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Effect of Ionicity of Three Protic Ionic Liquids as Neat Lubricants and Lubricant Additives to a Biolubricant

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Abstract: Friction and wear of sliding surfaces are responsible for important energy losses and negative environmental effects. The use of environmentally friendly and cost-effective protic ionic liquids as neat lubricants and lubricant additives has the potential to increase the efficiency and durability of mechanical components without increasing the environmental damage. In this work, three halogen-free protic ionic liquids with increasing extent of ionicity, 2-hydroxyethylammonium 2-ethylhexanoate, 2-hydroxymethylammonium 2-ethylhexancate, and 2-hydroxydimethylammonium 2-ethylhexanoate, were synthesized and studied as neat lubricants and additives to a biodegradable oil in a steel–steel contact. The results show that the use of any protic ionic liquid as a neat lubricant or lubricant additive reduced friction and wear with respect to the biodegradable oil. The ionic liquid with the lowest ionicity reached the highest wear reduction. The one possessing the highest ionicity presented the poorest friction and wear behaviors as a neat lubricant, probably due to the more ionic nature of this liquid, which promoted tribocorrosion reactions on the steel surface. This ionic liquid performed better as an additive, showing that a small addition of this liquid in a biodegradable oil is enough to form protective layers on steel surfaces. However, it is not enough to accelerate the wear process with detrimental tribocorrosion reactions.

Keywords: protic ionic liquids; lubricants; additives; biolubricant

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1. Introduction

Friction and wear of sliding surfaces are responsible for important energy losses and negative environmental effects. Some researchers have quantified friction and wear losses to comprise as much as 23% of the world's total energy consumption [1]. Approximately 20% of these energy losses are used to overcome friction and 3% to replace worn parts of machines. The use of advanced lubricants, new materials, and the application of novel surface technologies may reduce friction and wear losses of rubbing surfaces up to 40%, which corresponds to savings in the range of 1.00%–1.55% of a country's gross domestic product [2,3]. Beyond the economic consequences, the application of tribological advances also has important environmental benefits. According to Holmberg and Erdemir [1], new advances in tribology can result in significant CO_2 emission reductions.

Transportation is one of the main energy consuming sectors. Road vehicles are responsible for 20% [4] of the global energy consumption. Approximately 17% of the fuel energy used in passenger cars is used to overcome friction of the moving parts, mainly in the piston assembly and bearings [5]. The development of high-performance lubricants with low viscosity has the potential to increase fuel efficiency in cars.

In the recent decade, ionic liquids (ILs) have shown great potential as lubricants [6–14] or lubricant additives [15–26] due to their excellent physicochemical properties [27,28], including low melting point, low flammability, negligible vaper pressure, and high thermal stability. One of the most important characteristics of ILs is that their properties can be tailored by varying the species of the cations and anions, giving rise to numerous families that can be used across different tribological systems. In addition, ILs can form stable ordered layers in a liquid state on metal surfaces due to electrostatic interactions with such surfaces. Most of the ILs currently used in lubrication are aprotic ionic liquids (AILs), a subset of ILs, and have been widely studied for more than a decade and proven to have potential to be lubricants and lubricant additives [29–33]. However, the implementation of AILs in general engineering lubrication is limited by two main factors: (1) most AILs contain halogen elements, such as fluorine or chlorine, which can easily form toxic acids, such as hydrofluoric or hydrochloric acid, when exposed to moisture in the atmosphere, causing corrosion of the metal workpieces; and (2) AILs can be very expensive because of complexity in their synthesis [34].

Contrary to AILs, protic ionic liquids (PILs), which are another subset of ILs, can be easily synthesized through proton transfer from a Brønsted acid to a Brønsted base. The key benefit of PILs is their potential to be significantly cheaper while still having good tribological properties. Based on the easy synthetic route, PILs can be designed to avoid halogens in their molecular components. Therefore, PILs are not only low-cost and eco-friendly, but also have a wide range of properties and tunable structures, which may make them ideal alternatives to AILs.

Although the study of ILs in lubrication is dominated by AILs, the study of PILs and, in particular, halogen-free PILs as novel lubricants and lubricant additives is receiving the attention of tribological researchers [33,35–41]. For instance, Zhao et al. [41] synthesized a series of PILs having dodecyl-ammonium cations with S-(1-carboxylpropyl)-N,N-dialkyldithiocarbamate anions, where the alkyl group was either ethyl, butyl, or octyl. The tribological properties of these PILs as additives to a lithium-based grease were investigated under a steel–steel system. All three PIL blends exhibited good lubricating and anti-wear performance, and the PILs also dramatically improved the capacity of extreme pressure of the base grease.

In addition, the presence of hydroxyl groups in PILs could form hydrogen bonds between PILs and the contact substrates to stabilize the lubricant layer. PILs with hydroxyl cations have drawn the increasing attention of tribological researchers. Iglesias's research group [32] found that when PIL tri-[bis (2-hydroxyethylammonium)] citrate is used as an additive in 2 wt.% to a mineral oil in aluminum–steel contact, it will form a tribolayer on the substrate surface, which may be responsible for a reduction of 16% in friction and 40% in wear compared with that just using mineral oil.

In a study by Espinosa et al. [39], PIL bis(2-hydroxyethylammonium) succinate was tested as a neat lubricant and lubricant additive in 1 wt.% to water under sapphire–stainless-steel contact. The addition of 1 wt.% PIL in water successfully reduced the running-in period and exhibited mild wear and superior lubricating performance with an ultra-low mean friction value of 0.02. Compared with water, the blend reduced the friction coefficient by 97%, even more than the reduction due to neat PIL, which was 88%.

In this research, a series of PILs that are derived from alkyl ammonium carboxylate salts of hydroxyalkyl-amines with differing basicity were synthesized and tested as neat lubricants and lubricant additives to a biodegradable oil in a steel–steel contact at room temperature. The physicochemical properties of the three PILs, 2-hydroxyethylammonium 2-ethylhexanoate (Eet), 2-hydroxymethylammonium 2-ethylhexanoate (Met), and 2-hydroxydimethylammonium 2-ethylhexanoate (Det), and their biodegradable oil blends were also characterized and correlated to their tribological performance.

2. Materials and Methods

2.1. Materials

The chemical reagents, 2-ethylhexanoic acid (≥99%), ethanolamine (≥99%), N-methyl ethanolamine (≥98%), and N, N-dimethylethanolamine (≥99.5%), were commercially available from Sigma-Aldrich (Saint Louis, MO, USA). Repsol (Madrid, Spain) kindly provided the commercially available biodegradable oil BIO TELEX 46 (BOA) and its corresponding biodegradable base (BO), and their properties are summarized in Table 1. All the materials were used as received with no further treatment.

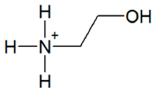
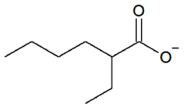
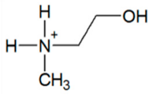
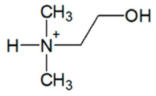
Table 1. Properties of the commercial biodegradable lubricant BIO TELEX 46 (top row) and its corresponding base biodegradable oil (bottom row).

Density (g/mL at 15°C)	Kinematic Viscosity (mm^2/s at 100 °C)	Kinematic Viscosity (mm^2/s at 40 °C)	Viscosity Index	Flash Point (°C)	Pour Point (°C)
0.91	9.91	49.90	190	312	−45
0.92	9.87	49.22	192	290	−45

2.2. Synthesis and Spectroscopic Characterization of PILs

In this study, a series of three novel protic ionic liquids, 2-hydroxyethylammonium 2-ethylhexanoate, 2-hydroxymethylammonium 2-ethylhexanoate, and 2-hydroxydimethylammonium 2-ethylhexanoate, were synthesized in our laboratory. During the synthesis process, the stoichiometric quantities of 2-ethylhexanoic acid were added dropwise to three hydroxyalkyl-amines (ethanolamine, N-methylethanolamine, and N, N-dimethylethanolamine) with differing basicity. The order of their base strength is as follows: N, N-dimethylethanolamine > N-methylethanolamine > ethanolamine. A water bath cooling system was used to keep the temperature of the reaction mixtures below 80 °C. The molecular structure, name, and abbreviation of each PIL are shown in Table 2. Based on the molecular structures of these PILs, they are composed of the same anion but different cations. Among them, Eet, possesses a higher number of hydrogen atoms bonded to the nitrogen and is estimated to have the highest extent of hydrogen bonding, followed by Met and Det. The ionic structure of the PILs was confirmed by proton nuclear magnetic resonance (^{1}H NMR) using a Bruker Ultra-shield 500 MHz spectrometer (Bruker, Billerica, MA, USA) with chloroform-d (CIL, 99.8 atom % D) as the solvent.

Table 2. The molecular structure, name, and abbreviation of protic ionic liquids (PILs).

Code	Structure		IUPAC name
	Cation	Anion	
Eet			2-hydroxyethylammonium 2-ethylhexanoate
Met			2-hydroxymethylammonium 2-ethylhexanoate
Det			2-hydroxydimethylammonium 2-ethylhexanoate

2.3. Ionicity, Thermal Stability, and Viscosity of PILs

The ionic conductivity of Eet, Met, and Det was measured using an Accumet Basic 30 Conductivity Meter (Fisher Scientific, Pittsburgh, PA, USA) at room temperature. After that, each PIL was added to BO with a concentration of 1 wt.% and 2 wt.%. In order to obtain six homogeneous mixtures, each PIL blend was magnetically stirred for one hour and ultrasonically mixed for half an hour at ambient temperature. Thermogravimetric analyses (TGA) of the neat PILs, blends, BO, and BOA were performed by using a TA Instruments Q500 (TA Instruments, New Castle, DE, USA) with a platinum pan from room temperature to 600 °C at a heating rate of 10° C/min and a flow rate of 20 mL/min in air to obtain the onset decomposition temperature of these lubricants. The dynamic viscosity data of these lubricants were collected within a temperature range of 25–100 °C by using a Brookfield DV2T-LV Viscometer (AMETEK Brookfield, Middleboro, MA, USA) with a Thermosel System to control the temperature.

2.4. Friction and Wear Tests

The tribological properties of Eet, Met, and Det used as neat lubricants and lubricant additives to BO under AISI 52100 steel–steel contact mode were evaluated by using a custom-designed reciprocating ball-on-flat tribometer at room temperature. The steel disks (31.7 mm diameter, Ra ≈ 0.06 μm) slid against stationary steel balls (1.5 mm diameter and Ra ≈ 0.56 μm) during each trial. The frictional tests were carried out under a normal load of 3 N, which corresponds to a maximum Hertz contact pressure of 2.31 GPa at a sliding speed of 0.03 m/s, a frequency of 5 Hz, a stroke length of 3 mm, and a sliding distance of 108 m. For comparison, frictional tests were also performed with the commercial biodegradable lubricant, BOA, and its base biodegradable oil, BO.

At least three frictional tests were carried out under the same conditions for each lubricant to minimize the experimental error. Each steel disk was cleaned in an ultrasonic cleaner with isopropyl alcohol (99.5%) and then dried in air before and after each frictional test. Before each test, 0.1 mL of lubricant was placed between the contact steel surfaces, and no additional lubricant was added during the test. Friction coefficients were continuously recorded over time and calculated as the average of each running.

After the frictional tests, an Olympus BH-2 Optical Microscope was used to measure the wear track width on each disk, and at least 15 measurements were taken along each wear track. Then, the wear volume was calculated according to the formula in the paper by Qu and Truhan [42]. A Nanovea ST 400 profilometer (NANOVEA, Irvine, CA, USA) was used to obtain the three-dimensional (3D) morphology of the wear track. A Tescan Mira3 scanning electron microscope (SEM, TESCAN, Warrendale, PA, USA) and energy-dispersive X-ray spectrometer (EDX, TESCAN, Warrendale, PA, USA) were used to study the wear mechanism and surface interactions of the worn steel disks after lubrication with different lubricants.

3. Results and Discussion

3.1. NMR Spectra of PILs

The proton nuclear magnetic resonance (^{1}H NMR) spectra in Figure 1 confirmed the molecular structures of the three PILs [40].

Eet ^{1}H NMR (chloroform-d, 500 MHz): d = 7.43 (s, 1H, NH), 3.77–3.79 (t, 2H, CH_2), 2.99–3.01 (t, 2H, N–CH_2), 2.04–2.09 (m, 1H, CH), 1.40–1.54 (m, 4H, CH_2, CH_2), 1.24–1.32 (m, 4H, CH_2, CH_2), 0.86–0.90 ppm (m, 6H, CH_3, CH_3).

Met ^{1}H NMR (chloroform-d, 500 MHz): d = 7.82 (s, 1H, NH), 3.83–3.85 (t, 2H, CH_2), 2.98–3.00 (t, 2H, N- CH_2), 2.61 (s, 3H, CH_3), 2.05–2.10 (m, 1H, CH), 1.36–1.47 (m, 4H, CH_2, CH_2), 1.23–1.29 (m, 4H, CH_2, CH_2), 0.86–0.91 ppm (m, 6H, CH_3, CH_3).

Det ^{1}H NMR (chloroform-d, 500 MHz): d = 9.77 (s, 1H, NH), 3.62–3.64 (t, 2H, CH_2), 2.68–2.70 (t, 2H, N–CH_2), 2.41 (s, 6H, CH_3, CH_3), 1.96–2.01 (m, 1H, CH), 1.37–1.41 (m, 4H, CH_2, CH_2), 1.25–1.32 (m, 4H, CH_2, CH_2), 0.71–0.76 ppm (m, 6H, CH_3, CH_3).

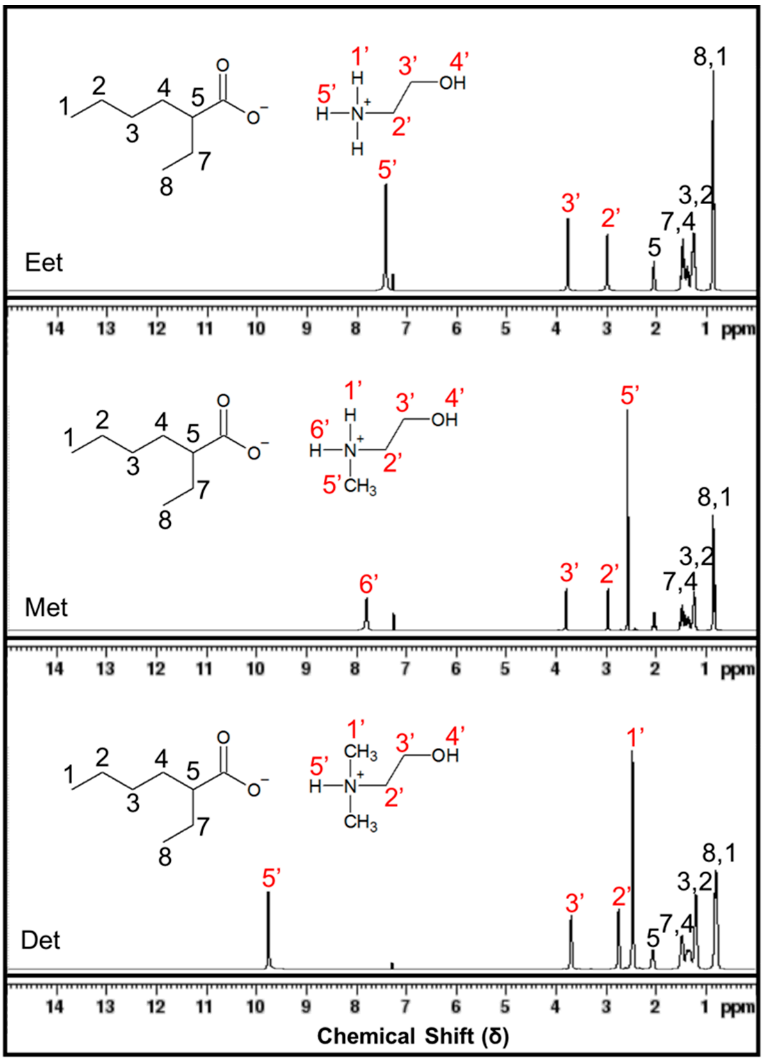


Figure 1. ^{1}H NMR spectra for PILs of Eet, Met, and Det.

3.2. Ionicity of PILs

The ionicity of a PIL is reflected in its conductivity, which provides the degree of ionization of a PIL [43]. The PILs in this study are salts of a weak acid (2-ethylhexanoic acid) and three bases (in increasing order of basic strength) of ethanolamine, N-methylethanolamine, and N, N′-dimethylethanolamine. The process of proton transfer is an equilibrium reaction, and the degree of ionization is dependent upon the relative basicity of the three alkanol amines.

As shown in Table 3, the ionic conductivity of Eet, Met, and Det at room temperature is 95, 405, and 680 µS/cm respectively, where the ionicity of the three PILs follows the order of Det > Met > Eet. As expected, Det, where the basicity of the corresponding alkanol amine is the strongest, has the highest degree of ionization and exhibits a more ionic nature than Met and Eet. On the contrary, the base (ethanolamine) of Eet is the weakest of the three bases, leading to its corresponding salt Eet having the lowest degree of ionization.

Table 3. Ionic conductivity of Eet, Met, and Det at room temperature.

PILs	Ionic Conductivity (µS/cm)
Eet	95
Met	405
Det	680

3.3. Viscosity and Thermal Stability of PILs and Mixtures

The average dynamic viscosity as a function of temperature of the three PILs, the base lubricants, and 1 wt.% PIL mixtures are shown in Figure 2 and Table 4. Viscosity and how temperature affects viscosity are highly influenced by the ion–ion interactions and the number of hydrogen bonds between molecules [43]. Eet, with the highest number of hydrogen bonds between its molecules, shows the highest viscosity (Figure 2a), followed by Met and Det. As expected, the viscosity of all the lubricants decreased with the increment of temperature. However, it should be noted that the decrease was particularly important for Eet, where its viscosity decreased around 97.5% from 40 to 100 °C. Adding 1 wt.% of any PIL to the base biolubricants slighly changed the values of viscosites, as can be seen in Figure 2b and Table 3. It is important to note that the conditions studied in this work correspond to a boundary lubrication regime, where the viscosity of the fluid is insufficient to avoid contact between surfaces.

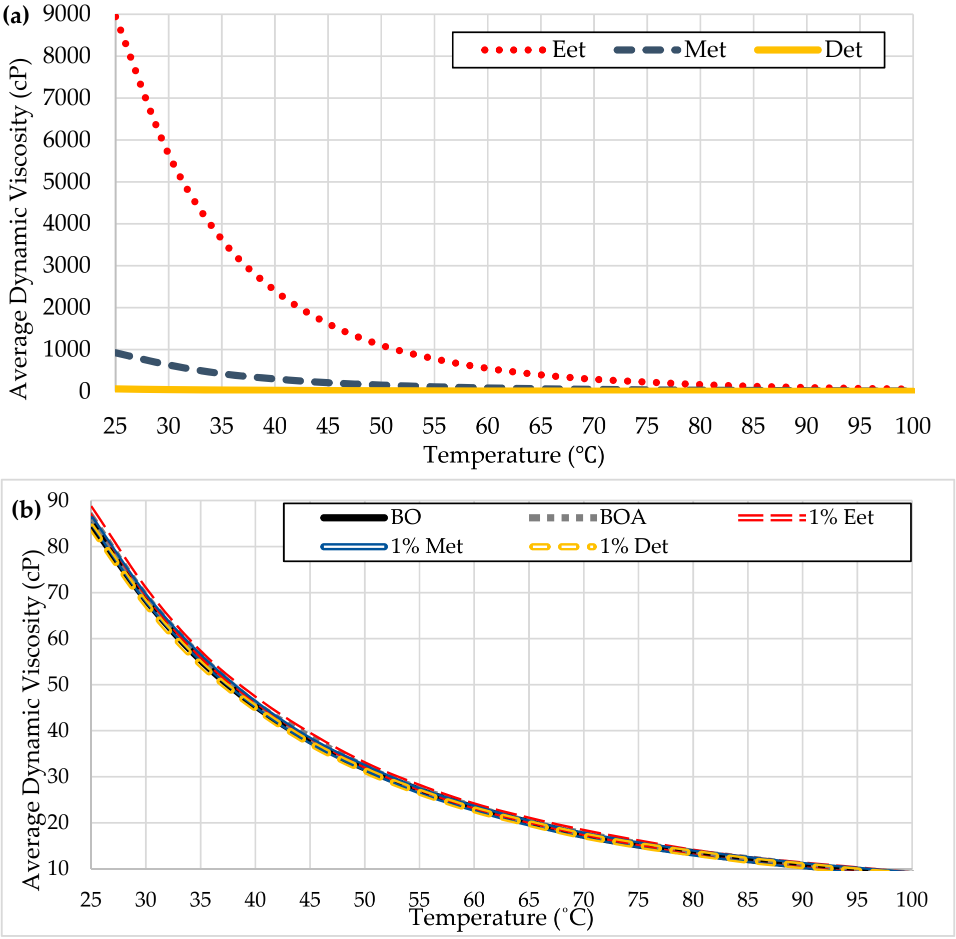


Figure 2. Average dynamic viscosity as a function of temperature for (**a**) the neat PILs and (**b**) biodegradable base (BO), BIO TELEX 46 (BOA), and 1 wt.% PIL blends.

Table 4. The viscosity of BO, BOA, neat PILs, and PIL blends.

Lubricant	**Dynamic Viscosity (cP)**		
	25 °C	**40 °C**	**100 °C**
BO	85.02	45.48	8.76
BOA	86.44	45.86	8.89
1% Eet	87.88	46.76	8.69
1% Met	85.88	45.80	8.67
1% Det	84.29	44.94	8.61
Eet	8943.75	2405.56	59.4
Met	926.86	301.58	14.72
Det	61.74	27.74	3.71

The results from the themalgravimetric analysis are summarized in Table 5 and Figure 3. Both biolubricants (BO and BOA) presented higher thermal stabilties than the neat PILs. Among the three protic ionic fluids, Det showed the lowest thermal stability with an onset temperature of 141.4 °C. The addition of 1 or 2 wt.% PIL slightly reduced the thermal stability of the biolubricant BO (Figure 3b).

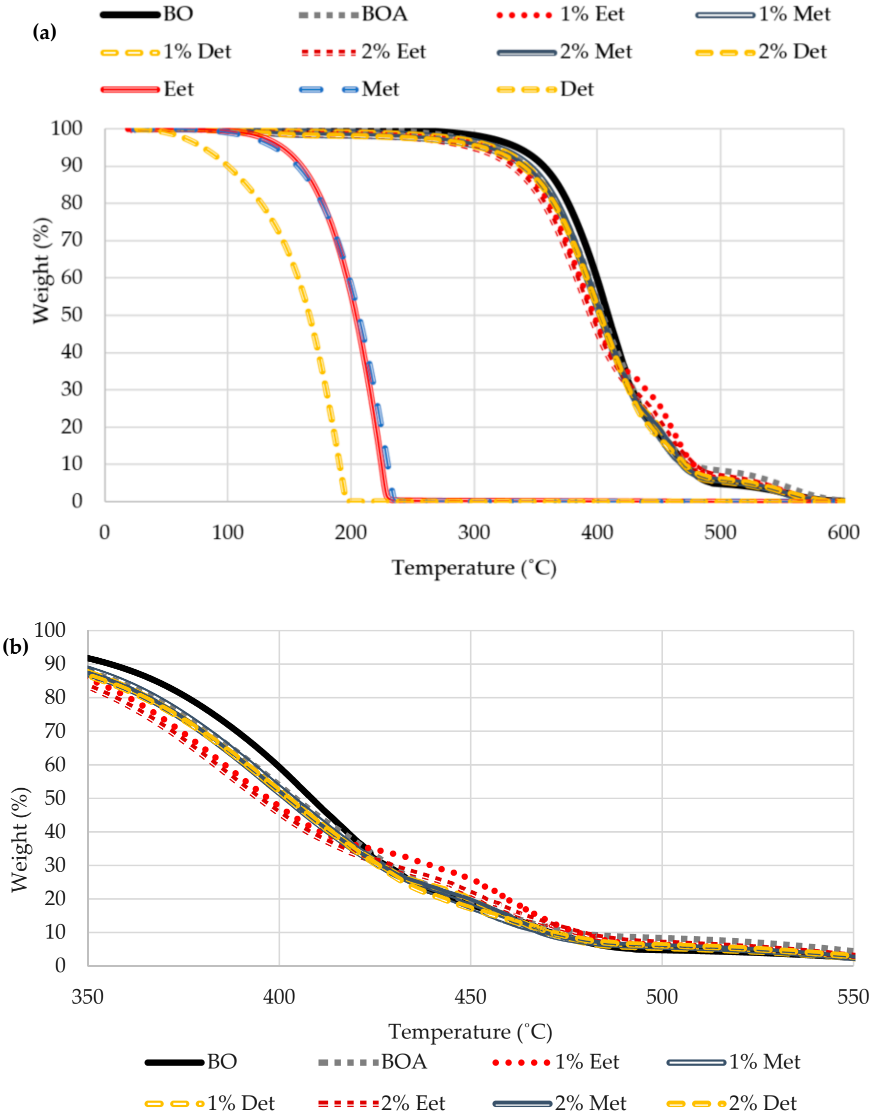


Figure 3. (**a**) Experimental TGA for BO, BOA, neat PILs, and PIL blends, (**b**) detail of the thermalgravimetric behavior of the lubricants from 350 to 550 °C.

Table 5. Thermal stability of BO, BOA, neat PILs, and PIL blends.

Lubricant	Onset Temperature (°C)
BO	364.8
BOA	350.7
1 wt.% Eet	343.5
1 wt.% Met	353.8
1 wt.% Det	350.5
2 wt.% Eet	341.3
2 wt.% Met	353.6
2 wt.% Det	351.5
Eet	177.5
Met	174.8
Det	141.4

3.4. Tribological Properties

Figure 4 shows the average friction coefficient values and standard deviations of steel–steel contact after at least three tests lubricated with BO, BOA, neat PILs, and PIL blends 1 wt.% Eet + BO, 1 wt.% Met + BO, and 1 wt.% Det + BO. The use of any neat PIL reduced friction compared with BO or BOA, showing maximum friction reductions of 57% and 36% with respect to the commercially available BOA when Eet and Met were used as lubricants, respectively. Det, whose corresponding neutral base has a higher basic strength than that of Eet or Met, presented the lowest friction reduction, probably due to the more ionic nature of this liquid, which promoted tribocorrosion reactions on the steel surface [7]. The effects of the three ionic liquids as additives were quite different. While Det performed better as an additive, showing that the addition of only 1 wt.% of this liquid in the base BO reduced friction by 69% with respect to BO and 61% with respect BOA, Eet and Met performed better as neat lubricants, although the addition of 2 wt.% Met to BO resulted in almost the same friction reduction as that obtained for neat Met.

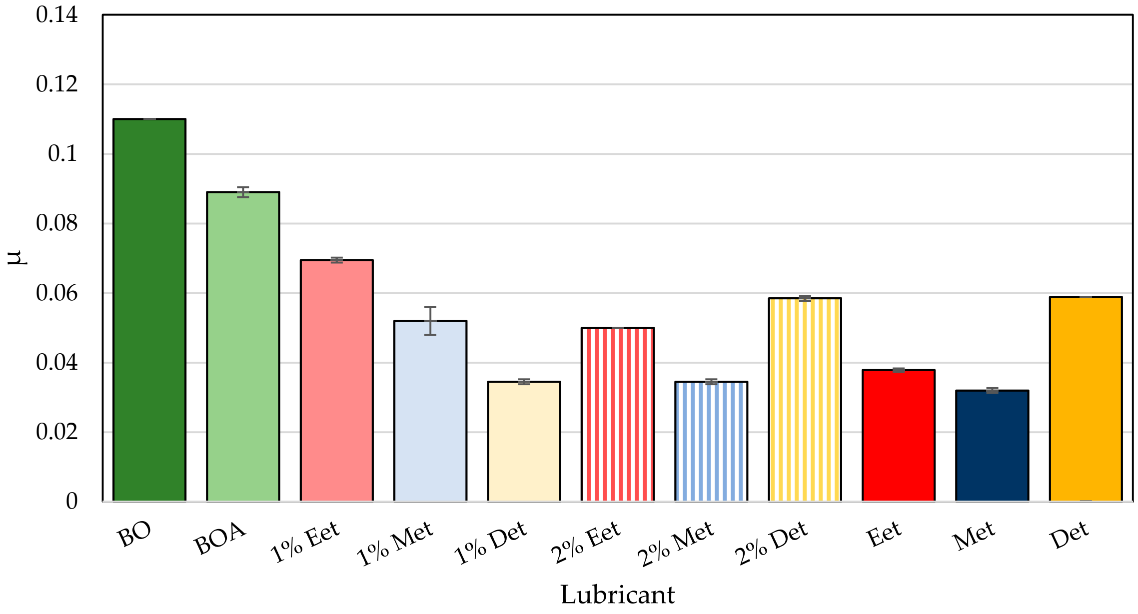


Figure 4. Average friction coefficients of steel–steel contact after tests lubricated with BO, BOA, neat PILs, and PIL blends 1 wt.% Eet + BO, 1 wt.% Met + BO, and 1 wt.% Det + BO.

Real-time friction coefficient variations for steel disks against steel balls after tests lubricated with the two bio-lubricants, the three neat PILs, and the mixture of 1 wt.% Det in BO are shown in Figure 5.

The use of any neat PIL or 1 wt.% Det + BO not only reduced but also stabilized the friction coefficient, particularly for Met and Eet.

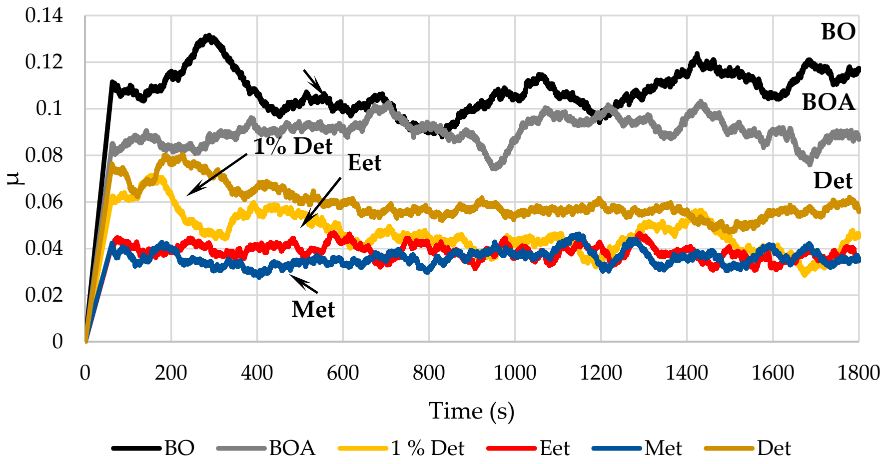


Figure 5. Friction vs. time curves of BO, BOA, 1 wt.% Det + BO, Eet, Met, and Det.

Figure 6 summarizes the average values of wear volume of steel disks after using the different lubricants. The presence of any PIL in BO reduced wear by one order of magnitude with respect to the base bio-oil, reaching similar wear values as those obtained with the commercially available BOA. No major differences were found between using 1 wt.% or 2 wt.% of the additive. After analyzing the steel disk wear volumes obtained when PILs were used as neat lubricants, the wear volumes showed the same tendency as the PILs' conductivity (ionicity), with the highest wear reduction being obtained with the PIL with the lowest conductivity (Eet). This PIL was able to reduce the wear volume by 95% and 67% with respect to BO and BOA, respectively. This significant wear reduction can be clearly seen in the optical images of Figure 7. The worn track image after a test lubricated with BO shows severe wear with visible abrasion marks and fatigue cracks, while when the steel surface was lubricated with neat Eet, the worn track was very mild with only superficial abrasion marks. In this figure, we can also see that the additives included in the formulation of BOA reduced considerably the wear track on the steel disk and changed the wear mechanisms from mainly abrasive to a milder adhesive.

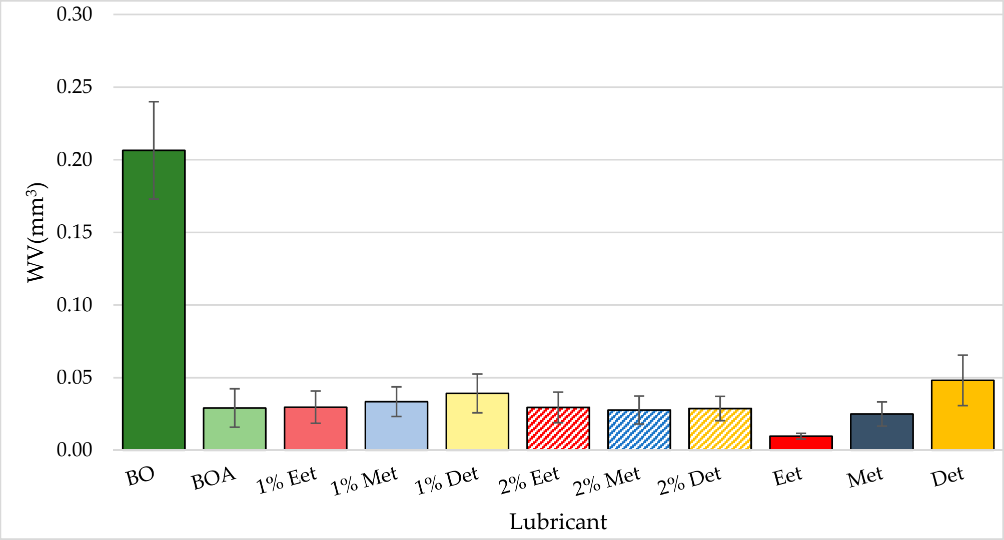


Figure 6. Average values of the wear volume of steel disks after tests lubricated with BO, BOA, neat PILs, and PIL blends 1 wt.% Eet + BO, 1 wt.% Met + BO, and 1 wt.% Det + BO.

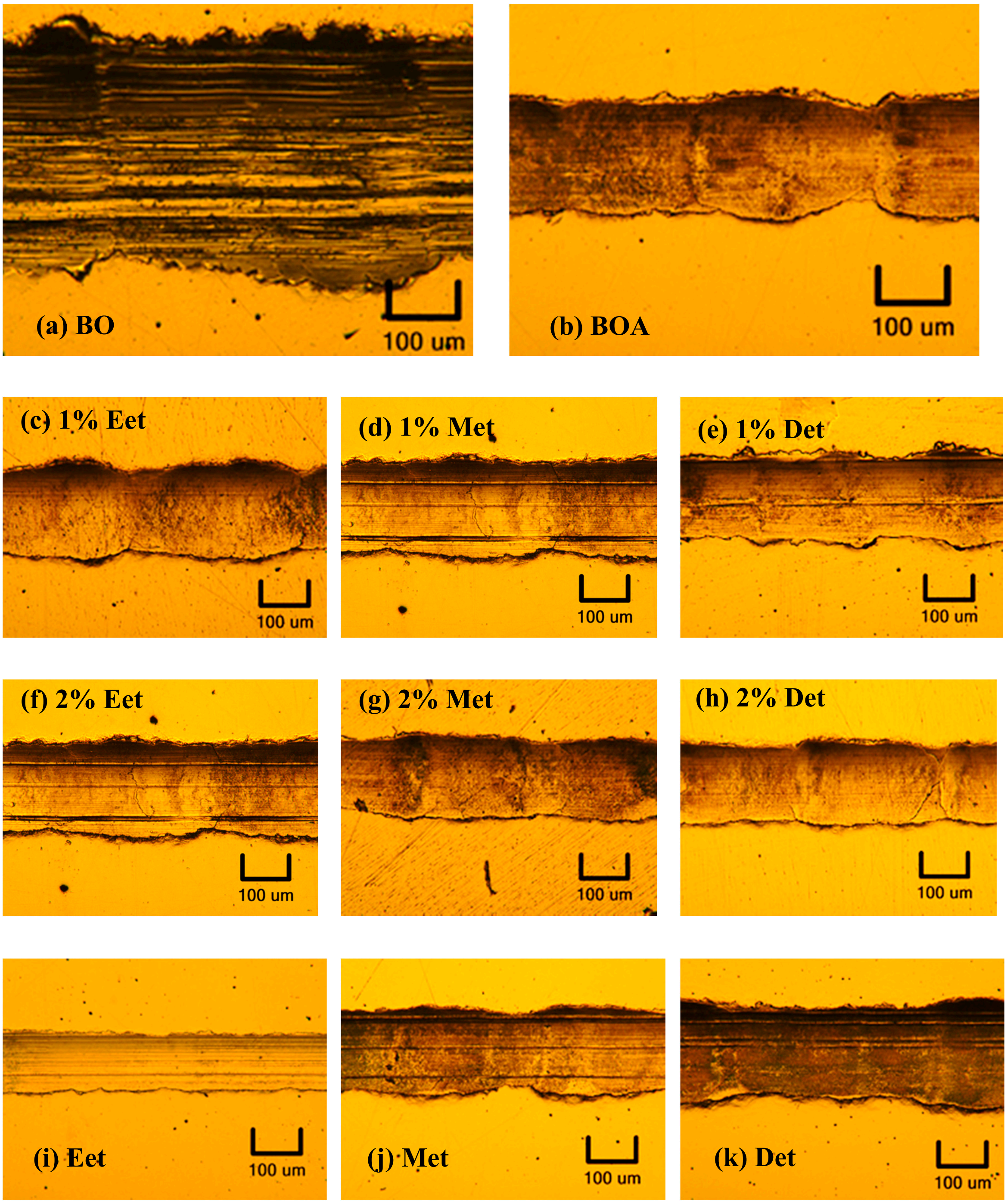


Figure 7. Optical images of worn surfaces on steel surfaces after tests lubricated with (**a**) BO, (**b**) BOA, (**c**) 1 wt.% Eet + BO, (**d**) 1 wt.% Met + BO, (**e**) 1 wt.% Det + BO, (**f**) 2 wt.% Eet + BO, (**g**) 2 wt.% Met + BO, (**h**) 2 wt.% Det + BO, (**i**) Eet, (**j**) Met, and (**k**) Det.

Figure 8 shows the 3D surface topography profiles on steel disks after tests lubricated with BO, BOA, and neat PILs. The use of any neat PIL reduced not only the width but also the depth of the wear tracks compared with BO. After using Eet, the wear scar was neglegible, showing only some superficial scratches.

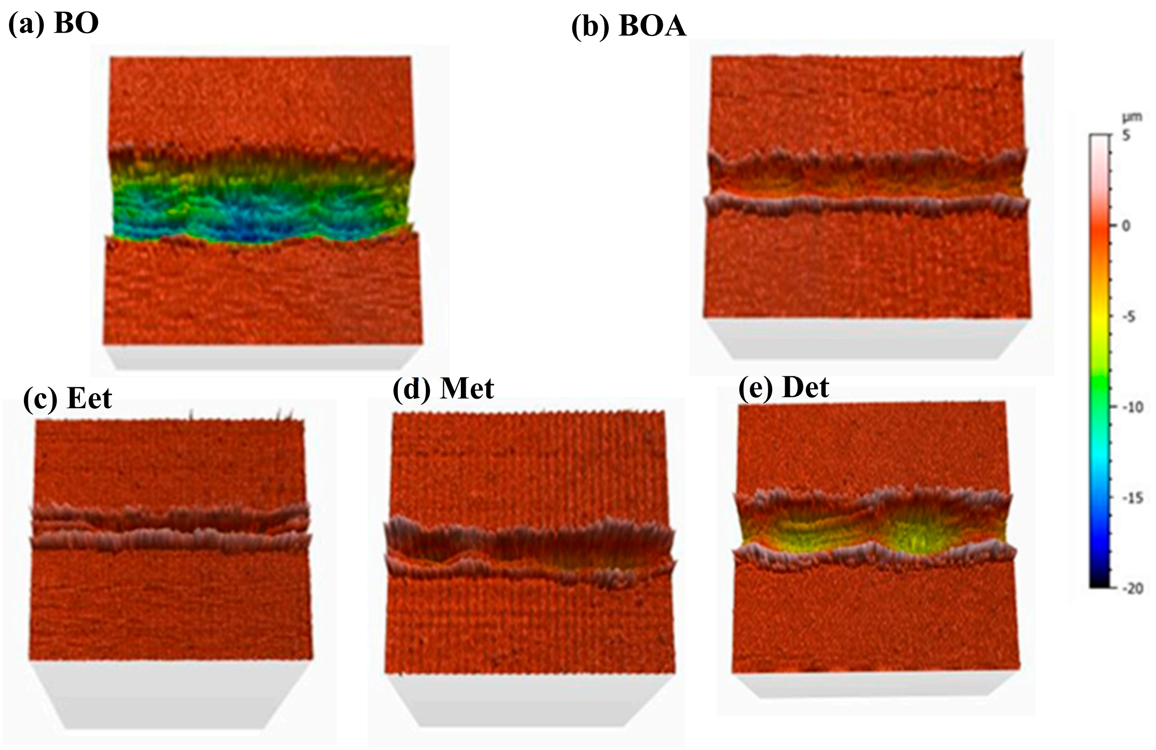
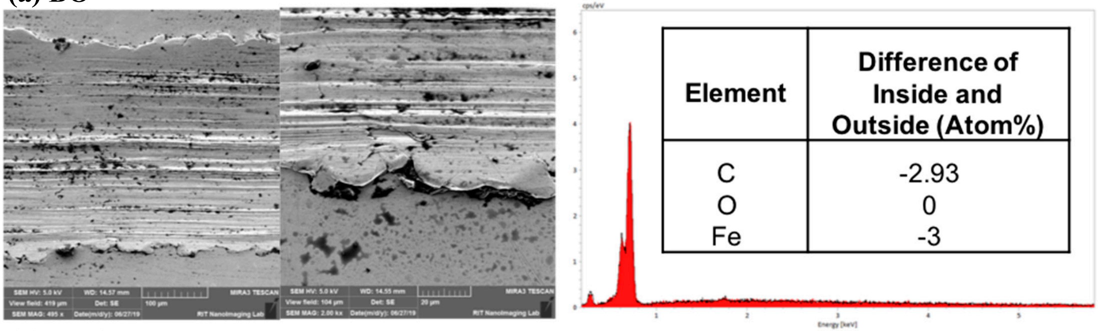


Figure 8. Three-dimensional (3D) surface profiles on steel surfaces after tests lubricated with (**a**) BO, (**b**) BOA, (**c**) Eet, (**d**) Met, and (**e**) Det.

The SEM images of the worn surfaces and the corresponding energy-dispersive X-ray (EDX) spectrum analysis obtained for both the inside and the outside of the wear tracks are shown in Figure 9. Severe three-body abrasive wear with some plastically deformed material accumulated over the edges of the wear track are shown after a test lubricated with BO. Slightly smaller amounts of C and Fe were detected inside the wear track for this lubricant. The additives included in the formulation of BOA reduced wear effectively, showing much milder conditions, probably due to the oxygen-rich layer formed inside the worn surface.

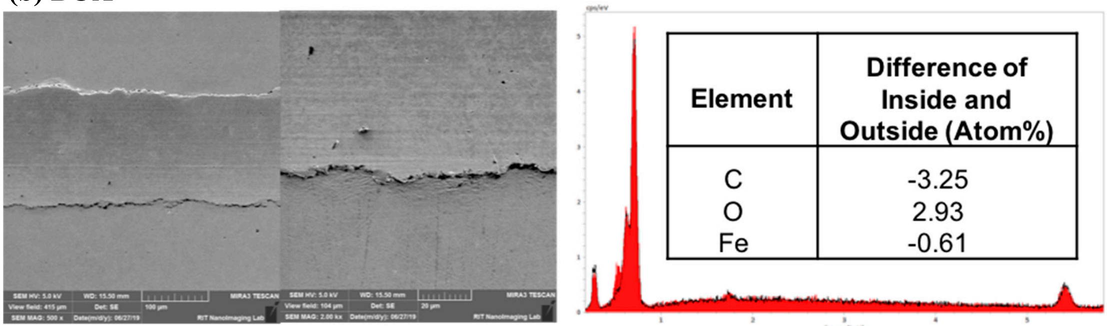
Lubricating with any PIL reduced wear and changed the wear mechanism from severe abrasive to mild adhesive with respect to BO. A higher amount of O was found inside the wear tracks for the three PILs, proving some kind of interaction between the ionic liquids and the steel surfaces. It has been demonstrated [7,44] that the tribochemical reactions between ILs and metal surfaces may be either beneficial (protective) or detrimental (tribocorrosive). In this study, the difference in O between the inside and outside of the wear track increased as the ionicity (conductivity) of the PIL increased, showing that a PIL with a more ionic nature promotes more tribochemical reactions with the steel surface. It is important to note that this effect is also related to the wear volume of the steel disks. Among the three PILs, Det (highest ionicity) presented the poorest anti-wear property probably due to tribocorrosion reactions between the PIL and the steel surface, which can be confirmed by the higher amount of O inside the wear track. However, when Det was used as an additive, a small amount of this PIL was enough to form a protective layer that avoided detrimental tribocorrosion reactions with the steel surface (see the EDX results in Figure 9). C was also found inside the wear track after tests lubricated with Det, 1 wt.% Det + BO, and particularly Eet. This carbon-rich layer has been previously proven to effectively protect surfaces against wear [18].

(a) BO



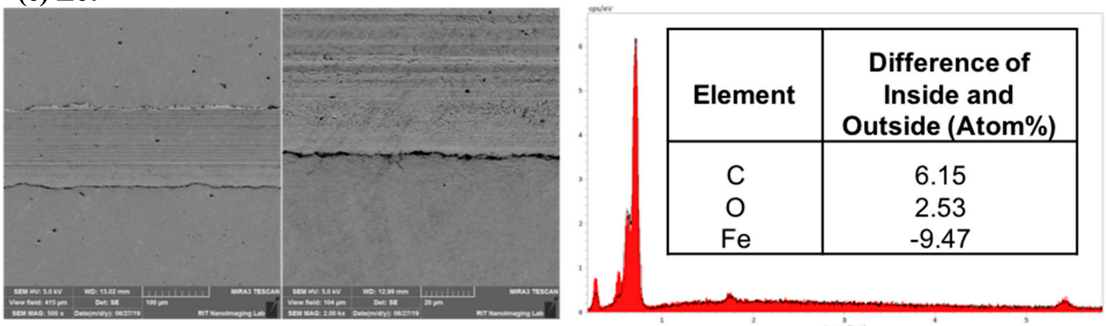
Element	Difference of Inside and Outside (Atom%)
C O Fe	-2.93 0 -3

(b) BOA



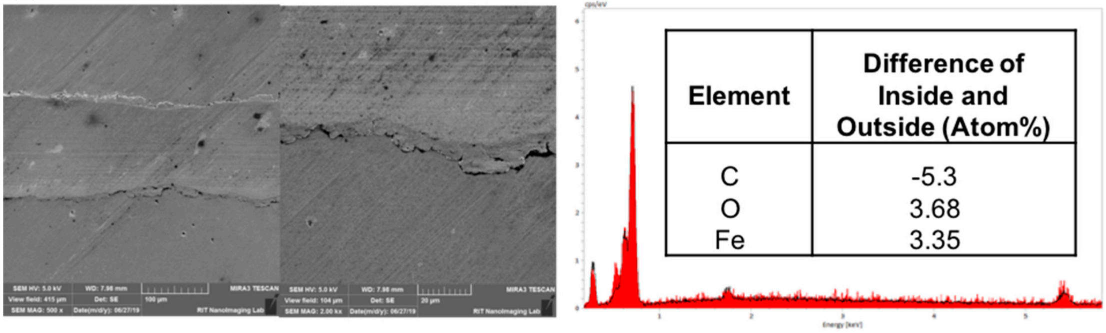
Element	Difference of Inside and Outside (Atom%)
C O Fe	-3.25 2.93 -0.61

(c) Eet



Element	Difference of Inside and Outside (Atom%)
C O Fe	6.15 2.53 -9.47

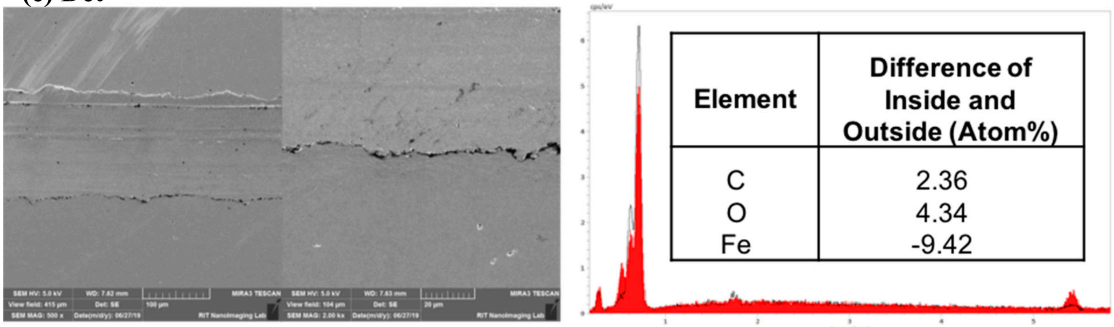
(d) Met



Element	Difference of Inside and Outside (Atom%)
C O Fe	-5.3 3.68 3.35

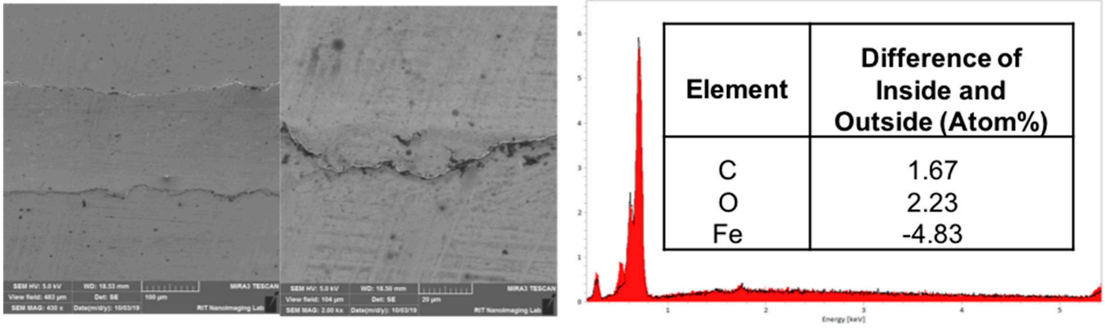
Figure 9. *Cont.*

(e) Det



Element	Difference of Inside and Outside (Atom%)
C O Fe	2.36 4.34 -9.42

(f) 1% Det



Element	Difference of Inside and Outside (Atom%)
C O Fe	1.67 2.23 -4.83

Figure 9. SEM images of worn surfaces and energy-dispersive X-ray (EDX) spectrum results of the inside and outside wear tracks for different lubricant conditions: (**a**) BO, (**b**) BOA, (**c**) Eet, (**d**) Met, (**e**) Det, and (**f**) 1 wt.% Det + BO.

4. Conclusions

In this work, three PILs derived from alkyl ammonium carboxylate salts of hydroxyalkyl-amines with differing basicity were synthesized and tested as neat lubricants and lubricant additives to a biodegradable oil in a steel–steel contact at room temperature. The ionicity of the three neat PILs was also investigated by reporting their conductivity at room temperature. The three neat PILs reduced friction and wear with respect to BO. Neat Eet, the PIL with the lowest ionicity, achieved the highest wear reductions with respect to BO and commercially available BOA. The PIL containing the strongest base, Det, presented the poorest friction and wear behaviors, probably due to the more ionic nature of this liquid, which promoted tribocorrosion reactions on the steel surface. However, this PIL performed better as an additive showing that small additions of this liquid in the biodegradable oil, BO, were enough to form a protective layer that avoids detrimental tribocorrosion reactions with the steel surface.

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