



UNIVERSITY OF LEEDS

This is a repository copy of *The role of surface roughness and slide-roll ratio in the decomposition of MoDTC in tribological contacts*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/110087/>

Version: Accepted Version

Article:

Khaemba, DN orcid.org/0000-0001-7709-4736, Jarnias, F, Thiebaut, B et al. (2 more authors) (2017) The role of surface roughness and slide-roll ratio in the decomposition of MoDTC in tribological contacts. *Journal of Physics D: Applied Physics*, 50 (8). 085302. ISSN 0022-3727

<https://doi.org/10.1088/1361-6463/aa5905>

© 2017 IOP Publishing Ltd. This is an author produced version of a paper published in *Journal of Physics D: Applied Physics*. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

The role of surface roughness and slide-roll ratio in the decomposition of MoDTC in tribological contacts

Doris N Khaemba^{1*}, Frederic Jarnias², Benoit Thiebaud², Anne Neville¹ and Ardian Morina¹

1. Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, LS2 9JT, Leeds, United Kingdom (UK).
2. TOTAL, Centre de Recherche de Solaize, Chemin du Canal BP 22-69360 Solaize, France.

* Corresponding author: d.n.khaemba@leeds.ac.uk,

Abstract. In this study, the role of surface roughness and slide-roll ratio in the decomposition and friction performance of molybdenum dialkyldithiocarbamate (MoDTC) has been investigated. Tribotests were carried out in a MiniTraction Machine (MTM) using steel discs of varying roughness rubbing against smooth steel balls in a sliding/rolling contact. Tests were conducted at slide-roll ratio (SRR) values of SRR=100% and 200%. Raman spectroscopy was used to perform chemical characterisation on the resulting wear scars. The friction performance of rough discs was not affected by the slide-roll ratio. On the other hand, increasing the slide-roll ratio from 100% to 200% in tests with smooth discs resulted in higher friction with large instabilities. Raman analysis showed significant differences in chemical composition of the wear scars generated after tests with smooth and rough discs. Wear scars generated using rough discs were mainly composed of MoS₂ indicating complete MoDTC decomposition while those generated using smooth discs were composed of a mixture of MoS₂, MoS_x (x>2) and FeMoO₄ indicating partial MoDTC decomposition. Numerical simulation of the contact revealed that under similar loading conditions rough surfaces have higher local pressures than smoother surfaces. It is proposed that higher local pressures in rough surfaces promoted complete MoDTC decomposition. The novel finding from results presented in this study is that at similar temperature and MoDTC concentration, the degradation of MoDTC within tribocontacts is highly dependent on the roughness of the tribopair. This is because surface roughness determines the local pressure at the asperity-asperity contact.

Keywords. Surface roughness; Slide-roll ratio; MoDTC; MoS₂; MoS_x; FeMoO₄; Raman spectroscopy

1 Introduction

Molybdenum dialkyldithiocarbamate (MoDTC) is mostly used as a friction modifier in engine oil. Friction reduction is achieved when MoDTC decomposes at the rubbing interface to form low friction films. A new mechanism for MoDTC decomposition in steel/steel contacts was recently proposed by the authors [1]. The proposed mechanism is different from a previously proposed mechanism by Grossiord et al. [2] and also proposes different decomposition products. According to the new mechanism, MoDTC decomposes to form MoS₂ as a final product with amorphous sulphur-rich

1
2
3 molybdenum, MoS_x ($x>2$) as the intermediate product. In certain test conditions, for example at high
4 MoDTC concentrations, high temperatures and high contact pressures, complete MoDTC
5 decomposition occurs and MoS_2 is formed at the tribocontact. Friction reduction is observed in such
6 conditions due to the presence of MoS_2 which has a lattice layer structure and low shear strength. At
7 other given test conditions, for example, at low temperatures and low MoDTC concentrations, partial
8 decomposition occurs and as a result MoS_x and FeMoO_4 are formed at the tribocontact. When this
9 happens, minimal friction reduction is observed. Varying surface chemistry at the tribocontact could
10 explain the varying friction performance of MoDTC lubricants observed in tests conducted in different
11 test conditions in previous studies [3-6].
12
13

14
15
16
17
18 Surface roughness has been shown to have a significant effect on the friction performance of MoDTC
19 lubricants in steel/steel contacts. In studies by Graham et al. [3] it was observed that under unidirectional
20 linear sliding conditions smooth discs ($R_a=10$ nm) did not show friction reduction ($\mu=0.12$) whereas
21 rough discs ($R_a=150$ nm) showed low friction after a short induction time ($\mu=0.03-0.04$). In the study
22 by Graham et al. [3], it was concluded that solid-solid contact was necessary for the formation of MoS_2
23 which resulted in low friction. So far, the explanation for high friction observed when smooth surfaces
24 are rubbed together has been attributed to formation of micro-elastohydrodynamic (EHD) lubricating
25 films at the tribocontact which prevent solid-solid contact [3, 7]. While this is a plausible explanation,
26 it is also possible that the surface chemistry plays a significant role in the friction performance. It is thus
27 important to understand the influence of surface roughness on the decomposition of MoDTC at the
28 rubbing interface.
29
30

31
32
33 Presently, there are no studies on the role of surface roughness on MoDTC decomposition. This work
34 therefore investigates the influence of surface roughness as well as slide-roll ratio on MoDTC
35 decomposition. Tribotests were conducted with MoDTC lubricant using rough and smooth discs and
36 the resulting wear scars on the tribopair were analysed using Raman spectroscopy, Energy Dispersive
37 X-ray analysis (EDX) and Transmission Electron Microscopy (TEM).
38
39

40 2 Experimental procedure

41 2.1 Tribotests

42 Tribotests were conducted using a MiniTraction Machine (MTM) from PCS Instruments, UK. Tests
43 were conducted using test conditions in Table 1. Two steel discs with different surface roughness; $S_q=10$
44 nm (smooth discs) and $S_q=150$ nm (rough discs) were used. The balls used had a diameter of 19 mm.
45 Steel balls were rubbed against the discs at slide-roll ratio (SRR) 100% and 200%. SRR is the ratio, as
46 a percentage, of sliding speed to entrainment speed where sliding speed is $U_s=|U_B-U_D|$ and entrainment
47 speed $U=(U_B+U_D)/2$. U_B and U_D are the speeds of the ball and disc, respectively. It should be
48 highlighted that although the speed of the ball was 0 m/s at SRR=200%, the ball was not fixed and as
49 such rotated due to the motion of the disc creating a circular wear scar around the ball.
50
51
52
53
54
55
56
57
58
59
60

Table 1. Test conditions for tribotests.

Test condition	Parameters
Temperature	100°C
Contact pressure	1 GPa (40 N)
Lubricant	0.5 wt% MoDTC in Group III mineral oil
Speed (SRR=100%)	0.45 m/s (disc), 0.15 m/s (ball)
Speed (SRR=200%)	0.6 m/s (disc), 0 m/s (ball)
Test duration	2 h
Ball material	AISI 52100 steel ($S_q=10$ nm)
Disc material	AISI 52100 steel ($S_q=10$ nm, $S_q=150$ nm)
Hardness	750-770 VPN (Ball and disc)

The Group III mineral oil was supplied by TOTAL Raffinage and had a viscosity of 0.026 Pa.s at 40°C and 0.008 Pa.s at 100°C. The sulphur content in the base oil was less than 0.05 wt%. The minimum lubricant film thickness (h_{\min}) was calculated using the Hamrock-Dawson equation [8]. The lambda ratio (λ), which is the ratio of h_{\min} to the composite roughness of the rubbing surfaces, was determined. At both slide-roll ratios, the lambda ratio (λ) was 0.05 and 0.5 for tests with rough and smooth discs, respectively. This indicates that the tests were conducted in boundary lubrication regime. However, in tests with smooth discs the boundary lubrication conditions were less severe than that in tests with rough discs. To check for repeatability, all tests were conducted at least twice. Using the average friction results obtained during the last 1h of tests, it was observed that the friction results were very repeatable with a maximum standard deviation of ± 0.003 .

2.2 Wear scar analysis

After tests, the samples were cleaned with heptane in an ultrasonic bath for 1 min to remove the excess lubricant before Raman analysis. This was done so as to improve the Raman signal from MoDTC decomposition products. Raman analysis of the tribopair wear scars after tribotests was carried using a Renishaw Invia spectrometer fitted with a 488 nm wavelength laser. The laser light was delivered and collected from the sample using the 50x objective lens in a backscattering configuration. Spectra were obtained at 1 mW laser power and 1s exposure time. Several accumulations were obtained in each spectrum to improve the signal-to-noise ratio (SNR). At these Raman spectra acquisition parameters there was no laser damage to analysed surfaces [9]. Peak analysis was conducted using the Renishaw WiRE program by fitting peaks using Gaussian/Lorentzian curves to determine the peak frequency.

Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray (EDX) analysis were conducted using a FEI Tecnai TF20 TEM. Focused Ion Beam (FIB) was used to prepare the thin sample

sections for TEM and EDX analysis. The FEI Nova 200 nanolab FIB was used for sample preparation. Optical white light interferometry was used to obtain surface roughness of the surfaces and 3D images of the surfaces after tribological tests..

3 Results

3.1 Friction results

Figure 1 shows friction coefficient obtained during tribotests using smooth and rough discs. Figure 1a shows results obtained in tests with rough discs. At both SRR=100% and SRR=200%, friction was high ($\mu=0.11-0.12$) at the beginning of the test but decreased rapidly within the first few minutes to low steady-state values of $\mu=0.04-0.05$.

Figure 1b shows friction curves during tests with smooth discs. At SRR=100%, friction coefficient was low (0.04) during the duration of the tests. At SRR=200%, friction was high ($\mu=0.10$) during the first 30 minutes of the test (this trend was repeatable). At longer rubbing times the friction decreased to values of $\mu=0.05-0.07$. The friction observed with smooth discs at SRR=200% was generally higher than that at SRR=100% and had large friction fluctuations.

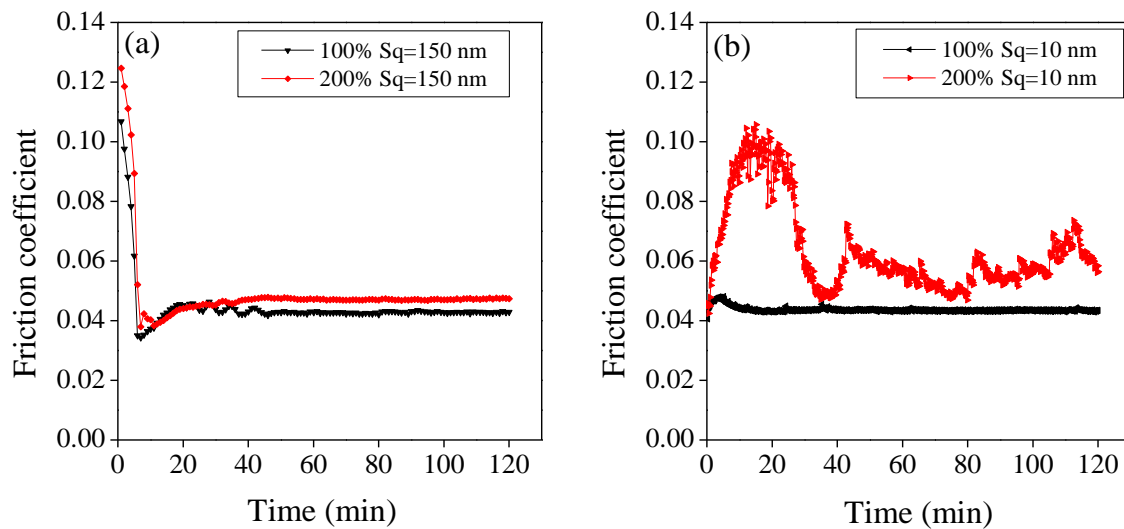


Figure 1. Friction curves of tests conducted at SRR=100% and 200% using (a) rough discs (b) smooth discs.

3.2 Morphology of tribopair wear scars

Figure 2 shows optical images, 3D images and depth profiles across wear scars after 2h tests. There were no significant differences in ball wear scar widths observed for tests conducted with smooth and rough discs. The measured wear scars widths on the balls was 304 ± 2 μm for tests conducted at SRR=100% and 265 ± 4 μm for tests conducted at SRR=200%. In tests conducted with rough discs, wear scars on the tribopair were clearly observed optically but no significant height differences between

rubbed and unrubbed regions were observed. In tests with smooth discs, depth profiles across wear scars revealed high regions on wear tracks of the tribopair. These high regions could indicate the presence of transfer material or formed tribofilms.

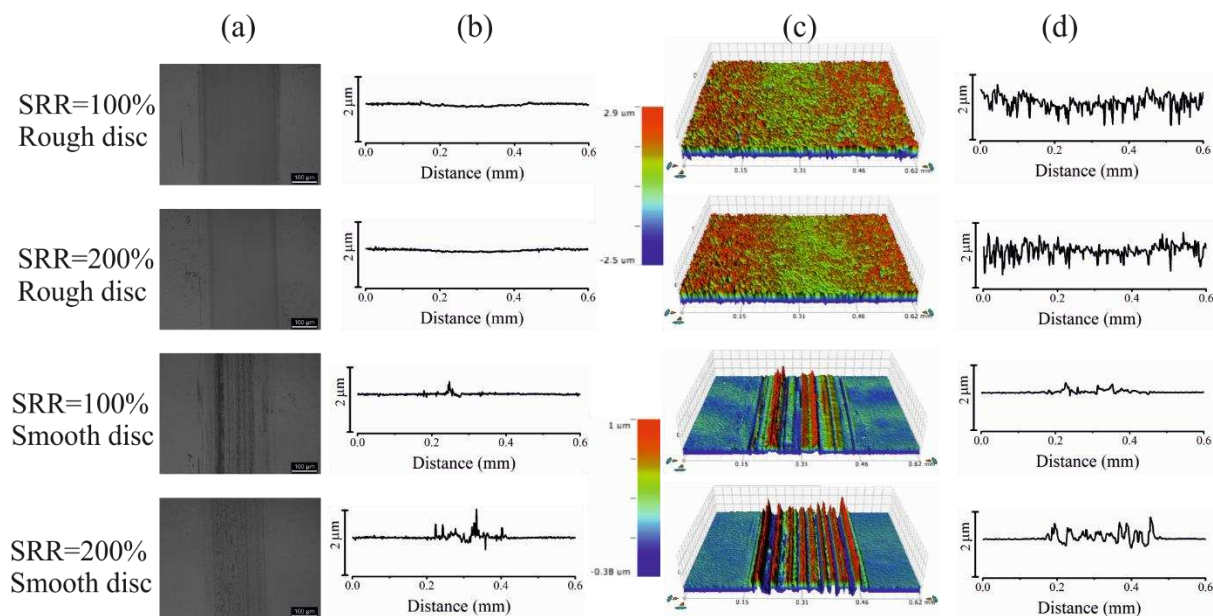


Figure 2. (a) Optical images of ball wear scars (b) depth profile across ball wear scars (c) 3D images of disc wear scars (d) depth profiles across disc wear scars.

3.3 Surface analysis of wear scars

Raman analysis was carried out on wear tracks generated on the tribopair at the end of the 2h tests. As the morphology of the wear scars was observed to be non-uniform in some samples, Raman analysis was conducted by obtaining several Raman spectra from different regions within each wear scar. This was done so as to determine the uniformity of the surface chemistry within the wear scars. Only a few of the spectra from each tribopair wear scar are presented in this section.

Figure 3a and Figure 3b show Raman spectra obtained from tribopair wear scars after tests with rough discs. Spectra obtained from different regions on the tribopair wear scars were very similar indicating uniformity in the chemical composition of the wear scars. MoS_2 peaks were observed at 380 cm^{-1} and 412 cm^{-1} [4]. The broad peak at $150\text{--}250\text{ cm}^{-1}$ was attributed to structural disorder in MoS_2 crystal structure [9-11]. The peaks observed at 510 cm^{-1} and 556 cm^{-1} were attributed to $\nu(\text{S-S})$ vibrations of bridging and terminal sulphur atoms [12] while the peak at 750 cm^{-1} was attributed to bridging oxygen atoms [13, 14]. The peak at 960 cm^{-1} is due to vibration of terminal oxygen atoms $\nu(\text{Mo=O})$ most probably from unreacted MoDTC that is trapped between asperities on the rough surface [15]. The broad peaks at 1370 cm^{-1} and 1580 cm^{-1} are due to formation of amorphous carbon [16].

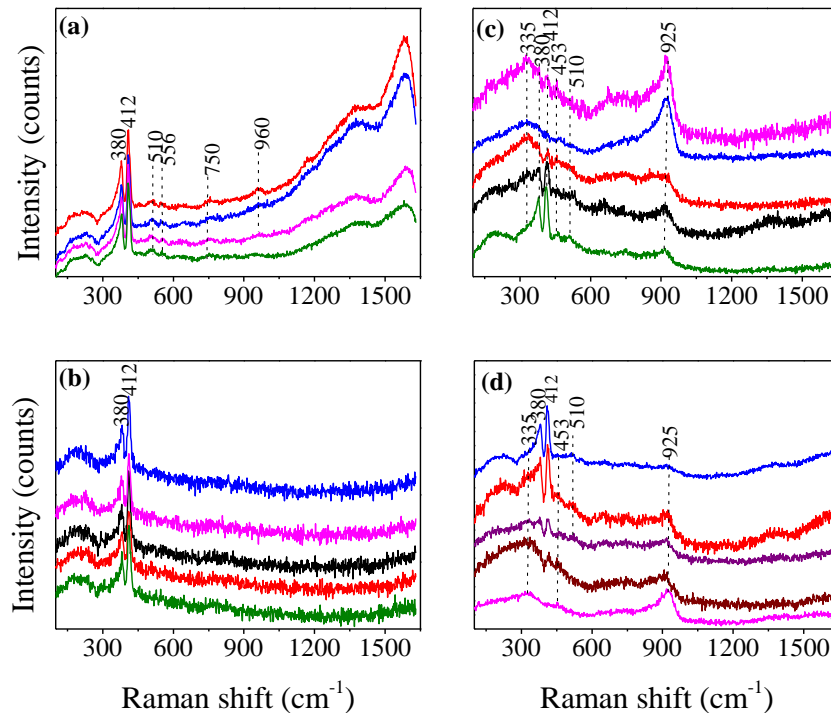


Figure 3. Raman spectra obtained from different positions on tribopair wear scars after 2h tests (a) rough disc, SRR=100% (b) rough disc, SRR=200% (c) smooth disc, SRR=100% (d) smooth disc, SRR=200%.

Figure 3c and Figure 3d show Raman spectra obtained from tribopair wear scars after tests with smooth discs. Raman spectra obtained from different regions within the wear scars varied greatly. In some regions, MoS_2 peaks were observed while in other regions broad peaks were observed at 335, 453 and 925 cm^{-1} . The peak at 925 cm^{-1} was assigned to FeMoO_4 [17] while the peaks at 335 cm^{-1} and 453 cm^{-1} were assigned to formation of amorphous sulphur-rich molybdenum compounds, MoS_x ($x > 2$) such as MoS_3 or MoS_4 [18-23].

The Raman results show that the chemical composition of MoDTC tribofilms was only affected by the roughness of the disc. Wear scars generated after tests with smooth discs were composed of a mixture of MoS_x , MoS_2 and FeMoO_4 while wear scars generated with rough discs were composed of MoS_2 .

Transmission Electron Microscopy (TEM) analysis of MoDTC tribofilms formed on rough discs has revealed the presence of crystalline MoS_2 layers [24]. This is in agreement with Raman results obtained in this study in tests with rough discs. However, Raman results shown in Figure 3c and Figure 3d indicated the formation of amorphous MoS_x in tests with smooth discs. To confirm that MoDTC tribofilms formed in the smooth discs were indeed amorphous in nature, TEM and EDX analysis were conducted on tribofilms formed on the smooth disc after tests at SRR=100%. Using Focused Ion Beam (FIB), a thin section of the tribofilm and the steel substrate was removed from within the disc wear scar

as shown in Figure 4a. The removed section had a thickness of about 50-70 nm as can be seen in Figure 4c.

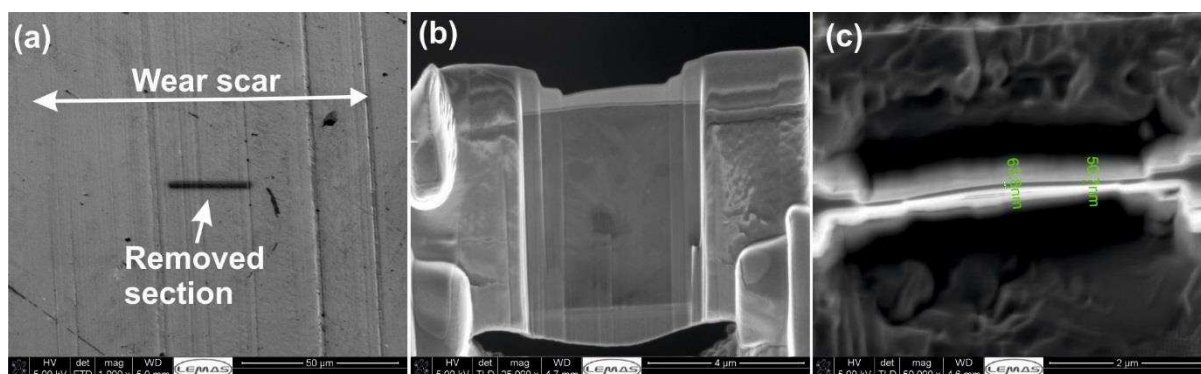


Figure 4.(a) SEM image showing the section of the disc wear scar that was removed using Focused Ion Beam (FIB) (b) side-view and (c) top-view of the removed thin film from the wear scar. Tribotest conducted with smooth disc at SRR=100%.

Figure 5a shows the TEM image of the analysed thin film. It can be seen that a tribofilm was present on top of the steel substrate. The thickness of the formed tribofilm was in the range 30-120 nm. In TEM images crystalline regions normally appear darker while amorphous regions appear lighter in colour. In Figure 5b it can be observed that the MoDTC tribofilm was amorphous in nature with only a few regions being crystalline. The TEM image confirms the presence of crystalline MoS₂ in the tribofilm which was detected using Raman analysis. EDX mapping images in Figure 5d-5g showed that the tribofilm had a high concentration of Mo, S and O. Fe was also present in the tribofilm but because of a much lower concentration compared to the steel substrate Figure 5g did not clearly show the presence of Fe in the tribofilm. These results thus confirm that MoS_x and FeMoO₄ detected using Raman analysis were indeed amorphous in nature.

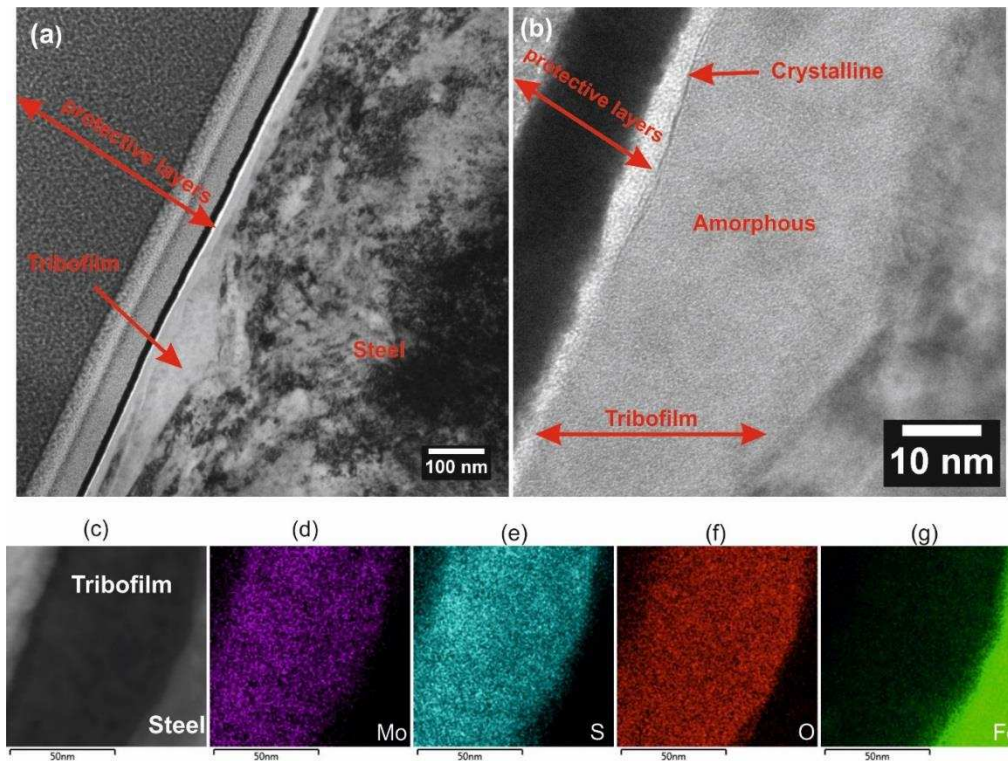


Figure 5. (a, b) TEM images showing the tribofilm formed on the smooth disc after tests at SRR=100%, (c) SEM image of the tribofilm region where EDX analysis was conducted, (d-g) EDX maps showing the elemental distribution of Mo, S, O and Fe.

3.4 Simulation of local contact pressures

The varying chemical composition due to surface roughness was an interesting observation considering that all other test parameters were similar. It should however be highlighted that the calculated Hertzian contact pressure assumes that the applied load is supported by the entire contact area. This is not accurate for real surfaces where the load is supported by the asperities and local pressures at the asperities can be significantly higher than the Hertzian contact pressure. The local contact pressure is thus dependent on the surface roughness. It is thus possible that the differences in local pressures could have affected the decomposition of MoDTC. Therefore to investigate the influence of surface roughness on local pressures, simulation of local pressures in contacts with the smooth and rough discs was conducted. Although it is obvious that rougher surfaces will have higher local pressures (due to smaller contact areas) than smooth surfaces, it is not possible to estimate how much higher the local contact pressure is in rough surfaces compared to smooth surfaces without using simulations. The main objective of this simulations was therefore to have a theoretical estimate of the difference in average local contact pressure between the two surfaces used in the experimental tests.

The numerical model used was based on the model developed by Ghanbarzadeh et al. [25] which incorporates a Boundary Element simulation for contact of rough surfaces. The model considers an elastic-perfectly plastic contact and the hardness of the material is used as a criterion for the plastic

1
2
3 flow. The plastic model is explained in detail in the study by Sahlin et al. [26]. Digitised surfaces were
4 used as inputs of the numerical model. Surfaces were created using the method introduced by Hu and
5 Tonder [27] which is flexible to simulate surfaces with desired surface roughness and asperity lateral
6 size.
7
8

9
10 In this simulation, two surfaces with different surface roughness were generated, surface 1 ($S_q=150$ nm)
11 and surface 2 ($S_q=10$ nm). The roughness of the two surfaces was similar to that of the two discs used
12 to conduct tribological tests. A third surface (surface 3) with the surface roughness $S_q=10$ nm was also
13 generated to simulate the roughness of the ball used in the tribological tests. Simulation of the local
14 contact pressure was carried out for a cut-off size of $64 \mu\text{m} \times 64 \mu\text{m}$ with each node being $1 \mu\text{m}$. Surface
15 3 was placed on top of surfaces 1 and 2 and a contact pressure of 1 GPa was applied on surface 3. The
16 load used ensured that the surfaces in contact were in boundary lubrication regime and the load applied
17 was carried by the asperities.
18
19

20 A Gaussian distribution was used to generate the surface roughness. It should be noted that while this
21 kind of asperity distribution is applicable to smooth surfaces it does not adequately represent the
22 distribution of asperities on rough surfaces. However, since the objective of these simulations was to
23 investigate the influence of surface roughness on local contact pressures, there was no attempt on
24 replicating the actual surface topography of the rough surfaces used in tests. Instead, the Gaussian
25 distribution was used to define rough surfaces for simplicity.
26
27

28 Asperities in rough surface can easily be deformed under a high load and the surface roughness can
29 change after rubbing for a short duration. To investigate the changes in surface roughness in the rough
30 discs, tests were conducted under the conditions presented in Table 1 at different test durations (5, 20,
31 40, 60, 90 minutes). Surface roughness of the generated wear scars on the discs was measured using
32 white light interferometer. It was observed that the roughness of the disc after rubbing for 5 minutes
33 was 147 nm. Significant changes in roughness were only observed after rubbing for 60 minutes ($S_q=130$
34 nm), which could be due to deposition of MoS_2 crystals (formed at the asperities) within the valleys as
35 a result of the rubbing motion. These results indicate that there was minimal asperity deformation during
36 rubbing in the first 60 minutes of rubbing. Therefore, the use of a surface roughness of 150 nm in the
37 simulations is representative of the testing conditions, particularly in the first half of the tests.
38
39

40 Figure 6 shows results of the simulation. Figure 6a shows the 2D map of local pressures between surface
41 1 and 3 (rough surface contact). Figure 6b shows the 2D map of local pressures between surface 2 and
42 3 (smooth surface contact). Figure 6c shows the average of local asperity pressures obtained in Figure
43 6a and Figure 6b. From the simulation results, it can be seen that despite the Hertzian contact pressure
44 being the same, the average local pressure in the rough surface was more than 2 times higher than in
45 the smooth surface.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

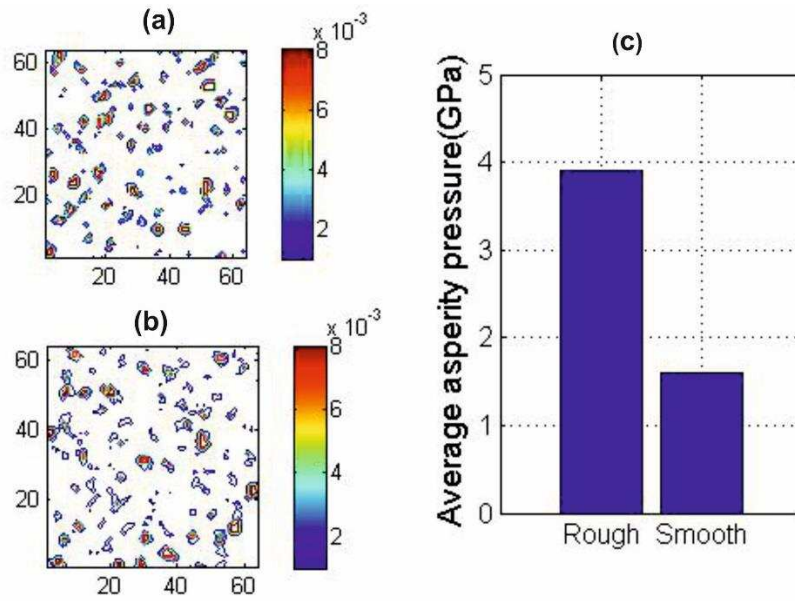


Figure 6. Simulation results of local contact pressures (a) rough disc (b) smooth disc (c) average asperity pressure for smooth and rough discs.

4 Discussion

4.1 Effect on MoDTC decomposition

At similar temperature and MoDTC concentration, rough discs resulted in formation of MoDTC tribofilms composed of MoS_2 while smooth discs resulted in formation of MoDTC tribofilms composed of MoS_2 , MoS_x and FeMoO_4 . Cousseau et al. [28] reported that MoS_2 was only formed when rough surfaces were used and that no MoS_2 was formed when smooth surfaces were used. It should however be noted that in the mentioned study, tests were conducted with a fully formulated oil unlike tests conducted in this study where only MoDTC in base oil was used. Cousseau et al. [28] suggested that rough surfaces promoted the formation of MoS_2 through removal of surface oxides. The authors arrived at this conclusion by considering that the removal of iron oxides was a prerequisite for the formation of MoS_2 . However, the authors of this present study have observed that MoS_2 is formed on samples which have been oxidised by rubbing in base oil prior to rubbing in MoDTC lubricant. Rubbing in base oil results in the formation of iron oxides on the rubbing surfaces [9]. It is thus believed that the removal of iron oxides is not a prerequisite for the formation of MoS_2 . The formation of MoS_2 in rough surfaces is therefore explained by a different mechanism other than the removal of iron oxide films.

The decomposition of MoDTC is dependent on parameters such as temperature, MoDTC concentration and shear stress. Presently, there are no kinetic models for the tribochemical reaction leading to the formation of MoS_2 therefore it is not possible to predict through calculations the test conditions that will ensure the complete decomposition of MoDTC to MoS_2 . As such the only way of determining suitable test conditions for MoDTC decomposition is through experimental measurement. From

1
2
3 previous studies conducted by the authors [1], it has been observed that MoS₂ is formed at temperatures
4 above 60°C, MoDTC concentrations above 0.1 wt% and Hertzian contact pressures above 0.9 GPa. It
5 should be highlighted that these conditions can vary depending on the sliding configuration and surface
6 roughness (as shown in this study). Based on the previous study [1] it was expected that MoS₂ would
7 be formed at the test conditions used in the present study (100°C, 0.5wt% MoDTC, 1 GPa). MoS₂ was
8 formed in rough surfaces as expected but in smooth surfaces MoS_x was observed in most regions of the
9 tribofilm.
10

11
12
13
14
15 Surface roughness has been shown to affect the distribution of pressure at the tribocontact with rough
16 surfaces having extremely high local pressures in comparison to smooth surfaces [29]. Simulation
17 results in this study showed higher local contact pressures in rough surfaces than in smooth surfaces
18 (Figure 6). In a recent study by the authors [1] where tests were conducted using samples with similar
19 roughness but at varying pressures, it was observed that increasing the Hertzian contact pressure from
20 0.98 GPa to 2.12 GPa resulted in the chemical composition of the wear scars changing from a mixture
21 of MoS₂, MoS_x and FeMoO₄ to wear scars composed of only MoS₂. The results obtained in [1] are in
22 agreement with results obtained in this present study and indicate that pressure is an important parameter
23 in the decomposition of MoDTC. At lower Hertzian/local contact pressures, partial decomposition
24 occurs and MoS_x is formed while at higher Hertzian/local contact pressures recrystallization of MoS_x
25 to MoS₂ is favoured resulting in complete decomposition.
26
27

28
29
30
31
32
33 The reaction kinetics for the decomposition of MoDTC in tribological conditions is presently still
34 unknown. However, from the results obtained in this study with rough and smooth surfaces it can be
35 seen that the decomposition of MoDTC is not only dependent on the temperature and additive
36 concentration but also on the local pressure. The reaction kinetics for MoDTC decomposition is
37 therefore most probably defined by the modified Arrhenius equation proposed in references [1, 30]
38 which includes both temperature and stress components rather than the commonly used Arrhenius
39 equation for thermally-activated reactions where the rate of reaction is dependent on only the
40 temperature.
41
42
43
44
45

46 47 4.2 Effect on friction

48
49 In tests conducted with rough discs, low friction was observed at slide-roll ratios used. The low friction
50 achieved can be explained by the presence of MoS₂ within the wear scars (Figure 3a, b). Results
51 obtained from tests with smooth surfaces ($\lambda=0.5$) showed that the induction time increased with increase
52 in slide-roll ratio from 100% to 200%. These results indicate that for smooth surfaces, the friction
53 reducing capability of MoDTC reduces as the slide-roll ratio increases. In a previous study, it was
54 reported that friction reduction ($\mu=0.1$) did not occur in smooth surfaces under pure sliding conditions
55 [3] where the lambda ratio (λ) was 0.7. It has been suggested that the friction behaviour observed with
56 smooth surfaces in tests with MoDTC is due to the formation of micro-elastohydrodynamic (EHD)
57
58
59
60

1
2
3 films [3]. This means that there is no direct contact between the tribopair. However, results obtained
4 from this study show that metal-metal contact occurred in smooth surfaces since MoDTC
5 decomposition products were observed in the generated wear scars (See Figure 5). The contact was
6 however not as severe as that in rough surfaces as evidenced by the presence of amorphous MoS_x .
7
8

9
10 Low friction was still observed in tests with smooth discs despite the MoDTC tribofilms formed being
11 mostly composed of MoS_x and FeMoO_4 which have no friction-reducing capabilities [1]. The low
12 friction can be explained by the presence of patchy MoS_2 layers on the top surface of the tribofilm
13 (Figure 5b). Despite the chemical composition of wear scars generated in tests with smooth discs being
14 similar, the friction values were more steady and lower at $\text{SRR}=100\%$ than at $\text{SRR}=200\%$. In tests with
15 smooth surfaces, crystalline MoS_2 which is responsible for friction reduction is only observed on the
16 top surface of the amorphous tribofilm and is patchy. During rubbing the tribofilm and the MoS_2 layers
17 are removed due to the presence of shear stress. The tribofilm is then reformed due to MoDTC
18 decomposition. The removal of the MoS_2 patches can lead to friction increase while the reformation of
19 the patchy MoS_2 films can result in friction reduction. This formation and removal process of MoS_2
20 layers can lead to friction fluctuation. Friction fluctuation was not observed at $\text{SRR}=100\%$ indicating
21 that the MoS_2 layers were being formed at the same rate as they were being removed thus maintaining
22 low friction. On the other hand, the friction fluctuation observed at $\text{SRR}=200\%$ was probably due to
23 the rate of removal of MoS_2 layers being slightly higher than the rate of MoS_2 formation leading to
24 longer periods of high friction. This hypothesis would explain the high friction observed by Graham et
25 al. [3] in tests with smooth discs under pure sliding conditions. This hypothesis would also explain the
26 longer induction time observed at $\text{SRR}=200\%$ than at $\text{SRR}=100\%$. Further TEM studies are needed to
27 confirm this hypothesis.
28
29
30
31
32
33
34
35
36
37
38

39 40 **5 Conclusions**

41 This study has investigated the influence of surface roughness and slide-roll ratio on friction
42 performance, surface chemistry and morphology of wear scars generated in tests with MoDTC
43 lubricant. The following conclusions can be made from this study:
44
45

- 46 • At $\text{SRR}=100\%$, friction was comparable for both rough and smooth discs irrespective of the
47 surface chemistry. At $\text{SRR}=200\%$, stable low friction values were achieved in tests with rough
48 discs but not in tests with smooth discs.
49
- 50 • The slide-roll ratios used in this study did not affect the surface chemistry. Surface chemistry
51 of the wear scars was affected by the surface roughness of the tribopair. Tests with rough discs
52 resulted in wear scars which were composed of MoS_2 while tests with smooth discs had wear
53 scars which were composed of a mixture of MoS_2 , MoS_x ($x>2$) and FeMoO_4 .
54
55
56
57
58
59
60

- Formation of MoS₂ in tests with rough discs can be attributed to high local pressures at the asperity-asperity contact which ensures complete decomposition of MoDTC to MoS₂. MoS_x formed in tests with smooth discs was as a result of partial decomposition of MoDTC due to lower local pressures.

This study highlights the importance of surface roughness in tribochemical reactions of MoDTC. The decomposition of MoDTC at a given test condition can be significantly enhanced by increasing the surface roughness which will ultimately result in low friction. These results are thus very significant to both lubricant formulators and component designers and offers an alternative approach to achieving friction reduction using organo-molybdenum additives.

Acknowledgements

The authors are grateful to Ali Gharbarzadeh for conducting the simulation work presented in this study. This study was funded by the FP7 program through the Marie Curie Initial Training Network (MC-ITN) entitled “ENTICE - Engineering Tribochemistry and Interfaces with a Focus on the Internal Combustion Engine” [290077] and was carried out at Total (Solaize), France and University of Leeds, UK.

References

1. D. N. Khaemba, A. Neville, and A. Morina, New insights on the decomposition mechanism of Molybdenum Dialkyldithiocarbamate (MoDTC): a Raman spectroscopic study. *RSC Advances*, 2016. **6**(45): p. 38637-38646.
2. C. Grossiord, K. Varlot, J. M. Martin, T. Le Mogne, C. Esnouf, and K. Inoue, MoS₂ single sheet lubrication by molybdenum dithiocarbamate. *Tribology International*, 1998. **31**(12): p. 737-743.
3. J. Graham, H. Spikes, and S. Korcek, The friction reducing properties of molybdenum dialkyldithiocarbamate additives: Part I - Factors influencing friction reduction. *Tribology Transactions*, 2001. **44**(4): p. 626-636.
4. K. T. Miklozic, J. Graham, and H. Spikes, Chemical and physical analysis of reaction films formed by molybdenum dialkyl-dithiocarbamate friction modifier additive using Raman and atomic force microscopy. *Tribology Letters*, 2001. **11**(2): p. 71-81.
5. A. Morina, A. Neville, M. Priest, and J. H. Green, ZDDP and MoDTC interactions in boundary lubrication—The effect of temperature and ZDDP/MoDTC ratio. *Tribology International*, 2006. **39**(12): p. 1545-1557.
6. Y. Yamamoto and S. Gondo, Friction and Wear Characteristics of Molybdenum Dithiocarbamate and Molybdenum Dithiophosphate. *Tribology Transactions*, 1989. **32**(2): p. 251-257.
7. J. Graham, H. Spikes, and R. Jensen, The friction reducing properties of molybdenum dialkyldithiocarbamate additives: Part II - Durability of friction reducing capability. *Tribology Transactions*, 2001. **44**(4): p. 637-647.

- 1
 - 2
 - 3
 - 4
 - 5
 - 6
 - 7
 - 8
 - 9
 - 10
 - 11
 - 12
 - 13
 - 14
 - 15
 - 16
 - 17
 - 18
 - 19
 - 20
 - 21
 - 22
 - 23
 - 24
 - 25
 - 26
 - 27
 - 28
 - 29
 - 30
 - 31
 - 32
 - 33
 - 34
 - 35
 - 36
 - 37
 - 38
 - 39
 - 40
 - 41
 - 42
 - 43
 - 44
 - 45
 - 46
 - 47
 - 48
 - 49
 - 50
 - 51
 - 52
 - 53
 - 54
 - 55
 - 56
 - 57
 - 58
 - 59
 - 60
8. B. J. Hamrock and D. Dowson, Isothermal Elastohydrodynamic Lubrication of Point Contacts: Part III—Fully Flooded Results. *Journal of Lubrication Technology*, 1977. **99**(2): p. 264-275.
9. D. Khaemba, A. Neville, and A. Morina, A methodology for Raman characterisation of MoDTC tribofilms and its application in investigating the influence of surface chemistry on friction performance of MoDTC lubricants. *Tribology Letters*, 2015. **59**(3): p. 1-17.
10. N. T. McDevitt, J. S. Zabinski, M. S. Donley, and J. E. Bultman, Disorder-Induced Low-Frequency Raman Band Observed in Deposited MoS₂ Films. *Applied Spectroscopy*, 1994. **48**(6): p. 733-736.
11. N. T. McDevitt, J. E. Bultman, and J. S. Zabinski, Study of Amorphous MoS₂ Films Grown by Pulsed Laser Deposition. *Applied Spectroscopy*, 1998. **52**(9): p. 1160-1164.
12. A. Müller, W.-O. Nolte, and B. Krebs, *[(S₂)₂Mo(S₂)₂Mo(S₂)₂]²⁻, a Novel Complex Containing Only S₂⁻ Ligands and a Mo□Mo Bond. *Angewandte Chemie International Edition in English*, 1978. **17**(4): p. 279-279.*
13. N. Ueyama, M. Nakata, T. Araki, A. Nakamura, S. Yamashita, and T. Yamashita, Raman and resonance Raman spectra of oxomolybdenum(VI) and -(V) complexes of cysteine and related thiolate ligands. *Inorganic Chemistry*, 1981. **20**(6): p. 1934-1937.
14. N. Ueyama, M. Nakata, T. Araki, A. Nakamura, S. Yamashita, and T. Yamashita, Raman and resonance Raman spectra of sulphur-bridged binuclear molybdenum (V) complexes of cysteine-containing chelate anions. *Chemistry Letters*, 1979. **8**(4): p. 421-424.
15. A. Müller, R. G. Bhattacharyya, N. Mohan, and B. Pfefferkorn, On the preparation of binuclear S, S bridged molybdenum(V) complexes crystal and molecular structure of [Mo₂S₄(Et₂dte)₂]. *Zeitschrift für anorganische und allgemeine Chemie*, 1979. **454**(1): p. 118-124.
16. J. S. Zabinski and N. T. MacDevitt, Raman spectra of inorganic compounds related to solid state tribochemical studies, 1996, USAF Wright Laboratory Report No. WL-TR-96-4034.
17. Y. Wang, P. He, W. Lei, F. Dong, and T. Zhang, Novel FeMoO₄/graphene composites based electrode materials for supercapacitors. *Composites Science and Technology*, 2014. **103**(0): p. 16-21.
18. C. H. Chang and S. S. Chan, Infrared and Raman studies of amorphous MoS₃ and poorly crystalline MoS₂. *Journal of Catalysis*, 1981. **72**(1): p. 139-148.
19. T. Weber, J. C. Muijsers, and J. W. Niemantsverdriet, Structure of Amorphous MoS₃. *The Journal of Physical Chemistry*, 1995. **99**(22): p. 9194-9200.
20. R. N. Bhattacharya, C. Y. Lee, F. H. Pollak, and D. M. Schleich, Optical study of amorphous MoS₃: Determination of the fundamental energy gap. *Journal of Non-Crystalline Solids*, 1987. **91**(2): p. 235-242.
21. C. Sourisseau, O. Gorochoy, and D. M. Schleich, Comparative IR and Raman studies of various amorphous MoS₃ and Li_xMoS₃ phases. *Materials Science and Engineering: B*, 1989. **3**(1-2): p. 113-117.
22. J. Lince, A. Pluntze, S. Jackson, G. Radhakrishnan, and P. Adams, Tribochemistry of MoS₃ Nanoparticle Coatings. *Tribology Letters*, 2014. **53**(3): p. 543-554.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
23. D. A. Rice, S. J. Hibble, M. J. Almond, K. A. H. Mohammad, and S. P. Pearse, Novel low-temperature route to known (MnS and FeS₂) and new (CrS₃, MoS₄ and WS₅) transition-metal sulfides. *Journal of Materials Chemistry*, 1992. **2**(8): p. 895-896.
 24. Y. Rai, In-situ interface chemical characterisation of a boundary lubricated contact, 2015, University of Leeds: PhD Thesis.
 25. A. Ghanbarzadeh, M. Wilson, A. Morina, D. Dowson, and A. Neville, Development of a new mechano-chemical model in boundary lubrication. *Tribology International*.
 26. F. Sahlin, R. Larsson, A. Almqvist, P. M. Lugt, and P. Marklund, A mixed lubrication model incorporating measured surface topography. Part 1: Theory of flow factors. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 2010. **224**(4): p. 335-351.
 27. Y. Hu and K. Tonder, Simulation of 3-D random rough surface by 2-D digital filter and fourier analysis. *International Journal of Machine Tools & Manufacture*, 1992. **32**(1-2): p. 83-90.
 28. T. Cousseau, J. S. Ruiz Acero, and A. Sinatora, Tribological response of fresh and used engine oils: The effect of surface texturing, roughness and fuel type. *Tribology International*, 2015.
 29. J. Seabra and D. Berthe, Influence of Surface Waviness and Roughness on the Normal Pressure Distribution in the Hertzian Contact. *Journal of Tribology*, 1987. **109**(3): p. 462-469.
 30. M. Mahrova, M. Conte, E. Roman, and R. Nevshupa, Critical Insight into Mechanochemical and Thermal Degradation of Imidazolium-Based Ionic Liquids with Alkyl and Monomethoxypoly(ethylene glycol) Side Chains. *The Journal of Physical Chemistry C*, 2014. **118**(39): p. 22544-22552.