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Study of the Interfacial Mechanism of ZDDP Tribofilm in Humid Environment and its Effect on Tribochemical Wear; Part I: Experimental

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Abstract

Wear performance of any tribological system can be influenced in a complex way by water contamination. Water can be the cause of steel corrosion which, in turn, can accelerate wear. It can decompose the additives in the oil and create a more corrosive environment which leads to the higher wear in the system. A key novelty of this study is to investigate the effect of relative humidity and the tribochemical changes on the tribological performance and tribofilm characteristics of boundary lubricated systems by means of designing a humidity control system integrated to the Mini Traction Machine (MTM) and Spacer Layer Interferometry Method (SLIM) for the first time. The system is capable of simulating rolling-sliding conditions continuously where lubricant can be contaminated with water. This paper is the first part of a two-part study and the theoretical aspects of the work is the subject of the second part of this investigation. It was observed that humidity hinders the tribofilm formation, especially at higher values of relative humidity and lower temperatures and it can significantly affect the wear process. The correlation between tribofilm thickness, water concentration, temperature and wear of the system was studied. The experimental results suggest that the higher the humidity, the higher the wear of the system and it is more noticeable at lower temperatures where the tribofilm in thinner. The surface chemistry of zinc polyphosphates was investigated as a function of humidity.

Key words: ZDDP, Boundary lubrication, Relative humidity, Wear

1 Introduction

Water plays a significant role in altering the tribological performance in bearing applications [1-3]. It can affect the tribological performance in different ways shown in Figure 1 [4] . A comprehensive study of the adverse effects of water on oil-lubricated tribological systems has been done by Parsaeian et al [4] and Lancaster et al [5] .

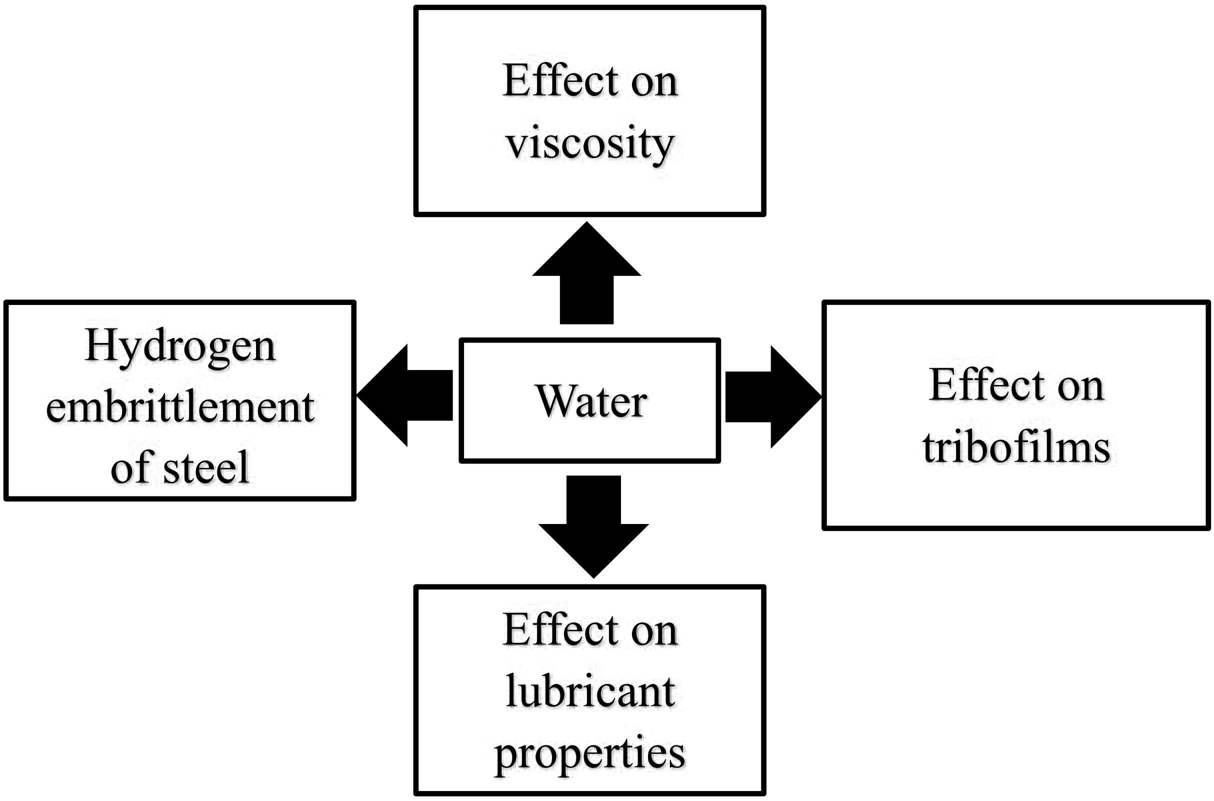


Figure 1 The main adverse effects of water contamination on a tribological system

1.1 Effect of water on decomposition of ZDDP (Zinc Dialkyl Dithiophosphates) additive

ZDDP reacts with the surface in the boundary lubrication regime and produces a comparatively thick tribofilm on the counter bodies. It was shown that the wear behaviour of the tribological system depends on the properties of the reaction layer formed on the surface. [4, 6-8].

The effect of water on tribofilm characteristics has been the subject of recent studies [4, 9-11]. It was reported that water increases the rate of decomposition of ZDDP which results in generating thinner tribofilm on the activated surfaces [12]. Faut and Wheeler [11] proposed that water contamination delays the formation of the tribofilm created by ZDDP. Nedelcu et al. [10] recently found that water changes the performance of ZDDP by altering the chain length of polyphosphates. It reduces the chain length of phosphate through hydrolysis. It was attributed to the interference of water with additive on the contacting surface due to the fact that water molecules prevent the ZDDP molecules to attach to the surface and changing the tribochemical reactions and reducing the progress of the formation of tribofilm. The same trends was observed recently by Parsaeian et al [4] . They suggested that by increasing the water concentration in the oil-containing ZDDP from 0 Wt% to 3 Wt%, the growth rate of the tribofilm is reduced significantly.

1.2 Hydrogen embrittlement and oil oxidation

Water is known as the significant source of generating hydrogen in lubrication system, especially bearing applications [13, 14]. The main reason for water causing pitting failure is considered to be hydrogen embrittlement. Hydrogen penetrates to the edge of the crack and accelerates the crack propagation [13-15].

When the oxygen and hydrogen are both present in the lubricant, published studies suggest opposite trends. Schatzberg et al. [16, 17] believe that oxygen is beneficial in terms of lessening the effect of water on fatigue failure but it was proposed by Ciruna et al. [13] that water is detrimental for the system and increases the corrosive wear of any tribocorrosion system. Water contamination can significantly accelerate the Oil oxidation [18]. The by-products of oil oxidation are always acids, which can make the environment more corrosive. This corrosive environment in oil can increase material degradation rate [2].

1.3 Effect of free water on viscosity

Water contamination may affect oil viscosity and in turn, the change in the oil viscosity can change the lubrication regime from elastohydrodynamic to severe lubrication regimes such as mixed or boundary lubrication regime.

Liu et al. [19] studied the effect of free water at concentrations between 8 and 36 vol. % on the viscosity of four different paraffinic mineral oil. At this large concentrations, water and oil form emulsion. In order to stabilize this emulsion, Liu et al. added emulsifying agent with concentrations between 1 and 8 vol. %. They noticed that although the viscosity of the emulsion is larger than the one of oil, a thinner EHD film is formed.

Chen et al. [20]studies the effect of relative humidity, i.e. 20, 60 and 100%, on PAO oil with ZDDP anti-wear additive in lubricated steel and steel contacts under extreme pressure and pure sliding conditions using ball-on-disc test rig. They concluded that water does not change the bulk properties, i.e. viscosity and TAN, of the oil.

The effect of water on viscosity seems to be strongly dependent on the amount of water in oil. Smaller amount appears to have no effect on viscosity, which is evident from Chen et al. [20] results. On the other hand, at larger amount of dissolved or free water, viscosity is expected to increase, which is evident from the results of Liu et al. [19]. The same results has also been found when hydrated ethanol was added to the lubricant [21]. This suggests that it is not sufficient to report only the relative humidity values but the exact amount of water in oil is required as well.

The tribochemistry of ZDDP has been the main focus of recent research; some focused on the chemical structure of the ZDDP and the chain length of glassy polyphosphates [22-24], some others focused on the effect of physical parameters such as temperature on the structure [25-27] and on the functionality of such films [28-31]. The effect of different parameters such as load, temperature and running-in time have been investigated but there is a lack of comprehensive understanding on the effect of relative humidity and the related tribochemistry on the tribological performance of boundary lubricated system under rolling/sliding conditions. The main aim of the current study is to assess the effect of relative humidity on tribochemical performance of boundary-lubricated systems in rolling/sliding contacts. For this purpose, a humidity control system was designed and integrated with the MTM/SLIM to be able to accurately control the humidity during the experiments and the correlation between tribofilm thickness, humidity, tribochemistry and wear was investigated.

2 Experimental procedure

2.1 Test rig

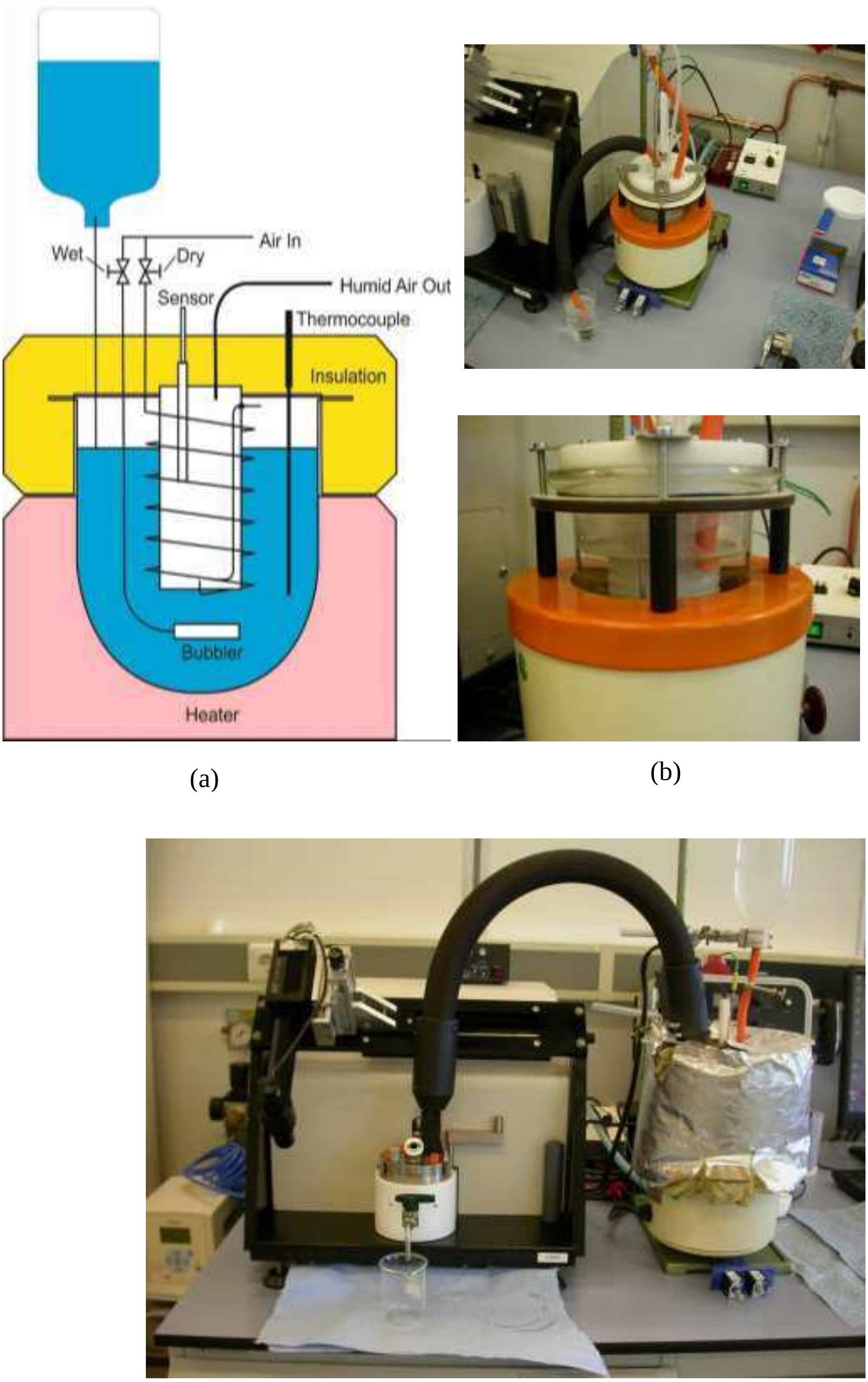
A Mini Traction Machine (Figure 2) was used to generate tribofilm on the surface and simulate rolling-sliding conditions in boundary lubrication regime. To measure the thickness of the reaction layer formed on the contacting surfaces, Spacer Layer Interferometry Method (SLIM) was used in this study. A detailed discussion regarding the test rig can be found in Ref [4, 32].

2.2 Humidity control system

To evaluate the effect of different levels of relative humidity on tribological performance and tribofilm characteristics, a humidity control system was designed. This system is capable of producing continuous steady humidity to expose the lubricant in the tribological experiment to a humid environment. To simulate rolling/sliding conditions and monitor tribofilm evolution during the test under controlled humid environment, the humidity system is mounted on an MTM/SLIM configuration. The humidifier is connected to the PC by a controller system and relative humidity is monitored by LUBCHECK program at a time interval of one second. The humidity could be varied between 0%-100% (±1%). The humidity control system consists of different parts described as followings (Figure 2):

- Heater: to heat up the water up to the desired temperature. The advantage of using heated water to produce humid air is to avoid the presence of water droplets in the humid air
- Insulation part: to isolate the chamber from the environment to keep the temperature and humidity constant during the experiment
- Humidity sensor : to control and monitor humidity during the test
- Thermocouple : to control the temperature of the water during the experiment
- Dry air and wet air valves: to apply the desired level of humidity in the range of 0% (dry air) to 100%
- Bubbler : to produce bubble in the water which facilitates generating the humid air

The humid air is transferred from the chamber to the MTM oil bath using a heated tube. The tube is heated to the same temperature as the oil bath and the chamber to avoid any condensation of the water in the system. The calibration of the humidity sensor was conducted by adjusting the output screw when inserting the humidity probe into two extreme humidity environments: the low RH environment—Lithium Chloride solution, 11.3%RH; the High RH environment—Sodium Chloride solution, 75.3%RH.



(a)

(b)

(c)

Figure 2 Humidity control system a) schematic figure b) humidity chamber c) MTM SLIM integrated to the humidity control system

2.3 Material and test conditions

The ball and disc were made of AISI 52100 steel which are commercially available for roller bearings. The hardness of the ball and disc specimens reported to be 6 GPa (See Table 1). Before starting the tribo-test, the ball and disc specimens were thoroughly cleaned up by immersing in isopropanol and petroleum ether using ultrasonic bath at temperature of 60°C for 20 minutes to remove any contamination from the contacting surfaces. The comparison between minimum Elastohydrodynamic film thickness and the composite roughness of the surfaces represents the severity of the contact known as the lambda ratio. The minimum EHL film thickness is calculated by using Hamrock-Dowson equation as the following:

$$h_{min} = 3.63R_x(\frac{U\eta_0}{E^*Rx})^{0.68}(\alpha E^*)^{0.49}(\frac{W}{E^*R_x^2})^{-0.073}(1-e^{-0.68k}) \quad (1)$$

Where Rx is the radius of curvature in the x-direction [m], U is the entrainment speed [m/s], E^* the reduced Young's Modulus [Pa], η_0 the dynamic viscosity of the lubricant [Pa s], α the pressure-viscosity coefficient [Pa^{-1}], W the applied load [N], k=1. The entrainment speed of the lubricant is an input into Equation 1. Smaller entrainment speed results in lower EHL film thickness which leads to contact moving towards boundary lubrication regime.

To be in boundary lubrication regime, the tribo-tests were conducted under applied load of 60 N which provides λ ratios of 0.04. Table 2 and Table 3 show the experimental working conditions and lubricant were used in this work.

Table 1 Material properties

Material properties	**Value**
Hardness	6 GPa
Elastic modulus	210 GPa
Ball surface roughness	20 nm
Disc surface roughness	130 nm

Table 2 Experimental working conditions

Parameters	**Value**
Maximum contact pressure (GPa)	1.2
Temperature (°C)	80, 98
Relative humidity (%)	0, 20, 30, 40, 50, 60, 70, 80, 95
Entrainment speed ($\frac{m}{s}$)	0.1
SRR	5%
Test duration (min)	120
λ ratio	0.04
Oil used	PAO+ZDDP
Dimensions (mm)	Ball = 19.05 / Disc = 46

Table 3 Lubricant properties

Details	**Designation**
PAO+ZDDP(0.08 mass% phosphorus)	PAO+ZDDP

2.4 Tribofilm characterisation

The chemistry of the tribofilm generated by ZDDP containing-oil at different levels of applied relative humidity was evaluated by using X-ray Photoelectron Spectroscopy (XPS) in this work. Analyses have been conducted at the end of each tribological test for different levels of relative humidity at two different temperatures of 80°C and 98°C. The samples were cleaned by Isopropanol and put into the ultrasonic bath for 5 minutes after the test and before the XPS analysis. The XPS analyses were performed in a PHI 5000 VersaProbeTM XPS (Ulvac-PHI Inc, Chanhassen, MN, US) fitted with a monochromatized Al Kα X-ray (1486.6eV) source. For the calibration purposes, the carbon spectrum peak was set to 284.8 eV. CasaXPS (version 2.3.15, Casa Software, Wilmslow, UK) was used to process the measurement data. The details of XPS and its post-test analysis has been reported in Ref [7].

2.5 Experimental approach

A set of experiments were designed to assess the effect of different values of relative humidity on tribofilm characteristics and its effect on wear behaviour by integrating MTM SLIM with humidity control system. All the experiments have been done in boundary lubrication regime at two different temperatures of 80°C and 98°C. The experimental approach used in this study has been discussed in the recent work of the authors in Ref [4]. The key novelty of this study is developing a humidity control system which provides lubricant exposed to the humid environment. In this system, water can be absorbed from the air by lubricant during the experiment. The humidity level was monitored to be constant during the experiment. Each test was carried out two times to check the reproducibility of the results and the error bars are plotted in the graphs.

3 Results and discussion

3.1 Humidity effect on oil

Coulometric Karl Fischer Titration will be used to measure water concentration before and after each test, which has an accuracy of ± 0.01. It is worth mentioning that this method can be used to measure water concentration in the oil but it cannot determine whether the water is free or dissolved.

In Figure 3 the water content at two temperatures of 80°C and 98°C for different levels of relative humidity are shown. It should be noted that before starting each experiment, oil was exposed to the relative humidity for 30 minutes to be saturated and all experiments were conducted at steady state relative humidity. Figure 3 shows that there is no significant changes in water concentration while the humidity level is adjusted between 20% and 50%. Water concentration dramatically increases at higher values of humidity. It can be clearly seen that the level of water adsorption due to the relative humidity reaches to a maximum of 0.079% at 95%RH. The same trend was observed for 98°C (Figure 3). The comparison between two temperatures of 80°C and 98°C confirms that the level of water content is reduced at higher temperature. It is likely attributed to the evaporation of the water molecules from the oil. It can also be interpreted from the results that only 18°C differences in temperature leads to a significant change in water concentration in the oil and it is more noticeable at higher values of relative humidity.

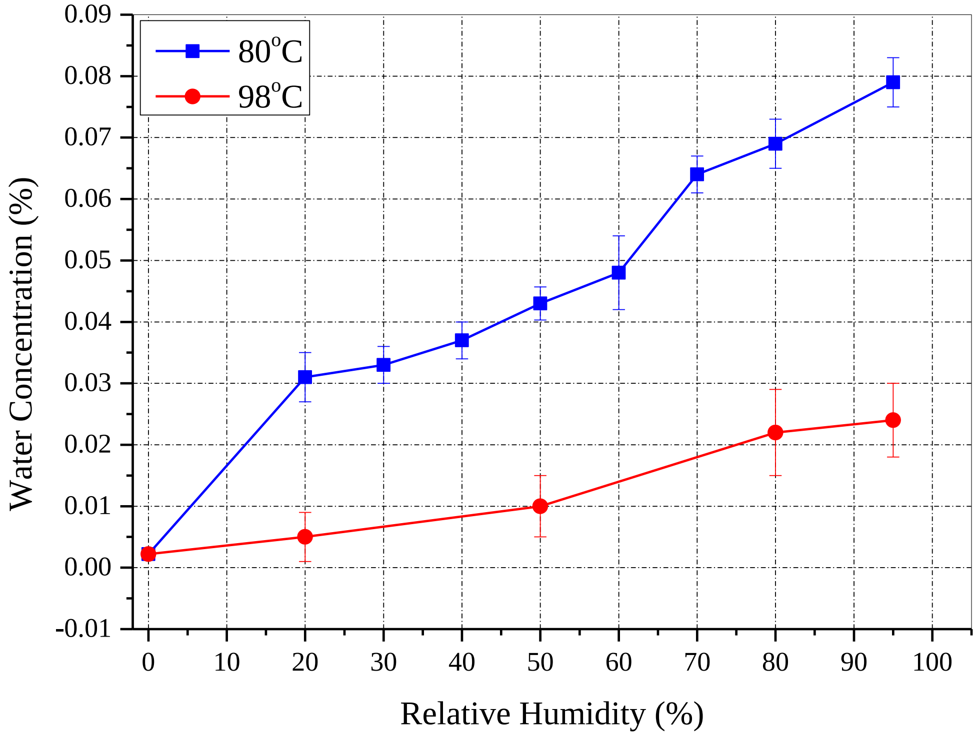


Figure 3 Measured water concentration at 80°C and 98°C

3.2 Effect of relative humidity on tribofilm evolution and wear performance

The samples were analysed after each experiments and wear measurements were carried out by an interferometer. Samples are taken out of the experimental set up after the complete tribo-tests. The tribofilm formed on the surfaces are carefully cleaned by using EDTA. A White Light Interferometer is then used to analyse the profile of the wear track. 2D and 3D images were taken from the wear track and the average wear depth of different areas inside the wear track is calculated. The experiments were repeated 2 times for each working condition and wear was measured in all cases. The wear reported results include the error bars and the variation of the experimental results from the mean value. It should be also noted that the wear depth was measured for 6 different points inside the wear track for each experiment and the average value was reported for the analysis.

The tribofilm thickness is measured using a Spacer Layer Interferometer mounted on Mini Traction Machine. The principle of the technique is explained in detail in Fujita et al. [33].

The effect of relative humidity on tribofilm growth at 80°C is shown in Figure 4. It can be clearly seen that the curves cluster together into three distinctive groups. The curves in the first group called low humidity range correspond to the relative humidity between 0%RH to 40% RH. Second and third groups represent curves for humidity in the range of 50%RH to 70% (medium humidity) and 80%RH to 95%RH (high humidity) respectively.

The higher tribofilm thickness was observed in the first group due to the lower water concentration in the oil (Figure 4). The lower tribofilm thicknesses were found in the high humidity group including the humidity in the range of 80% to 95%. Results indicate higher water concentration in higher humidity tests (Figure 4). It can be concluded that the higher the relative humidity thinner tribofilm is formed. The same trend was observed at 98^{o}C in terms of tribofilm thickness (Figure 5). Tribofilm thickness was decreased by increasing the relative humidity.

The comparison between these two temperatures show that the differences between the steady state tribofilm thicknesses for the low humidity values and high humidity values are more distinguishable at low temperature (80^{o}C). The results are in a good agreement with the recent study by the authors [4]. They proposed that when the mixed-water in oil increases, the steady state tribofilm thickness decreases. Cen et al [7] found the same trend in their work.

The effects of relative humidity and the corresponding water concentration on steady state tribofilm thickness at two different temperatures of 80^{o}C and 98^{o}C are plotted in Figure 6 and Figure 7. It can be understood from the graph that the steady state thickness of the tribofilm reduces while the water concentration (relative humidity) increases for both temperatures. This is in line with the findings of Costa et al. [34] when hydrated ethanol was added to the oil. However, it is more significant and noticeable at lower temperature due to the fact that more water is present in the oil. An increase of temperature has been shown to increase the ZDDP decomposition rate thus increasing the tribofilm thickness. It can be clearly understood that at the same values of humidity, tribofilm thickness is higher at higher temperature. The same trend was observed by Morina et al [35, 36].

Figure 8 indicates how steady state tribofilm thickness influences wear performance. The following conclusion can be drawn from the graph; first and foremost, thicker the ZDDP tribofilm leads to lower wear in the system. Secondly, it can be noted that at the same thicknesses of the tribofilm, the higher wear occurs at lower temperature (80^{o}C) which can be attributed to the higher dissolved water concentration in the oil at lower temperature. This difference indicates that thickness of the tribofilm is only one of the dominant factors in affecting wear performance and composition of the tribofilm is also significant and needs to be explored.

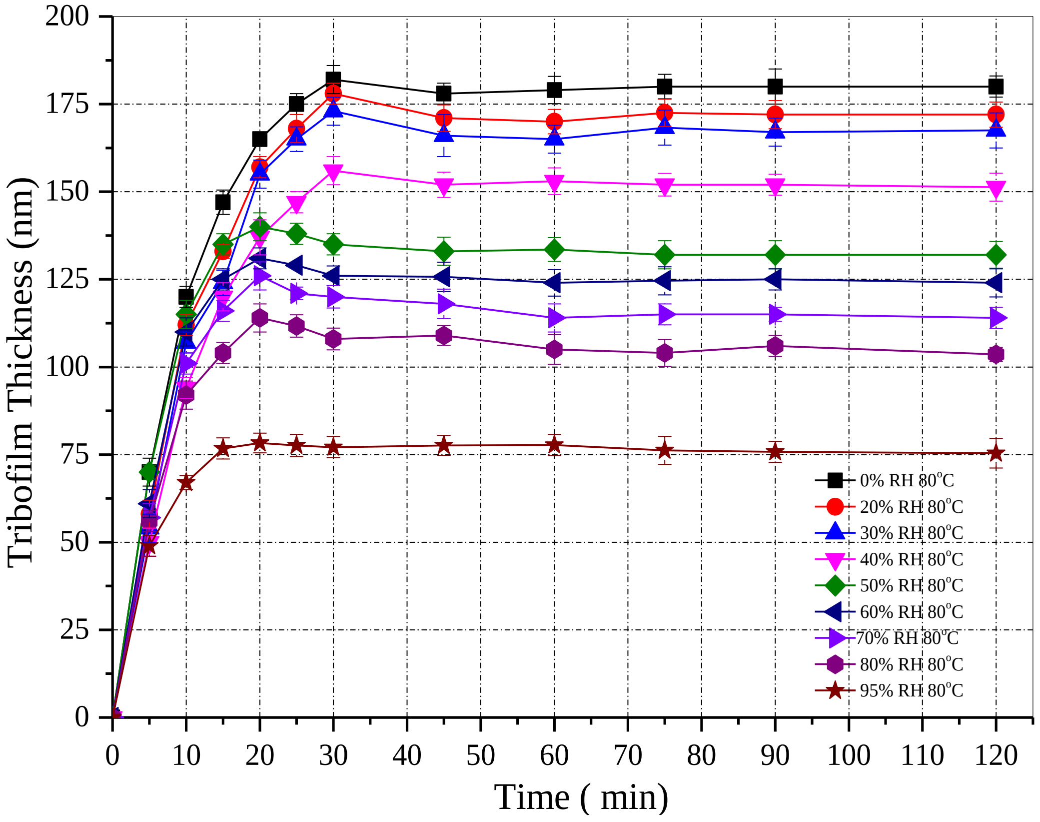


Figure 4 Tribofilm thickness measurement results for 80ºC for different levels of relative humidity

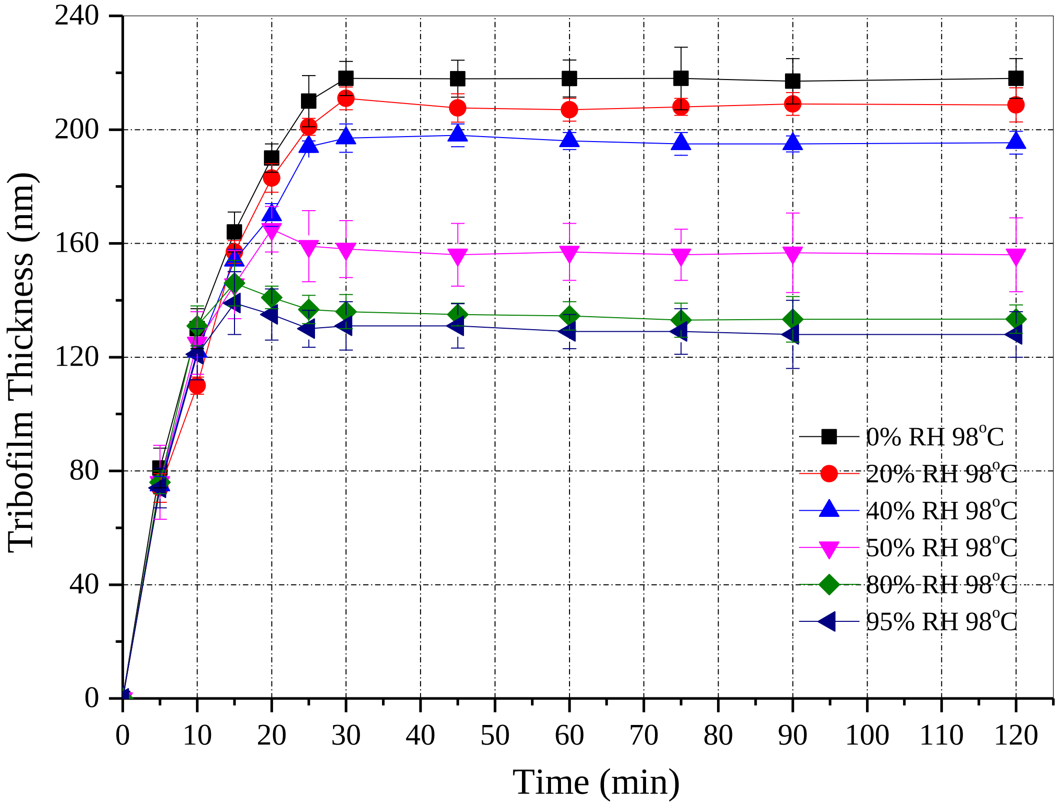


Figure 5 Tribofilm thickness measurement results at 98ºC for different levels of relative humidity

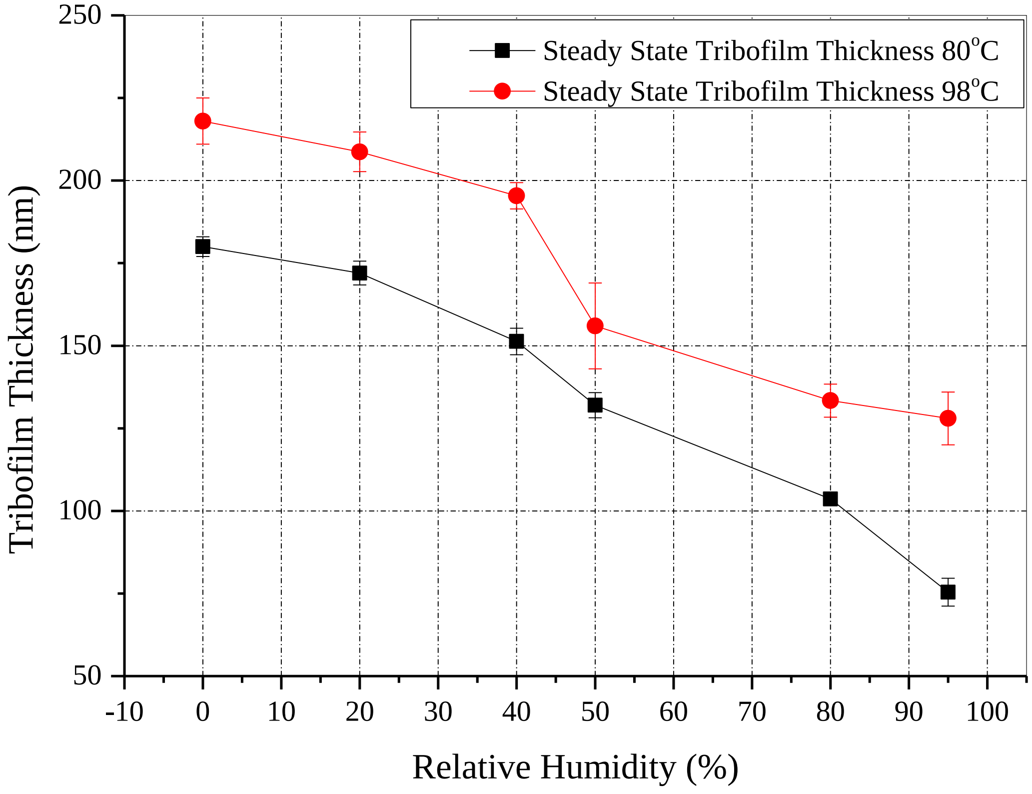


Figure 6 Effect of relative humidity on steady state tribofilm thickness for different temperatures

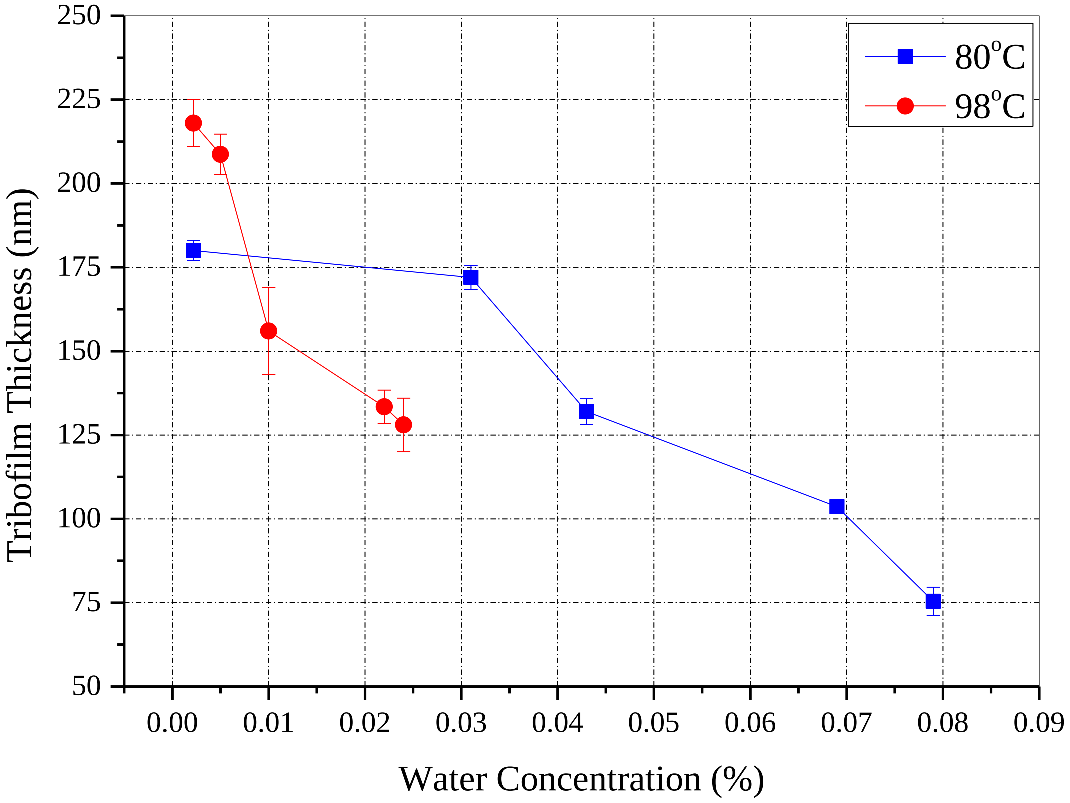


Figure 7 Effect of water concentration measured at different levels of relative humidity on steady state tribofilm thickness for different temperatures

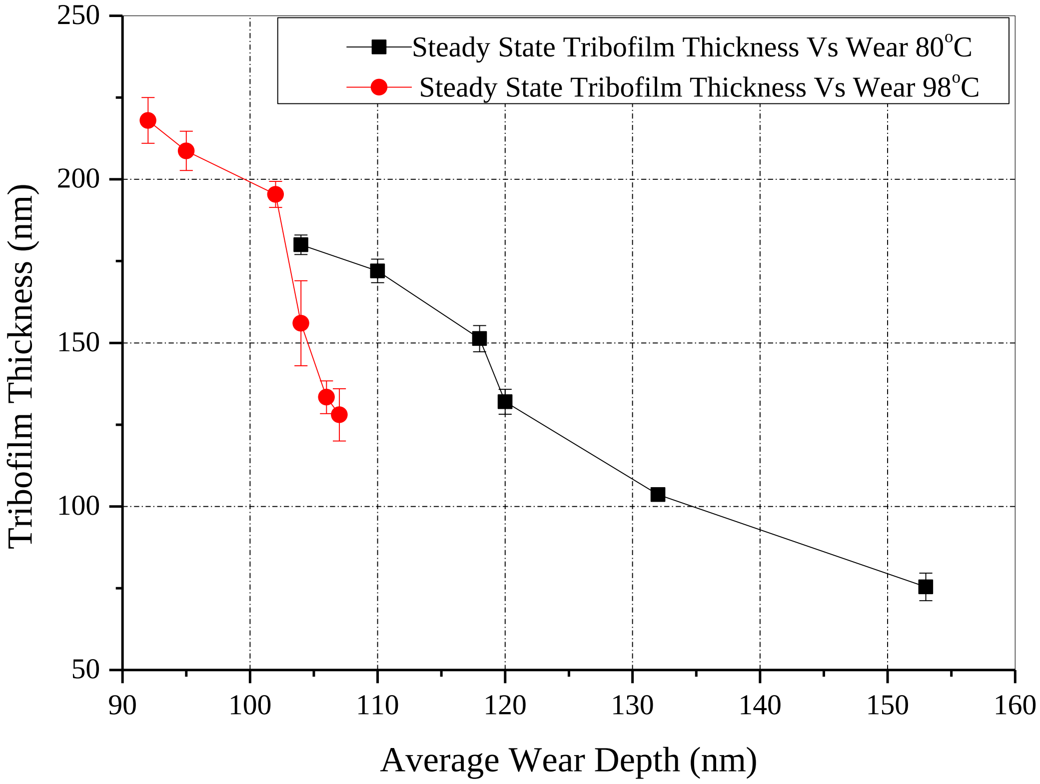


Figure 8 Steady state tribofilm thickness results vs measured wear depth

3.3 Effect of relative humidity on tribochemistry

Crobu et al. [22, 23] showed the surface chemistry of zinc polyphosphates can be characterised using XPS based on the integrated intensity ratio of bridging oxygen (P-O-P) and non-bridging oxygen (P=O and P-O-M). It has been suggested that the chain length of glassy phosphates tribofilm can be identified by a combined usage of bridging oxygen/non-bridging oxygen (BO/NBO) intensity ratio, Zn3s-P2p$_{3/2}$ binding energy difference and a modified Auger parameter. This combined method allows characterisation of polyphosphate chain composition ranging from zinc orthophosphate to zinc metaphosphate.

In this study, the ratio of bridging oxygen to non-bridging oxygen is used to identify the chain length of glassy polyphosphate by dividing the ratio of BO to NBO intensity obtained from XPS analysis (Figure 9 and Figure 10). For the above mentioned experiments in Section 3.2 XPS analysis was conducted and the oxygen peaks are plotted. This approach has extensively been demonstrated in literature [37-45].

Table 4 represents the results for BO/NBO at different levels of relative humidity. It can be seen that the value of BO/NBO decreases while the humidity increases for both temperatures of 80°C and 98°C. It can be interpreted that higher values of humidity correspond to shorter polyphosphates chain length ranging from zinc orthophosphate to zinc metaphosphate [22, 23].

Based on the BO/NBO ratios, the shortest polyphosphate chain length was observed for 95% relative humidity at 80°C while 0% relative humidity at 98°C was found responsible for the longest polyphosphate chain length. The test at 80°C and 0% RH showed a very short–chain structure predominant in orthophosphate composition and the long-chain structure (metaphosphate) belongs to 0% RH and 98°C. It suggests that humidity can affect the mechanical properties of the tribofilm especially at lower temperatures and higher levels of humidity due to the higher water concentration in the oil. Figure 3 illustrates the water concentrations at different values of humidity. The lowest water content belongs to 98°C and 0% RH which is responsible for the longest polyphosphate chain (metaphosphate) and the highest water concentration is for 95% RH at 80°C found 0.079 which has the shortest glassy polyphosphate chain length.

The results are in a good agreement with literature. Fuller et al [46] and Nichollas [47] et al pointed out that longer chain polyphosphates could also be depolymerised by water to shorter chain polyphosphates. The proposed mechanisms of depolymerisation of polyphosphates chain are described in Equation 1 and Equation 2. In the presence of water, hydrolysis of polyphosphates occurs, creating short-chain polyphosphates and phosphoric acid.

$$Zn\,(PO_3)_2 + 6H_2O \longrightarrow Zn_7\,(P_5O_{16})_2 \text{ (short chain polyphosphates)} + 4H_3PO_4 \qquad (1)$$

$$Zn\,(PO_3)_2 + 3H_2O \longrightarrow Zn_2P_2O_7 \text{ (short chain polyphosphates)} + 2H_3PO_4 \qquad (2)$$

It supports the fact that when higher water concentration is present in the oil at higher values of humidity and lower temperature, the tribofilm formed on the surface consists of shorter polyphosphates due to the depolymerisation of the longer polyphosphates chains [7, 10].

The effect of humidity on tribofilm chain length for different temperatures of 80°C and 98°C are shown in Figure 11 and Figure 12 respectively. Interpreting the graphs confirms that the difference between BO/NBO ratios of 0%RH and 95%RH at 80°C is more significant than 98°C due to the evaporation of water at higher temperature and lower water concentration presented in the oil.

Figure 7 showed that higher temperature leads to the thicker steady state tribofilm thickness. The comparison between the ratios of BO/NBO of two temperatures reveals that the higher the tribofilm thickness the longer the polyphosphates chain (Table 4). Figure 7 and Table 4 results indicate that the higher test temperature results a thicker tribofilm containing longer polyphosphates.

Table 4 BO/NBO ratios at different levels of relative humidity

Tests	BO/NBO	
	80^{o}C	98^{o}C
0% Relative Humidity	0.43	0.56
20% Relative Humidity	0.39	--------
30% Relative Humidity	0.30	--------
50% Relative Humidity	0.14	0.2
70% Relative Humidity	0.1	--------
95% Relative Humidity	0.04	0.15

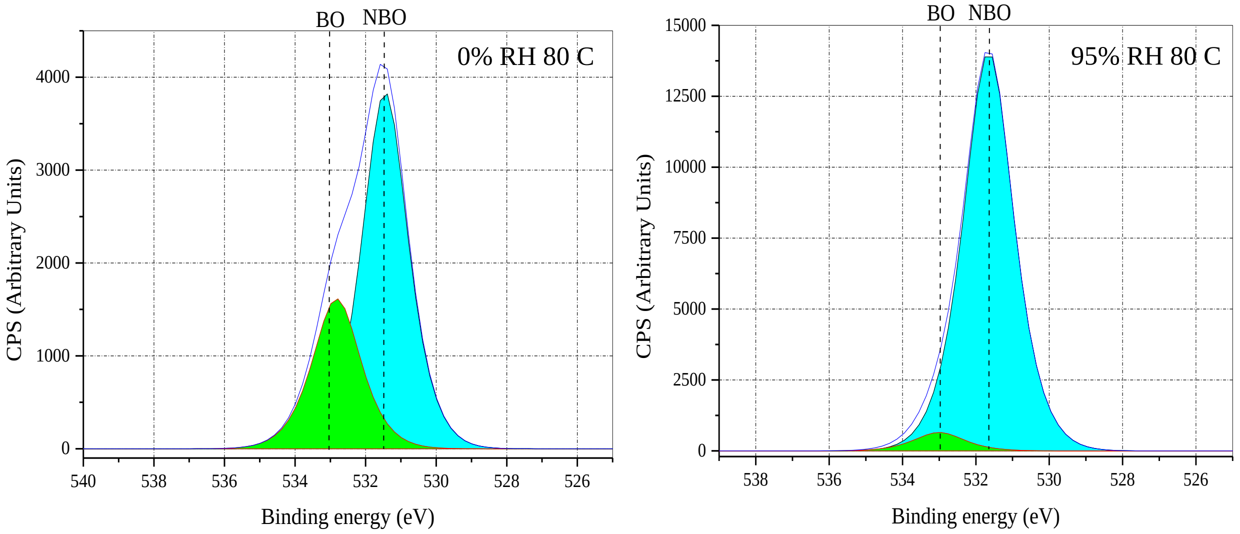


Figure 9 High resolution X-Ray Photoelectron Spectroscopy (XPS) spectra for ZDDP tribofilm formed at different values of humidity for 80^{o}C

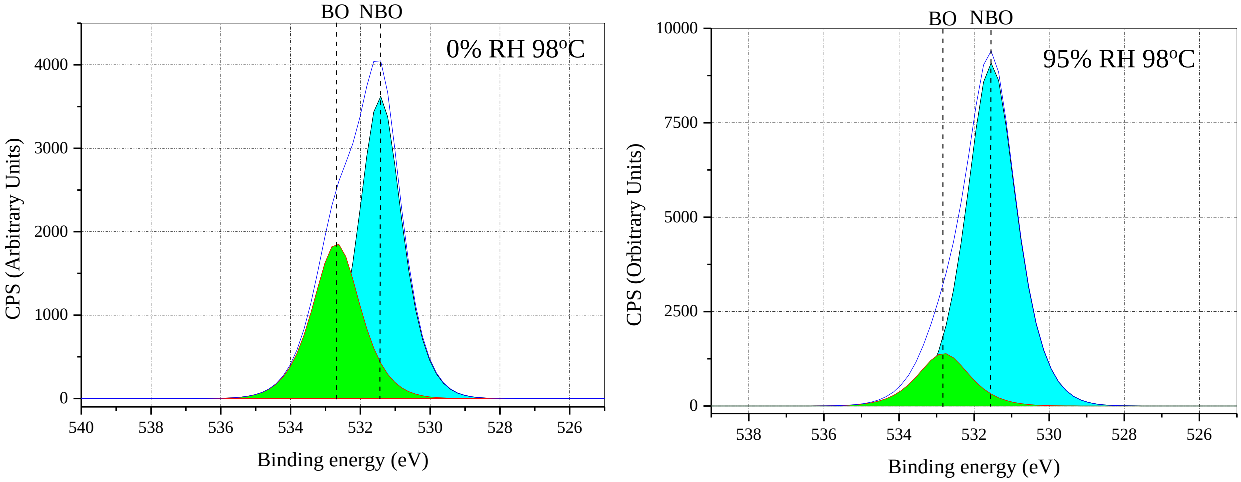


Figure 10 High resolution X-Ray Photoelectron Spectroscopy (XPS) spectra for ZDDP tribofilm formed at different values of humidity for 98°C

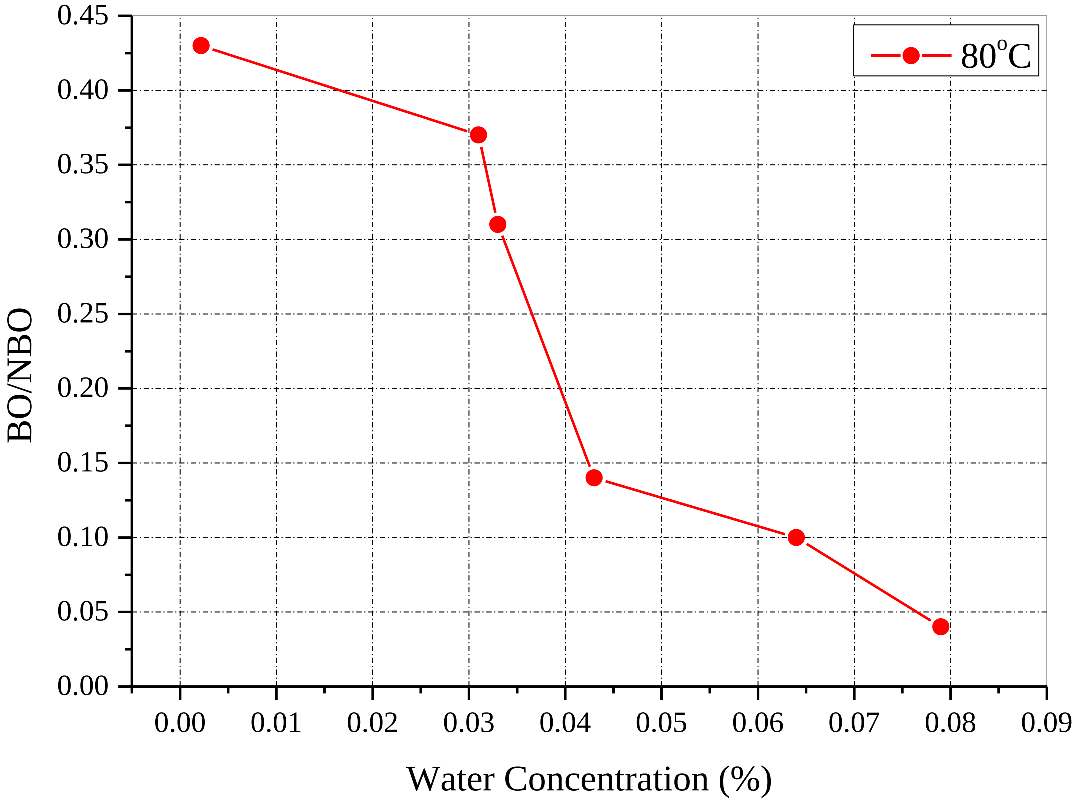


Figure 11 Effect of water concentration at different values of relative humidity on polyphosphate chain length at 80°C

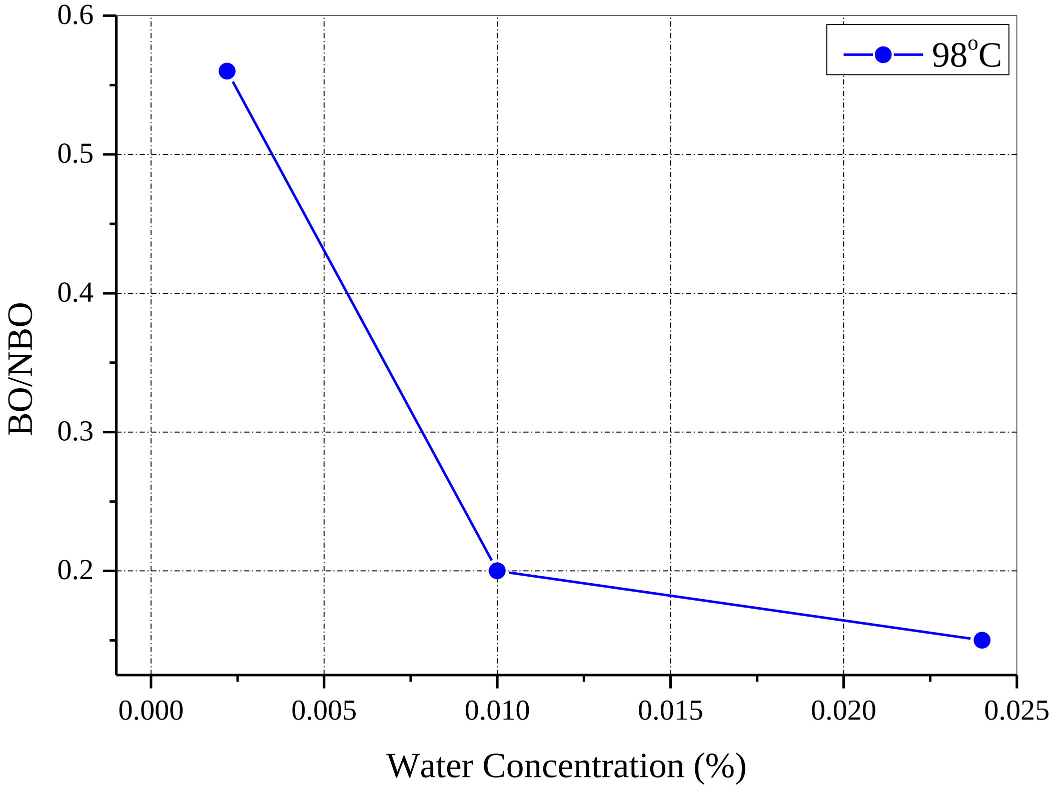


Figure 12 Effect of water concentration at different values of relative humidity on polyphosphate chain length at 98°C

3.4 The effect of relative humidity on wear performance

The tribological tests were performed using MTM SLIM with different levels of relative humidity to investigate the relationship between relative humidity and wear performance. Figure 13 and Figure 14 illustrates the effect of different levels of humidity and the corresponding water contents on wear performance of the lubricant. Based on the wear results, it can be noted that the higher the relative humidity the higher the wear of the system. The reason for the increase of wear at higher relative humidity is attributed to the higher level of water adsorption. The following conclusion can be drawn that relative humidity results in the acceleration of wear of the system. Figure 13 confirms that the average wear depth is dramatically increasing when the relative humidity is reaching the higher values (more than 50%) at 80°C. It supports the fact that the level of water absorption of the oil in the presence of humid environment increases to a maximum of 0.079 volume percent at 95% RH which produces 153 nm average wear depth. The water contents and wear depth follow the same trend at 98°C as 80°C but it should be mentioned that the effect of higher relative humidity on wear performance is more noticeable at 80°C compared to 98°C.

These results are in a good agreement with the studies done by Lancaster et al [5] and Cen et al [7, 9]. It was proposed that water contamination plays a significant role in accelerating wear of the system in comparison with the effect of water on friction. Cen et al [7] found recently that increasing the relative humidity leads to the higher water adsorption and higher wear under pure sliding condition. Recent work published by Parsaeian et al [4] indicates that average wear depth is increasing by mixing more water in the oil. It was also found by Cai et al [27] that water contamination above the saturation level in the oil (emulation) is detrimental for the system in terms of wear behaviour. In this study, it is also observed that the lower temperature results in higher wear. It can be related to the more evaporation of water at higher temperature. It can also be said that the higher temperature leads to the thicker tribofilm formed by ZDDP. The same trends were proposed by Cen et al [7] and Ghanbarzadeh et al [8]. On the other hand, the increase in the wear in the presence of water can be attributed to the higher tribocorrosion rate of steel substrate which then results in the more availability of iron ions in the glassy phosphate tribofilm. The presence of iron phosphate and the competition between iron ions and zinc ions to form the phosphates can lead to the formation of the shorter chain polyphosphates as found in the surface chemistry results. This is an interesting finding and more detail chemical studies on the tribofilm will result in gaining more insights into the real mechanisms involved.

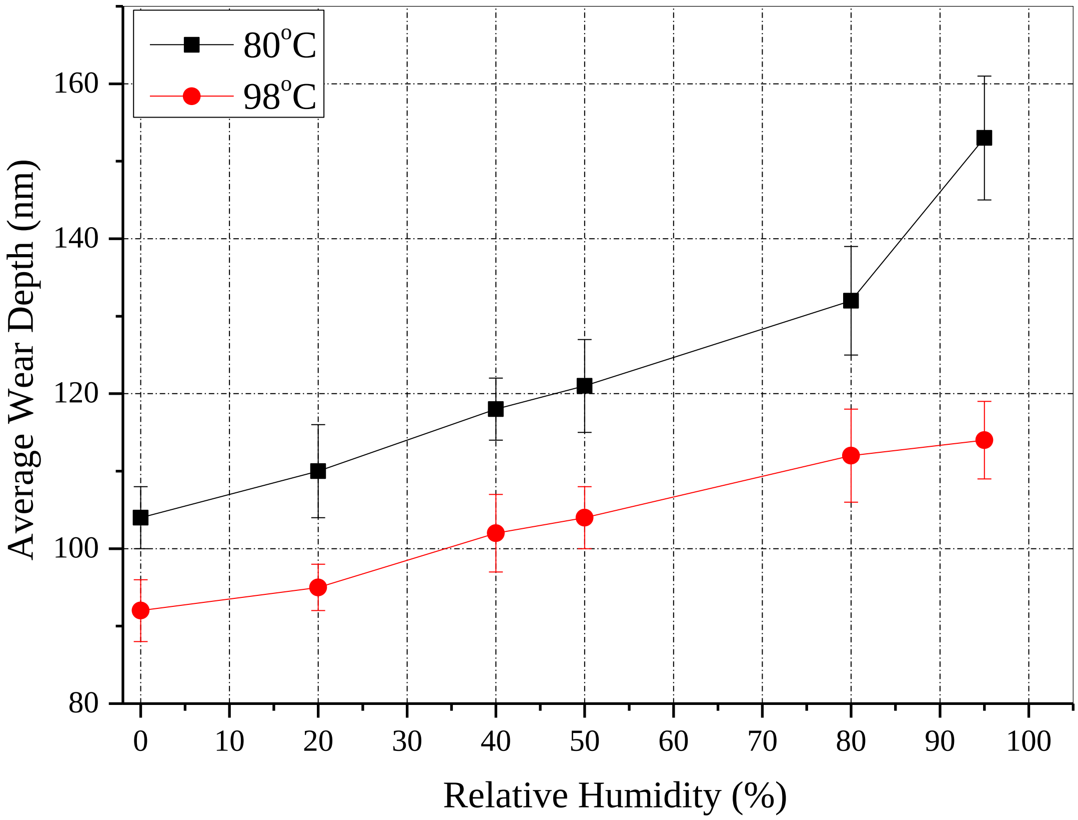


Figure 13 Effect of relative humidity on the average wear depth at two different temperatures of 80°C and 98°C

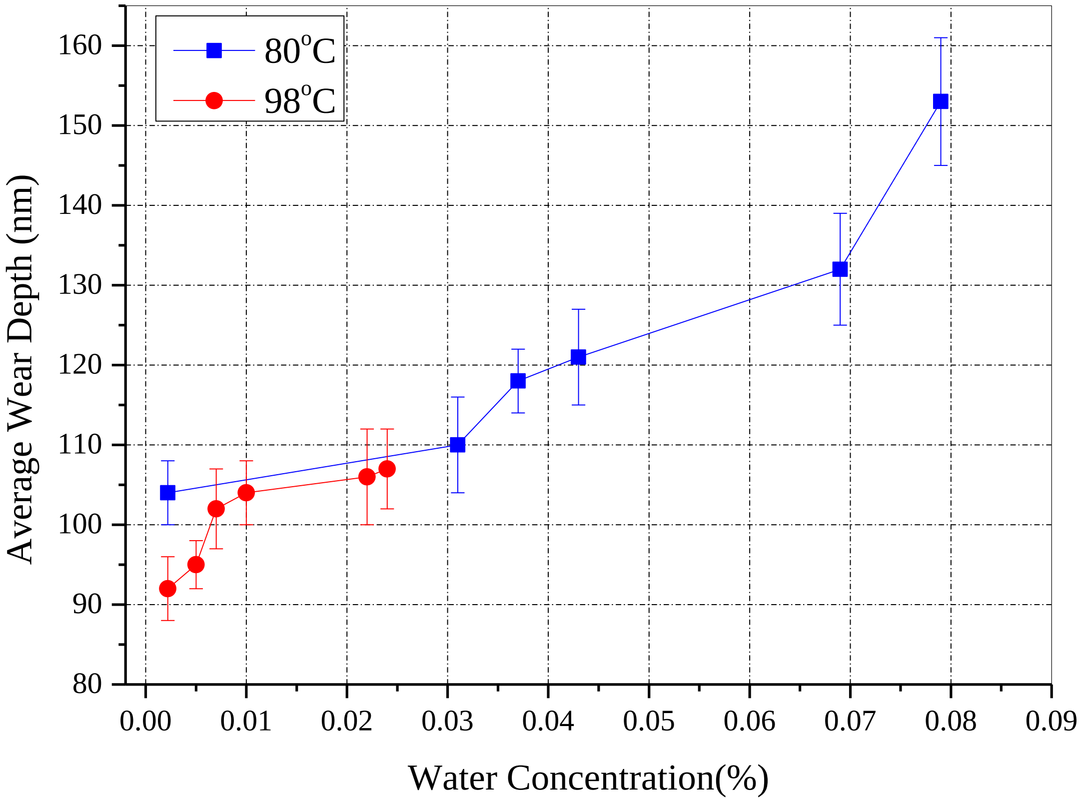


Figure 14 Effect water concentration measured at different levels of humidity on the average wear depth at two different temperatures of 80ºC and 98ºC

4 Conclusions

The effect of relative humidity on tribofilm characteristics and wear performance of a boundary lubricated system in rolling/sliding conditions has been investigated for the first time. Notable observations can be summarised as follows:

- The increase of relative humidity increases the tribocorossive wear of the system for both temperatures of 80ºC and 98ºC. It can be attributed to the higher water concentrations when higher humidity values are applied. It is worth mentioning that the higher the temperature the less the tribocorrosive wear due to the thicker tribofilm thickness formed on the surface. The effect of humidity on wear performance is more significant at lower temperature in comparison with higher temperature.
- Higher water contents in oil results in reducing the growth of the tribofilm which causes higher wear in the system. Reducing tribofilm growth might be because of the difficulty that ZDDP molecules have to access to the surface and react with the substrate in the presence of higher amount of water.
- Relative humidity can significantly affect the mechanical properties of the tribofilm. It was found that the effect of humidity on tribofilm formation is more significant at higher humidity and lower temperature (80ºC) due to the more water content in the oil.
- It can be interpreted from the results that humidity hinders the growth of the tribofilm and it can considerably affect the tribocorrosive wear of the system. The higher the relative humidity the lower the steady state tribofilm thickness and the higher the tribocorossive wear.
- XPS results show that shorter chain poly phosphates present in the tribofilm at higher relative humidity. It can be linked to the depolymerisation of longer polyphosphate chain to shorter chain. The higher the relative humidity the lower the ratio of BO/NBO.

To summarise, the results indicate that the higher water concentration is observed in the higher humidity test and thinner tribofilm containing shorter chain poly phosphates is formed on the surface. This experimental results are used to develop a semi-analytical model considering the effect of relative humidity on the tribofilm thickness and the corresponding wear for the first time which is the subject of the second part of this study.

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