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Glycerol oleate tribofilms: Relationships between chemical composition and tribological performance

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ABSTRACT

Glycerol oleates (GO) are organic friction modifiers (OFMs) with lower toxicity than traditional P- and S-containing friction modifiers. They are increasingly used in lubricant formulations but the mechanisms by which they lower friction and protect surfaces in the boundary lubrication regime are still not well understood. We have determined tribological performance and the chemical nature of tribofilms formed on steel for model formulations of glycerol monooleate, trioleate (GMO, triolein) and their mixture with glycerol dioleate (GDO) as a function of sliding-rolling ratio (% SRR) and temperature. Formulations of GMO, triolein and the mixed GOs in PAO4 base oil were tested at a low entrainment speed of 0.02 m/s and two different temperatures, 60°C and 100°C, in a mini traction machine (MTM) tribometer, with SRRs from pure sliding to pure rolling conditions. The thickness of tribofilms formed was tracked by spacer layer image mapping (SLIM), and their chemical composition was examined using ToF-SIMS. Temperature is correlated with film thickness, which subsequently influences the frictional performance of additives. Higher temperatures promote the formation of thicker films, resulting in lower friction for all additives. ToF-SIMS analysis identified a transition from physisorption at low temperatures and SRRs to chemisorption-dominated friction reduction at higher temperatures and SRRs.

1. Introduction

Whether the global position on CO_2 emissions has reached a "tipping point" or we are embarking on new climate milestones, the overwhelming body of evidence concludes that advances in science and technology need to be embraced to support control of climate change. In this context, reducing global emissions from the transportation sector is very important. Friction is inextricably linked to the fuel economy, which is currently one of the main drivers of development in the internal combustion automotive sector. Engine friction originates from several components operating at different load, speed, and temperature conditions. The current emphasis is to reduce environmental emissions by increasing fuel efficiency. Approximately 11.5 % of the fuel energy in passenger cars generated by an engine is lost through friction [1]. An essential function of advanced engine oils is to enhance fuel efficiency by minimising the frictional losses between contacting surfaces, which is responsible for high friction and severe wear within the boundary lubrication regime. Reducing this metal-to-metal friction helps engines run more efficiently, leading to huge energy savings and a reduction in CO_2 emissions. To enhance the performance and extend the service life of the mechanical components, various lubricant additives have been applied, with a particular focus on improving surface protection under boundary lubrication regime [1–6]. Molybdenum Dithiocarbamate (MoDTC) and Zinc Dialkyldithiophosphate (ZDDP) are among the most effective friction modifiers, known for their excellent friction-reducing capabilities and robust surface protection[7–9]. However, increasingly stringent environmental regulations on engine oils have necessitated reducing the use of additives containing sulphur, phosphorus, and heavy metals. As a result, considerable efforts have been directed towards the development and application of organic friction modifiers, as sustainable alternatives to traditional organo-metallic additives such as ZDDP and MoDTC [10–12]. Typical OFMs are amphiphilic surfactants with a long alkyl chain and a polar head group. They adsorb on the surface through their polar head group, while the hydrocarbon tails are positioned perpendicular to the surface [2,13–15]. Amine, amide, carboxylic acid, ester, and alcohol are common functional groups of OFMs used for

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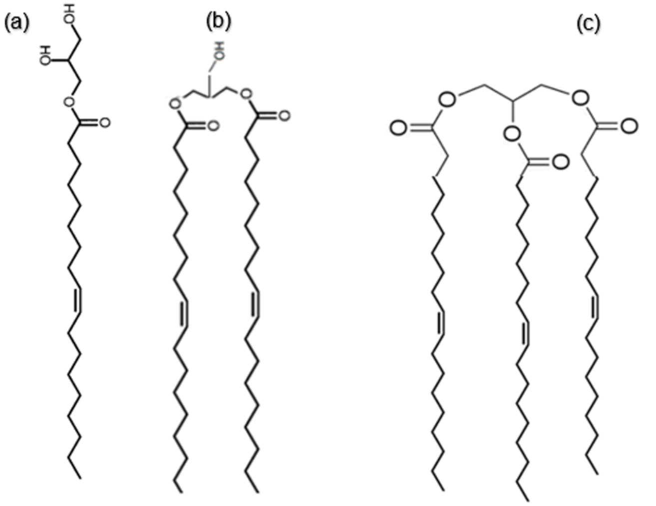


Fig. 1. Molecular structures of (a) GMO, (b) Glycerol dioleate, and (c) Triolein.

engine oils [13,16].

Organic friction modifiers reduce friction at the asperity-asperity contact by forming boundary tribofilms[2]. Although the friction reduction capability of OFM is typically attributed to the formation of monolayer film on the surface contact [17], some studies have reported the development of a thick viscous tribofilm on the metal surface with thickness ranging from 10 to 100 nm [18,19]. The film formation and performance of OFMs are affected by various factors, including the polarity of the head group, chain lengths, concentrations, running conditions, temperature, and the presence of other lubricant additives [14,15,17,18,20–24]. However, the correlation between reaction film formation from organic friction modifiers under varying tribological conditions and their performance is generally not well understood.

Glycerol monooleate (GMO) is a fatty acid derivative that is widely used as an organic friction modifier in lubricants [25,26]. The positive impact of GMO on friction reduction results from the protective films it forms on the lubricated surface. This is achieved through the functional groups, which facilitate close adsorption onto the surfaces [27,28]. However, there is still no agreement about the reactions of GMO that lead to the formation of a tribofilm and the mechanism by which the film reduces friction. It is usually assumed that GMO adsorbs on the metal surface via its polar head group by forming hydrogen bonds with the surface hydroxyl or oxygen atoms in the metal's oxide layer [29]. However, other studies suggested that the GMO may undergo hydrolysis to form glycerol and oleic acid (OA) in steel-steel contacts and the resulting fatty acid monolayer on steel surfaces is responsible for improved boundary lubrication [13,16,30–32]. On the other hand, Fry et al.[26] suggested that it is unlikely that GMO hydrolysis into a carboxylic acid within rubbing contact in the presence of amine. Wang et al.[28] found that GMO reduces friction by physical adsorption on the surface at a low temperature, while chemisorption films play a vital role when the temperature is higher than 110℃. Based on operating temperatures and running conditions, engine tribological systems may undergo different lubrication regimes, from boundary, mixed, to elasto-hydrodynamic regimes. Moreover, temperature can impact the thickness and durability of friction modifiers' films, as elevated temperatures may cause the desorption of molecules from the metal surface [28]. Conversely, high temperatures are necessary to create chemically reactive protective layers [18,33,34].

While the effect of temperature on GMO tribological performance is relatively well understood, there is no systematic study to show if tribological conditions, such as SRR (%) and the contact mode, influence the mechanisms by which GMO protects the surfaces.

In this study, a variety of analytical techniques were utilised to investigate the relationship between friction reduction and film formation by different OFMs under sliding-rolling, sliding and rolling tribological conditions.

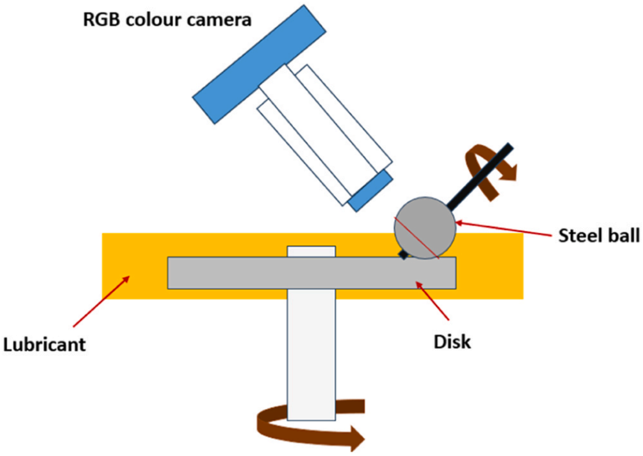


Fig. 2. Schematic image of MTM-SLIM set-up.

High-resolution transmission electron microscopy (HRTEM) was used to analyse the thickness and properties of the tribofilms. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was employed to characterise the chemistry of the adsorbed additive layers and surface chemical reaction films following tribological testing. Additionally, the width of the wear track and surface roughness post-tribological measurements were analysed using a 3D surface profiler. Finally, the tribological mechanism is discussed, based on the experimental findings.

2. Materials and methodology

2.1. Lubricants

Glycerol monooleate (GMO), glycerol trioleate (triolein), and a mixed glycerol oleate(GO), comprising 50 % GMO, approximately 40 % glycerol dioleate (GDO), and over 10 % triolein, were selected as organic friction modifiers. The friction of oleic acid was also investigated to examine whether GMO reduces friction by hydrolysis. The molecular structures of OFMs used are shown in Fig. 1. GMO, triolein, and oleic acid were purchased at a ≥ 99 % purity from Sigma-Aldrich, while the mixed GO was supplied by Infineum. All additives were used as received. PAO4 (viscosity index 124, flash point 222 ℃, pour point −69 ℃) was used as a base oil. The lubricant solutions were prepared by stirring 1 wt % of the OFM in the PAO4 oil at 60℃ and 400 rpm for 15 min to prepare homogeneous samples. Since some solutions precipitated when they were cooled at room temperature, all the tribological experiments were performed immediately after sample preparation.

2.2. Tribological test

A PCS Mini Traction Machine (MTM) tribometer, shown in Fig. 2, was used to characterise the frictional characteristics of the model OFM formulations, and a Spacer Layer Image Method (SLIM) apparatus coupled with the MTM was used to measure and map the thickness of reaction films formed on the ball. The SLIM images were analysed by using a 3D mapper analysis program. Tribological tests were carried out under a boundary lubrication regime (Lambda ratio, $\lambda < 1$) calculated using the Hamrock-Dowson expression [35] and three different types of contact motion: sliding-rolling, sliding, and rolling. The SRR ratio (as a percentage) is calculated as a ratio between the sliding speed (U_{Disc}-U_{Ball}|) and entrainment speed ($(U_{Disc}+U_{Ball})/2$), where U_{disc} and U_{ball} are the speeds of the disc and the ball.

In pure sliding conditions, SRR is calculated as 200 %, the ball was

Table 1
Test conditions and material properties of specimens for MTM tribotest.

Test conditions	Parameters
Temperature	60 °C,100°C
Contact pressure	0.69 GPa
Load	40 N
Lubricant	GMO, mixed GO, triolein, oleic acid
Test duration	2 h
Ball material	AISI 52100 steel (Ra=10 nm)
Disc material	AISI 52100 steel (Ra=10 nm)
SRR (%)	5, 50, 100,150, 200
Entrainment speed	0.02 ms^{-1}[39]

kept stationary, and only the disc was rotated, while in pure rolling, SRR is calculated as 5 %, the ball and the disc were rotated in the same direction at the same surface speed. In the sliding-rolling condition, both the disc and the ball were rotated independently, allowing for a slide-roll ratio (SRR) of 50 %, 100 %, and 150 %.

For MTM-SLIM tests, a steel disc of 46 mm diameter and a drilled ball of 19.05 mm diameter were used. The MTM specimens were supplied by PCS Instruments Ltd (Acton, UK). The ball and disc were ultra-sonicated with ethanol and acetone before the measurement. The tests were conducted for 2 h at five different SRRs (%), followed by the generation of the Stribeck curve. However, the Stribeck results were not included in the manuscript as they were not directly relevant to the objectives of the present study. A load of 40 N was used, giving a mean contact pressure of 0.69 GPa, calculated using Hertzian contact theory for a point contact. Two specific temperatures, 60°C and 100°C, were chosen to replicate the engine's real operational conditions. During SLIM image acquisition, the ball was pushed against the glass lens with a load of 20 N.

The SLIM is primarily used for measuring ZDDP tribofilms formed from ZDDP lubricant additives which typically are around 100 nm thick, however, previous studies used SLIM also for measuring organic films with thinner film thickness [22,36–38]. The key advantage of the SLIM is its ability to quantify tribofilm thickness in situ, without cleaning, cooling, or removing the MTM ball from the test rig. Furthermore, SLIM enables continuous monitoring of tribofilm formation during the test, providing a series of thickness measurements as the test progresses. This allows quick and convenient analysis of both film growth and removal rates, making it a very effective technique for studying tribofilm behaviour. Test conditions and material properties of specimens are detailed in Table 1. Tribological tests were repeated three times to ensure the repeatability of the tests.The machine was also indexed prior to the testing to ensure that images were captured at the same location.

2.3. Surface analysis

2.3.1. Surface imaging

The White Light Interferometry, NPFLEX™ 3D Surface Metrology System from Bruker, was used to evaluate the width of the wear scar and surface roughness on the steel disc after the tribological test. Before the wear measurement, the tribofilm formed on the steel surface was cleaned by using EDTA. 2D and 3D images of the wear track were taken. The wear width was measured for three different points for each experiment and the average value was reported. The Vision 64 software from Bruker was used to interpret and analyse the data produced by NPFLEX. Since the disc has a higher susceptibility to wear, due to the lower hardness compared with the ball, all the wear measurement was performed on the disc.

2.3.2. Surface chemical analysis

High-Resolution Transmission Electron Microscopy (HRTEM) was used for post-tribological analysis of films formed from additives on the steel surface. This instrument was equipped with Energy Dispersive X-ray (EDX), and a High-Angle Annular Dark-Field Scanning (HAADF) for a comprehensive examination. The cross-sections of the worn surfaces on the disc were prepared for TEM analysis using the high-resolution monochromated Focused Ion Beam (FIB) technology.

The chemical compositions of the tribofilm were studied using Time-of-Flight Secondary Ion Mass Spectrometry IV (ToF-SIMS, ION-TOF GmbH., Münster, Germany). ToF-SIMS is a technique that can analyse the thin film and provide information about the organic chemical structures [10]. The primary ion beam was a bismuth liquid metal ion gun (Bi^{3+}) run at 25 kV (pulsed target current of ~1 pA). Surface analysis was performed on MTM disc's wear track. For each sample, data were acquired over 3 regions of 500 × 500 μm^2 at 256 × 256 pixel resolution. The measured mass range (m/z) was between 1 and 410. Data acquisition and analysis were performed using Surface Lab 7 software (IONTOF GmbH). Positive and negative spectra of inside and outside the wear were extracted and compared. Selected spectra were normalised for comparison and identical Y scales were used.

3. Results and discussion

3.1. Impact of temperature and SRR (%) on friction

To investigate the effect of the slide-roll ratio on the frictional behaviour, the tribological response of OFMs and base oil was compared. Fig. 3 presents the mean friction coefficient values for steel-steel contact lubricated with PAO4 and PAO4 +OFMs at a constant speed of 0.02 ms^{-1} at five different SRRs, and at two different

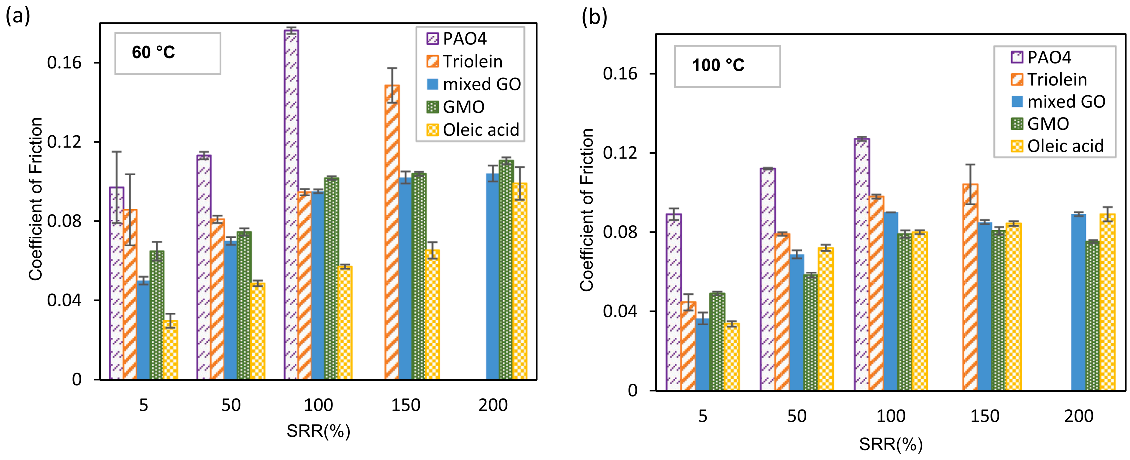


Fig. 3. Mean coefficient for last 20 min of tribotest for different lubricants in PAO4 at five different SRRs at (a) T:60°C and (b)T:100°C.

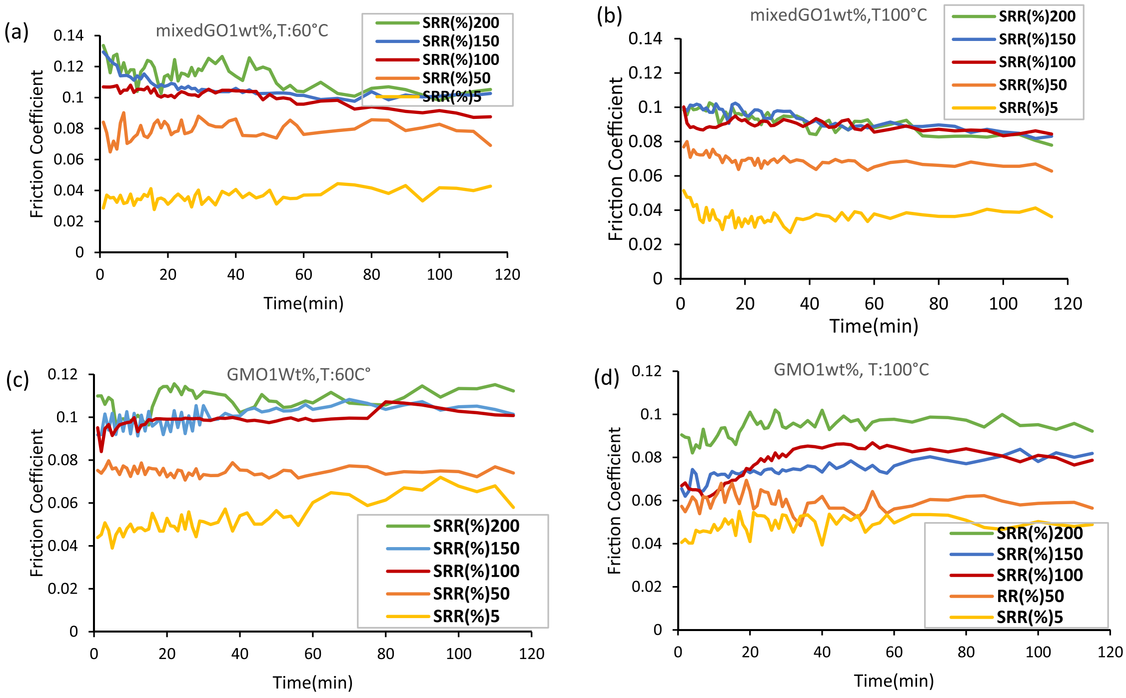


Fig. 4. coefficient of friction vs time at different SRRs for GMO1wt% solution in PAO4 at (a)T:60°C T, (b) T:100°C and mixed GO1wt% solutions in PAO4 at (c) T:60°C and (d)T:100°C.

temperatures. The mean friction coefficients were determined by calculating the average of the last 20 min of COF values, representing the steady state. The results show that each lubricant solution containing OFMs lowered friction relative to the pure base oil. The friction coefficient gradually increased at both temperatures with the increase of SRR. These results align with previous studies that suggested higher SRRs would induce higher shear stresses on the surface, leading to wear and removal of the OFM film, indicative of a more boundary lubrication regime [40].

The COFs of triolein at SRR of 200 % and PAO4 at SRRs of 150 % and 200 % at both temperatures were too high and exceeded the machine limitation, leading to the termination of the test after 50 min. We do not expect triolein to be used as a friction modifier on its own; it is rather one of the components of the mixed GO, making it worthwhile to investigate as a reference. GMO and the mixed GO formulation provided comparable COF at lower temperature, shifting from 0.06 to 0.11 from pure rolling to pure sliding conditions, respectively. Additionally, apart from oleic acid, all additives exhibited lower friction at a higher temperature test at all SRRs.This phenomenon could be attributed to the shear properties of the formed tribofilms or thickness. The higher temperature decomposes the GMO [31] while physical adsorption of the additive plays a major role in reducing friction at the lower temperature test [28]. GMO showed a similar friction coefficient to oleic acid at higher SRRs at a temperature of 100°C, while mixed GO demonstrated a comparable COF to oleic acid across all SRRs at this temperature. At a temperature of 60 °C, both GMO and mixed GO provided a COF similar to oleic acid, but only under pure sliding conditions. These results suggest that the interaction of oleate, the hydrolysed product of GMO, and the steel surface is the key mechanism governing friction reduction at these tribological conditions. The type of chemical reactions at the interface will also determine the tribofilm formation rate, hence it is crucial to also quantify the thickness of the formed films.

Fig. 4 shows the friction values as a function of time for GMO and mixed GO lubricants. A high friction coefficient at the beginning of the test and fluctuation in friction trace was noted for mixed GO during the first 60 min of contact, however, with continued rubbing the COF reduced and a stable friction trace was obtained (Fig. 4(a) and (b)). The formation of thick and stable tribofilm, especially at higher SRRs and elevated temperatures, is one of the reasons for this phenomenon [32]. In contrast, Fig. 4(c) and (d) show that GMO produced a lower friction coefficient than the mixed GO at the start of the test. However, the friction was observed to increase during the first 60 min of rubbing,

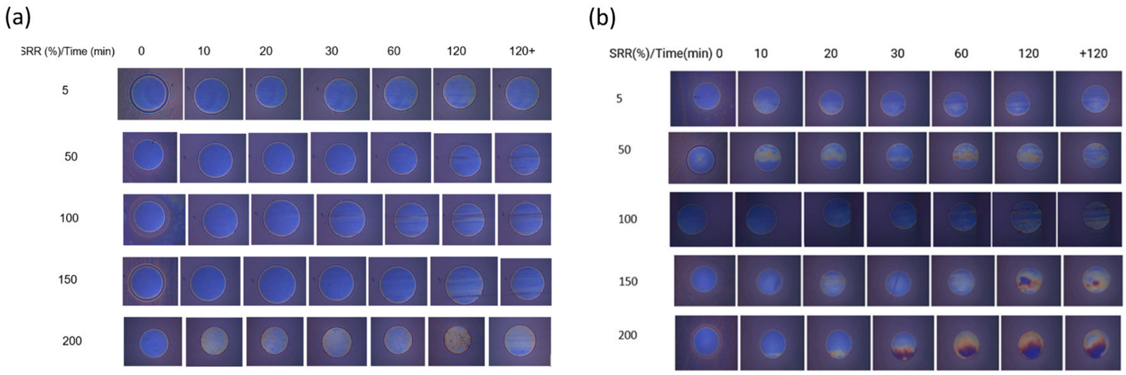


Fig. 5. Interference images from wear track for mixed GO1wt% in PAO4 at different SRRs at temperatures T:60°C(a) and T:100°C(b).

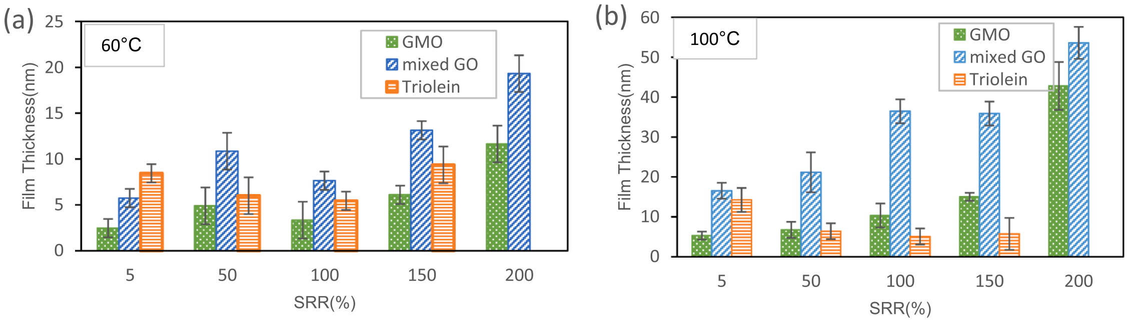


Fig. 6. Film Thickness of GMO1wt%, mixed GO1wt%, and triolein1wt% in PAO4 solution at 5 different SRRs at temperatures (a) 60°C and (b) 100°C.

particularly at a temperature of 60°C. Additionally, the instability of the COF trace was observed throughout the test. This behaviour is likely due to the dynamic formation and removal process of thin tribofilm in the contact. These findings align with previous studies indicating that temperature has a significant impact on the frictional performance of GMO [22,28]. However, they also show that the extent of this correlation with temperature can vary considerably depending on the type of GMO used.

Fig. 5 presents the SLIM images of tribofilm formed from a 1wt% mixed GO solution in PAO4 at varying SRRs at 60°C and 100°C. The supplementary data in Fig. A1 show the SLIM images for GMO tested under the same range of SRRs and temperatures. It can be observed that the colour of the images changes gradually from pale blue to orange and ultimately to brown and dark blue with increasing rubbing time, indicating the progressive formation and accumulation of tribofilms on the wear track. At 60°C, the film took longer to establish, and a thick viscous tribofilm did not form at this temperature. Additionally, some horizontal scratches across the centre of the contact suggest that wear has occurred. In contrast, at 100°C, particularly under harsh contact conditions such as SRR(%)200,tribofilm formation occurred rapidly after 20 min of rubbing. Notably, no wear scars were visible on the surface, indicating effective surface protection. The chemical nature of this film, along with its formation mechanism, is described in Section 3.2.2, accompanied by ToF SIMS results.

Except for an SRR of 5 % and temperature of 100°C, triolein exhibited the highest friction coefficient compared to other additives at both tested temperatures. This behaviour could be attributed to its molecular structure: unlike GMO, triolein does not have any hydroxyl groups. Replacing the polar hydroxyl group with the oleate ester groups appears to have a negative impact on friction within the boundary lubrication regime. The results of previous molecular dynamic simulations demonstrated the critical role of hydrogen bonding in stabilising the film monolayers [17]. GMOs tend to form hydrogen bonds with oxide anions (=O) situated on the metal surface, which act as hydrogen bond acceptor, while triolein with no hydroxyl group is unable to engage in intermolecular hydrogen bonding interactions. Moreover, triolein with three ester groups, it is expected to undergo three decomposition reactions. In light of this, an extended rubbing duration might be necessary to fully develop its effect. Further analysis of this aspect is required to understand the potential mechanism of reduced friction and wear performance better.

3.2. *Surface analysis*

3.2.1. *Tribofilm thickness*

The thickness of the tribofilm could be a key factor in assessing the surface protection of organic friction modifier additives, which in turn influences the wear and friction behaviour of the system. Film thickness can be measured by various methods, depending on the type of lubricant and the accuracy requirement. This study employed two techniques, space layer image mapping, SLIM, and HRTEM, to quantify the tribofilm thickness. The mean tribofilm thickness on steel balls was measured using the interference images across the horizontal axis of the circular contact with a diameter of 100 µm. The film thickness obtained from SLIM for all three additives at 60°C and 100°C with varying amounts of SRRs is shown in Fig. 6. The results indicate that all additives produced a thicker film at elevated temperatures. A comparison of the film thickness across all SRRs revealed substantially thicker film at an SRR of 200 % compared to 5 %. These findings suggest that harsher tribological conditions achieved at higher SRRs facilitated tribofilm growth, consistent with previous studies [22,40].

To better understand the effect of temperature on the film formation, the mean film thickness for the 1 wt% GMO and mixed GO formulation was calculated from the SLIM images corresponding to different rubbing times at an SRR of 200 % and temperatures of 60°C and 100°C (Fig. 7). It is evident that the film developed initially very rapidly at 100°C and increased in thickness with increasing rubbing time. In contrast, at 60 °C, the film growth is slower and more gradual, with a lower overall thickness compared to 100 °C. The film growth rate for mixed GO is higher, both in terms of thickness and speed, particularly at elevated temperatures. These findings indicate that temperature is a critical factor influencing film formation.

HRTEM was employed for analysing the structure of the tribofilms but the images were also useful for measuring the tribofilm thickness.

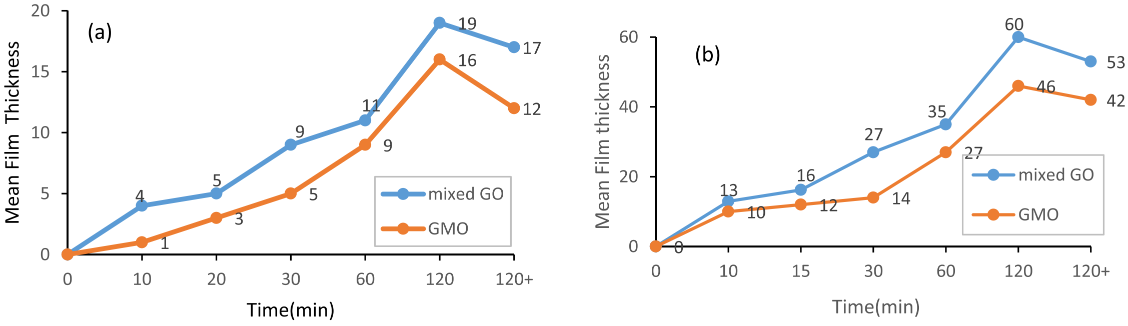


Fig. 7. Mean film thickness calculated from interference images for mixed GO and GMO at SRR(%)200 and T:60°C(a) and T: 100°C(b).

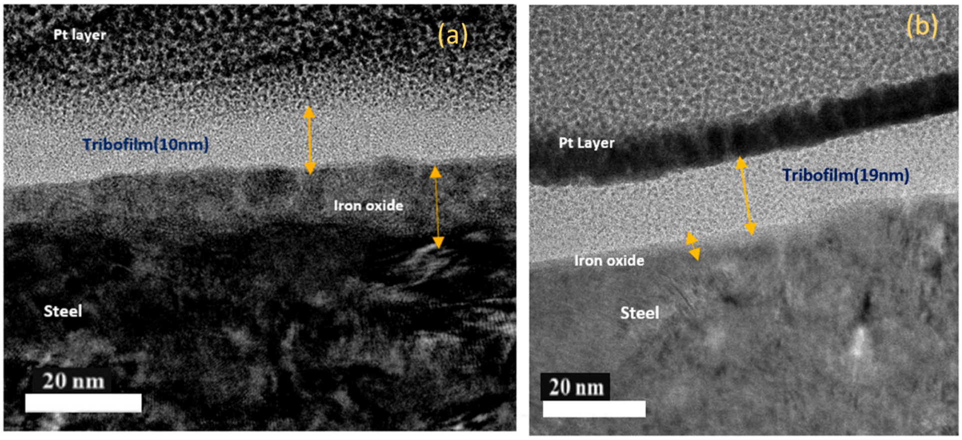


Fig. 8. HRTEM images for formed tribofilm at 60 °C and SRR(%) 200 for (a) GMO1wt% and (b) mixed GO1 wt%.

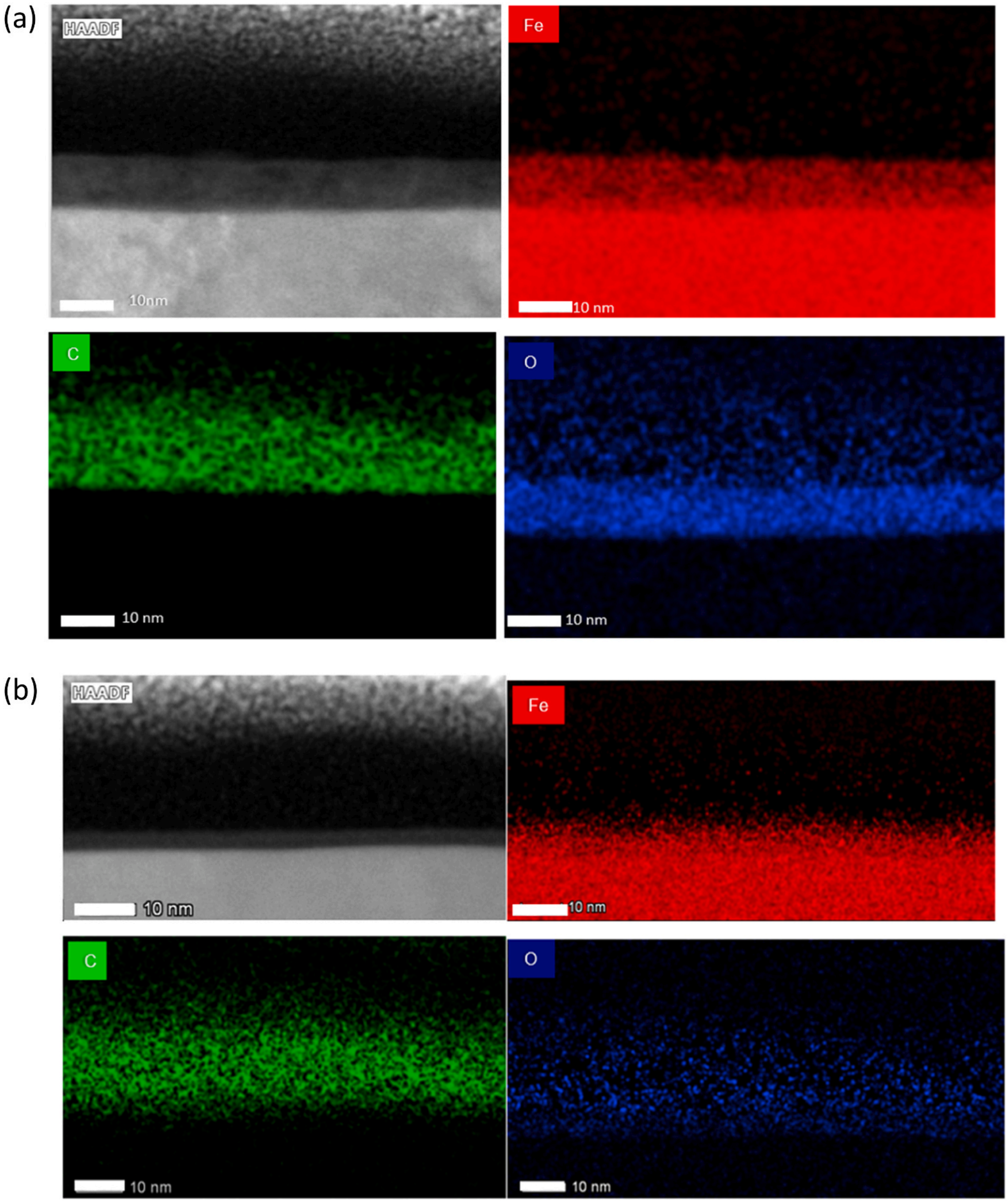


Fig. 9. HAADF image and EDX measurement by HRTEM for (a) GMO1wt% and (b) *mixed* GO1wt% tribofilm at SRR(%)200 and temperature 60°C.

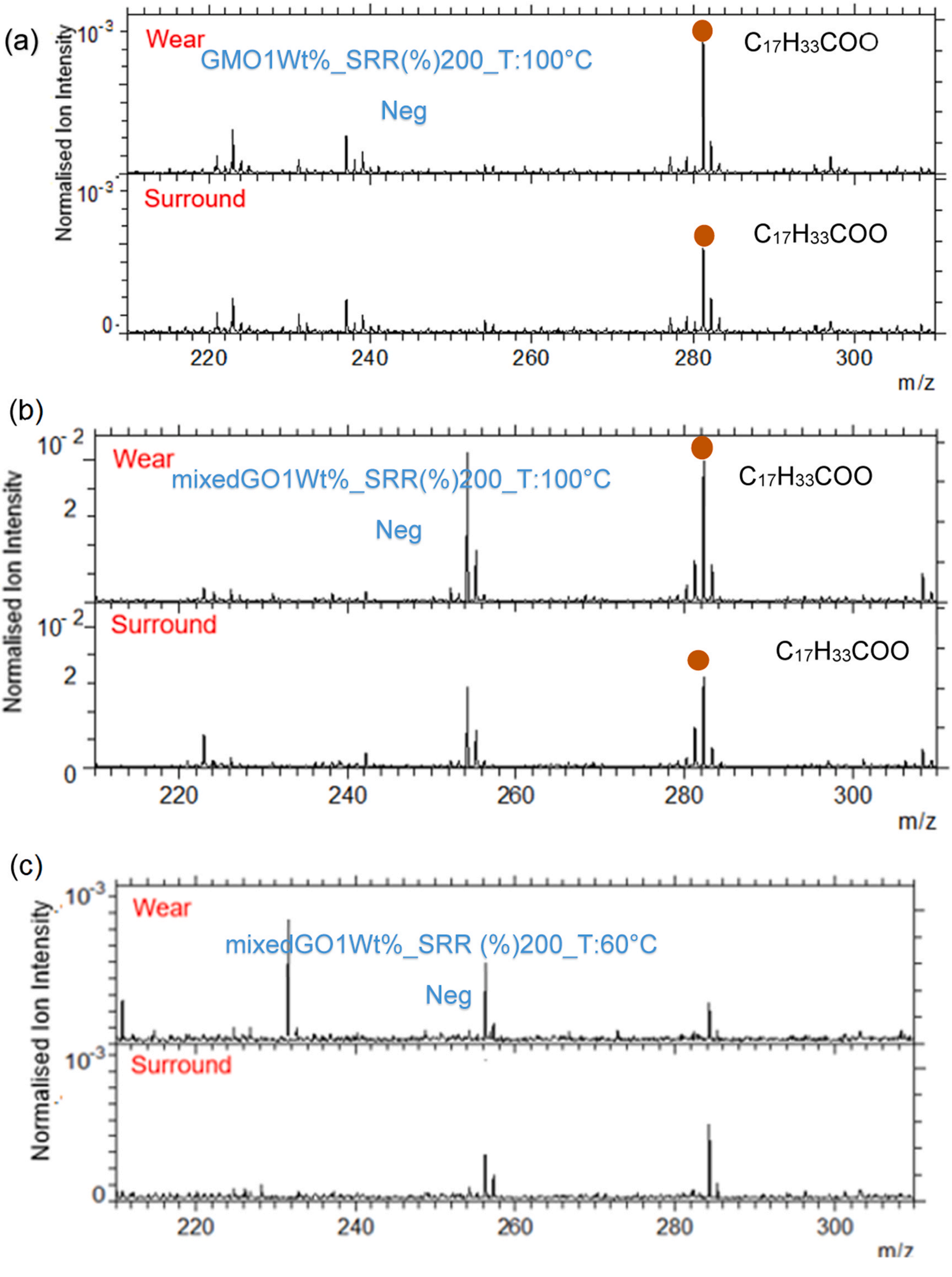
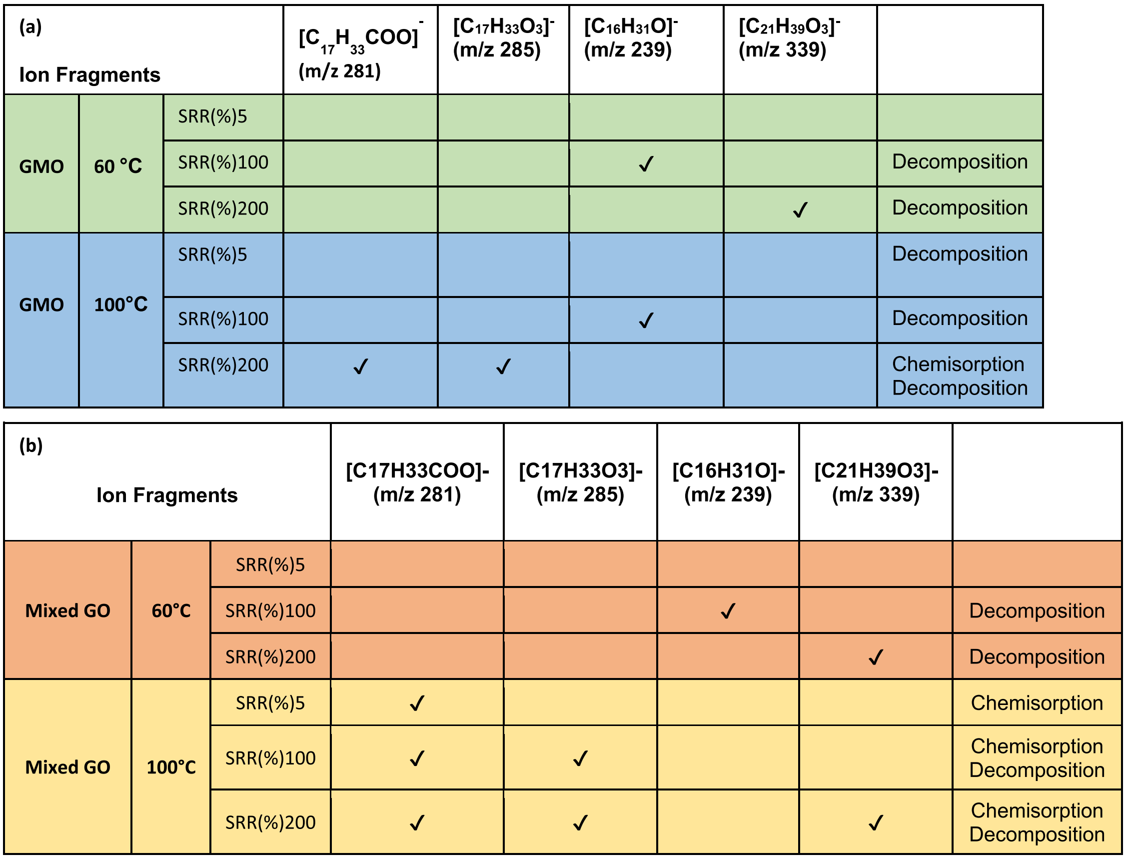


Fig. 10. Negative ions from ToF-SIMS analysis of inside and outside of the friction surface tested with, (a) 1 wt% GMO, (b)1 wt% mixedGO, at SRR(%)200 and temperature 100°C and (c) mixed GO1wt% at SRR(%)200 and temperature 60°C.

Cross-sectional views of the tribofilms in TEM images from FIB lamellas reveal a discernible difference in tribofilm thickness, as shown in Fig. 8 for films formed from two different model lubricant formulations containing 1 wt% GMO and 1 wt% mixed GO in PAO4. The images were taken after friction and wear experiments at 60°C and a SRR of 200 %. After 2 h of sliding in the presence of 1 wt% GMO lubricant, followed by a Stribeck curve at an SRR of 200 %, a thin tribofilm with an average thickness of 9–11 nm was observed, as illustrated by Fig. 8(a). In contrast, 1 wt% mixed GO formed a thicker tribofilm, with an average thickness of 16–18 nm, as shown in Fig. 8(b). These results agree with the measurement obtained by SLIM (Fig. 5). These findings show that the chemistry of OFM influences the thickness of the surface reaction layer, which has an impact on tribological performance [41]. Fig. 8 also demonstrates the thicker iron oxide layer on the surface after testing with GMO compared to the mixed GO formulation. This indicates that the GMO induced more surface oxidation than the mixed GMO.

The cross-sectional structure and elemental distribution in the tribofilm were investigated by EDX mapping. EDX and high-angle annular

Table 2
Molecular fragments detected in the negative and positive ion spectra for GMO (a), and mixed GMO (b) lubricant-derived tribofilm.



(a) Ion Fragments			$[C_{17}H_{33}COO]^-$ (m/z 281)	$[C_{17}H_{33}O_3]^-$ (m/z 285)	$[C_{16}H_{31}O]^-$ (m/z 239)	$[C_{21}H_{39}O_3]^-$ (m/z 339)	
GMO	60 °C	SRR(%)5					
		SRR(%)100			✓		Decomposition
		SRR(%)200				✓	Decomposition
GMO	100°C	SRR(%)5					Decomposition
		SRR(%)100			✓		Decomposition
		SRR(%)200	✓	✓			Chemisorption Decomposition

(b) Ion Fragments			[C17H33COO]- (m/z 281)	[C17H33O3]- (m/z 285)	[C16H31O]- (m/z 239)	[C21H39O3]- (m/z 339)	
Mixed GO	60°C	SRR(%)5					
		SRR(%)100			✓		Decomposition
		SRR(%)200				✓	Decomposition
Mixed GO	100°C	SRR(%)5	✓				Chemisorption
		SRR(%)100	✓	✓			Chemisorption Decomposition
		SRR(%)200	✓	✓		✓	Chemisorption Decomposition

dark field (HAADF) maps (Fig. 9) show that the tribofilm consists of C and O-enriched layers. The significant amount of C and O within the wear tracks can be attributed to the adsorption of OFM on the surface [20]. As shown in Fig. 9(a), a significantly higher concentration of O on the surface indicates the presence of a thick oxidation layer for GMO.

3.2.2. *Chemical properties of the tribofilms*

To obtain the chemical composition of tribofilms formed from GMO, mixed GO, and triolein additives in boundary lubrication, the MTM discs tested with OFMs at three different SRRs (%), 5, 100, and 200 and at temperatures 60°C and 100°C were analysed by ToF-SIMS. Spectra were recorded at three different positions inside and outside the wear track.

From the literature, it is known that the presence of ions corresponding to $[C_{17}H_{33}COO]^-$ suggests the chemical adsorption of GMO [42,43]. Additionally, ion fragments such as $[C_{17}H_{33}O_3]^-$, $[C_{18}H_{33}O]^-$, $[C_{16}H_{31}O]^-$ and $[C_{16}H_{29}O]^-$, generated by the interaction of cleaved alkyl tails of GMO with oxygen at the iron oxide surface, can be attributed to GMO decomposition [27,42–44]. Fig. 10 shows the negative ion spectra with ion mass from 210 to 310 u inside and outside the wear tracks tested with 1 wt% GMO at an SRR of 200 % and with 1 wt% mixed GO with SRRs of 5 % and 200 %, and at temperatures of 60°C and 100°C, respectively. Interestingly, the oleate ion fingerprint peak ($[C_{17}H_{33}COO]^-$) at position 281.2 u was detected for 1 wt% GMO at an SRR of 200 % and for the 1 wt% mixed GO at all 3 different SRRs but only at 100°C (Fig. 10 (a) and (b)). This ion was not visible at 60°C for these additives. These results suggest that chemisorption plays a vital role in tribofilm formation and as a result in reducing friction under these tribological conditions. Furthermore, the higher concentration of hydrocarbon moieties with the general formula $[C_nH_m]^+$ detected within the wear track at higher SRRs, implies that GMO underwent decomposition [22]. Based on the tribological results, where friction for both GMO and mixed GO is lower at 100 °C than at 60°C, it can be suggested that tribofilms formed from the chemisorption of ester fragments on the contact surface exhibit lower friction.

Table 2 shows the molecular fragments observed in the positive and negative ion spectra for GMO and mixed GO 1 wt% solution at 60°C and 100°C. The ion oleate fragment was detected for the mixed GO at all SRRs at the temperature of 100°C, while this peak was not apparent for GMO for SRRs of 100 % and 5 % at this temperature. This is likely because slightly less GMO is decomposed under the mild rolling conditions. Additionally, this can also be attributed to the chemical composition of mixed GO, which includes three types of glycerol oleates: GMO (with one oleyl group), GDO (with two), and triolein (with three). At higher temperatures and under severe contact conditions, any of these additives can undergo hydrolysis to produce oleate ions. Consequently, a higher concentration of oleate ion can be detected in ToF-SIMS spectra, while GMO with only one oleyl group produces a lower concentration of oleate ion, making detection more difficult. A higher ion intensity of oleate ion for mixed GO compared to GMO, as shown in Fig. 10 (a) and (b) confirmed this.

The ion intensity was compared outside and inside the wear tracks to verify whether the detected ion originates from thermal cracking or whether the SRR influences GMO tribochemical decomposition. If the intensity peak of this ion on the wear track is higher than that on the unrubbed surface it suggests that the SRR has an impact on the GMO and mixed GO decomposition. Fig. 10(a) and (b) show a higher intensity peak of the $[C_{17}H_{33}COO]^-$ fragment inside the wear scar compared to the outside of the wear scar. Additionally, the ion fragments associated with GMO decomposition were detected at *m/z* 285, 239 and 339 in positive ion spectra of GMO and mixed GO at both temperatures, but only at

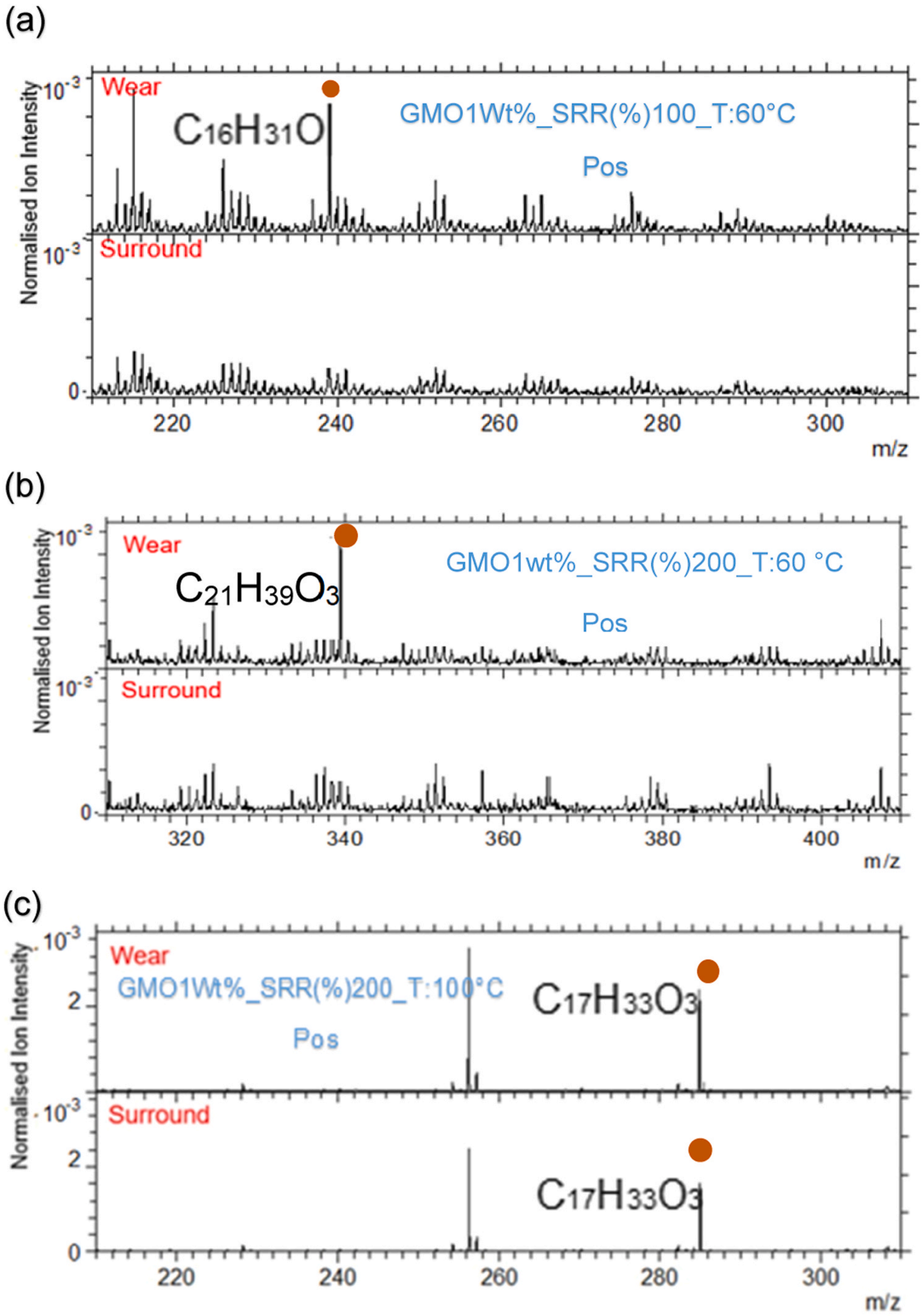


Fig. 11. Positive ions from ToF-SIMS analysis of inside and outside of the friction surface tested with 1 wt% GMO, (a) SRR(%)100, temperature 60°C (b) SRR(%)200, temperature 60°C and (c) SRR(%)200 and temperature 100°C.

higher SRRs (Fig. 11). At a temperature of 60°C the ion fragments $[C_{16}H_{31}O]^-$ and $[C_{21}H_{39}O_3]^-$ were seen at 239 and 339 u both inside and outside the wear tracks, as illustrated in Fig. 11(a) and (b). The intensity of the peak was noticeably lower outside the wear, confirming that the harsh contact conditions, as represented by an SRR of 200 %, promote GMO and mixed GO decomposition.

At the beginning of rubbing, GMO and GDO adsorb to the metal surface via one or more of the glyceryl hydroxyls, forming a hydrogen bond with the ferrous surface [29,39]. Continued rubbing, especially at higher SRR (200 %), results in the breakdown of these additives, leading to production of oleic acid and glycerol. Oleate ions form a strong chemisorbed bond to the surface, while glycerol adsorbs through hydrogen bonding. However, due to the weaker nature of this bond, glycerol gradually desorbs from the surface. The schematic illustration of these mechanisms is presented in Fig. 12. It is worth noting that the HRTEM and SLIM results indicated that GMO and mixed GO did not form monolayer tribofilm. Accordingly, this schematic only presents the interaction of molecules with the steel surfaces via physisorption and chemisorption.

These findings suggest that the more severe conditions achieved at higher SRRs facilitate the decomposition process of GMO and promote thicker film growth [13,32,45].

From the ToF-SIMS spectra for triolein at SRRs of 5 % and 100 % at both temperatures, no ion fragments attributed to triolein

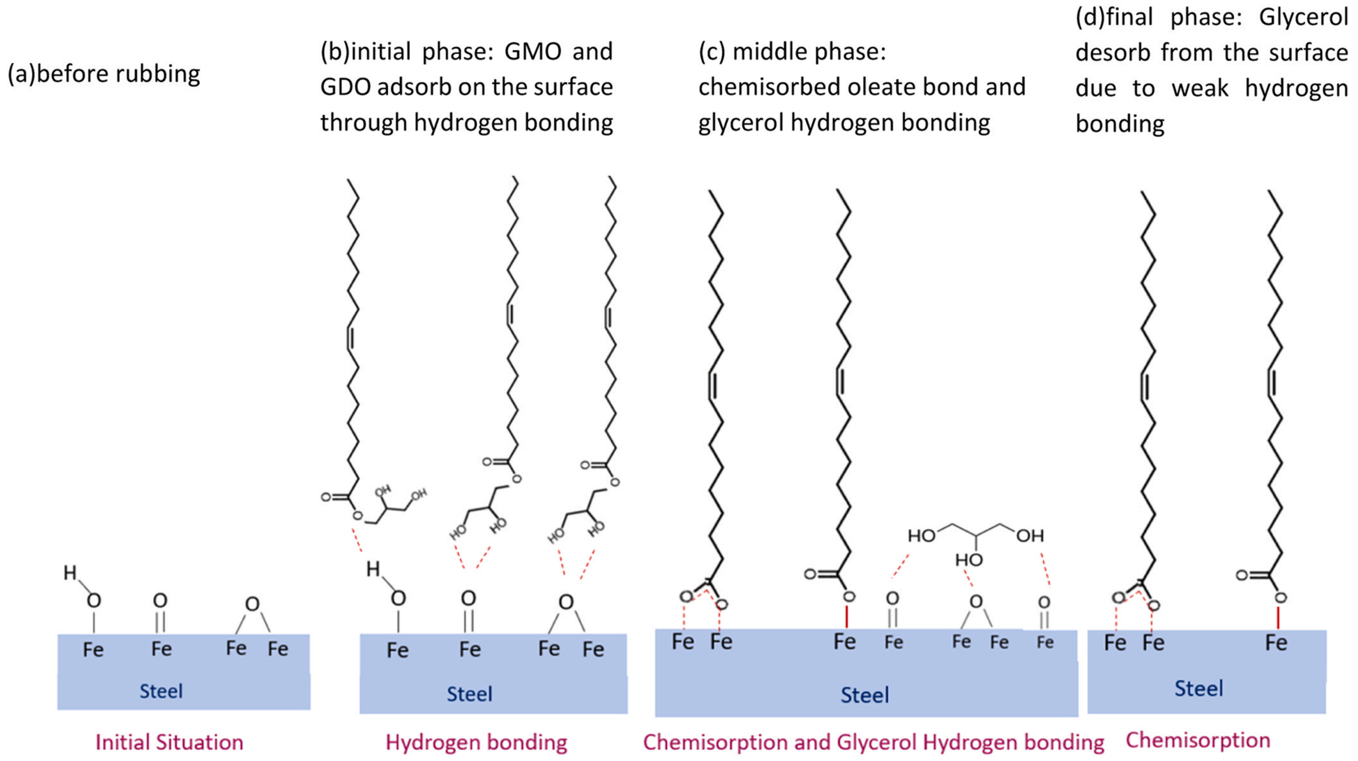


Fig. 12. The schematic illustration of adsorption mechanism of GMO and GDO on the steel surface.

decomposition were found in positive and negative ion spectra. This could be related to triolein molecular structure. As triolein cannot form the hydrogen bond to the surface in the first step, it is expected to undergo three ester cleaves in one step. However, this is unlikely to happen when the molecule cannot spend enough time at the surface through forming a hydrogen bond.

Since the COF of triolein at SRR of 200 % was too high and exceeded the machine limitations, leading to the termination of the test after 50 min, no ToF-SIMS analysis was done for this condition.

3.3. *Wear analysis*

Surface roughness and wear track width were quantified by optical white light interferometry following tribological measurements to evaluate the anti-wear properties of the various additives. Considering that the wear was minimal, the width of the wear track was used to characterise the amount of surface damage. Figs. 13 and 14 show the wear scar width and surface roughness respectively, reflecting average values obtained from three randomly selected locations along the wear scar. The observed trend in the width of the wear scars implies that the tribofilm generated from all additives successfully reduces wear.

At both temperatures, there was a notable trend of increasing wear scar width with rising SRRs. Triolein showed the widest wear tracks compared to other additives. This may be attributed to generating the films with low shear strength, which are easily worn off under severe conditions. At both temperatures, GMO generated larger wear scars than mixed GO on the MTM discs, even the signs of wear being more apparent for the GMO in SLIM images compared to mixed GO. As previously discussed, GMO reduces friction through physical adsorption at lower temperatures [28]. Since physisorption is a reversible process, the film formed can be easily removed. This observation suggests that the film formed by GMO is less effective in protecting the surface than mixed GO tribofilm. On the other hand, based on SLIM and HRTEM results, the tribofilms formed by GMO solutions are thinner compared to those formed by mixed GO. Our finding is in agreement with prior studies that thicker OFM layers lead to narrower wear tracks compared to the wider tracks seen with thinner OFM layers [26]. The wear scars generated by GMO and mixed GO are narrower at elevated temperature. The observed results can be ascribed to the formation of strong and thick tribofilm created by these organic friction modifiers on the surface at higher temperature. The thicker films formed at 100 ºC exhibit high durability and are more resistant to removal under harsh loading conditions[22].

The average surface roughness of MTM discs has been illustrated in Fig. 14.All lubricants showed increased roughness at 60°C compared to 100°C. This suggests that the thicker film formed at the higher temperature resulted in a smoother surface. Despite forming a thicker film compared to GMO at 100°C, mixed GO exhibited a rougher surface. This phenomenon can be attributed to the combined effects of thermal decomposition, film heterogeneity, and the chemical nature of the hydrolysis products. As confirmed by ToF-SIMS analysis, mixed GO undergoes hydrolysis at elevated temperatures, producing oleic acid and glycerol. While oleic acid may react with the steel surface to form iron oleate, the released glycerol, being insoluble in the PAO4 base oil, can accumulate unevenly across the contact area. This may result in patchy, viscous deposits, contributing to increased surface roughness. Additionally, at higher temperatures, mixed GO undergo hydrolysis to oleic acid, which could contribute to a more corrosive surface. Its low shear strength enables the maintenance of low friction despite the roughened wear surface[31]. Our results also indicate that an increase in wear track width is associated with the maximum COF of additives.

and 100°C(b)

4. Conclusion

The effect of organic friction modifier head group, slide-roll ratio, and temperature on friction, wear, and tribofilm formation have been studied. It was found that all three tested OFM additives were effective at reducing friction compared to the base oil, however the mechanisms were different. The following findings were obtained.

- All additives showed lower friction at a higher temperature however, the friction coefficient gradually increased at both with the rise of

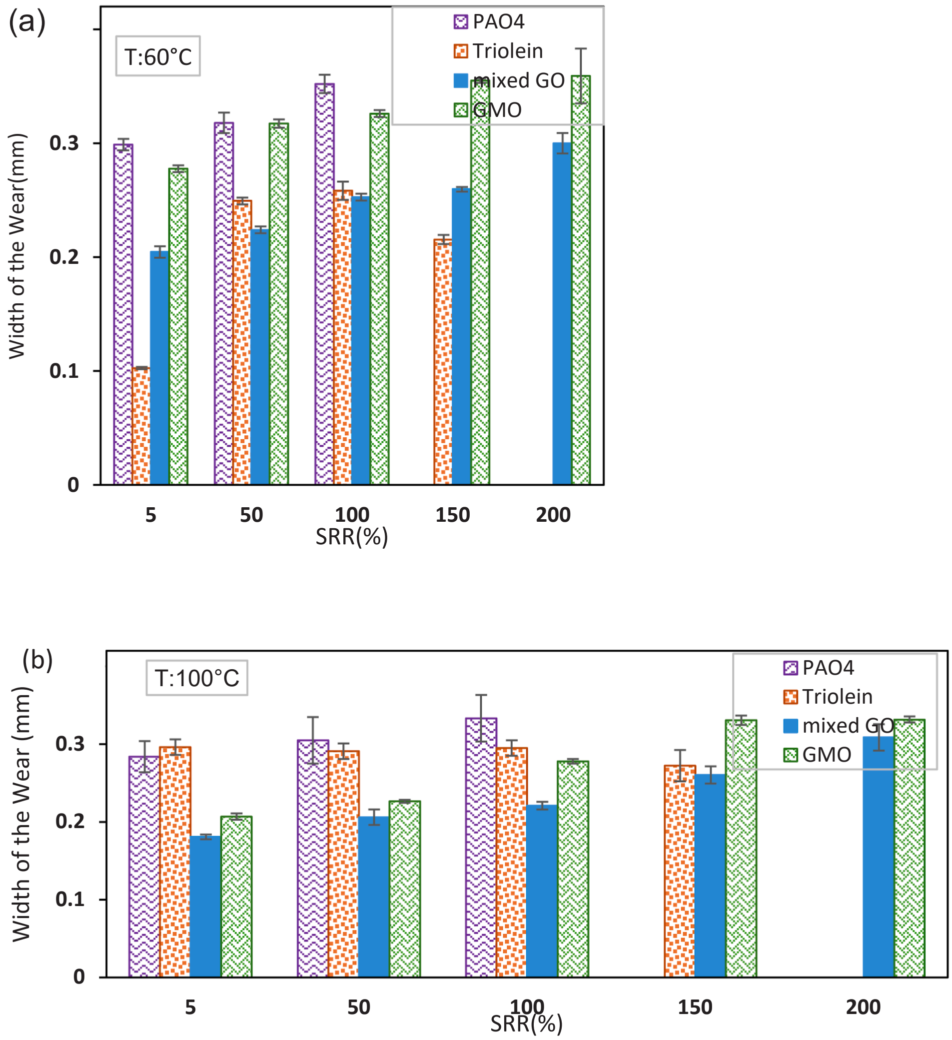


Fig. 13. Average of the wear track width on the disc lubricated with GMO, mixed GO, triolein and PAO4 at a temperature 60°C(a) and 100°C(b).

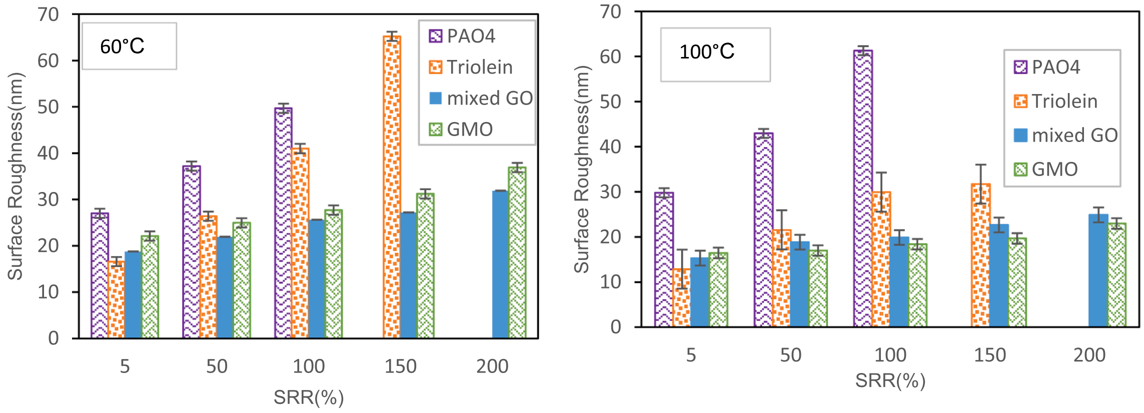


Fig. 14. Average surface roughness on the disc lubricated with GMO, mixed GO, triolein, and PAO4 at a temperature 60°C(a).

SRR. This outcome aligns with expectations as elevated SRRs and higher sliding induce greater lateral stresses on the surface, leading to wear and removal of the OFM.

- As evident from SLIM images, thicker protective tribofilm formed at the worn surface at a temperature of 100 C, resulting in lower friction.
- ToF-SIMS results indicate that both, SRR and temperature, affect the surface chemistry. The GMO and mixed GO exhibited two different mechanisms of friction reduction dependent on slide-roll ratio and temperature. At 60°C, GMO and mixed GO reduced the friction by physical adsorption on the steel surface at lower SRRs, whilst at higher SRRs, ion fragments associated with GMO decomposition were detected in the ToF-SIMS spectra. At 100°C, mixed GO

lubricant underwent hydrolysis to form oleic acid across all SRRs, however, for GMO solution in PAO4 the oleate fingerprint was only observed at SRR(%)200.

- The ion fragments associated with GMO decomposition were detected in ToF-SIMS ions spectra of GMO and mixed GO wt% inside and outside the wear tracks at both temperatures, but only at higher SRRs, however, the intensity peak outside the wear was notably lower. These findings strongly confirmed that GMO and mixed GO decomposition does not occur thermally, but rather, the harsh contact conditions, such as SRR(%)200, promote GMO and mixed GMO decomposition.
- The tribofilm thickness obtained by SLIM was validated by HRTEM. The results showed that the film formed by mixed GO is thicker compared to the GMO solution.

Statement of Originality

The paper has not been published previously and is not under consideration for publication in another journal. If this work is accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher.

CRediT authorship contribution statement

Marjan Homayoonfard: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sven L M Schroeder:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Peter Dowding:** Writing – review & editing, Validation, Resources, Funding acquisition, Conceptualization. **Ardian Morina:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.triboint.2025.110915.

Data availability

Data will be made available on request.

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