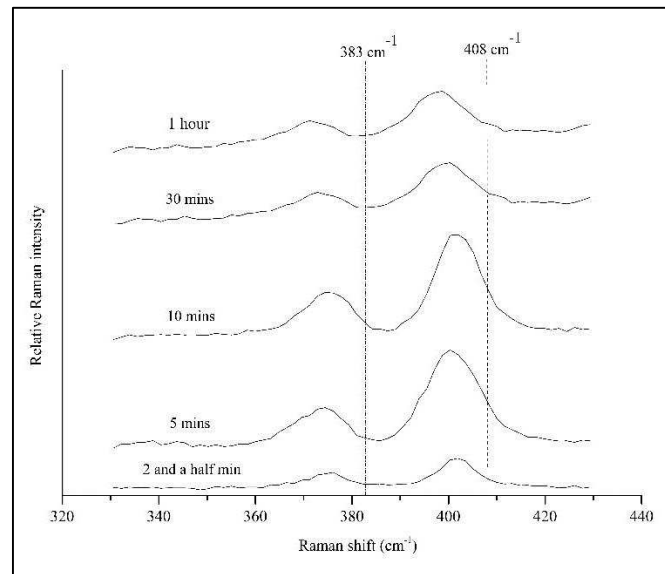


Figure 5 . Raman  $E_{2g}$  and  $A_{1g}$  vibrating modes of the Mo-S bond as a function of rubbing time for room temperature test conditions on the disk wear scar. The position of the  $E_{2g}$  and  $A_{1g}$  peaks of the pure  $MoS_2$  is highlighted at  $383$  and  $408\text{ cm}^{-1}$ .

Figure 6 shows the comparison between the Raman shift of  $A_{1g}$  and  $E_{2g}$  peaks obtained from samples tested at different testing duration at room temperature, with the friction performance obtained. Raman shift defines the vibration modes of the chemical bond as a result of the laser beam. Any change of the Raman shift position will indicate a change in the physical and/or chemical structure of the molecule being analysed. For the room temperature sample analysis shown in Figure 6, the  $E_{2g}$  peak value was observed at  $375\text{ cm}^{-1}$  for most of the analysed samples. Similarly, the  $A_{1g}$  peak assigned to the motion of the S atoms along the z axis of the unit cell was observed at the range of  $400\text{ cm}^{-1}$ . No significant change in the Raman peak position of the Mo-S frequencies was seen on various wear scar areas, indicating a similar tribofilm is formed at any test duration.

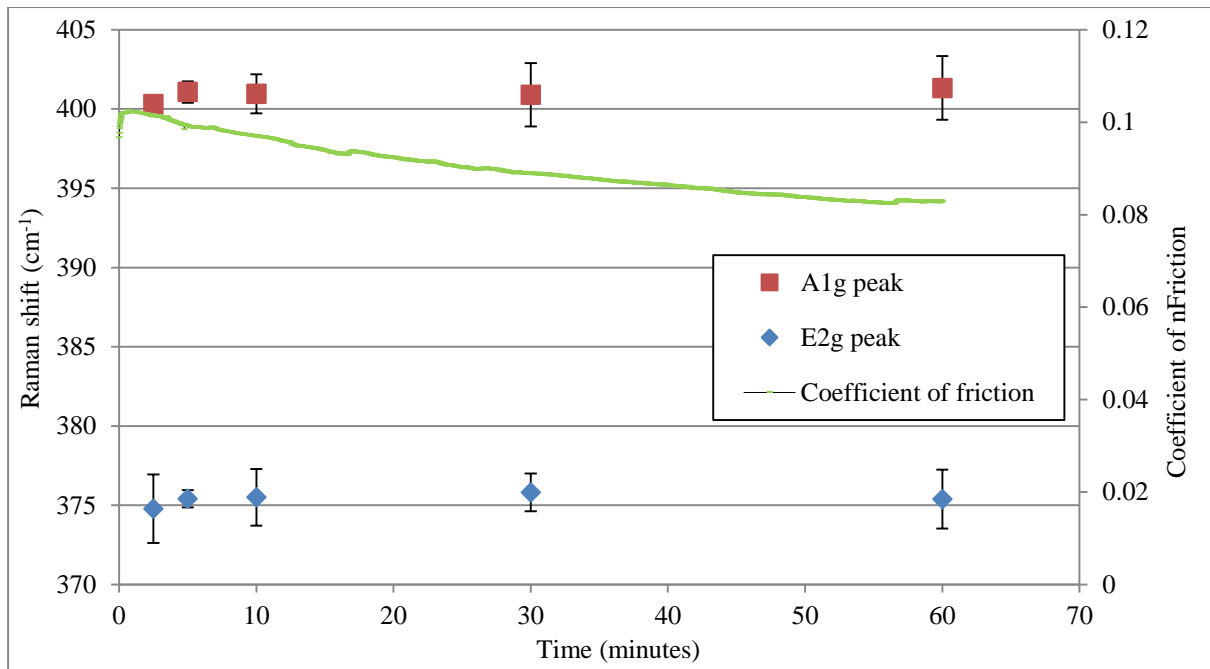


Figure 6. Raman shift of  $A_{1g}$  and  $E_{2g}$  mode obtained from samples tested at room temperature tests, along with the friction coefficient of the 1 hour room temperature test. The standard deviation shows the variation of Raman shift obtained from tens of Raman point analyses across the wear scar.

Raman analysis conducted on the wear scar of the ball samples however shows the absence of any Raman Mo-S response. Instead, a response at around the Raman shift value of  $670\text{ cm}^{-1}$  is observed [Figure 7] on most of the analysed wear scar area for all of the time period samples. This Raman peak at  $670\text{ cm}^{-1}$  has been attributed to the response of the  $\text{Fe}_3\text{O}_4$  iron oxide [32], and can be related to the wear of the ball sample occurring with longer duration of testing time.

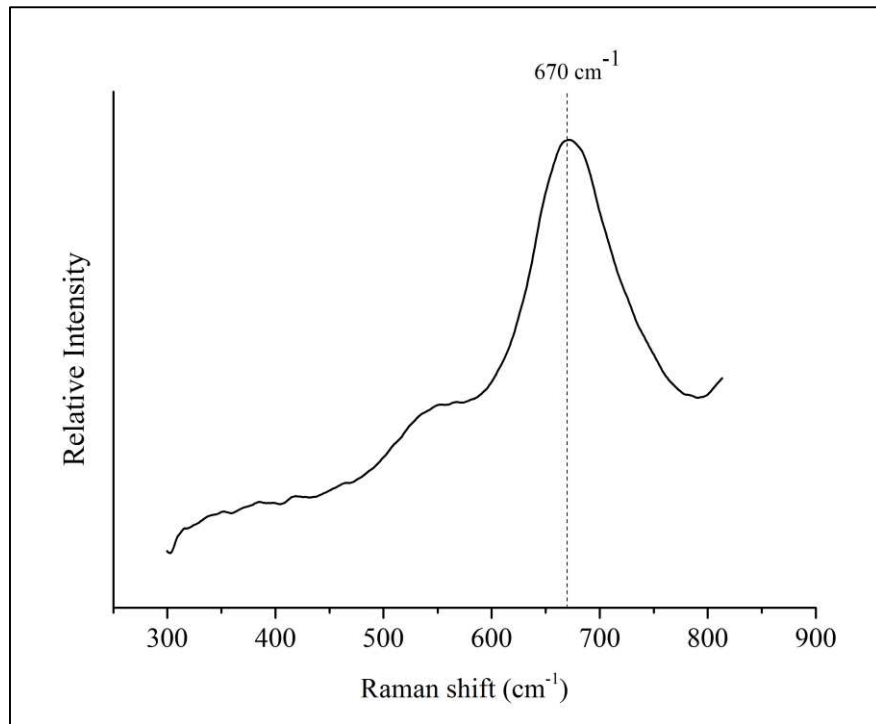


Figure 7. Raman response of the room temperature test ball wear scar for the 1 hour time period. The Raman response of the  $\text{Fe}_3\text{O}_4$  at  $670\text{ cm}^{-1}$  is observed.

No  $\text{MoO}_3$  at  $820\text{ cm}^{-1}$  was observed on the Raman spectra for room temperature test samples. For tests of less than 10 minutes, a Raman peak position  $871\text{ cm}^{-1}$  has been observed which gradually becomes less intense with testing time and disappears with longer duration of testing, as shown in Figure 8. In contrast, longer duration of testing results in detection of a new Raman peak at around  $920 - 930\text{ cm}^{-1}$  shift. This Raman peak is significant for longer duration of test and is observed with every Raman analysis undertaken for the room temperature test. Initial assessment of these two peaks indicate formation of Mo-O-Mo and Mo=O, respectively, but further analysis with additional techniques is required to confirm the mechanism of their formation from the MoDTC additive.

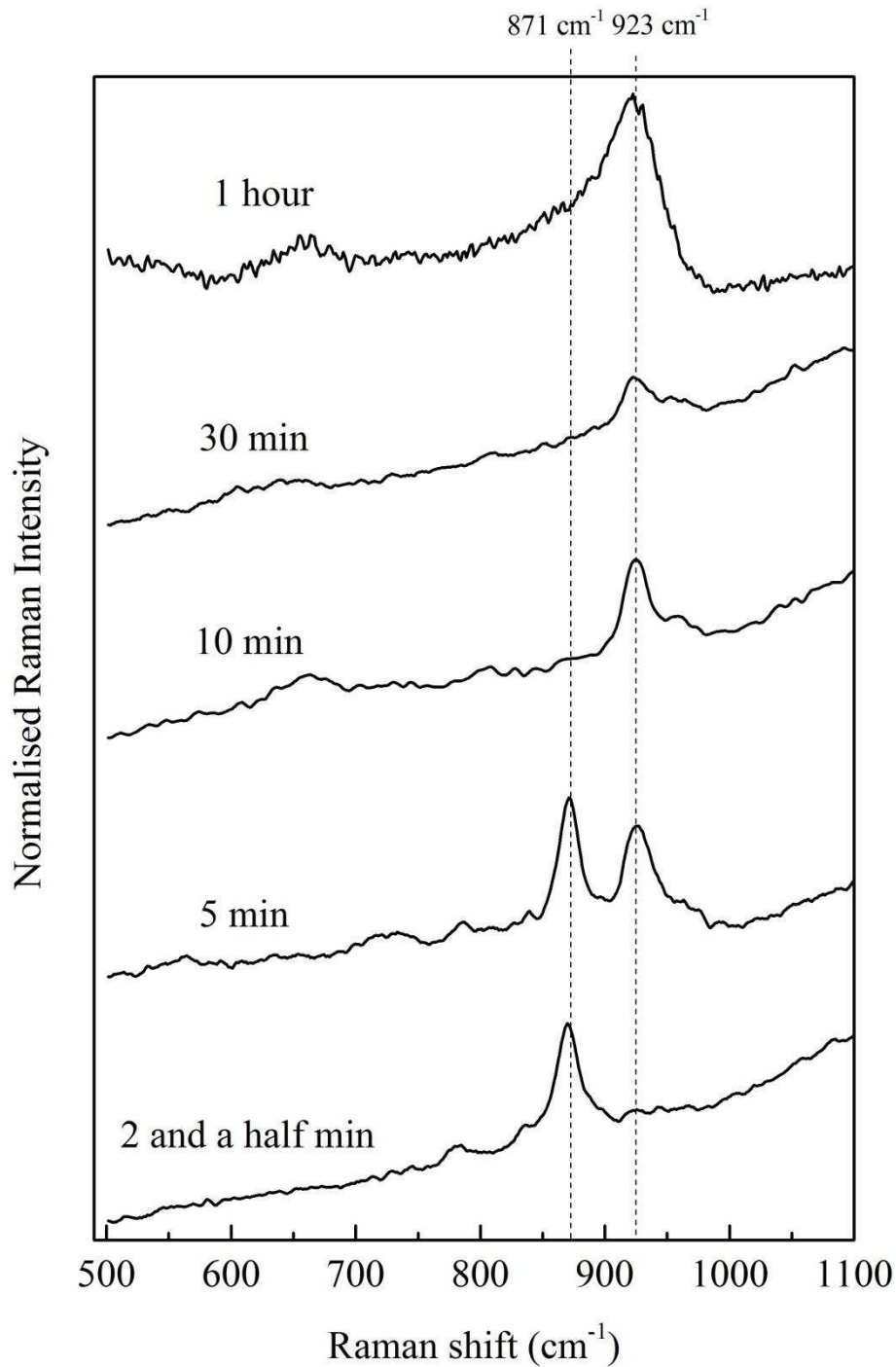


Figure 8. Various Molybdenum oxide bonds observed at different time duration room temperature test disk samples. No MoO<sub>3</sub> Raman peak (at around 820 cm<sup>-1</sup>) has been observed.

Another Raman peak characteristic that could indicate the physical and/or chemical nature of the surface being analysed is the Full Width at Half Maximum (FWHM). Figure 9 shows the FWHM of the Raman Mo-S peaks obtained from the room temperature test wear scar after different test duration. The distribution does not show any statistically meaningful change of

the FWHM with testing time, indicating no significant qualitative tribofilm difference in these conditions.

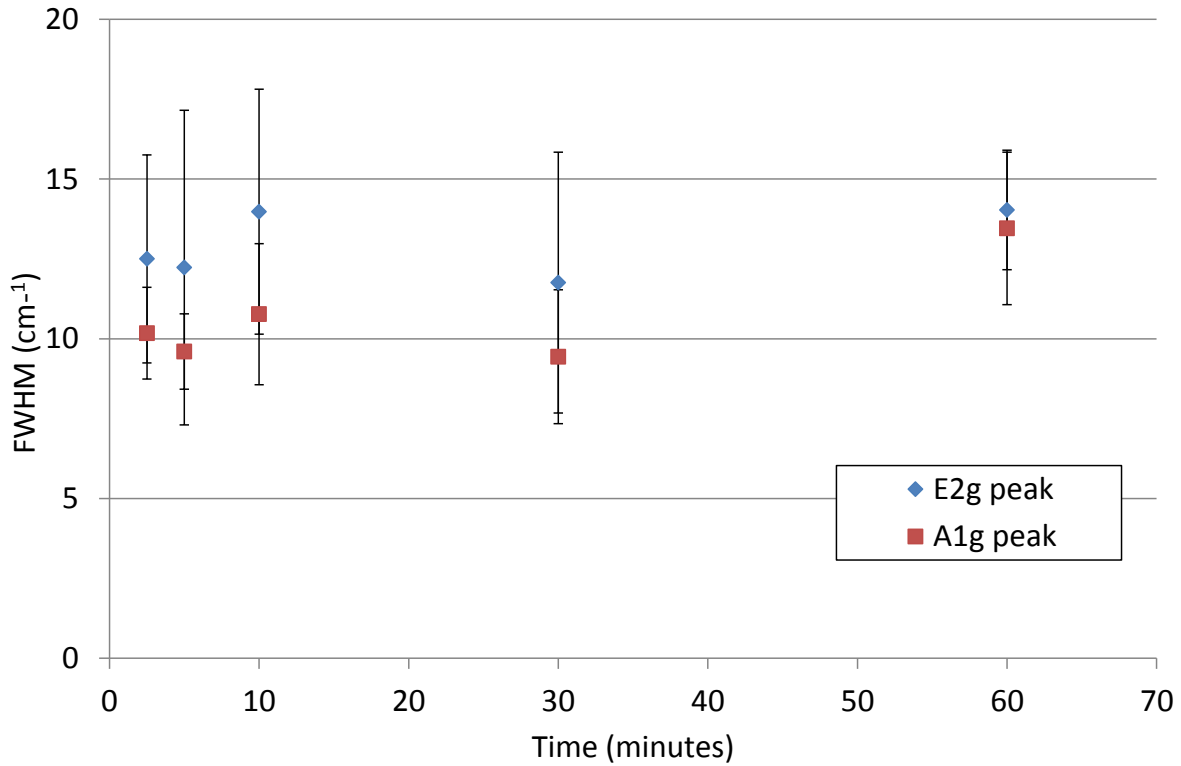


Figure 9. FWHM of the E<sub>2g</sub> and A<sub>1g</sub> Raman peaks obtained from disk wear scar tested at room temperature

To further indicate the formation and distribution of the MoS<sub>2</sub> tribofilm on the sample surface, a Raman map analysis was also carried out onto the surface. The analysis was undertaken with the same parameters to the single point analysis, and a similar mapping analysis was carried out on two to three different areas. The Raman map was analysed with the distribution of the normalised intensity variations of the 400 cm<sup>-1</sup> (A<sub>1g</sub>) Raman response of the tribofilm at room temperature. The response of the Raman peak indicates the distribution of the tribofilm is not uniform on the surface (Figure 10).

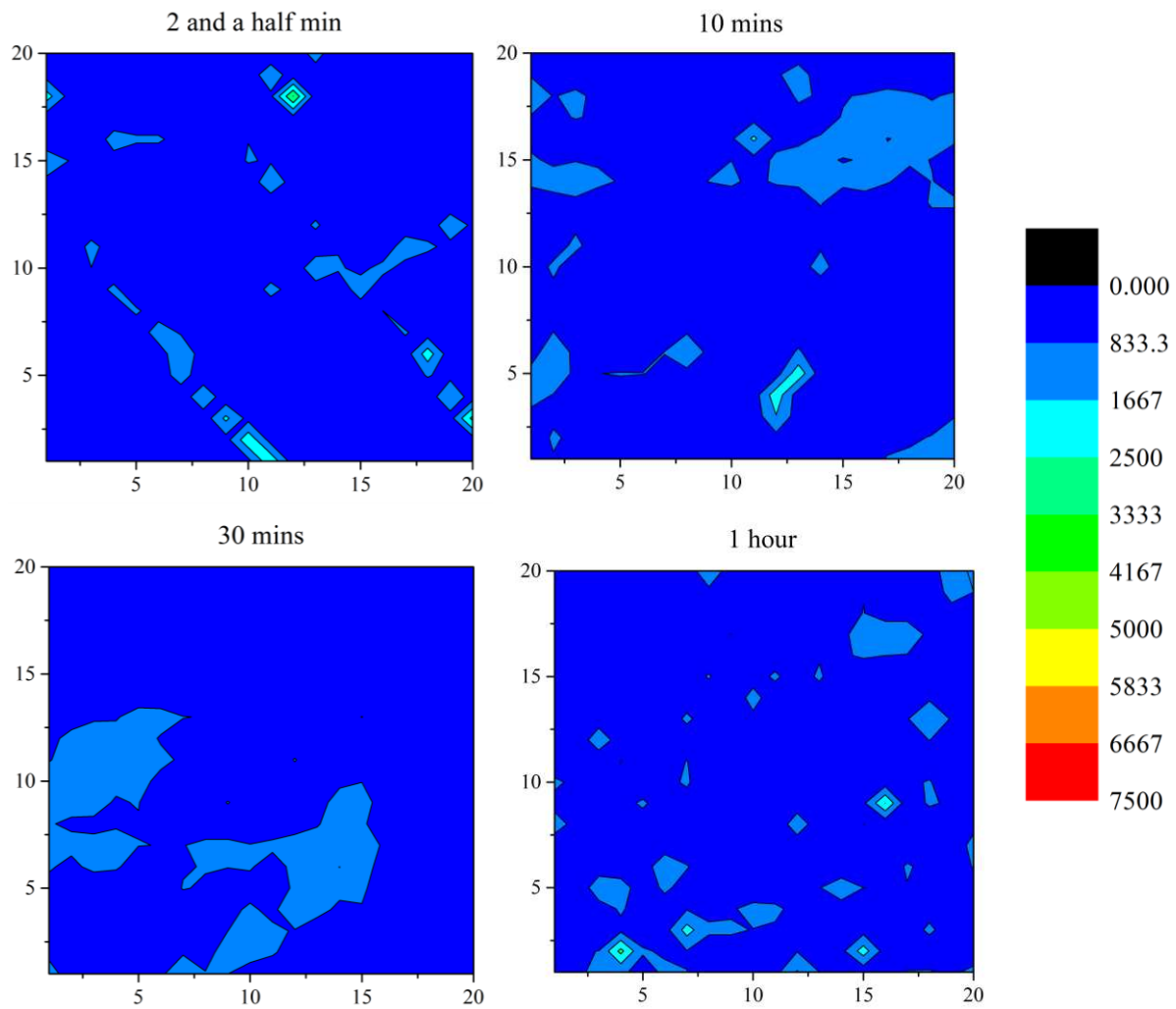


Figure 10. Raman map intensities of  $A_{1g}$  peak at  $400\text{ cm}^{-1}$  at a wear scar area of  $20 \times 20\text{ }\mu\text{m}$  of the disc samples obtained from 2 and a half minutes, 10 minutes, 30 minutes and 1 hour tests at room temperature conditions

### 3.3.2. Raman analysis of HSPOD high temperature ( $100^{\circ}\text{C}$ ) wear scar samples

High temperature tests with the MoDTC lubricant resulted in low friction. The friction graph in Figure 1 shows a drop in friction within the time period of 5 to 10 minutes and reaches a steady state friction of 0.04 within 30 minutes. Figure 11 shows the Raman spectrum obtained from analysing the 1 hour/ $100^{\circ}\text{C}$  disc wear scar. The two characteristic peaks of  $379$  and  $410\text{ cm}^{-1}$  have been observed and indicate formation of the  $\text{MoS}_2$  tribofilm [7, 8].



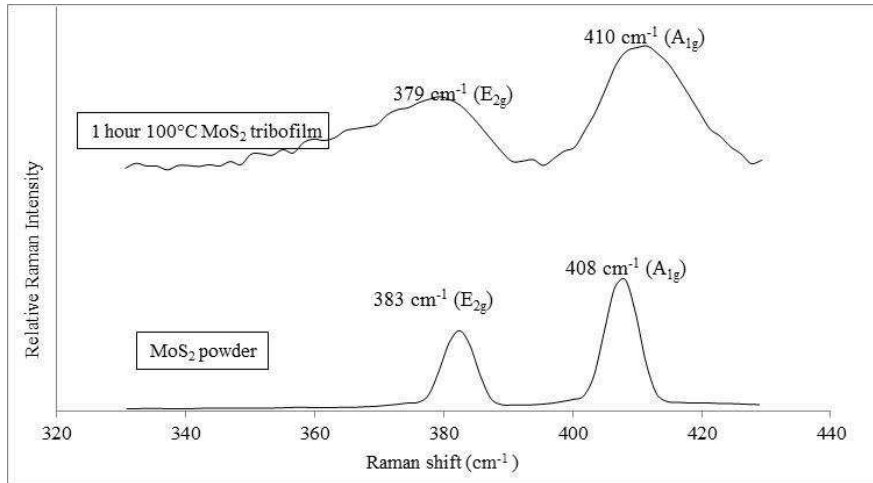


Figure 11. Raman spectra of the  $E_{2g}$  and  $A_{1g}$  peak for the 1 hour high temperature  $MoS_2$  tribofilm, in comparison to the  $E_{2g}$  and  $A_{1g}$  peak of a pure  $MoS_2$  powder.

A comparative Raman analysis of the disk wear scar for various testing time periods is presented in Figure 12. An apparent Raman shift for the  $A_{1g}$  frequency mode can be observed on the graph, which is not the case with the  $E_{2g}$  peak. Figure 13 shows the distribution of the  $A_{1g}$  and  $E_{2g}$  Raman peaks for the various tests along with the friction coefficient.

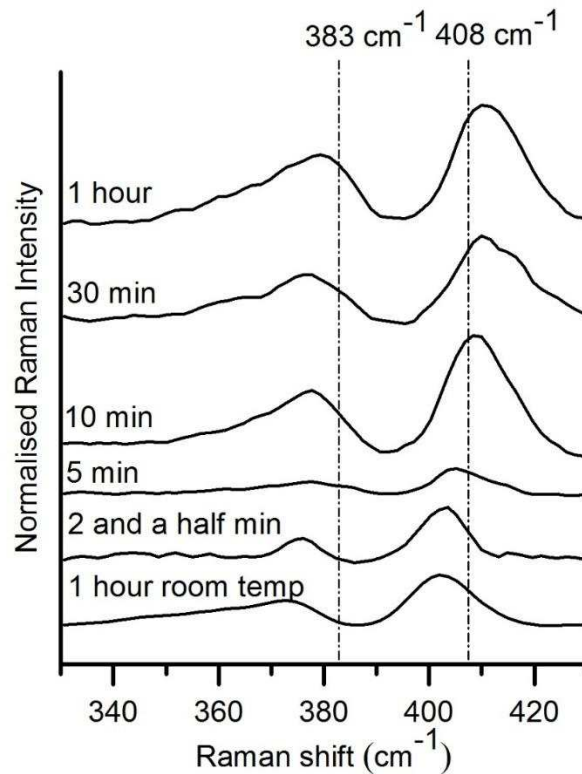


Figure 12. Raman response of the  $E_{2g}$  and  $A_{1g}$  peaks of the Mo-S bond at the wear scar of the disk samples as a function of rubbing time for high temperature ( $100^\circ C$ ) test conditions. The position of the  $E_{2g}$  and  $A_{1g}$  peak of the pure  $MoS_2$  is highlighted at  $383$  and  $408\text{ cm}^{-1}$ .

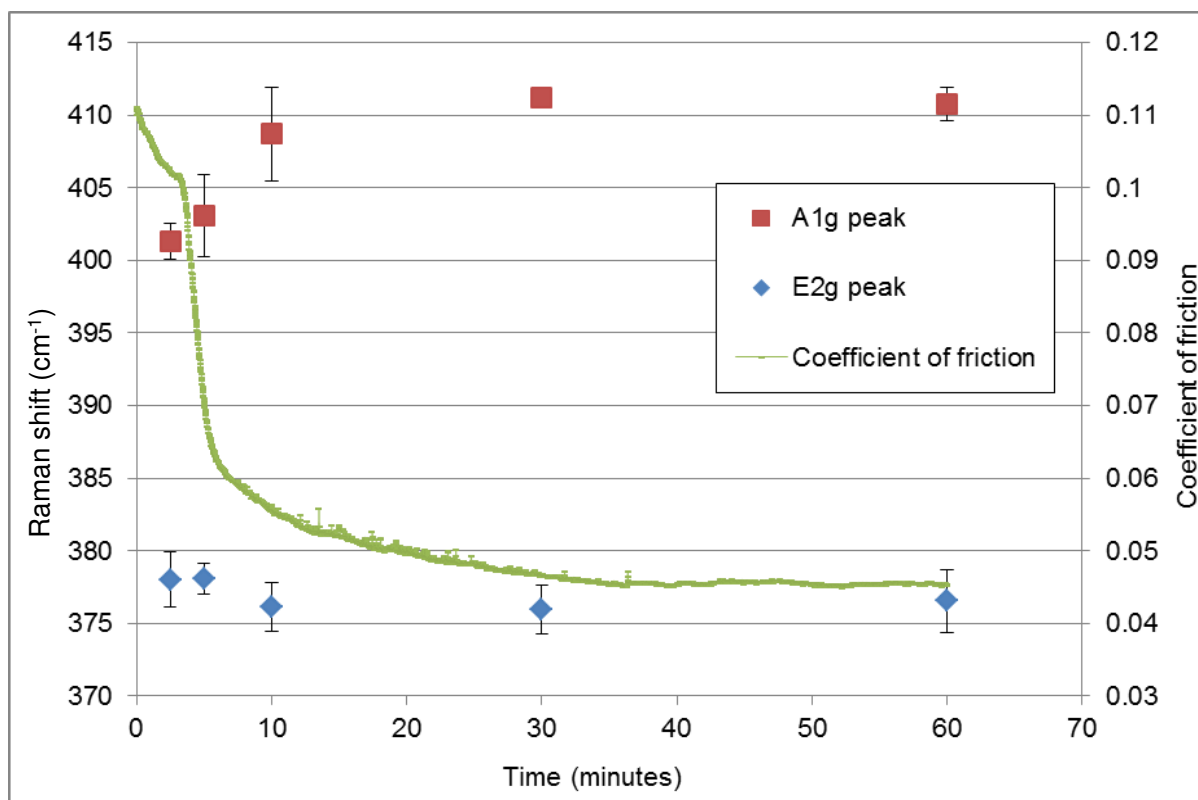


Figure 13. Variation of the Raman peak position for different time periods, along with the friction drop at the higher temperature (100°C) test.

After a time period of 2 and half minutes, the Raman peak response for the two Mo-S characteristic peaks is similar to the ones observed for the room temperature samples. The friction coefficient graph also shows a high friction value during these testing time periods. Within the time period of 5 and 10 minutes, the friction value starts to drop for the high temperature test. The low friction of the high temperature test is apparent at time periods of 30 minutes where the system starts reaching a steady state friction value. The wear scar analysed showed a sharp Raman response around 410  $\text{cm}^{-1}$  and the lower  $E_{2g}$  mode between 375 and 380  $\text{cm}^{-1}$ , and similar peaks were also observed at the wear scar analysis for the 1 hour time period samples. The observed peaks are typical for the  $\text{MoS}_2$  tribofilm. As the friction drops an evident shift in the  $A_{1g}$  is observed which indicates the breakdown of the MoDTC additive towards the formation of a  $\text{MoS}_2$  tribofilm.

Figure 14 highlights the  $A_{1g}$  and  $E_{2g}$  Raman peaks observed at the wear scar of the ball samples for various testing time periods. These show a similar shift to that observed on the wear scar of the disk samples. During the longer test duration, where the friction measured is low, the  $A_{1g}$  and  $E_{2g}$  Raman peak values are at around 412 and 378  $\text{cm}^{-1}$ , respectively. This Raman shift is in accordance to the formation of the  $\text{MoS}_2$  tribofilm on the ball wear sample leading then to the reduction in friction. Shorter testing time period samples, especially under 2 and a half

minute show an absence of the  $A_{1g}$  and  $E_{2g}$  Raman peaks. This response is similar to that of the room temperature samples, which showed an absence of the  $A_{1g}$  and  $E_{2g}$  peaks of the Mo-S bond. At high temperature test, friction dropped after around 5 and 10 minutes rubbing. As shown in Figure 12, position the  $A_{1g}$  and  $E_{2g}$  peaks detected on the disk sample after 10 minutes is similar to those of the low friction Raman response ( $412$  and  $379\text{ cm}^{-1}$ ). However, for the same testing period, position of the  $A_{1g}$  and  $E_{2g}$  Raman peaks ( $405$  and  $375\text{ cm}^{-1}$ ) detected on the ball wear scar do not indicate formation of the same film as on the disk. Ball wear scar is in continuous contact with the disk, further work is underway to establish if the continuous contact affects the tribofilm chemical structure.

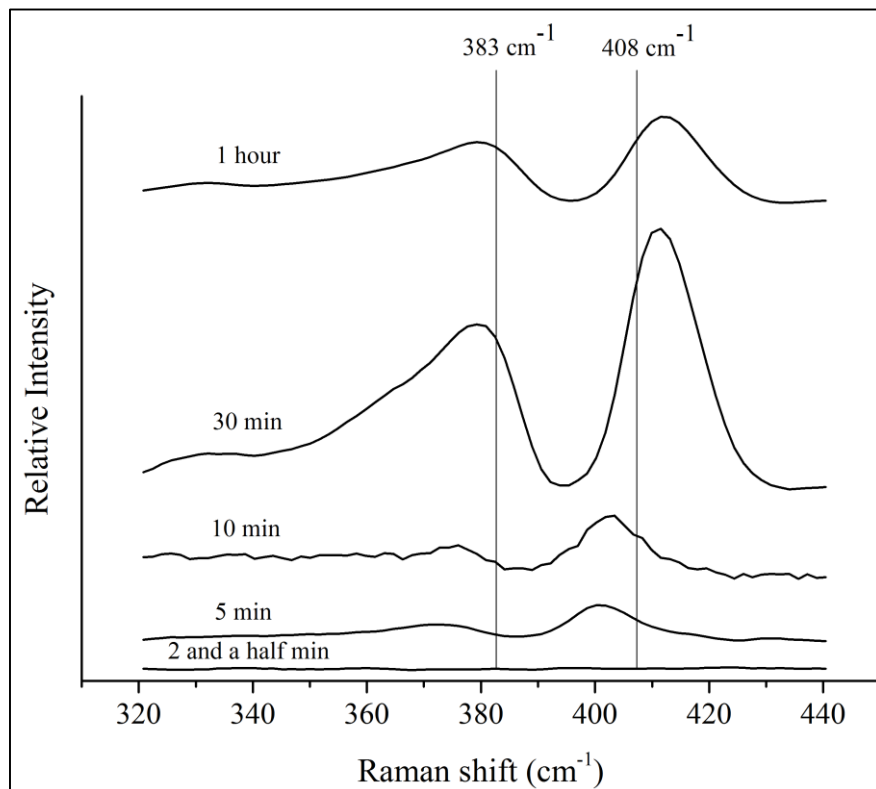


Figure 14. Raman response of the  $E_{2g}$  and  $A_{1g}$  vibrating frequency of the Mo-S bonds at the wear scar of the ball samples as a function of rubbing time for high temperature ( $100^{\circ}\text{C}$ ) test conditions. The position of the  $E_{2g}$  and  $A_{1g}$  peak of the pure  $\text{MoS}_2$  is highlighted at  $383$  and  $408\text{ cm}^{-1}$ .

TEM images (Figure 15) show that a tribofilm thick around  $35\text{ nm}$  is formed at time periods of even 2 and a half minute testing at high temperature. TEM images for the HSPOD  $100^{\circ}\text{C}$  tribofilm for the time period of 1 hour show formation of a MoDTC tribofilm with a thickness of about  $100\text{ nm}$ . Figure 16 shows a higher magnification of the tribofilm which, in contrast to the tribofilm formed at room temperature, exhibits a layer like structure. The images confirm the formation of  $\text{MoS}_2$  sheets, where this layer-lattice structure of the molybdenum disulphide

has facilitated the low friction between the contacts. Similar TEM images were confirmed showing MoS<sub>2</sub> eyelashes at the wear debris showing a lot of highly-dispersed and very flexible bonded MoS<sub>2</sub> single sheets [11].

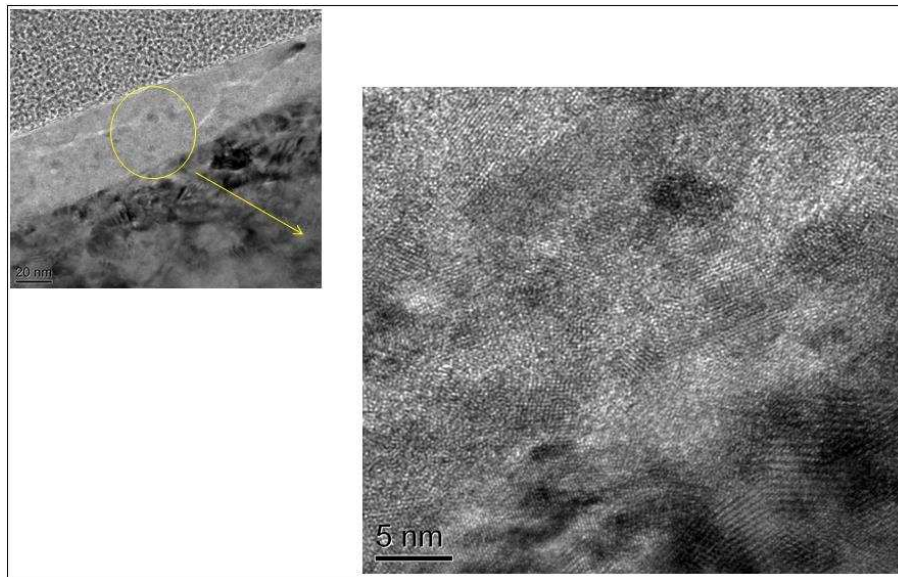


Figure 15. TEM images for the HSPOD 100°C tribofilm for the time period of 2 and a half minute

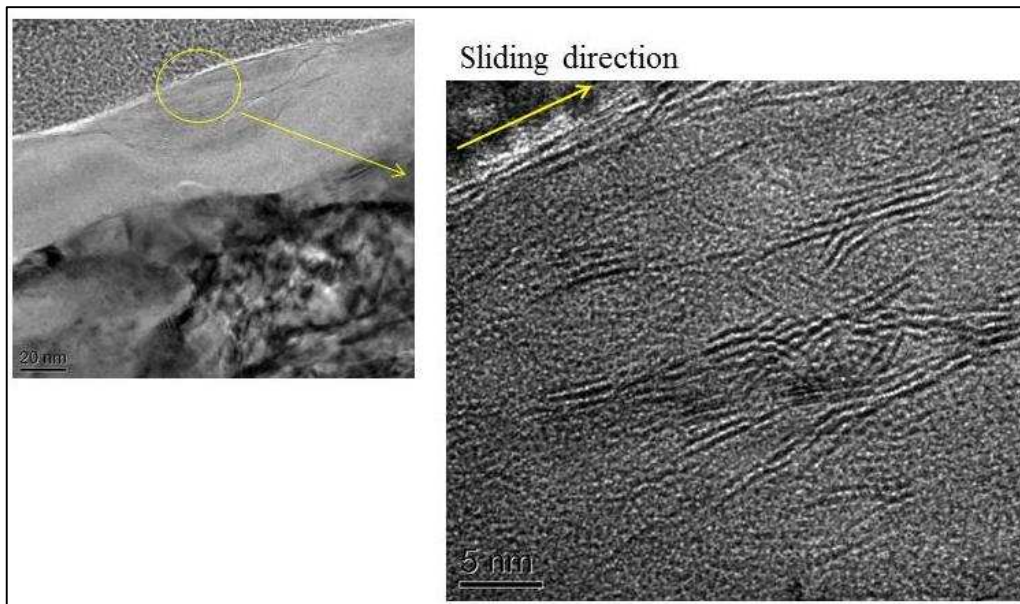


Figure 16. TEM images for the HSPOD 100°C tribofilm for the time period of 1 hour.

Similar to the room temperature samples, the Raman response of pure MoO<sub>3</sub> at 820 cm<sup>-1</sup> was not observed at high temperature testing conditions. As observed under room temperature test condition, shorter duration test at high temperature did not show a peak response around 870 cm<sup>-1</sup> for the Mo-O-Mo entity. Low intensity Raman response of the Mo=O bonds (920 – 930 cm<sup>-1</sup>) could be observed only after certain rubbing, in contrast to room temperature wear scar

which showed distinctive Mo=O peak even after 5 minutes of testing. No peak at  $870\text{ cm}^{-1}$  was observed too, indicating no formation of Mo-O-Mo entity in high temperature wear scar. However, a broad Raman peak between  $660$  and  $690\text{ cm}^{-1}$  is more apparent in high temperature tests. These peaks have been reported for the bonding vibration of the  $\text{Fe}_3\text{O}_4$  iron oxide peak [32]. The Raman response for the iron oxide peak is very apparent at high temperature/longer duration tests, as observed in Figure 17.

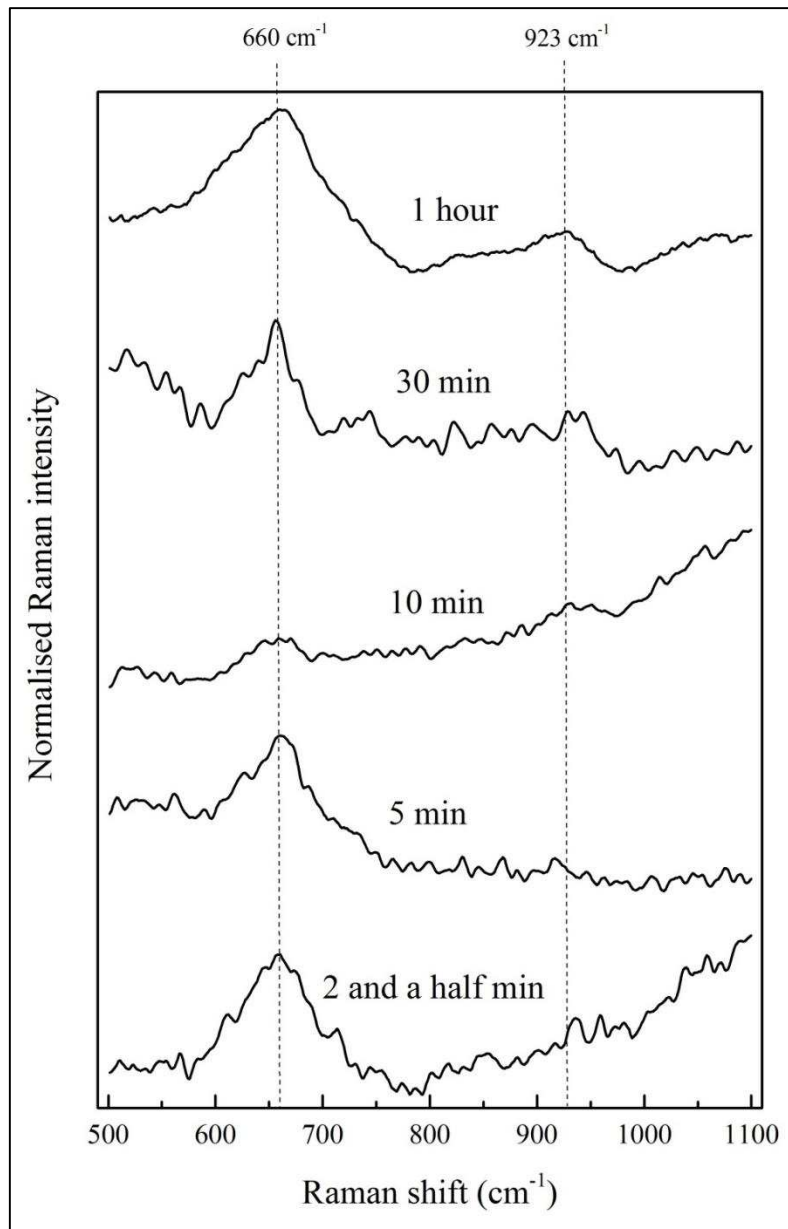


Figure 17. Raman intensity variation for  $\text{Fe}_3\text{O}_4$  and Mo=O peaks of test conducted at  $100^\circ\text{C}$  temperature at different time period.

The FWHM of the various time period high temperature ( $100^\circ\text{C}$ ) samples can be observed in Figure 18 for the two distinct Mo-S Raman peaks. At a time period of 2 and a half minute, the FWHM values for the two characteristic peaks of Mo-S are similar to each other, a feature similar to the room temperature sample. With longer testing, the FWHM for the  $A_{1g}$  frequency

mode can be observed to be in the range of 10 to 20  $\text{cm}^{-1}$ , similar to the room temperature FWHM values. However, the  $E_{2g}$  peak shows an increase in the FWHM values which appear in the range between 10 and 25  $\text{cm}^{-1}$ . The increase in FWHM of the  $E_{2g}$ , assigned to the motion of the Mo - S atoms in the x-y layered plane of the unit cell, could be explained in relation to lattice layer formation.

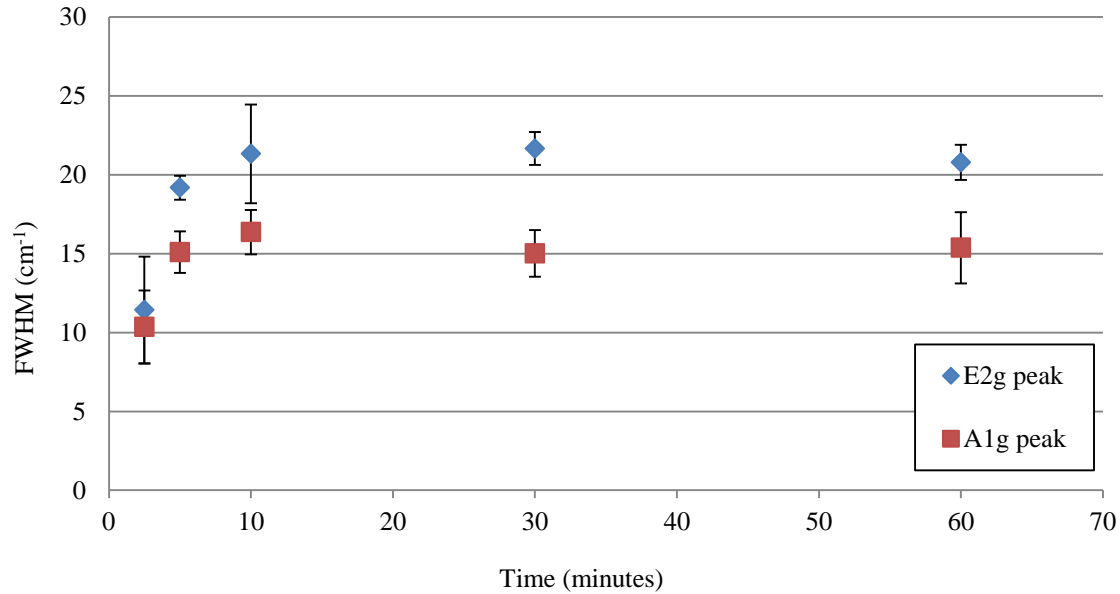


Figure 18. FWHM of  $E_{2g}$  and  $A_{1g}$  Raman peaks obtained from disk wear scar tested at 100°C

Raman map analysis of the normalised intensity variations for the  $\text{MoS}_2$  ( $A_{1g}$ ) Raman response of the tribofilm showed an overall increase of the intensity value with time for higher temperature test. The intensity of the  $\text{MoS}_2$  tribofilm with time shows a stronger response of the development of the  $A_{1g}$  peak onto the sample surface (Figure 19). In comparison to the Raman map analysis of the room temperature samples, the normalised intensity of the high temperature samples are more apparent on to the surface of the tribofilm. The room temperature map area demonstrated an uneven response of the  $A_{1g}$  peak on to the surface of the tribofilm and a similar response is also observed on the high temperature scanned area. However, with time duration, high temperature samples shows higher intensity of the  $A_{1g}$  peak and the change in the structural transformation is already observed with the Raman shift of this peak.

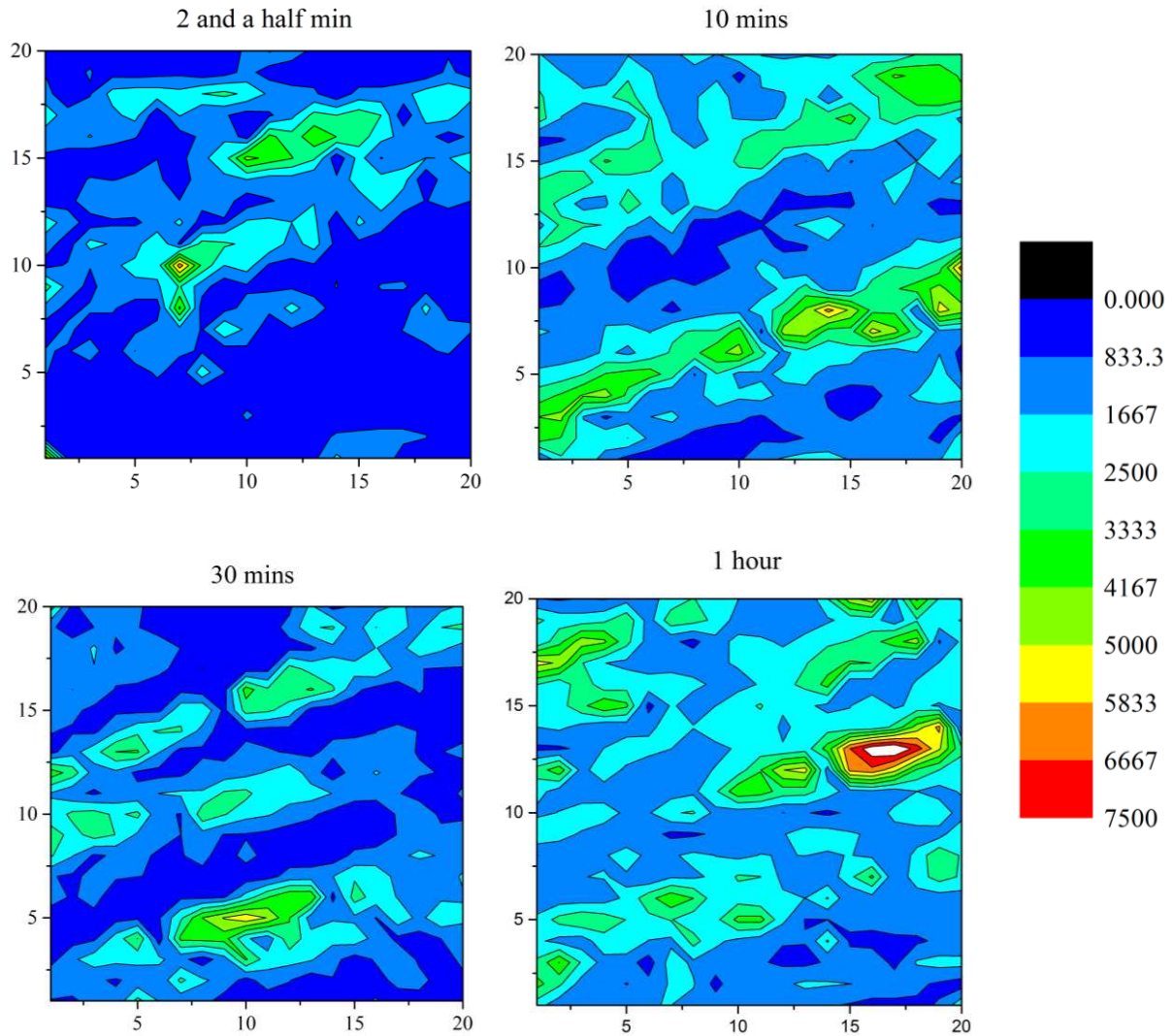


Figure 19. Raman map intensities of MoS<sub>2</sub> tribofilm A<sub>1g</sub> peaks (410 cm<sup>-1</sup>) at the wear scar area of 20 X 20 μm of the disk samples obtained from 2 and a half minutes, 10 minutes, 30 minutes and 1 hour tests at high temperature (100 C) conditions

### 3.4. Wear Performance

Figure 20 shows the wear rate values obtained at the end of 1 hour test under both condition of 100°C and room temperature. In both temperatures, the MoDTC containing lubricant showed less wear than the base oil with the wear at 100°C being higher than the wear observed at room temperature test.

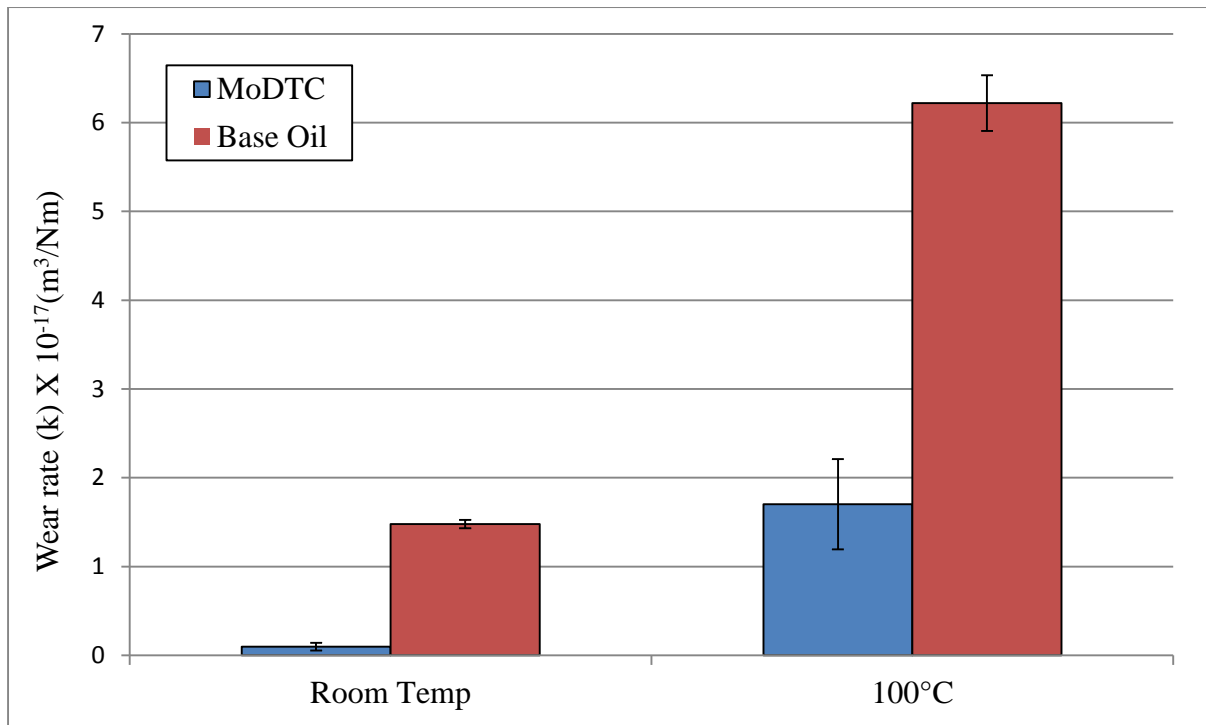


Figure 20. Dimensional wear rate of the ball samples at time period of 1 hour at room and 100°C temperature. Change of temperature will affect both the viscosity and the MoDTC tribochemical reactions. The MoDTC oil is reducing wear even at room temperature.

#### 4. Discussion

The MoDTC additive in higher temperature test resulted in wear reduction as well as in friction reduction compared to base oil test. At room temperature, although the friction obtained with MoDTC oil is not reduced, the wear observed is much lower than the base oil, indicating a positive effect of MoDTC tribofilm formed at this temperature on material protection. The focus of this study is the friction performance of the MoDTC additive.

Raman map analysis of high temperature samples showed an apparent rise in intensity value with time for the MoS<sub>2</sub> tribofilm, indicating the low friction tribofilm development onto the surface of the wear scar. In this study, the Raman mapping has been used to indicate the tribofilm distribution and identification of the representative spectra for each wear scar. The change of MoS<sub>2</sub> Raman peaks intensity with rubbing and temperature is relevant and is subject of a future study.

##### 4.1 Effect of rubbing on the tribochemical development of the MoDTC tribofilm

Surface analysis of samples produced from both room temperature and high temperature lubricated tests show formation of a relatively thick tribofilm formed on the wear scar. The characteristic Raman peaks observed at the room temperature sample showed that a pure MoS<sub>2</sub> tribofilm was not formed on the wear scar, explaining the lack of friction reduction. In contrast the analysis of the tribofilm formed on high temperature test samples confirms the formation of MoS<sub>2</sub> tribofilm on both of the contacting surfaces. In these tests, it took around 5-10 minutes



of rubbing for the friction to reduce to the low friction value typical for the MoS<sub>2</sub> tribofilm. It is obvious that an appropriate combination of rubbing and lubricant temperature is necessary for formation of the MoS<sub>2</sub> tribofilm on the interface.

Under room temperature conditions, the gradual friction drop of the friction in comparison to the base oil test indicates the presence of the additive itself initiates the slow friction drop when the tribological components are in contact. The tribological contact therefore initiates the decomposition of the MoDTC additive within the contact, but at this temperature formation of the MoS<sub>2</sub> layers is not promoted. The Raman response obtained from the room temperature samples shows a Mo-S spectrum with the two characteristic peaks along with the Mo-O bonds that indicate formation of the Mo-S-O core radical from the decomposition of MoDTC. Therefore under these tribological conditions, the MoDTC additive decomposes to form free radicals of Mo-S-O which adsorb onto the wear scar but do not form the MoS<sub>2</sub>. Formation of MoDTC decomposition products prior to the formation of MoS<sub>2</sub> has been proposed before [11]. The current study provides experimental evidence of the MoDTC decomposition products formation and show that the complete kinetics of MoS<sub>2</sub> tribofilm formation is highly dependent on rubbing and lubricant temperature.

High temperature conditions not only will result in more solid – solid contact [19] due to lower viscosity but will also affect the additive decomposition rate and adsorption related processes. At high temperature testing, the rubbing conditions result in the Mo-S-O radical adsorbed on to the wear scar to decompose further to form the MoS<sub>2</sub>. An amorphous tribofilm structure is observed at time period of 2 and a half minute, where the friction is high. TEM images for 1 hour time period show a formation of ‘eyelashes’ like structure which has been attributed to the formation of MoS<sub>2</sub> sheets [11] which enable low friction. These highly dispersed layers of MoS<sub>2</sub> are detected on most part of the 100°C tribofilm, but close to the substrate an amorphous like structure similar to the ones observed at high friction is observed. A prerequisite to form an initial layer before these layers of MoS<sub>2</sub> has been reported by various authors [6, 33]. Gondo and Yamamoto [34] indicated that a prerequisite to form MoS<sub>2</sub> on the rubbing surfaces was that MoO<sub>3</sub> be formed in advance. In the current study, the Raman response of the pure MoO<sub>3</sub> tribofilm at 820 cm<sup>-1</sup> is not observed on any of the wear scars. This is in contrast to previous work conducted in vacuum with XPS on tribofilms [35] and dry sliding MoS<sub>2</sub> coating Raman studies [25]. A broader Raman peak is however observed onto the Raman spectrum of the tribofilm at a frequency range of 850 – 1000 cm<sup>-1</sup> Raman shift (Figure 8). This Raman shift corresponds to the long chain of Mo-O bonds [31]. Under room temperature the Mo-O-Mo entity Raman response at 871 cm<sup>-1</sup> (Figure 8) can be observed for shorter duration of test which further disintegrates to form Mo=O bonds with longer duration test [30, 36, 37]. The Raman results in this study indicate that important precursor to MoS<sub>2</sub> tribofilm formation are the transient tribochemical reactions between iron oxide and MoDTC decomposition products. Further work is underway to better understand the mechanisms by which these reactions lead to the formation of low friction tribofilms.

#### 4.2. Effect of temperature on the tribochemical development of the MoDTC tribofilm

Previous work has demonstrated the effectiveness of temperature for the formation of the MoS<sub>2</sub> tribofilm from the MoDTC additive [7, 38]. The characteristic Raman active modes for the MoS<sub>2</sub>, approximately at 379 and 410 cm<sup>-1</sup>, are observed at samples where the friction drops to a value of 0.04. The MoS<sub>2</sub> tribofilm formed under high temperature however shows a shift of 2-3 cm<sup>-1</sup> to that of the pristine MoS<sub>2</sub> spectrum (Figure 3). This shift could be as a result of the induced pressure which probes vibrational changes in the multilayered MoS<sub>2</sub> [39]. At high temperature test sample, during the high friction induction period, the Raman response corresponds with that observed when analysing the room temperature test sample. Low friction could be achieved only at 100°C after a certain induction time, indicating a synergy between temperature and rubbing in formation of low friction tribofilm.

One key observation from Raman results is that under high temperature conditions, the shift in the A<sub>1g</sub> Raman peak position (Figure 12) and increase in FWHM of both A<sub>1g</sub> and E<sub>2g</sub> Raman peaks (Figure 18) align very well with the drop of friction coefficient, as seen in Figure 13. Shift of the Raman peak position together with the FWHM indicate that the physical and chemical structure of the tribofilm changes with rubbing. This shift can be due to the crystallinity of the MoS<sub>2</sub>, purity, stress, thickness etc. A recent published study on model MoS<sub>2</sub> film suggests that position of A<sub>1g</sub> Raman peak in relation to E<sub>2g</sub> could be used as a convenient diagnostic of the layer thickness of the MoS<sub>2</sub> samples [40]. Lee et al [40] characterised single and few layers of MoS<sub>2</sub> films by Raman spectroscopy and concluded that the frequency of the E<sub>2g</sub> mode decreases and that of A<sub>1g</sub> mode increases with increasing the number of MoS<sub>2</sub> monolayers. In the current study, formation of the MoS<sub>2</sub> layers with rubbing is shown by the TEM images of the tribofilm (Figure 16). Therefore, position shift of the E<sub>2g</sub> and A<sub>1g</sub> modes of the MoDTC tribofilm formed at high temperature could indicate not only formation of a pure MoS<sub>2</sub> structure on the wear scar but also a result of the number of MoS<sub>2</sub> layers formed, leading to low friction performance.

Future work will be conducted in evaluating the tribofilms formed on the ball wear scar and their correlation with the films formed on disk samples. This would help elucidate the effects that continuous contact (in case of ball wear scar) has on the physical and chemical nature of the films formed.

#### 4. Conclusions

Surface analysis techniques of Raman spectroscopy and TEM have been used to study the transient tribochemical processes when the Molybdenum dialkyldithiocarbamate (MoDTC) friction modifier additive is tested in boundary lubrication regime. Raman analysis of in-lub wear scars showed that a tribofilm is formed in both, room temperature and high temperature (100°C) conditions. The results obtained provide experimental evidence of the proposed theoretical models in literature but also highlight new chemistries on the wear scar which develop from MoDTC as a function of rubbing and lubricant temperature. The key conclusions are:

1. The Raman spectra can be used to obtain both qualitative and quantitative information on

the tribofilms formed on the wear.

2. Under room temperature conditions, the MoDTC additive gives a slight friction drop when the tribological components are in contact and significant wear reduction. The decomposition of the MoDTC lubricant within the contact is initiated with rubbing and shows the presence of Mo-S-O bonds within the contact, but does not promote the formation of the MoS<sub>2</sub> tribofilm. Further rubbing does not change the tribofilm properties.
3. Formation of MoDTC tribofilm is initiated at the sliding sample, and with further rubbing at 100°C low friction coefficient is obtained. The shift of E<sub>2g</sub> and A<sub>1g</sub> Raman modes of the MoS<sub>2</sub> tribofilm has the potential to provide both qualitative and quantitative information on the film formed.
4. The transition from Mo-S-O tribofilm to low friction MoS<sub>2</sub> depends from both the rubbing time and lubricant temperature. The effect of lubricant temperature is suggested to be more related to the tribochemical processes at the interface.

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