A multi-technique characterization of the tribofilm formed by a fully formulated CVT fluid

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ABSTRACT

In this work, the morphology, thickness, chemical composition and mechanical properties of the tribofilm formed by a fully formulated CVT fluid are investigated by multiple techniques and linked to the frictional and wear characteristics of a pin-on-disc tribosystem. It is found that the tribosystem shows higher friction and wear when tested at 150 °C than at 80 °C. The main reason is that although the morphology and thickness are similar, the tribofilms formed at different temperatures have different chemical compositions and mechanical properties. The tribofilm formed at 150 °C is Fe richer and has greater hardness and shear strength, which leads to a higher tribochemical wear rate and a greater interfacial shear force.

1. Introduction

Tribofilms have long been known to be crucial in the friction and wear control of boundary lubrication, where film thicknesses are not sufficient to separate surfaces and asperity contacts occur. Generated by chemical reactions between additives and contact surfaces, tribofilms are constantly formed and removed in boundary lubrication and serve as self-sacrificing layers. A variety of additives are applied for the formation of tribofilms with different friction and wear performances, while Zinc dithiophosphates (ZDDPs) are arguably the most commonly used additive. In the past decades, an huge number of research papers has been published investigating the role that tribofilms play in the tribosystem and the mechanisms of their friction and wear control.

Morphology, thickness and chemical composition of the tribofilms have been investigated by researchers for decades, due to their close linkage to the frictional and wear characteristics of the tribosystem. Various surface analytical techniques have been applied in this field. Scanning electron microscopy (SEM) [1–6] and atomic force microscopy (AFM) [7–10] are extensively employed for the morphology of the tribofilms. Gosvami et al. [11] even performed in-situ AFM observations of the ZDDP tribofilm formed under different contact pressures and temperatures. A focused ion beam microscope (FIB) is frequently used to measure the thickness of the tribofilms [12–17], by providing straightforward cross-section profile images. As to the chemical composition of tribofilms, energy dispersive X-ray spectroscopy (EDX) is commonly employed to carry out the qualitative analysis in combination with SEM [18–22]. X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) also serve as powerful tools to analyze the chemical state of elements in tribofilms [23–29].

Further, the mechanical properties of the tribofilms are also of great concern. In microscale and nanoscale tribology, it is proposed that the friction is controlled by the effective shear strength of the contacting surface layers and the real contact area [30–32]. In boundary lubrication with existing tribofilms, this theory is also widely supported by literature. Mortier et al. [33] suggested that some tribofilms have low shear strength properties and allowed shearing within the film structure itself, and therefore led to lower friction. The shear strength of the ZDDP tribofilm were linked to their friction modifying effects by different research groups [34–37]. Therefore, investigating the mechanical properties of tribofilms helps understanding the friction in layered boundary lubrication. However, due to the small thicknesses (usually 50–200 nm) and the non-uniform distribution of the tribofilms, research in this area has been rather limited. The nano-hardness of tribofilms, serving as an indirect indication of the shear strength of tribofilms, has been investigated by researchers. Bec et al. [38] performed in-situ imaging of different tribofilms and found that the hardness of the tribofilms varied in depth. For ZDDP, the hardness started from about 1 GPa on the top surface and increased to 3 GPa at 20 nm depth. Aktary et al. [39] reported that the hardness of ZDDP tribofilms formed on AISI 52100 steel ranged from 2.3 to 5.0 GPa. Pereira et al. [40] measured the
hardness of ZDDP tribofilms at different temperatures and found a 2–4.5 GPa range. Recently, Ueda et al. [41] reported hardness values of ZDDP films of 2.4 and 3.3 GPa after 25 min and 6 h rubbing. As to the researches on shear strength of the tribofilms, Pidduck and Smith [42] proposed the idea of employing AFM and lateral force microscopy (LFM) to study the lateral force of the tribofilm. Kano and Yasuda [43] employed the AFM to study the shear strength of the ZDDP tribofilm. However, only the electrical signals were presented, without being translated into forces.

In this work, the connection between the friction and wear characteristics of the tribosystem and the properties of the tribofilm (morphological, chemical, mechanical, etc.) are investigated. The tribofilm being studied is formed by the fully formulated Shell NS-3 oil. First, the friction and wear characteristics of the system are studied by pin-on-disc tests. The post-test surfaces are subsequently analyzed by AFM, FIB-SEM and XPS for the morphology, thickness and chemical composition of the tribofilms respectively. Nanoscale hardness and Young’s modulus are calculated employing a mechanical contact model, based on the evaluation of collected AFM images and force-indentation depth curves. The shear strengths of the tribofilms are further measured by the AFM running under LFM mode.

2. Experimental design

2.1. Pin-on-disc tribometer

The lubricated metal to metal sliding contacts at a temperature range of 80–150 °C were evaluated by a pin-on-disc tribometer, CSM HT 3–110 (CSM Instruments, United States). The ball was immersed in fully formulated oil Shell NS-3, held and loaded by the holder. The disc was heated by the base and rotated at a predefined speed. The tribological data, including lateral force and coefficient of friction, were monitored and recorded by the sensors.

The steel ball was 10 mm in diameter and made of AISI 52100 with a hardness of 62–66 HRC. The chemical compositions are listed in Table 1. The centre-line average roughness Rz is 130 nm. The disc is of the same material of the ball (AISI 52100), with a centre-line average roughness Rz of 20 nm, see Fig. 1.

Both the ball and the disc were ultrasonically cleaned by 2-propanol for 10 min prior to the test. After the ball and disc were assembled in the test rig, 10 ml lubricant was applied and the temperature was raised to the set value without applying any load. When the system reached the test temperature, the normal load was then applied and the test started. Friction forces were recorded for 12 h, while the initial running-in periods were excluded. The detailed tests conditions are listed in Table 2.

The lateral forces and coefficient of friction data were recorded automatically during the test by the friction sensor at a rate of 5 Hz. The tests were repeated three times for each condition.

2.2. Post-test surface characteristics

An optical microscope was used to measure the size of the wear scars. AFM, FIB-SEM and X-ray photoelectron spectroscopy were employed to characterize the morphology, thickness and chemical compositions of the tribofilm respectively. Prior to the surface analysis, the samples were ultrasonically cleaned by 2-propanol for 10 min in order to remove the residual lubricant and wear debris. The samples were further heated to 60 °C in a vacuum oven for 30 min to dissipate the residual detergent of the surfaces.

A Park NX-10 AFM (Park Systems, South Korea) was used to investigate the tribofilm morphology. For the morphology measurement, the AFM ran under the tapping mode, equipped with a beam-shaped, non-contact cantilever (PPP-NCHR) with a nominal resonance frequency of 330 kHz. The central parts of the wear scar on the post-test surface were scanned over a 50 × 50 μm² area at a scanning rate of 10 μm/s. The z-
height data in the scanning area were collected at a resolution of 256 pixels × 256 pixels.

A Nova 600 Nanolab Dualbeam SEM/FIB (FEI, United States) was used to observe the thicknesses of the tribofilm. For each sample, four 3 µm × 20 µm² areas of the surface were milled using a gallium ion beam. The depth of the sputtered area was about 4 µm. This process revealed the cross-section profile of the tribofilm and the substrate material beneath. The micrograph of the cross-sections of the film (and substrate) were then recorded by a secondary electron detector located at an angle of 52° to the direction vertical to the surface of the sample.

The chemical composition of the wear scars were studied by an X-ray photoelectron spectroscopy PHI Quantera SXM (Physical Electronics, United States), with a monochromatic Al Kα X-ray (1486.6 eV) source. The size of the X-ray beam was 100 µm. The chemical bonding conditions of the tribofilm were analyzed by detecting the kinetic energy of emitted photoelectrons. The measured spectra were shifted with respect to aliphatic carbon C1s at 284.8 eV. During the measurement, the residual pressure remained below 5 × 10⁻⁷ Pa. Survey scans were firstly carried out between 50 and 1100 eV binding energy under a 25 W constant-analyzer-energy mode, to identify the elements present. The survey scans were performed in three cycles. Next, narrow scans of the selected elements together with the etching technique were conducted in order to identify the chemical compositions in depth profile. For each measuring step, the sample was sputtered with a 3 kV, 3 × 3 mm² argon ion beam, removing around 14.5 nm of material, after which narrow element scans were carried out. This process was repeated nine times for each sample, adding up to 130 nm in depth.

2.3. Nanoscale hardness and elastic modulus by AFM

The hardness and elastic modulus measurements of the tribofilm were conducted in force spectroscopy mode using Dimension 3100 AFM retrofitted with NanoScope IIIa controller (Bruker, USA). Stiff silicon-made rectangular-shaped cantilevers with polycrystalline diamond-coated tips were used to allow a low-wear testing, namely DT-NCHR from Nanosensors (Switzerland). Prior to and after the nanomechanical testing, height images of the surface topography were collected in contact mode using the same tip at the deflection setpoint of 0.5–1.0 V. Imaging and nanomechanical testing were performed using NanoScope software version 8.15. Cantilever (normal) spring constant values, \( k_0 \), were obtained based on their geometry, using formula [44]:

\[
k_0 = \frac{E_0 w^3}{4t^2}
\]

(1)

where \( E_0 \) is Young’s modulus of the cantilever, \( w \) is width of the cantilever, \( t \) is the thickness of the cantilever, and \( l \) is the length of the cantilever (measured from the end of the chip to the apex of the tip). We assumed the Young’s modulus of the cantilever to be 165 GPa [45,46]. The geometry of the cantilever and the tips were measured by SEM imaging after each experiment by JEOL JSM-7610-LA microscope using a low voltage. The radii of the AFM tips, \( R \), were determined by calculating the radius of the circle that coincides with the tip apex profile. The range of the obtained dimensions of several cantilevers used is presented in Table 3.

Thus, based on Eq. (1) \( k_0 \), values ranging from 48.9 to 88.3 N/m were obtained. The (normal) sensitivity of the AFM optical system, \( S_n \), was measured on a quartz reference, fitting the extended part of the force-distance curve.

The NanoScope Analysis software version 1.8 was used to process and evaluate plastic (hardness by indentation) and elastic (Young’s modulus by elastic sample response) events obtained by AFM tip-to-surface loading under different normal forces, \( F_n \). In the case of the hardness calculation (average), around 30 indentations were performed at different spots on the specific sample. The surface topography was imaged before and after to inspect the indentation hole. The projected area of the remaining deformation (hole), \( A_p \), was calculated by three-dimensional analysis of the hole profile by means of dedicated software. The \( A_p \) ranged from 8000 to 33000 nm². The hardness, \( H \), was then calculated using the following formula [47,48]:

\[
H = \frac{F_n}{A_p} k_0 \frac{k_n V_n}{A_p}
\]

(2)

where \( V_n \) is the photo-potential measured vertically with a position sensitive photo detector (PSPD) that is proportional to the (normal) deflection of the cantilever. The applied \( F_n \) ranged from 19 to 75 mN.

The Young’s moduli values were obtained by evaluating around 50 force-distance curves collected at different spots on the specific sample. The Derjaguin, Muller and Toporov (DMT) model was employed to quantify the tribofilm elasticity. In this model the deformed contact profile is the same as in the Hertz model, however with a higher applied load, \( F_\text{DMT} \), due to an additional adhesion interaction. The following formula was used [49,50]:

\[
F_\text{DMT} = \frac{4}{3} \frac{E}{1 - \nu} \frac{1}{\delta} \sqrt{R\delta} F_\text{adh}
\]

(3)

where \( E \) is the Young’s modulus of the tested sample, \( \nu \) is the Poisson ratio of the tested sample, \( \delta \) is the indentation depth, \( F_\text{adh} \) is the adhesion force (pull-off force) and \( F_n \) \( F_\text{DMT} \) \( F_\text{adh} \). We assumed the \( \nu \) to be 0.3 [51]. The \( F_n \), \( \delta \) and \( F_\text{adh} \) were calculated directly from the force-distance curves. Due to small indentation depth, up to 8 nm, a “spherical indenter” in the DMT model and a pure elastic material respond could be assumed. The Young’s modulus was determined by fitting the slope of the extended part of force-distance curves (fitting parameter). The fitting used a nonlinear least squares fit that goes through the contact point.

2.4. Lateral force and shear strength by AFM

The shear strengths of the tribofilm were measured by the Park NX-10 AFM running under LFM mode using the method proposed by Pietrement and Troyon [52]. Data of large scanning areas (50 × 50 µm², located in the centre of the wear scars) were captured to minimize the effects of local inhomogeneity. The DT-NCHR (Nanosensors) cantilevers were used in this experiment as well.

In LFM mode, the cantilever moves laterally parallel to the surface and it is deflected sideways due to tip-sample interaction (friction). This
deflection is recorded by the PSPD as the photo-potential measured laterally, \( V_t \). The main point of concern - in the calculation of the lateral force and the shear strength - is the determination of the (lateral) sensitivity of the AFM optical system, \( S_o \), because it cannot be calculated directly from a typical (vertical) force-distance curve [53–55]. However, when one knows the \( S_o \), the \( S_t \) can be calculated from the following formula [53], assuming that the PSPD is rotationally symmetric:

\[
S_t = \frac{E_t h^3}{2G} S_o \tag{4}
\]

where \( h \) is the height of the tip (see Table 2) and \( G \) is the shear modulus of the cantilever.

The lateral force, \( F_L \), can then be calculated using the formula:

\[
F_L = k_s V_t \tag{5}
\]

where \( k_s \) is the cantilever (torsional) spring constant given by:

\[
k_s = \frac{Gw^3 l^3}{3h^2} \tag{6}
\]

Using Eq. (4) and (6), Eq. (5) can then be rewritten as:

\[
F_L = \frac{E_s w^3}{6l} \frac{h^3}{l^2} S_o V_t \tag{7}
\]

The contact area, \( A_c \), and the mean contact pressure of the cantilever tip and the surface, \( P \), can be calculated by the Hertzian contact model [54]:

\[
A_c = \frac{\pi a^2}{2} \tag{8}
\]

\[
P = \frac{F_c}{\pi a^2} \tag{9}
\]

where \( a \) is the contact radius, which can be expressed as:

\[
a = \sqrt[3]{\frac{3Fr}{4E} \frac{1}{v^2}} \tag{10}
\]

The shear strength can then be calculated as:

\[
\tau = \frac{F_L}{A_c} \frac{1}{\pi a^2} \frac{E_s w^3}{6l} \frac{h^3}{l^2} S_o V_t \tag{11}
\]

3. Experimental results and discussions

3.1. Friction and wear characteristics of the pin-on-disc samples

The friction and wear of the pin-on-disc sample pair were measured at different temperatures (80–150 °C, with 10 °C interval). An example result (at 80 °C, 0–1 h) is shown in Fig. 2. A running-in period occurs from 0 to 0.15 h, where the coefficient of friction changes. Afterwards, the system enters the steady-state, indicating by the stable coefficient of friction values. In this study, the running-in periods are trimmed and only the coefficient of friction of the steady-state are considered.

The coefficients of friction as a function of temperature are shown in Fig. 3. It is evident that in the temperature range between 80 and 150 °C, the coefficient of friction increases with increasing temperature. At 80 °C, a COF of 0.12 is observed. The COF rises smoothly with temperature. While at 150 °C, the COF is 0.14, more than 15% higher than at 80 °C.

The wear of the samples also increases with temperature. The optical microscope images of the wear scars on ball samples tested at 80 and 150 °C are shown in Fig. 4. For the ball tested at 80 °C, a wear scar of around 200 µm diameter is observed, with a wear volume of around 2.51 \( \times 10^{-13} \) m\(^3\). When tested at 150 °C, however, more wear occurs: the diameter of the wear scar significantly increases to around 300 µm, and the wear volume is around 1.27 \( \times 10^{-12} \) m\(^3\).

The differences in friction and wear at different temperatures suggest that the temperature plays a role in this tribological process. The reason may be attributed to the fact that the tribofilms formed at different temperatures differ in morphology, thickness, chemical contents and mechanical properties. To better understand this tribological process, further investigation on the tribofilms was carried out and is presented in the following subsections.

3.2. Morphology, thickness and chemical composition of the tribofilms

To better understand the origin of the different tribological performances, the tribofilms formed on the wear scars were studied by AFM, SEM-FIB and XPS.

Representative z-height AFM images of post-test ball samples are shown in Fig. 5. The rubbing direction is along the y axis. The corresponding cross-section profiles - taken perpendicular to the sliding direction - are also presented for comparison.

A similarity can be identified in the morphology of the tribofilms formed at different temperatures. The post-test surfaces are inhomogeneous and pad-like structures are observed along the sliding direction. The bright, elevated pads are tribofilms and the dark valleys are due to
the steel substrate not being covered (this is further confirmed by the SEM-FIB images below). Tribofilm pads with the size of 10–20 μm form and elongate in the sliding direction, while tribofilm pads with the size of 1–5 μm are also observed between the substrate valleys. For both samples, the height differences between peaks and valleys are around 100–125 nm, which provide hints of the tribofilm thicknesses.

The reason for the minor differences in the tribofilm morphology formed at 80 and at 150 °C is that larger and more continuous tribofilm pads are formed on the wear scar at 150 °C than at 80 °C. This can be identified by both the z-height images and the cross-section profiles.

A focused ion beam microscope was used to generate images of the cross-section of the tribofilm. Representative SEM images are presented in Fig. 6. It can be identified that the morphology and thickness of the tribofilms formed at different temperatures are rather similar. Most of the surfaces are covered with a dark-coloured tribofilm, a small ratio of the surfaces are steel substrate without tribofilm. This is in good agreement with the AFM topography results. The thicknesses of the tribofilms are measured and labelled in Fig. 6. For both samples, the thicknesses of the tribofilms are around 120–135 nm. No significant differences are observed.

The results of the z-height AFM measurements and the SEM-FIB images indicate the continuity of the tribofilms for the samples tested at both 80 and 150 °C. The surfaces are well covered by tribofilms, which prevents direct metal to metal contact. In addition, there is little variation between the thickness of the tribofilms formed at different temperatures. Therefore, the morphology and thickness of the tribofilms are not likely to be the main reason for the different tribological performances. Other factors should be considered.

XPS was employed to analyze the chemical composition of the tribofilms on post-test surfaces. The XPS depth profiling of the tribofilms
on the post-test ball samples is shown in Fig. 7 and Fig. 8. In the phosphorus spectrum of the samples tested at 80 C, a sharp peak at 133.0 eV is observed, which corresponds to iron pyrophosphate (Fe₄(P₂O₇)₃). Therefore, the tribofilm generated under this test condition (80 C) is composed mainly of short chain iron phosphate. In the calcium spectrum, a sharp peak at 347.2 eV is found. This peak corresponds to the calcium carbonate (CaCO₃) and calcium oxide (CaO).

For the 150 C case, the XPS depth profiles are shown in Fig. 8. The phosphorus spectra observed are similar to those for the 80 C case: the peaks appear at 133.0 eV, which corresponds to Fe₄(P₂O₇)₃. Therefore, it is evident that the similar phosphorus compound is generated at the higher temperature. In the calcium spectrum, however, the peaks occur at 346.8 eV instead of 347.2 eV in the 80 C case. This suggests the existence of more CaO alongside of CaCO₃.

More information about the tribofilms generated at different temperatures was revealed by atom concentrations along the depth, see Fig. 9. The atom concentrations follow a similar trend: P and Ca decreases with depth and the Fe concentration increases with depth. At a depth of 125 nm, P and Ca almost vanish in both cases, while the Fe concentrations go beyond 80%. This suggests the tribofilm thickness for both 80 C and 150 C is around 130 nm, which is in good agreement with the AFM and FIB-SEM results. However, the element concentrations vary for the two samples tested at different temperatures. It can be seen that at the surface the tribofilm generated at 80 C contains around 12.5% of Fe, and almost 40% in the tribofilm generated at 150 C. The concentrations of P and Ca are lower in the 150 C case (both around 5%), in contrast to the 80 C case (over 10%). This clearly suggests that even though the chemical compositions of the tribofilms generated at
80 C and 150 C are comparable, the concentrations of the elements are rather different. The tribofilm generated at 150 C is more Fe rich than that generated at 80 C. This will probably lead to different mechanical properties of the tribofilm and further affect the friction and wear performances.

The mechanical properties of the tribofilms are investigated in the following subsections.

3.3. Hardness and Young’s modulus of the tribofilm

Fig. 10 represents an example of submicron scale visualization (AFM, contact mode) of tribofilm surfaces with residual plastic impression after an AFM-tip indentation (dark area in the images). Due to the diamond AFM-tip coating the geometry of the indenter varies from one cantilever to another, resulting in differences in the shape of the indentation profile (projected area). The tribofilm formed at 150 C turned out to be of a high hardness; high normal loads needed to be applied to obtain a decent indentation with the used AFM setup. The calculated average nano-indentation hardness, \( H \), is 4.7 1.1 GPa for this sample. Differently, for the tribofilms formed at 80 C the calculated average \( H \) is 2.7 0.7 GPa; this sample can evidently be deformed under lower normal loads. These values fall into similar ranges as those of the hardness of ZDDP tribofilms in Ref. [39].

The values of the Young’s modulus follow the trend of the hardness result. For the tribofilm formed at 150 C the average \( E \) is 75 16 GPa, while for the tribofilms formed at 80 C it is 56 14 GPa. These values are similar to the Young’s modulus of ZDDP tribofilms reported in literature [57,58]. The \( E \) value distributions are shown in Fig. 11.

Note that we assumed that the Poisson’s ratio of the tribofilm is 0.3. The results of the elastic modulus results are dependent on the Poisson’s ratio being taken, see Eq. (3). Potential errors could arise from this assumption: if the real Poisson’s ratio of the tribofilms is in the range of 0.2-0.4, an error range of 86%-114% will be caused in comparison with the value reported.

3.4. Lateral force and shear strength of the tribofilms

In the lateral force measurements, the interfacial shearing force of the tribofilms was measured for the further calculations of the shear strength. Three different normal loads \( F_n \) were applied: 1 \( \mu \)N, 2 \( \mu \)N and 5 \( \mu \)N. These loads were chosen so as to ensure that the top surface of the tribofilm was effectively “sheared” during the measurement instead of just elastically deformed. In addition, the shear forces were measured at three different sliding velocities: 0.01 mm/s, 0.05 mm/s and 0.25 mm/s.

To illustrate the shearing of the surface, the topography of the tribofilm before and after a lateral force measurement is shown in Fig. 12 for comparison. The inner area was first tested by the AFM under LFM mode with 2 \( \mu \)N normal load. Then the topography of the larger area was imaged for comparison under the tapping mode. It can be seen that the topography of the tribofilm measured by the LFM mode is clearly altered, indicating the occurrence of shear deformation.

The raw data of the lateral force measurements are electrical signals with the unit of volts. They are equal to \( V_i \) representing the lateral torsion. An example image is presented in Fig. 13b. The z-height image of the sample acquired at the same time is also presented for comparison.

It can be noticed that the lateral force results show an identical pattern to the z-height result, implying that the lateral forces are influenced by the surface roughness. This is anticipated because when the tip travels through bumps or grooves the tilting angle changes due to the surface tilting. However, in the relative flat areas the signals are rather steady. This indicates that the lateral force on these areas is almost constant and can therefore be interpreted as the force for shearing the surface. A line profile of a trace and retrace lateral forces for 80 C and 150 C can be seen in Fig. 14.

It can be found in Fig. 14 that despite the surface roughness affects the lateral forces, the “base line” of the lateral forces for both the 80 C and 150 C cases is clearly recognizable. The tribofilm formed at 150 C presents a larger lateral force when being sheared, implying a higher
shearing force than for the tribofilm formed at 80°C.

To perform the calculation of the shear strength (Eq. (11)) the Young’s modulus of the tribofilms is taken from the results presented in Subsection 3.3.

The average results along the scanning areas and the standard deviations are plotted Fig. 15.

In general, the results present noticeable standard deviations, which are caused by the surface roughness and the material inhomogeneity. However, the trends are rather clear. The tribofilms formed at 150°C show a higher shear strength than the 80°C cases under all testing conditions. This is because of the different chemical compositions, which are shown in subsection 3.2. This higher shear strength may be connected to the higher coefficient of friction observed in Fig. 3.

In addition, it can be concluded that the shear strength of the tribofilm is affected by the average contact pressure, but very little affected by the shearing velocity in the range of 0.01 mm/s to 0.25 mm/s.

4. Discussion

The results in this work reveal that the frictional and wear properties of the tribosystem are related to the chemical composition and mechanical properties of the tribofilm. The friction and the wear mechanisms are discussed below.

4.1. Friction mechanisms

The testing conditions of the LFM for shear strength of the tribofilm are already similar to the real applications (0.25 mm/s shearing velocity and 2.5–5 GPa mean contact pressure, for instance), and the shear strengths acquired in this work can be assumed to be close to reality. The results reveal the correlation between the friction and the shear strength of the tribofilm, as has been suggested in literature.

For the case tested under 0.25 mm/s shearing velocity and ~3 GPa mean contact pressure, the shear strength of the tribofilm formed at 150°C is 370 MPa, while at 80°C the shear strength is 291 MPa, 21% smaller than the 150°C case. This difference is very similar to the difference in the coefficients of friction, which are 0.14 at 150°C and 0.12 at 80°C, i.e., 14.3% smaller. This similarity supports the equation proposed in literature for the friction in boundary lubrication:

\[ F = \tau s A_{\text{col}} \] (12)

Because the post-test surface topography at different temperatures is similar, the real contact areas are comparable. Therefore, the higher shear strength \( \tau \) at 150°C contributes to the higher friction force and
4.2. Wear mechanisms

In this work, the testing duration of the pin-on-disc test is 12 h, which is long enough for the system to reach the steady, mild wear state. During this stage, the main wear mechanism is tribochemical wear, see Fig. 4.

The XPS atomic concentration results show that the Fe content in the tribofilm formed at 150 °C is richer than that formed at 80 °C. The reason might be that at elevated temperature the chemical reactivity of the Fe with the additive package is higher and that more Fe atoms reacted with the additives, form the tribofilm and are sheared during sliding. This is in line with the fact that the wear volume is higher at 150 °C than at 80 °C.

5. Conclusions

In this work, pin-on-disc sliding tests lubricated by the fully formulated oil Shell NS-3 are carried out. The friction observed is linked to the morphology, thickness, chemical compositions and shear strength of the tribofilm that are measured by a variety of characterizing techniques. The findings are summarized as follows.
The AISI 52100 friction pair lubricated by Shell NS-3 shows different friction levels when running at different temperatures. The coefficient of friction increases when the testing temperatures rise from 80 °C to 150 °C. The wear scar also increases with higher temperature, indicating a higher wear rate at higher temperature.

(2) The tribofilms formed at 80 °C and 150 °C are similar in morphology and thickness but differ in chemical composition. The tribofilm formed at 150 °C contains higher Fe in all depths than the tribofilm formed at 80 °C. It is assumed that the chemical reactivity of the Fe substrate is higher at elevated temperatures. It leads to higher tribochemical wear rate, which explains the larger wear scar observed at 150 °C.

(3) The tribofilms showed a noticeable difference in hardness and Young’s modulus. The film formed at 150 °C reveals high hardness (~4.7 GPa) and Young’s modulus (~75 GPa). We attribute this to the high Fe content in the tribofilm formed at 150 °C. Differently, the tested nanomechanical properties of film formed at 80 °C indicate a drop in hardness (~43%) and Young’s modulus (~25%) in comparison with the tribofilm formed at 150 °C.

Fig. 13. AFM results of lateral force measurement (sample tested at 150 °C). The normal load is 5 μN and the shearing velocity is 0.25 mm/s (a) height image (tapping mode) and (b) representative PSPD lateral force (LFM) image.

Fig. 14. Line profiles of the lateral force signal. Both cases are measured with 5 μN in normal load and 0.25 mm/s shearing velocity.

Fig. 15. AFM shear strength of the tribofilms under different test conditions: (a) Shear strength vs. mean contact pressure (with the shearing velocity of 0.25 mm/s) and (b) Shear strength vs. shearing velocity (with the normal load of 1 μN).
Different shear strengths of the tribofilms formed at different temperatures are observed. The tribofilm formed at 150 °C shows higher shear strength than its counterpart at 80 °C. In addition, it is found that the shear strengths of the tribofilm are dependent on the mean contact pressure but are very little affected by the shearing velocity in the range of 0.01–0.25 mm/s.

The different mechanical properties of the tribofilms formed at different temperatures may be linked to the higher Fe content in the tribofilm formed at 150 °C. This could also be the reason for the higher coefficient of friction that is observed in the pin-on-disc test at 150 °C.

Declaration of competing interest

The authors declare no conflict of interests.

CRediT authorship contribution statement

Can Wang: Conceptualization, Methodology, Software, Formal analysis, Investigation, Visualization, Writing - original draft, Writing - review & editing. Hubert Gojzewski: Writing - original draft, Writing - review & editing, Software, Investigation, Visualization. Dirk J. Schipper: Supervision, Project administration, Writing - review & editing.

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