New strategy for reducing the EHL friction in steel contacts using additive-formed oleophobic boundary films

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Abstract: In this study we present a mechanism for the elastohydrodynamic (EHD) friction reduction in steel/steel contacts, which occurs due to the formation of oleophobic surface boundary layers from common boundary-lubrication additives. Several simple organic additives (amine, alcohol, amide, and fatty acid) with different molecular structures were employed as the model additives. It was found that the stronger chemisorption at 100 °C, rather than the physisorption at 25 °C, is more effective in friction reduction, which reaches 22%. What is more, EHD friction reduction was obtained in steel/steel contacts without use of the diamond-like carbon (DLC) coatings with their wetting or thermal effect, which was previously suggested as possible EHD friction reduction mechanism; yet about the same friction reduction of about 20% was obtained here—but with much simpler and less expensive technology, namely with the adsorbed oleophobic surface layers. A small variation in the additive’s molecular structure results in significant changes to the friction, indicating good potential in future EHD lubrication technology, where these additives could be designed and well optimised for notable reduction of the friction losses in the EHD regime.

Keywords: elastohydrodynamic (EHD); friction; additives; oleophobic layer; boundary slip

1 Introduction

In engineering applications many lubricated contacts correspond to conditions of elasto-hydrodynamic (EHD) or hydrodynamic (HD) lubrication regime [1–3]. These are the most desirable lubrication regimes for both friction and wear. In these full-film conditions, film pressure is able to resist the load and separate the contacts, preventing any severe collisions between the surface asperities that enhance the friction and wear. Accordingly, in the HD and EHD full-film regimes, the viscous friction dominates the contact, rather than the solid–solid asperities.

Until now, for the vast majority of engineering applications and engineering HD/EHD lubrication models, the viscosity was considered to be the main parameter of the oil that governs the lubrication [1]. Viscosity changes with the pressure and temperature are critical influences in that respect, since they define the actual thickness of the lubricating film. However, recently, the contacting materials also became of interest for EHD lubrication, in at least two different ways. One of the two suggestions is that higher thermal insulation surfaces (compared to steel), such as diamond-like carbon (DLC), might generate higher surface temperatures, affecting the oil temperature in the contact and so reducing the oil’s viscosity, which then affects the EHD friction [4].

Another suggestion for reducing the EHD friction...
that goes beyond the viscosity effects is focusing on the boundary-layer effects at the solid–liquid interaction [5–9]. In several studies with a systematic variation of the DLC coatings’ surface-energy values and consequently the wetting behaviours with base oils [10], it was found that a significant and consistent EHD friction reduction, even up to 50% [6, 7], can be achieved. These and other EHD studies pointed out the importance of the surface energy (mainly the polar component) [6, 7, 10, 11], the wetting [10, 11], and in particular the spreading [10], which can affect the boundary slip of the lubricant over the surface and so reduce the friction drag in conditions of full-film lubrication. The effect of low wetting, as well as boundary slip, on the friction, drag or energy losses reduction was previously proposed on many occasions in nano-scale studies [12–15] or theoretically [16–18], as well as for low-load HD contacts in the MPa contact-pressure range [8, 19, 20].

However, within the EHD contacts, where the contact pressure can reach a few GPa, several other critical physical phenomena occur simultaneously, in particular temperature increases and dramatic viscosity changes, but their true values and effects are not easy to experientially verify. As such, disagreements for the theoretical models that rely on temperature or viscosity still exist. Accordingly, establishing wetting and boundary-slip effects in EHD lubrication—a very new phenomenon in EHD lubrication—in addition to the above-mentioned parameters that have dominated for a century, is a challenging task. This is because the effects and the individual contributions of pressure, temperature, and wetting are difficult to isolate.

The above consideration regarding wetting influence on the friction in contacts with DLC coatings possessing low-surface-energy, one may suggest that the same should occur if the surface wetting is modified with the adsorbed additive layers, such as used in conventional boundary lubrication, if these layers could provide low surface energy, once adsorbed at the surface. So far, the studies of effect of additives on the wetting performance, and even more, of their effect with temperature variation are almost completely absent. However, if we could achieve that additives are used on, for example bare steel surfaces, making them oleophobic, with low wetting behaviour that will facilitate slip and so reduce full-film friction, this would be of great importance and advantage over employing the DLC coatings, which are more expensive and more difficult to deposit, especially to complex geometries and higher roughness engineering components.

In fact, our very recent studies on the effect of additives (simple organic friction modifiers) on the oil–steel wetting show a notable rise in the oleophobic properties of steel surface due to additive adsorption, both at 25 °C due to physisorption [21] and at 100 °C due to chemisorption [22]. Moreover, relevant molecular structure effects, such as the number of polar groups, chain length, polarity and saturation, were identified in these studies. Accordingly, in this study we analyse how these, the same simple organic friction modifiers, as used in [21, 22] and with the same variation of their molecular structures, affect the friction in EHD steel-on-steel contacts at room temperature of 25 °C and also at increased temperature of 100 °C. Moreover, the adsorption of the additives is analysed via attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) to explain and support the friction results.

## 2 Experimental

### 2.1 Materials and lubricants

In this work we used specimens from a MTM tribology tester (PCS Instruments, London, UK), which is described later on, namely discs and balls from steel DIN 100Cr6/AISI52100. Discs have a 46 mm diameter, while balls 19.05 mm. Both the balls and the discs were hardened to about 760 Vickers, as reported by producer. The used samples were very smooth, as reported by producer and confirmed with a white light interferometer (Contour, GT-K0, Bruker, USA), Table 1. Moreover, we also checked that the roughness values of the samples did not

| Sample | $R_a$ (µm) | $R_q$ (µm) |
|--------|-------------|-------------|
| Ball   | 0.014 ± 0.003 | 0.018 ± 0.004 |
| Disc   | 0.012 ± 0.003 | 0.015 ± 0.004 |
change during the tests, confirming that the tests were indeed in full-film regime.

For the investigation of the influence of additives at two distinct temperatures, 25 and 100 °C, we selected two base oils to have the same kinematic viscosity at the selected temperatures, i.e., 62.5±0.3 mm²/s. Accordingly, the selected oils were poly-alpha-olefin base oils (PAO), with the same chemical structure, but two different viscosity grades, i.e., PAO 6 and PAO 65 (Total, Solaize, France), and are the same, as used in companion study in Refs. [21, 22]. Their key physical properties are given in Table 2. Tribotests were performed with the base PAO and a PAO with 4 wt% of the selected additive to ensure the additive effect. The same concentration was also used in earlier studies and was defined based on its applicability to some real engineering cases [23–25].

A number of simple additives with polar head groups were used in this study to analyse the effect of some fundamental additive variations [26–29] on the friction in EHD contacts. As mentioned earlier, these molecules are exactly the same as used in earlier companion wetting studies [21, 22], where more details can also be found. A summary of the molecules used and their variation is presented in Fig. 1.

| Table 2 Kinematic viscosity, surface tension, and density of selected base oils. |
|-----------------|-----------------|-----------------|
| Oil             | PAO 6           | PAO 65          |
| Kinematic viscosity at 25 °C (mm²/s) | 62.28           | 1,340.93        |
| Kinematic viscosity at 40 °C (mm²/s) | 30.52           | 591.49          |
| Kinematic viscosity at 100 °C (mm²/s) | 5.84            | 62.78           |
| Surface tension at 25 °C (mN/m) | 29.07           | 30.41           |
| Surface tension at 100 °C (mN/m) | 27.73           | 28.82           |
| Density at 25 °C (g/cm³) | 0.822           | 0.837           |
| Density at 100 °C (g/cm³) | 0.784           | 0.798           |

In the nine different additive molecules we varied the length of alkyl chain of 11, 16, and 18 C atoms, which is one of the most recognised additive effects [28, 29]. The second important parameter is the polarity [26, 27], which was varied by selecting different functional groups: amine (–NH₂), which has the lowest polarity, hydroxide (–OH) with higher polarity, but the lowest than amide (–CO–NH₂), and finally, carboxyl (–COOH) group with the highest polarity [27]. The polarity variation was made with molecules that all have double bond (C=C), because of their better solubility than those with single (C–C) bonds. Finally, saturation effect was also investigated. Four unsaturated and five saturated molecules were used, but for direct comparison, we used molecules with one carboxylic (COOH) group with alkyl chain length of 18 C atoms, but having all single or one double bond.

The mixtures of PAO oil and additive were prepared by using a magnetic-based stirring device at a temperature of 50 °C. The stirring was performed during 4 h, which ensured homogenic mixtures. The mixtures were then monitored for 2 days in normal room conditions to verify there is no precipitation occurring, which confirmed the mixtures were stable. The second method to verify the stability of the mixtures was ATR-FTIR spectra, which were measured for all the mixtures. If the intensity and position of the characteristic peaks did not change after two days we considered the mixtures to be stable [30–34]. However, it turned out that all the mixtures we used were stable. Prior to the tribological tests, we put the oils on a magnetic stirrer for another hour at 50 °C to further ensure the homogeneity of all the mixtures during the tests.

The kinematic viscosity of the mixtures was determined at 40 °C, as well as at 100 °C and since the values at both temperatures differed by less than 1% compared to the PAO oils without additives, the kinematic viscosity of both PAO base oils (Table 2) was assumed for all the tested mixtures.

2.2 Tribological tests

The tribotests were performed using a MTM tribology tester (MTM2, PCS Instruments, London, UK) using a ball-on-disc configuration. The tested contacts were
steel/steel under lubrication conditions with base oils and with the mixtures of the same base oils with selected additives (Fig. 1) at 25 and 100 °C. To achieve the same viscosity at both temperatures, PAO 6 and PAO 65 oils were used (Table 2). Before the tribological tests started the steel discs and balls were cleaned with n-heptane and were dried in stream of air. All the oils were placed in the same amount of 10 mL into the MTM cup, heated to the required temperatures of 25 and 100 °C and stabilised for 20 min at the required temperature, with no other treatment. After the temperature stabilised, the test was run according to the same procedure, described later on. All the tests were repeated at least three times. The normal load was 35 N, which results in 1 GPa of contact pressure. Slide-to-roll ratio SRR (corresponds to ratio of sliding vs. entrainment speed) of 50% was set in all tests. The mean contact velocities (the entrainment velocities, \(u_e\)) ensured the complete separation of the contact surfaces with full-film EHD lubrication conditions. The test were run from high entrainment speed (2.5 m/s) toward lower entrainment speed (1.0 m/s) in discrete steps of 0.1 m/s. Each step lasted for 10 s so that the friction value became stabilised. From the Tallian parameter \(\lambda\), calculated according to Eq. (1), the values were above 5 at all contact conditions, for both PAO 6 and PAO 65 oils, confirming that results were obtained in EHD lubrication regime. Moreover, this was clear from uniform friction data and checks of the surfaces after the tribotests.

\[
\lambda = \frac{h_0}{\sqrt{R^2_{q,ball} + R^2_{q,disc}}}
\]  

(1)

The \(R_q\) roughnesses of samples used in Eq. (1) are given in Table 1, while Hamrock–Dowson equation (Eq. (2), [35]) was used to calculate the minimum film thickness (\(h_0\)).

\[
\frac{h_0}{R'} = 3.63 \left(\frac{u_n \eta_0}{E'R'}\right)^{0.68} (\alpha E')^{0.49} \left(\frac{W}{E'R'^2}\right)^{-0.073} \left(1 - e^{-0.68k}\right)
\]  

(2)

2.3 ATR-FTIR spectroscopy

ATR-FTIR was employed to determine the chemical characteristics of the steel disc surfaces with the adsorbed films that formed during the tribotests. After every test at both 25 and 100 °C, the disc samples were cleaned. N-heptane was used to rinse the samples, and then were dried with an air stream. Samples were analysed with a FTIR spectrometer (Perkin Elmer, USA), equipped with a diamond ATR high-performance accessory (Harrick Scientific Products Inc., USA). Spectra were recorded at an incidence angle of 45°. The sampling area was set for 0.5 mm. 4,000–400 cm\(^{-1}\) was selected as the active sampling range. 2,500–1,800 cm\(^{-1}\) region was, however, omitted from the results spectra because of the noise from the diamond crystal. 64 scans were used to obtain the spectra and the measurement resolution was 4 cm\(^{-1}\). A background was also taken before every measurement with a clean ATR crystal that was cleaned with alcohol (isopropyl) and carefully dried using a cellulose cotton. Firm contact between the sample and the crystal was always ensured.

3 Results

3.1 Coefficient of friction (COF) at 25 °C

The results of the tribological tests for the base oil and the base oil with additives with (1) one and two COOH groups; (2) variation of chain lengths; (3) variation of polarities; and (4) different saturations for the tests at 25 °C are presented in Fig. 2. Increased entrainment speed causes the COF to decrease, which is due to thermal shear thinning and has been already explained in several previous studies for similar tests [4–7, 36]. The highest friction was observed with the base oil without additives, the exception being mixtures with two polar head groups (11C–/2xCOOH and 16C–/2xCOOH), which leads to the general observation that the additives decrease the EHD friction. The friction decrease is affected by the additive’s molecular structure since the different additives reduce the COF to different extents, i.e., from 3.6% to 12.4%, which is schematically summarised in Fig. 4.

The additives having just one COOH group result in an up to 9.7% lower friction than the additives having two COOH groups (Fig. 2(a)). As shown in Fig. 4, additives that have only one COOH group give lower COF than that the base
oil, while the additives that have two COOH groups give slightly higher COF (up to 1%) than the base oil.

When the chain length of the saturated additive with one COOH group is increased from 11 to 16C, the friction is reduced up to 4.5%. Increase in chain length from 16 to 18C-atoms gives an up to 2.9% lower friction. Thus the effect of the increasing chain length was the COF reduction by up to 7.4% (Fig. 1(b)). However, the total reduction in friction for the 18C molecule with one COOH group in comparison to the base oil without additives was 12.4%, as seen in Fig. 2(b). On the other hand, the chain length increase for additives with two COOH groups decreases the COF only slightly, i.e., by up to 0.8% (Fig. 2(a)).

The polarity of the additive functional groups reduces the COF (Fig. 2(c)), however, this decrease is not monotonic for fatty alcohol, which is discussed later on. The most polar additive, i.e., fatty acid gives up to 4.3% lower friction, the fatty amide shows up to 6.8% lower friction than the fatty alcohol, and up to 5.6% lower friction than the fatty amine, which is the least-polar additive.

The saturation, which was compared for the additives having 18C-atoms and one COOH group, decreases the friction by up to 2% (Fig. 2(d)). The saturated fatty acid with the longest chain length (18C) gives the lowest COF among all the selected additives and reduces the friction by up to 12.4% in comparison to the oil without additives (Fig. 4).

3.2 COF at 100 °C

The results of the tribological tests for the base oil and the base oil with additives with (1) one and two COOH groups; (2) variation of chain lengths; (3) variation of polarities; and (4) different saturations at 100 °C are shown in Fig. 3. Compared to the 25 °C tests, the COF does not decrease with the increasing entrainment velocity since the thermal effect is diminished by the external temperature, confirming the earlier suggestion and previous reports [4–7, 36], while newly introduced oleophobic surface behaviour may also contribute to overall friction behaviour. The highest friction is always measured.
for the base oil without additives, which is slightly different from the case at 25 °C, where mixtures with two polar head groups provided slightly higher friction. However, we can again confirm that the additive molecular structure affects the friction noticeably, and differently for various additive chemical structures, i.e., from 3.0% to 22.2%. This is a significantly higher effect of additives and their molecular configuration on friction than at 25 °C, which is presented in Fig. 4.

Fig. 3  EHD friction at 100 °C depending on additive variation of the (a) number of COOH groups; (b) alkyl chain length; (c) functional groups polarity; and (d) saturation.

Fig. 4  Average difference in the COF (in %) between the base oil with additive and the base oil without additives.
From Fig. 3(a), we see that for the same number of C atoms, the additives that have only one COOH group result in up to 20.0% lower friction than the additives, which have two COOH groups. Longer chain lengths provide even lower friction, with both one and two polar groups. The one COOH group molecule with 16C atoms gives a noticeably lower friction than all the others, resulting in an up to 17.8% lower COF in comparison to the base oil (Fig. 3(a)). This is a slightly greater friction reduction than at 25 °C. While at 25 °C the additives with two COOH groups slightly increase the friction, at 100 °C they decrease it, like the other additives.

Increase of the alkyl chain of the saturated additive with one COOH group from 11 to 16C give an up to 10.7% lower friction, while the increase from 16 to 18C give an up to 4.7% lower friction, and thus the effect of chain length was a COF decrease of up to 15.4% (Fig. 3(b)). However, the total reduction in friction for the 18C molecule with one COOH group in comparison to the base oil without additives was 22.2% (Fig. 2(b)). Increase of the alkyl chain for additives having two COOH groups decreases the COF only slightly, i.e., up to 1.8% (Fig. 2(a)).

The higher polarity of the additive functional groups reduces the COF (Fig. 2(c)). In contrast to 25 °C, the friction decrease is in accordance with the polar nature of the polar heads, namely from the lowest polarity amine (NH2) to alcohol (OH), amide (CONH2) and finally to highest polarity carboxylic acid (COOH). Indeed, alcohol and amine have almost the same values (10.9% and 11.4% less than the base oil), but the general effect of polarity is still maintained. However, it is very clear and significant that the amide has a 14.5% lower friction than the base oil and 3.0%–3.6% compared to the alcohol and amine, while carboxylic acid, which is the most polar, provided an up 8.1% lower friction than the amide, 10.9% lower than the alcohol and amine, and even 11.4% lower than the base oil. This friction reduction is thus clearly more significant at 100 °C than at 25 °C.

The saturation, which was compared for the additives having 18C-atoms and one COOH group, decreases the friction by up to 1.4%. The saturated fatty acid with the longest alkyl chain of 18C-atoms gives the lowest COF among all the tested additives and reduces the friction by up to 22.2% in comparison to the base oil without additives, as seen in Fig. 4. This is the same as for 25 °C, however, at 100 °C also the unsaturated long-chain (18C) fatty acid provides a similarly low friction, i.e., 21.1% lower than it was measured with the base oil.

### 3.3 ATR-FTIR results at 25 and 100 °C

The ATR-FTIR spectra of the discs’ surfaces after the tribological tests with the base oil and the base oil with the additives at 25 °C is presented in Fig. 5, while the spectra obtained at 100 °C is presented in Fig. 6. The absorbance peaks intensity in each spectrum is written next to every characteristic peak.

After the tribological tests at both temperatures, the ATR-FTIR spectra show characteristic peaks that correspond to the tested additives’ molecular structures. However, comparing the spectra after the tests at 25 and 100 °C (Figs. 5 and 6), it is obvious that the peaks’ intensities are significantly higher at high temperature (~0,25 a.u.) than at room temperature (~0,12 a.u.). This indicates more intensive adsorption of additives at 100 °C than at 25 °C, which agrees with the earlier reports in Refs. [23, 26, 37].

For the additives that have two COOH groups, the characteristic peaks are observed in the ranges 1,420–1,190 and 945–880 cm⁻¹, which are typical for dicarbonyl vibrations (HOOC–R–COOH) [38], as shown in Figs. 5(a) and 6(a). It can be noticed that longer chain 16C–/2xCOOH has higher intensity of these peaks than 11C–/2xCOOH, which is true for 25 and 100 °C (Figs. 5(a) and 6(a)). In the case of the additives with one COOH group, these peaks are not measured. However, we observe the bands at ~2,920 and ~2,855 cm⁻¹ for additives that contain one as well as two COOH groups, and these bands correspond to the stretching and bending of the C–C sp³ hybridisation (methylene (ν CH2) group) [38–40]. It is also noted that for additives with one COOH group the intensity of these bands is stronger than for two COOH groups. This is true for both temperatures, while these peaks are more pronounced at 100 °C (Fig. 6(a)) than at 25 °C (Fig. 5(a)). The bands found at ~1,700 and ~1,460 cm⁻¹ measured in both spectra, namely at 25 and 100 °C, correspond to the vibrations mode of
the \((\nu C=O)\) bonds \([41]\).

For the additives with different chain lengths (Figs. 5(b) and 6(b)), we observe the same characteristic peaks at \(\sim2,920\) and \(\sim2,855\ \text{cm}^{-1}\) \((\nu \text{CH}_2)\); \(\sim1,700\) and \(\sim1,460\ \text{cm}^{-1}\) \((\nu \text{C}=\text{O})\); \(\sim725\ \text{cm}^{-1}\) \((-\text{(CH}_2)_{n-}\) \([38]\); however, they decrease with the decreasing chain length of the additive at both 25 and 100 \(^\circ\)C. This suggests the involvement of all these species in the formation of the surface film, but their formation is influenced by the length of the additive \([42]\).

Again, the peaks are far more distinct at 100 \(^\circ\)C (Fig. 6(b)) compared to 25 \(^\circ\)C (Fig. 5(b)), indicating temperature dependent formation of the additive film \([26]\).

The spectra of the discs after the tribotests at 25 and 100 \(^\circ\)C with additives having different polarity of the head group, show characteristic peaks \([38, 43]\), which are attributed to alcohols \((3,500–3,200\ \text{cm}^{-1}, \sim1,470–1,365\ \text{cm}^{-1}, \sim1,265–1,140\ \text{cm}^{-1}, -\text{CH}_2-\text{OH})\); alcohols \((3,500–3,200\ \text{cm}^{-1}, \sim1,470–1,365\ \text{cm}^{-1}, \sim1,265–1,140\ \text{cm}^{-1}, -\text{CH}_2-\text{OH})\); amines \((\sim2,855\ \text{cm}^{-1}, \sim1,470–1,365\ \text{cm}^{-1}, -\text{CH}_2-\text{NH}_2)\); and amides \((\sim3,500–3,200\ \text{cm}^{-1}, \sim1,300–1,000\ \text{cm}^{-1}, -\text{CH}_2-\text{CO–NH}_2)\). The peaks between 750 and 630 \text{cm}^{-1}\) correspond to the \((\nu \text{C}=\text{C})\) stretching, which is present due to the unsaturated molecular structure of the additives (Figs. 5(c) and 6(c), and Table 2).

The spectra of the additives with different saturations (Figs. 5(d) and 6(d)) show higher intensities of the characteristic peaks for the saturated 18C–/COOH than the unsaturated 18C=COOH additive at both 25 and 100 \(^\circ\)C. The spectrum of the disc recorded after the tribotest using base oil without additives at 25 \(^\circ\)C (Fig. 5(d)) and 100 \(^\circ\)C (Fig. 6(d))

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**Fig. 5** ATR-FTIR spectra of steel discs after tribological tests at 25 \(^\circ\)C with base oil and a mixture of base oil and additives having different (a) numbers of COOH groups; (b) chain lengths; (c) polarities of the functional groups; and (d) saturations.
shows only three low-intensity peaks (~0.01 a.u.) that belong to the ($\nu$ CH$_2$) stretching.

4 Discussion

It is already well known and documented that when in solid–liquid interactions, the hydro/oleophobicity increases, while the friction drag and energy consumption are reduced. This was shown in many nano-scale studies [12–15] and even in low-load contacts in the range of a few MPa [8, 19, 20]. However, in recent years several studies have confirmed that achieving oleophobicity with poor wetting in oil-lubricated contacts also significantly changes the friction behaviour in full-film EHD lubrication in the GPa range [6, 7]. Our earlier studies confirmed this by using various DLC coatings with a tailored surface energy [10, 11]. Moreover, it was shown that successful wetting management is possible through the spreading parameter [6, 10, 11], which gives more insight into the oil adsorption and dynamic wetting properties. This is in contrast to the most commonly used static contact angle, which, however, in cases of spreading wetting behaviour that is typical for most oils on engineering surfaces, does not provide the relevant information [11, 21, 22].

In this view, it would be extremely beneficial if the poor wetting in the EHL regime could be achieved with a simpler technology, where existing metal surfaces (typically steel) could be used directly, without the need for expensive and complex coating depositions. The formation of permanent oleophobic surface layers in the EHL contacts in-situ, which would provide the poor wetting behaviour at the solid–liquid interface, is thus an ambitious but
rewarding new technology to reduce the friction in EHL steel contacts.

In fact, our recent studies have shown that as a proof of concept for wetting, tailoring can be achieved even with simple organic additives, such as fatty acids, alcohols, amines, and amides with various molecular architectures [21, 22]. The variation of wetting by employing these simple oiliness additives was confirmed both at room temperature and elevated temperature of 100 °C, where the wetting dynamic contact angles, as well as contact angle hysteresis (CAH) changed dramatically, by several times. In the current research we have used exactly the same base oils, the same additives and the same metal surfaces as in the wetting studies [21, 22]. This is purposely done to use the evidence of wetting behaviour from wetting studies that are already well documented and described in detail in above mentioned available literature.

In this study, therefore, we used the same additives as in previous wetting studies to investigate whether this concept, i.e., poor wetting and consequent boundary slip, is a valid way to reduce the EHL friction, and how sensitive the EHL friction is to relatively small variations in the additives’ molecular structures. However, to confirm the effect of additives on friction, their adsorbed layers at the tribologically-tested surfaces has to be proved, for which the ATR-FTIR analyses were performed in this work (Figs. 5 and 6).

Moreover, in previous studies using DLC to reduce the EHL friction, a complementary plausible mechanism was proposed due to the coating’s thermal isolation properties and the consequently increased contact temperature that reduces the viscosity and so the friction. However, in this study we completely excluded any possible thermal effect in the contacts, since the study is performed using steel/steel contacts and the nm-thick adsorbed additive layers only, which can thus confirm or rule-out the thermal EHD friction-reduction mechanism. It is well known that the nm-thickness molecular layer cannot provide any relevant isolation, as well as the negligible variations in the physical properties [26] between selected molecules cannot make any distinction in this respect.

The results in this study show that all the selected additive mixtures successfully adsorbed to the steel surfaces, without any additional treatment or procedures, simply via the adsorption of the polar heads to the metal surfaces [23, 26]. The ATR-FTIR spectra indicate the adsorption of organic species on the steel discs during the tribotests for all the mixtures of additives with oil, both at 25 and 100 °C, while for the base oil without additives it does not, as shown in Figs. 5 and 6. The presence of adsorbed species at 25 °C might seem unexpected, however, this was most probably due to a local temperature increase, clearly seen from thermal oil thinning and friction reduction in our friction tests (see the strong decrease of friction in Fig. 2), as well as due to possible pressure-induced tribomechanical interactions [26, 44–49]. Moreover, comparing Figs. 5 and 6, the adsorption at 25 °C is clearly much weaker than at 100 °C, supporting the overall lower tribocatalytic activity. Therefore, in the test at 25 °C it was mostly physical adsorption that occurred, but partially the additive film was formed also through the chemisorption, as confirmed by the ATR-FTIR results (Fig. 5), which is relatively mild binding, but well known to be effective in tribological contacts under even much more severe conditions, such as the mixed and boundary regimes [26]. In contrast, at 100 °C the chemical adsorption occurred in all cases (Fig. 6), which provides much stronger bonding of the adsorbed layer.

In agreement with the fact that additives selected for this study provide substantial oleophobic wetting behaviour [21, 22], and the chemical evidence of the adsorbed films on the surfaces after the tribotests (Figs. 5 and 6), the hypothesis of this study that EHL friction is affected by the films of oiliness additives was verified. The friction decreased by 3.6%–12.4% at 25 °C and by 3.0%–22.2% at 100 °C. This is a very significant reduction in the friction, especially for 100 °C. Furthermore, this shows that the more strongly chemisorbed film at 100 °C (Fig. 6) provides lower friction, which is a consequence of the more completely adsorbed film, promoting higher oleophobicity and so more non-polar interactions of the additive alkyl tails and the non-polar PAO oil, which means an easier flow of oil or slip over the adsorbed layer compared to steel surface with typical oil–steel boundary interaction interface.
This mechanism is schematically shown in Fig. 7.

Moreover, the molecular structure also clearly affected the friction, suggesting the high sensitivity of the EHD friction to relatively small, but consistent, additive changes. The general effect of the molecular structure was the same at 25 and 100 °C. That is to say, the qualitative effect of chain length, polarity, and saturation was the same—an increase of these three additive properties resulted in higher oleophobicity and lower friction. Only the additives with two COOH groups at 25 °C resulted in slightly higher friction in comparison to the base oil, which is in the contrary to all the other results. However, at 100 °C the additives having two COOH heads, and all the additives having just one COOH head always exhibited a lower friction than the base oil. The overall difference between the different types of additives (i.e., the different molecular structure) was by 2.9%–7.4% at 25 °C and by 1.8%–20.0% at 100 °C. So, again, this confirms the stronger effect on the friction by the additives at the higher temperature.

All the additives reduced the COF, with the minor exception described above. It has been suggested that the reduction of friction in full-film HD conditions at low contact pressures of MPa range could be caused by organic friction modifiers that can promote fluid slip [8, 50, 51]. It has been further argued that due to organic friction modifiers adsorption, the methyl –CH₃ groups form planes, which result in smooth and poorly wetted surfaces, so that liquid can easily slip over such surfaces [8, 26]. Moreover, organic friction modifiers are known to form surface layers that are in nature oleophobic, which thus result in poor wetting by the alkanes [52]. We have reported in our companion studies that the structure of additive molecule significantly influences the wetting of oil on steel at both 25 and 100 °C [21, 22]. The slightly higher friction for molecules that have two COOH groups at 25 °C (Figs. 2(a) and 3) can be explained by the way that bifunctional acids can adsorb to the steel via one or both COOH polar heads [53], or react with some other molecule, and so preventing the formation of a packed and dense film with methyl tails on top [54]. In this case the free COOH groups that may present at the surface can thus enhance the interactions with the oil in surrounding [54]. This agrees with our ATR-FTIR results (Fig. 4(a)), which clearly show peaks that correspond to dicarbonyl vibrations that are not measured for additives that have only one COOH polar head.

Numerous studies have shown that fatty acids in oil reduce the friction in boundary lubrication [1, 23, 37] and that this reduction is dependent on their chain length [26, 55], but the influence of the fatty acid’s chain length in EHD lubrication, shown in this study (Figs. 2(b) and 3), has not yet been reported. However, it was reported earlier that fatty acids with longer alkyl chains are more stable and stronger and thus form more protective adsorbed films [1, 28, 55]. This agrees with our ATR-FTIR measurements (Fig. 4(b)), which show a higher intensity of the peaks that correspond to the ν CH₃ group for additives with a longer alkyl chain. We have furthermore presented earlier that the surface becomes more oleophobic when additives with longer alkyl chains are used [21, 22], which is in agreement with the suggestion that fluid slip could cause a reduction of the EHD and HD friction [6–8, 50, 51].

More polar additive head groups decrease the EHD friction, which is true for all the tested additives, except the fatty alcohol at 25 °C (Figs. 2(c) and 3), however, the difference compared to the fatty amine is within 1.2%, and thus almost negligible. The reason for the polarity effect on the steel surface is that the more polar functional groups of the additive

![Fig. 7 Schematic presentation of the mechanism for (a) easy shear slip plane between the oleophobic alkyl chain tails and bulk oil film, compared to (b) direct interaction between the oil and the steel surface (commonly oxidised, with contaminants), absent of easy-shear plane.](image-url)
result in a more firmly adsorbed film [23, 26, 37, 56]. It is well established that the better the organic friction modifier’s adsorption, the more effective its friction-reduction properties will be in boundary lubrication conditions [1, 23, 26, 57]. The effect of the head group’s polarity on the friction for ferrous substrates has been extensively investigated [26] and the studies have shown that amine groups as well as carboxylic acid have stronger effects than nitrile, halide or alcohol groups [26, 37, 58, 59]. Recently, we have shown that the oleophobicity increases as the polarity of the additive head increases [21], and the ATR-FTIR spectra (Fig. 4(c)) show a stronger intensity of the organic species when polarity of the additive increases. Stronger additive head adsorption therefore results in a more complete layer of the opposite tails, namely the methylene groups [26], and this can thus cause a larger reduction in the EHD friction.

Finally, the saturation of the additive having the same alkyl chain length and COOH group decreases the EHD friction (Figs. 2(d) and 3) as well. This result is again in agreement with earlier evidence that saturated fatty acids that possess long and straight alkyl chains, can form very uniform films with alkyl tails oriented perpendicularly to the steel surface [1, 23, 56]. Furthermore, unsaturated fatty acid molecules rotate around the double C=C bond, which prevents the formation of a uniform film and complete surface coverage [53, 60, 61]. Our ATR-FTIR spectra (Fig. 4(d)) indeed show the characteristic peaks of (ν C=C) bonds for unsaturated fatty acid and their absence for a saturated acid. Moreover, the stronger intensities of the characteristic (ν CH2) bonds for saturated fatty acid indicates the more oleophobic behaviour, which has also been experimentally shown with dynamic wetting tests in a previous study [21, 22].

5 Conclusions

1) A new lubrication technology to reduce EHL friction using additives on the steel surfaces that form oleophobic boundary layers is described. The friction is sensitive to relatively small variations in the additive molecular structures, indicating a strong potential to tailor the additives and their interactions with the surfaces.

2) More strongly bonded layers (via chemisorption) with better organised layers (from long-chain, saturated, and highly polar additives) provide lower wetting and lower EHD friction.

3) A higher contact temperature of 100 °C promotes the formation of more strongly adsorbed (oleophobic) boundary layers and reduces the EHD friction more than those at 25 °C.

4) Molecular structures of the selected additive clearly affect the EHD friction, i.e., additives with only one COOH group, a longer alkyl chain length, a higher polarity of the head group, and a fully saturated structure reduce the EHD friction more than the opposite properties.

5) Friction reduction using additives compared to the base oil was 3.6%–12.4% at 25 °C and 3.0%–
22.2% at 100 °C.

6) Wetting-based EHD friction reduction due to oleophobic films was obtained in steel/steel contacts without a surface thermal effect, which was alternatively suggested for friction reduction with DLC coatings with low wetting, which however, also have lower thermal conductivity. Moreover, the most oleophobic films reduced EHD friction for about the same as was previously observed with DLC coatings, i.e., about 20%, however, additives are much simpler and less expensive technology.

7) Variations between the different molecular structures affect the EHD friction by 2.9%–7.4% at 25 °C and by 1.8%–20.0% at 100 °C. The most effective additive was found to be saturated fatty acid with 18 C atoms.

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