

Protic Ionic Liquids Used as Metal-Forming Green Lubricants for Aluminum: Effect of Anion Chain Length

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Among the applications for protic ionic liquids (PILs), lubrication is one of the newest and the most promising. In this work, ammonium-based protic ionic liquids were tested as lubricant fluids for aluminum-steel contacts. PILs were synthesized with 2-hydroxyethylamine (2HEA) and a carboxylic acid (formic and pentanoic), aiming to understand the effect of two different anion chain lengths on the lubricant behavior. The synthesized PILs were characterized by RMN, FTIR and TGA. Wear tests, conducted using a ball-on-plate configuration, showed that the increase of the anion carbon chain length in the PIL structure reduced significantly the coefficient of friction value. Besides, after the wear tests, the PILs structural integrity was not affected. In the same way, bending under tension (BUT) tests evidenced that the performance for stamping conditions of the PIL with the longest anion carbon chain was similar to that of the commercial lubricant. Since, both formed a uniform tribofilm, developed the same lubrication regime and the drawing forces values were close and constant. Hence, the ionic liquid obtained with 2HEA and pentanoic acid (2HEAPE) is as suitable as the commercial lubricant for metal forming processes.

Keywords: Aluminum, Protic Ionic Liquid (PIL), Coefficient of friction, Lubrication, Bending under tension (BUT)

1. Introduction

Research about ionic liquids has recently developed a trend oriented to protic ionic liquids (PILs) due to their wide spectrum of application. Their properties of extremely low vapor pressure, high viscosity, high thermal and ionic conductivity, non-flammability, thermal and chemical stability, and low toxicity make them suitable in many fields of applications, such as catalysis, electrochemical devices and separation processes. Protic ionic liquids can be tailored for a specific application taking into account that a small change whether in anion structure whether in cation structure or in both, modifies their corresponding physical-chemical properties¹⁻⁷.

Among the promising uses of ionic liquids, lubrication for metal-metal, metal-ceramic and ceramic-ceramic contacts has been a new trend since the authors Ye et al.⁸ showed a significant reduction in the average coefficient of friction for some of the aforementioned tribopairs using two different alkylimidazolium tetrafluoroborates. Liu et al.⁹ tested the

same ionic liquids for lubrication of steel-steel tribopair under vacuum, with a reduction of almost 50% of the coefficient of friction compared to perfluoropolyether (PFPE) and mineral oil. Meanwhile, another work¹⁰ showed their superior performance for steel-aluminum tribopair under cryogenic conditions compared to mineral oil. Thereafter, many different ionic liquids have been tested for different contacts^{11,12}.

Initially, most of the research involving ionic liquids as lubricants used alkylimidazolium as cation and tetrafluoroborate or hexafluorophosphate as anion, due to their availability¹³. More recently, diverse structures have also been used. Some alkylphosphonium-organophosphate ionic liquids were synthesized by Barnhill et al.¹⁴, to evaluate their performance as antiwear lubricant additives and its relationship with their structures. Another study¹⁵ evaluated phosphonium cation-based ionic liquids with different anions and concluded that the increase of their reactivity with the steel-steel and aluminum-steel contacts allowed the formation of a tribofilm and had the best tribological behavior.

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Research of protic ionic liquids as lubricants saw the light when lubrication with perfluoropolyether (PFPE)-ammonium-based protic ionic liquid for nickel-cobalt contacts was tested by Kondo¹⁶ for application in magnetic thin film media. More recent studies¹⁷⁻²⁰ have dealt with lubrication using different kinds of ionic liquids, focused on ammonium and imidazolium-based ones. Espinosa et al.^{19,20} showed the influence of the different structures inside the ionic liquid molecule on the tribological performance of metal-metal and metal-ceramic contacts, mainly concerning the anion chain structure. Secondary amines were the cation precursors for the ammonium-based ionic liquids tested^{17,19,20} and their anions either were obtained from mono-, di- or tri-carboxylic acids, or were inorganic. These studies displayed stable, low and ultralow coefficient of friction values when increasing polarity, number of ammonium protons and oxygenated groups for the obtaining of strong surface interaction as well as lubricant film stability. In the present work, it was used PILs synthesized with 2-hydroxyethylamine (ZHEA), a primary amine, and a monocarboxylic acid, in each case, with variation of the anion chain length.

Friction control is important to determine the deformation in stamping processes²¹ and avoids wrinkling²², as well as in the level of residual stress and springback of the deformed pieces²³. The lubrication regimes more found in metal forming are generally boundary or mixed, depending on the applied load and the obtained coefficient of friction²¹⁻²³. As reported by other authors¹⁷⁻²⁰, boundary lubrication can be achieved using ionic liquids, due to their elevated viscosity, which could give away interesting results for application in metal forming.

However, there is not a huge amount of literature work related to the use of protic ionic liquids as lubricants for metal forming, nor for aluminum. Research of aluminum-steel contacts is, in its most, focused on how the structure of different ionic liquids influences on the coefficient of friction and the interaction contacts-ionic liquids, through tests using the tribometer²⁴⁻²⁹. A work reports the use of imidazolium-based ionic liquids for micro-milling processes³⁰. In this research³⁰, the ionic liquids were used as cutting oil and yielded a similar performance in comparison with conventional cutting fluids. Besides, their use for this kind of application involves the realization of tests in laboratory, like those with the tribometer, before their macro-scale use, for example to manufacture a metallic cup.

The aim of this work is to evaluate the behavior of ammonium-based protic ionic liquids as lubricant fluids for aluminum-steel contacts as well as their feasibility for using in metal forming. PILs were synthesized with 2-hydroxyethylamine (ZHEA), a primary amine, and a carboxylic acid, with only one carboxylic function, aiming to know the different responses for two different anion chains. The used carboxylic acids were formic and pentanoic. In order to know the viability for using the studied protic ionic liquids, bending under tension (BUT) test was carried out

to evaluate the performance of the PILs on the aluminum stamping process and their potential for further application in mechanical forming processes.

2. Materials and Methods

Neutralization of ZHEA with each of the carboxylic acids under controlled reaction conditions was conducted to synthesize the PILs^{6,31}. Structures of the used reactants and the obtained PILs are presented in Table 1. These liquids were chosen since they are in liquid state at room temperature, they have low toxicity because their simple structure favors biodegradability^{32,33}, and their capability for being adsorbed onto the metal surface due to the presence of the oxygen and nitrogen atoms^{6,34}, that can improve both lubrication and corrosion performance.

Lubricant fluids included the aforementioned PILs and a commercial lubricant commonly used in mechanical forming, for comparison purposes. Characterization of the lubricant fluids boarded nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR) spectra, thermogravimetric analysis (TGA) and viscosity. ¹H and ¹³C NMR spectra were obtained using a Varian equipment with 400 MHz frequency, 1 H inductance and 9.4 T magnetic field and using trimethylsilane (TMS) as internal standard. ZHEAPE and the commercial lubricant were diluted in deuterated chloroform. ZHEAF was characterized using deuterated methanol. Density was determined experimentally using a pycnometer at 25 °C. TGA was conducted under nitrogen flow of 50 cm³.min⁻¹, from 23 °C up to 400 °C with a heating rate of 10 °C.min⁻¹ in Shimadzu TGA-50 equipment. Viscosity measurements for the PILs were conducted in an Anton Paar Stabinger ViscometerTM SVM 3000, a rotational, tube - rotor device, at 25 °C. Contact angle determination were conducted in an equipment tailored by the Laboratório de Pesquisa em Corrosão - LAPEC, at UFRGS, using a camera for capturing the drop photograph and image analysis software to measure the contact angle. FTIR spectra were acquired by a Bruker Vertex 70v equipment, with a resolution of 4 cm⁻¹.

Plates of as-received aluminum 1100 (Table 2) were used as work substrate. For coefficient of friction measurements, a tribometer CETR UMT (Universal Micro Tribometer) in ball-on-plate setting was used, using a quenched and tempered AISI 1050 steel ball of 4.76 mm diameter. The normal force was 0.5 N for a Hertzian stress of 404.54 MPa. The tests were conducted with frequency of 1 Hz and 2 mm track for a sliding distance of 7.2 m. The lubricant fluid (synthesized PILs and commercial lubricant) was placed on the testing area. A dry, non-lubricated wear test was also conducted to determine the coefficient of friction value for the tribopairs. Three measurements were conducted, to guarantee the reproducibility. The experiments were carried out at room temperature and air atmosphere.

Table 1. Structure of the obtained PILs and the reactants for their synthesis.

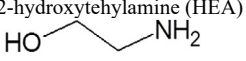
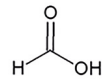
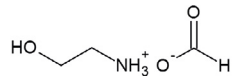
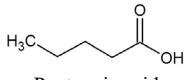
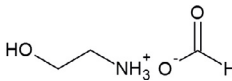
Cation precursor	Anion precursor	PIL
2-hydroxyethylamine (HEA) 	 Formic acid	 2HEAF (2-hydroxyethylammonium formate)
	 Pentanoic acid	 2HEAPe (2-hydroxyethylammonium pentanoate)

Table 2. Composition of the aluminum plates.

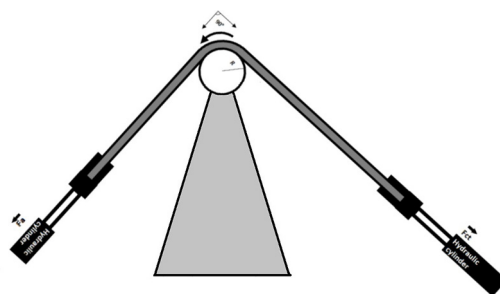
Element	%
Si	0.132
Fe	0.320
Cu	0.0085
Mn	0.027
Mg	0.013
Al	99.46

Since the studied PILs are ethanol- and water- soluble along a wide range of compositions^{3,35}, samples were cleaned with these solvents before the morphological characterization, with the removal of most of the PIL from the surface. For cleansing the commercial lubricant and given its nature of vegetable oil, the most appropriate is the removal with solvents like *n*-hexane or tetrahydrofuran³⁶. Ethanol is not a good solvent for vegetable oils. But considering the huge volume of ethanol vs. the amount of commercial lubricant (approximately 100 μ l), most of the latter was removed from the metal surface.

Morphology was evaluated by optical microscopy of the tracks on the substrate and on the AISI 1050 steel balls using Olympus CX31. Track profiles were acquired by a profilometer Bruker ContourGT-K. Wear volume was computed according with the ASTM G133 - 05 (2010) Standard, section 9.3, but considering the plastic deformation contribution, as explained by other authors²⁰. The obtained wear volume value was divided by the total sliding distance to calculate the corresponding wear rate.

In order to know the viability for using the studied protic ionic liquids in metal forming application, a test that simulates the stamping process named bending under tension (BUT) or radial strip drawing was conducted. In this test, coefficient of friction is measured when the material is deformed sliding it on a cylindrical die, where the stress is the highest. The equipment used for this test is presented in Figure 1. The triangular shape aims to diminish the influence of vibration and to give away stability when the force is transmitted.

In this test, there was a cylindrical steel die, with a diameter of 13 mm, on which an aluminum 1100 strip, with dimensions of 700 mm x 300 mm x 1 mm, slid. The aluminum strip was

**Figure 1.** Equipment for bending under tension test.

grabbed by pliers at the strip end as shown in Figure 1. At the other end of the arm that held the pincer, a hydraulic cylinder was placed; one of them applied the drawing force (F_a), to slide the aluminum strip a distance of 23 cm, and the other one applied the back tension force (F_{bt}) opposite to the movement. Both of these forces were measured with a load sensor. Torque measurements took place with a sensor placed on the cylindrical die. Five tests with each lubricant were carried out to confirm reproducibility. The corresponding lubricant was applied with a paint brush before placing each end of the aluminum strip in the pliers. Measurements were conducted under room temperature condition. Drawing speed was 185 mm.s⁻¹ and sliding was perpendicular to the rolling direction. Data acquisition was done using signal conditioning device Spider 8 and software Catman® 4.0 from HBM. Aluminum 1100 strips were used as received and the die polishing was made with SiC paper # 300, 600, 1200 and 2000 using a mechanical lathe.

3. Results and Discussion

3.1. Lubricant fluids structure and properties

NMR confirmed the structures of the PILs. Figure 1S shows the NMR spectra obtained for the PILs, being Figure 1S-a) and 2S-a) the proton (¹H) spectra and Figure 1S-b) and 2S-b) the carbon (¹³C) ones. Peaks for each spectrum matched with those reported by Álvarez and coworkers³ and demonstrate that PIL syntheses were successful. On the other hand, NMR for the commercial lubricant (Figure 3S) showed that the fluid corresponded to a vegetal oil.

Figure 2 shows the FTIR-spectra for the studied PILs and for the commercial lubricant. Spectra for the PILs (Figure 2-a) matched with the ones expected³⁷. Functional groups in PILs structures can be observed in Figure 2-a. There is a strong broad band between 3600 cm^{-1} and 2300 cm^{-1} corresponding to the overlapping of O-H stretching, due to the carboxylic function as well as the water content in the PILs, and the N-H stretching bands. There is a plateau between 1700 cm^{-1} and 1550 cm^{-1} for 2HEAF and between 1650 cm^{-1} and 1410 cm^{-1} for 2HEAPE, formed by the overlapping between the C=O stretching band, close to 1700 cm^{-1} and the broad NH_2 scissoring band at 1615 cm^{-1} . C-O band is located at 1250 cm^{-1} and 1240 cm^{-1} for 2HEAF and 2HEAPE, respectively. NH_2 wagging and twisting bands appear between 850 cm^{-1} and 750 cm^{-1} . C-N stretching bands can be found between 1220 cm^{-1} and 1020 cm^{-1} ³⁸. All these bands are in agreement with those reported by³⁷ for 2HEAF.

Figure 2-b shows the FTIR spectrum for the commercial lubricant. Band at 3370 cm^{-1} points out a $\equiv\text{CH}$ stretch inside the structure and band at 3150 cm^{-1} relates to $=\text{CH}$. Besides, the molecule presents methylene structures with asymmetric C-H stretching at 2850 cm^{-1} , a symmetric C-H stretching at 2930 cm^{-1} , scissoring at 1460 cm^{-1} . Bands at 1735 cm^{-1} and 1090 cm^{-1} refer to stretching C=O and C-O in aliphatic esters. C=C stretching appears at 1660 cm^{-1} and its bending is located at 1400 cm^{-1} ; meanwhile, at 1570 cm^{-1} , C=C stretching appears. The last three bands at the right of the spectrum (920 cm^{-1} , 570 cm^{-1} and 540 cm^{-1}) refer to nitrogenous groups inside the structure, probably coming from additives^{38,39}. Regarding the structural characterization of the commercial lubricant and the information provided by the manufacturer, it corresponds to a vegetable oil.

Thermograms (Figure 3, Table 3) revealed, for all the studied lubricant fluids, an important water percentage in the lubricant fluids, due to the weight loss up to $100\text{ }^\circ\text{C}$. The highest water content corresponded to PIL 2HEAF and being 2HEAPE the lubricant fluid with the least water content. For the commercial lubricant, there could be an important

contribution of structural degradation in this stage, because there is no prove on the FTIR spectrum (Fig. 2-b) of the presence of water in the oil structure.

Thermograms of the studied PILs (Figure 3-a) show the start of the accentuated mass loss, with a more vertical slope of the line, at approximately $150\text{ }^\circ\text{C}$ for 2HEAF and $122\text{ }^\circ\text{C}$ for 2HEAPE (blue and red circles), indicating that, at this temperature, PIL degradation started. This degradation can compromise their lubricity and tribological performance. In theory, 2HEAPE degradation should start at higher temperature is due to its longer anion chain length^{40,41}. However, it did not take place in that way, and 2HEAF presented higher degradation temperature. It can be due to the formation of another structure or a degradation mechanism in two steps or in a slow step for the 2HEAF; meanwhile, for 2HEAPE degradation could have a mechanism of only one and fast step. Hence, the use of these PILs must be at temperatures lower than $\sim 120\text{ }^\circ\text{C}$, point at which degradation started. The weight loss ends at approximately $180\text{ }^\circ\text{C}$ for 2HEAPE and close to $225\text{ }^\circ\text{C}$ for 2HEAF, and both left a residual mass.

On the other hand, the commercial lubricant (Figure 3-b) presented a phenomenon at the temperature interval between $\sim 100\text{ }^\circ\text{C}$ and $295\text{ }^\circ\text{C}$, which can be attributed to degradation of the oil structure, possibly related to degradation in the oxygenated groups. The most significant weight loss for the commercial lubricant started at $295\text{ }^\circ\text{C}$, temperature at which the alkyl backbone rupture started. This thermal behavior is consequence of the high density of alkyl functions belonging to the hydrocarbon backbone, whose covalent carbon-carbon bonds need high energy amounts to be broken¹⁶.

Table 3 shows the aforementioned water content and the physical-chemical properties of the fluids studied in this research. One of the most relevant properties of lubricants is the viscosity. As a rule of thumb, a high viscosity warrants good performance for reduction of coefficient of friction and, in consequence, wear rate⁴². 2HEAPE and the commercial lubricant had high values of viscosity, compared to 2HEAF, matter that makes them promising for the application in

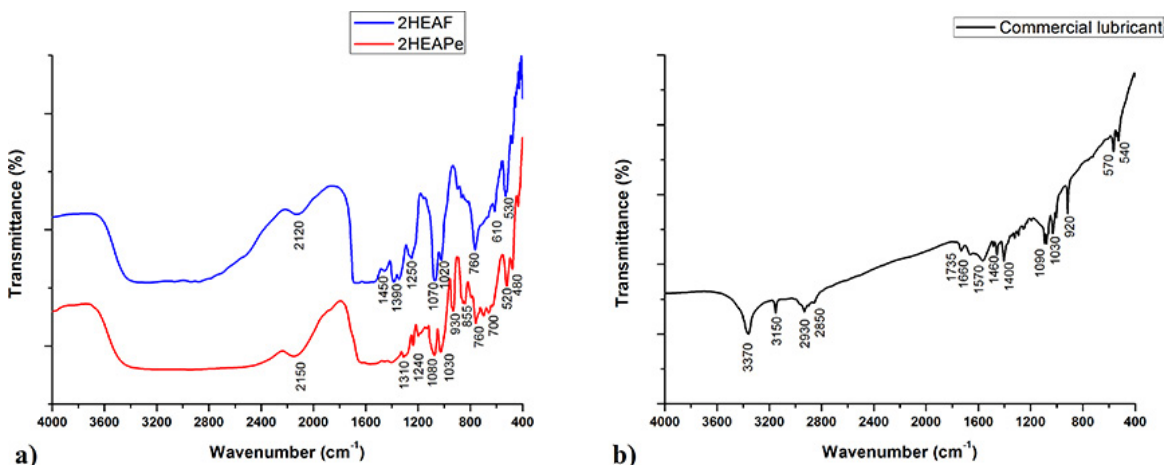


Figure 2. FTIR-spectra of the fluids studied as lubricants: a) PILs and b) commercial lubricant.

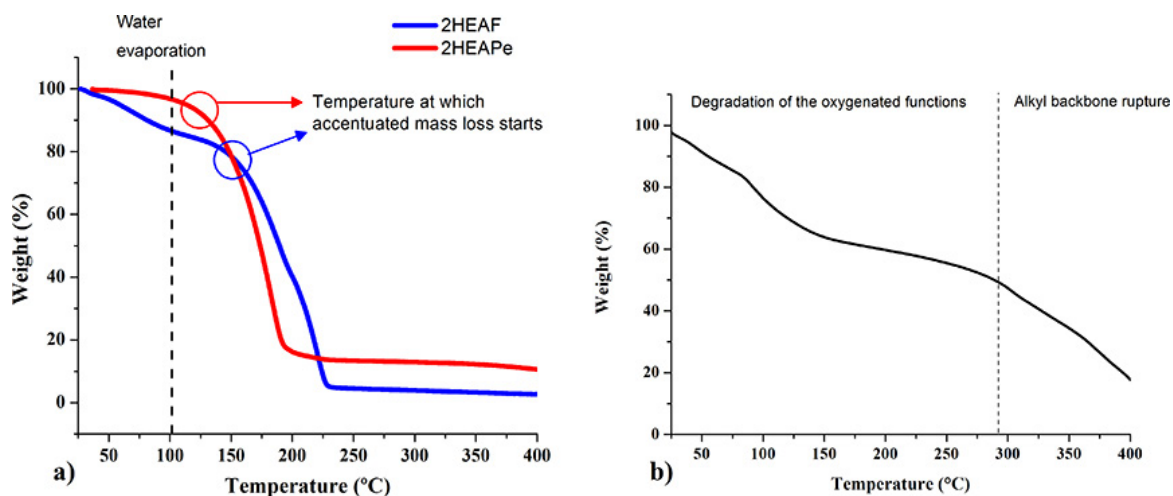


Figure 3. Thermograms for the studied lubricant fluids: a) Protic ionic liquids and b) Commercial lubricant.

Table 3. Physical-chemical properties of the studied lubricant fluids.

Lubricant fluid	Density (g.cm ⁻³) @ 25 °C	Water content (%)**	Viscosity (mPa.s)	Contact angle (°)
2HEAF	1.16	13.0	16.126 @ 25°C	56 ± 0.9
2HEAPE	1.04	3.12	1333.2 @ 25 °C	51 ± 0.5
Commercial Lubricant	0.99	-	239.76 @ 40 °C*	27 ± 2.5

* Information supplied by the manufacturer. ** Computed from TGA results.

lubrication. In the work of Espinosa et al.²⁰, the viscosity for the ionic liquids were in the same order of the 2HEAPE value and extremely low coefficient of frictions and wear rates were attained.

Density values for all the studied lubricant fluids were very close from each other (Table 3). However, the PIL 2HEAF was the one with the highest density value and the commercial lubricant, the one with the lowest, being 2HEAPE the one with intermediate value. It is expected that longer anion chain in the protic ionic liquids produce the decrease of the density⁴¹. The values of density of the commercial lubricant are close to those found for vegetable oils⁴³.

Wettability determined from the contact angle measurements (Table 3), using a drop of lubricant fluid on the aluminum plate, indicated that commercial lubricant presented more interaction with the aluminum substrate because of its low contact angle^{44,45}. On the other hand, 2HEAF had the highest contact angle. It means that this liquid presented the lowest interaction with the substrate surface, while 2HEAPE presented an intermediate behavior. This behavior can be associated to the chain length of each molecule. However, the contact angle standard deviation for the substrate with protic ionic liquids suggested more uniformity than for the commercial lubricant, perhaps because the latter presented different chemical functions throughout the complete molecule. This behavior was also observed in the works of Espinosa et al.^{19,20}, whose studied ionic liquids, corresponding to secondary-amine based cations, had higher contact angles (~54°) than the one for the synthetic base oil

poly-alpha olefin (20.2°). These authors^{19,20} stated that the lowest contact angle could be related to the formation of an uniform lubricant layer that works out as wear protection. However, it is important to consider other contact and wettability parameters to elucidate the interaction between the metal substrates and the lubricant fluids. For example, Blanco et al.⁴⁶ associated lower surface tension values to higher wettability for non-polar molecules, for the same substrate (same surface energy); also, the polarity of the molecules could increase wettability and for some molecules on a substrate, the contact angle can variate with time. In other work, Kalin and Polajnar⁴⁷ conducted a study regarding the wettability parameters for different diamond-like carbon (DLC) surfaces and some liquids; according with the DLC energy surface, for the same liquid, there were important differences on contact angle and contact angle variation with time (spreading), and those different behaviors will be reflected in the tribological response.

3.2. Wear tests

Aluminum-quenched and tempered AISI 1050 steel contacts are of practical interest, for instance, in mechanical forming, field where the forming tools are generally made of steel. Figure 4 shows the results of the wear test for coefficient of friction. For all the studied lubricant fluids applied for the different contacts, there was initially a step of oxide breakage up to 0.3 m approximately (Figure 4). Then, all the lubricants trapped the displaced materials to

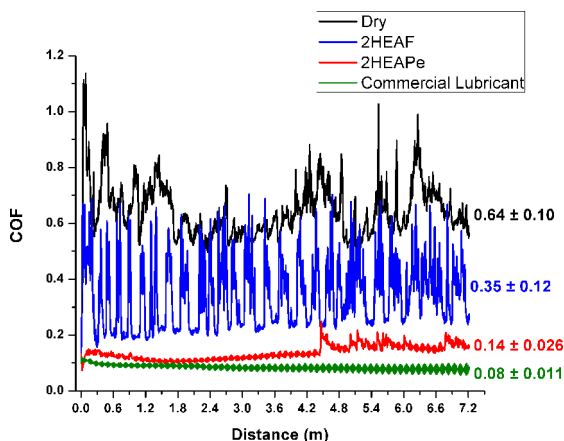


Figure 4. Coefficient of friction (COF) plots obtained from ball-on-plate wear test with average and standard values (left).

form a slurry that promoted the abrasion⁴⁸. The wear tests for aluminum-steel tribopair revealed the coefficient of friction decrease for the PILs with the increase of the alkyl carbon chain length in the anion: The lowest coefficient of friction corresponded to the contacts with application of the commercial lubricant, followed by PIL 2HEAPE.

The non-lubricated system as well as the 2HEAF-lubricated one developed important instability and oscillations in the coefficient of friction value (Figure 4), due to their poor lubricity. It also evidenced important mechanical and structural modifications on the sliding surfaces as the tests went by that yielded the different COF values along the experiments. The poor lubricity of the 2HEAF can be due to the need for longer anion chain length to support the normal load.

Aluminum-steel contacts lubricated with 2HEAPE and the commercial lubricant tended to be very stable and, regarding the average values, close to each other (Figure 4). However, significant oscillation of coefficient of friction started at 4.4 m for 2HEAPE (Figure 4). It revealed an important change on the surface after that distance. COF values reported for these fluids are characteristic of boundary lubrication. This lubrication regime has as mechanism the significant contact between the surfaces and the adsorption of a molecular layer that diminished the COF value⁴⁹. Standard deviation of the coefficient of friction values (Figure 4) revealed that, for the 2HEAPE and the commercial lubricant, there was the formation of a stable tribofilm adsorbed on the metal surface that avoided significant increases of the COF. COF Oscillation of the system lubricated with commercial lubricant augmented gradually with time. With the gradual increase of density of the materials in the lubricant fluid, abrasion and the oscillation of coefficient of friction also augmented (Figure 4).

Figures 5 and 6 allow discussing about the wear mechanisms. Aluminum-steel contacts lubricated with 2HEAPE and with commercial lubricant had mechanism governed by abrasion, since adhesion was almost totally suppressed in these systems, no material transferred to the ball and wear grooves formed,

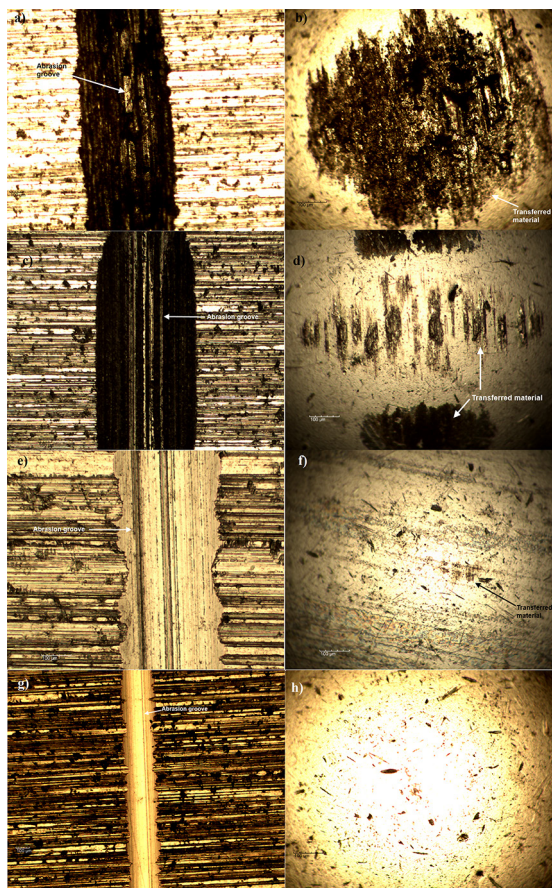


Figure 5. Images of the tracks on the aluminum plate and the AISI 105 steel balls after the wear tests: a) Dry test – track, b) Dry test – ball, c) 2HEAF – track, d) 2HEAF – ball, e) 2HEAPE – track, f) 2HEAPE – ball, g) Commercial lubricant – track, h) Commercial lubricant – ball.

as well as plastic deformation was promoted (Figures 5-e, 5-f and 6). This plastic deformation could have taken place due to the application of load through the alumina ball. For these lubricants, the predominant lubrication regime corresponded to boundary lubrication⁵⁰.

2HEAF system had a mixed abrasion-adhesion wear mechanism (Figure 5-c, 5-d), with an important contribution of plastic deformation that provoked the track widening observed on the profilometry results (Figure 6). In the dry condition, due to the amount of transferred material, the mechanism is considered as governed by adhesion^{42,51,52}, with formation of a third body that affected the track shape, as observed by profilometry (Figure 6).

The wear rates for 2HEAPE and the commercial lubricant (Figure 7) were in the same order of magnitude, despite the differences of the coefficient of friction. It revealed that the PIL 2HEAPE had a performance comparable to the commercial lubricant, maybe because of the PIL anion chain length and high viscosity. Meanwhile, for the 2HEAF the wear rate was similar to that obtained under the dry condition. The dry condition maintained as the highest wear promoting,

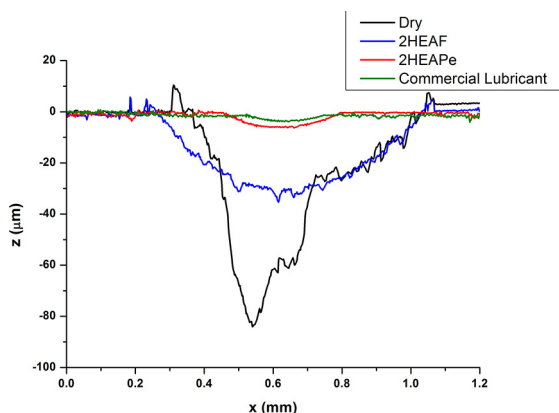


Figure 6. Track profiles obtained for each tested lubricant fluid as well as the dry condition.

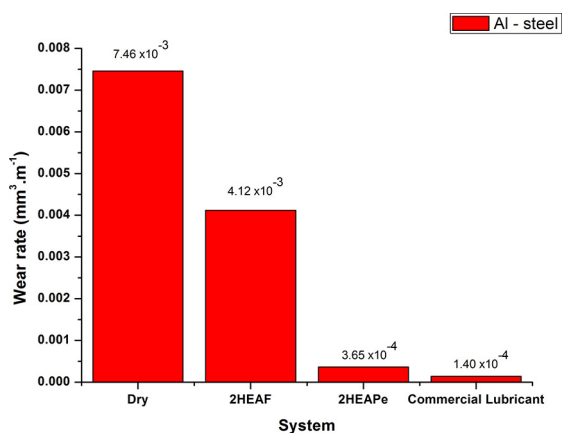


Figure 7. Wear rates and wear volume percentage vs. dry condition (in parentheses) obtained for PILs and commercial lubricant.

in agreement with the highest coefficient of friction. It all revealed the influence of the anion chain length for the PILs: 2HEAPE with longer anion chain (5 carbon atoms) reduced wear rate more significantly than 2HEAF with only one carbon in the anion chain. The longer the anion chain length, the less wear rate.

Since aluminum is a soft material, for the dry test condition, there was formation of a third body in form of debris on the bottom of the track. It produced the irregular-shaped grooves observed on the track profile (Figure 6) and avoided the formation of a semicircle-shaped track⁵³, similar to the ball indentation obtained for the tests using 2HEAPE and commercial lubricant. It indicates that, in the wear mechanism for 2HEAPE and the commercial lubricant there was not an important presence of debris as third body, which could have been forming part of the liquid (slurry).

Samples with dry condition and lubricated with 2HEAF presented close wear rate values (Figure 7), which made of 2HEAF the worst lubricant fluid of the studied ones, despite it reduced wear in 45.75% vs. dry condition. It means that there was the formation of an unstable tribofilm. Meanwhile,

2HEAPE reduced the wear rate in more than one order of magnitude and its performance was comparable to the commercial lubricant. It all evidenced that the structure of the PIL influenced on the lubrication behavior for the aluminum-steel contacts. The increase of the anion chain length, from one up to five carbons in this case, allowed the reduction of the coefficient of friction, as well as the wear rate. 2HEAPE and the commercial lubricant diminished wear in 95.1% and 98.23% vs. dry condition. It allows inferring that they had comparable performances but being the commercial lubricant slightly superior.

3.3. Chemical stability of lubricant fluids after the wear tests

According to the FTIR spectra after the wear tests (Figure 8-a), the PILs studied did not present any structural modification, since their respective spectra kept the same peaks observed for the neat PILs (Figure 2-b). It is environmentally desirable, since maintaining the integrity of the PILs would ensure their posterior recuperation, purification and reuse. However, tests of use, recuperation and reuse must be conducted in order to know the cyclability of these PILs for lubrication. In addition, the spectra (Figure 8-a) remark the oxidation stability of the PILs and points out that this stability is also present under the application of load. These results confirm what was found in the TGA (Figure 3) about the thermal stability of the PILs for the test conditions. Anyway, it is necessary to conduct tests with higher load values at higher temperatures to determine how these variables might affect the PILs structures.

On the other hand, the spectrum for the commercial lubricant (Figure 8-b) showed important structural changes, mainly induced by oxidation⁵⁴, represented by the growth of the bands related to oxygenated groups, such as OH⁻ ($3600 \text{ cm}^{-1} - 2200 \text{ cm}^{-1}$)³⁸. This behavior is due to the high oxidation susceptibility of the unsaturated C=C and C≡C groups, present inside the molecule^{54,55}. The oxidation was enhanced by the experimental conditions, such as air atmosphere, shear stress application to the fluid intrinsic of the wear test, and the localized increase of the temperature. The products of the oxidation reactions could yield in the loss of lubricity, that can be related to the oscillations observed in the coefficient of friction on Figure 8, since the iron of the ball can catalyze oxidation processes⁵⁶. These results are in agreement with the TGA (Figure 3), that showed a significant weight loss of the commercial lubricant up to 100 °C, not related to water evaporation but, as confirmed by the FTIR results after wear tests (Figure 8), with an important contribution of structure degradation starting at low temperatures (<100 °C), enhanced by the wear tests conditions. It means that it is not possible to submit the commercial lubricant to work at any temperature without promoting its degradation.

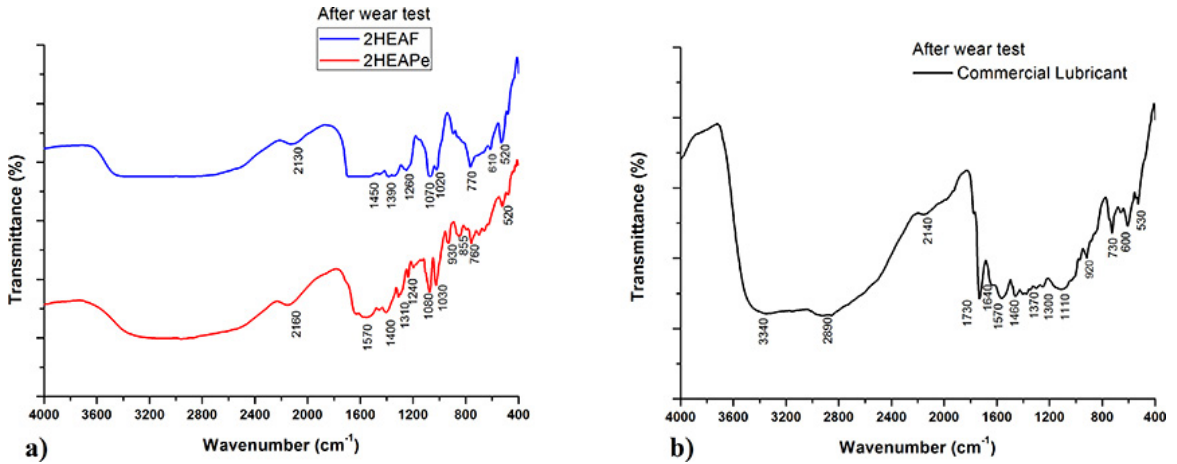


Figure 8. FTIR spectra for the lubricant fluids after the wear tests: a) PIL and b) commercial lubricant.

3.4. Bending under tension

Since all the studied lubricant fluids promoted wear reduction, they were tested under conditions that simulate a metal forming process to evaluate their feasibility for this application.

Bending under tension results yielded interesting information about the potential use of the PILs as lubricants for stamping process. Using 2HEAF, the strips broke (Figure 9-a). For the 2HEAF test, the cylindrical die presented marks due to the high adhesion between the metals (Figure 9-b). The formed 2HEAF film was not thick enough to avoid the contact between the die and the strip and the local contact pressure was extremely high. In the point of contact, microweldings formed and scratches and rupture were promoted²¹. These results match with those found in the aforementioned wear test conducted in a tribometer where adhesion, scar formation, material transfer and high wear rate were evidenced for the system that used 2HEAF as lubricant. Besides, wear tests showed high COF for 2HEAF, which can be related to friction shear stress²³ that could induce the fracture at an angle proximate to 45° (Figure 9-a)⁵⁷.

Tests with 2HEAPe and the commercial lubricant were successfully conducted until the end. Figure 10 shows the results of the measurements of both the actuation and back tension forces. During the first 0.5 s for the commercial lubricant and 1.5 s for the 2HEAPe system corresponded to a dead time when the computer started working for data acquisition and the force application. From then on, the forces were almost constant in all cases. Average values of drawing force using 2HEAPe and the commercial lubricant were of $2.3 \text{ kN} \pm 2.1 \times 10^{-2} \text{ kN}$ and $2.2 \text{ kN} \pm 4.7 \times 10^{-2} \text{ kN}$, respectively and, with the same order, the average back tension force values were $1.8 \text{ kN} \pm 2.4 \times 10^{-2} \text{ kN}$ and $1.8 \text{ kN} \pm 5.4 \times 10^{-2} \text{ kN}$. For practical interest, working either

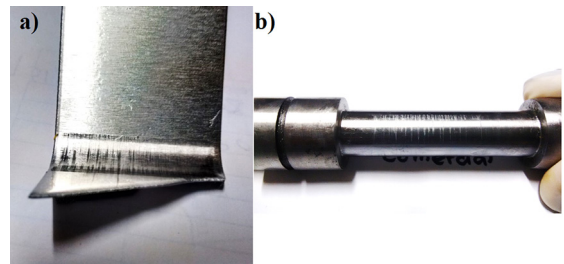


Figure 9. Images of a) the strip and b) the die after BUT tests using 2HEAF.

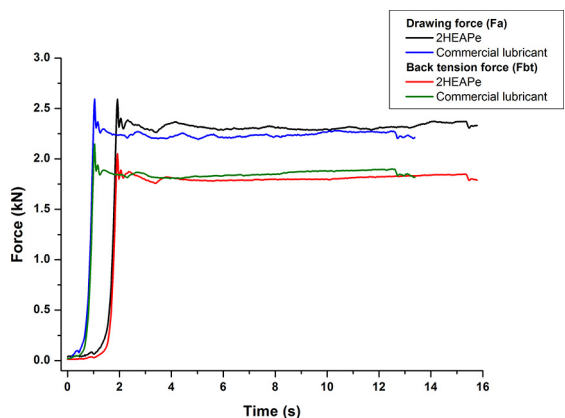


Figure 10. Actuation and back tension forces measurements for BUT test.

with the one or the other lubricant fluid in the stamping of aluminum 1100 with a steel tool would yield the same in terms of the force needed for holding the blank (Fbt) and the force needed by the punch (Fa), since the PIL 2HEAPe had as good performance as the commercial lubricant, regarding forces.

Torque measurements (Figure 11) revealed a response much more sensitive to variation of the friction coefficient

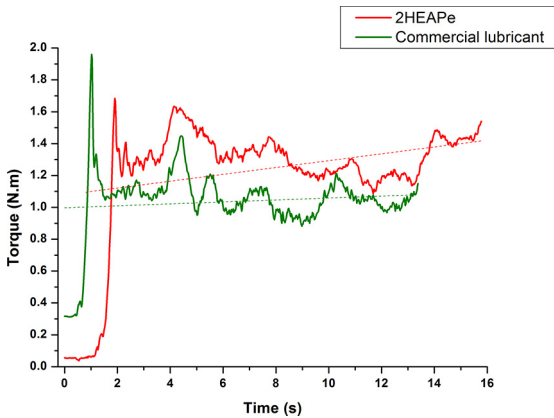


Figure 11. Torque measurements for BUT tests with dashed lines for the corresponding least squares fitting.

than the other forces⁵⁸. Average torque value for 2HEAPE is of $1.26 \text{ N.m} \pm 0.3 \text{ N.m}$ and $1.04 \text{ N.m} \pm 0.2 \text{ N.m}$, showing a similar performance between the tested lubricant fluids. However, linear fitting through least squares (dashed line in Figure 11) revealed slopes with values close to zero, being 0.022 N.m.s^{-1} for 2HEAPE and 0.006 N.m.s^{-1} for the commercial lubricant, with standard deviation of 0.002 N.m.s^{-1} for both cases. It means that the lubrication conditions in both cases were highly stable, as reported by other authors⁵⁸. Despite the small difference between the tested lubricant fluids, 2HEAPE presented a performance comparable to that presented by the commercial lubricant in the BUT test, which confirms its suitability for stamping processes.

Coefficient of friction (COF) was calculated using two equations. The first of them is reported in the work of Sniekers and Smits⁵⁹, based on the analysis of free force diagram of the strip contacting the cylindrical die, as follows:

$$COF = \frac{\frac{RoD}{R}}{\sqrt{F_a^2 + F_{bt}^2 + \left(\frac{RoD}{R}\right)^2}} \quad (1)$$

Where RoD corresponds to the torque measured in the cylindrical die, R is the die radius.

On the other hand, Andreasen et al.⁵⁸ took into account the average friction stress τ and the normal pressure p acting on the contact area between the strip and the die. These values can be calculated as follows:

$$\tau = \frac{2T}{\pi w R^2} \quad (2)$$

$$p = \frac{F_a + F_{bt}}{2wR} \quad (3)$$

Being T the torque value measured on the die, w the strip width and R corresponds to the die radius. The

relationship between Equations 2 and 3 corresponds to the COF (Equation 4)²²:

$$\mu = \frac{4T}{\pi R (F_a + F_{bt})} \quad (4)$$

The results of the former computations appear in Figure 12. The values found by Equation 1 are very close to those found by Equation 4, and the mean and the standard deviation values for each lubricant and equation are found in Table 4. From these results, it could be stated that the commercial lubricant was better lubricant than the 2HEAPE; however, it is not a guarantee for a good stamping process, where the control of friction is more important than minimizing or suppressing it^{21,22}. COF values (Table 4) showed a predominant mixed lubrication regime²³, since the COF values are less than 0.1 for both the studied lubricant fluids.

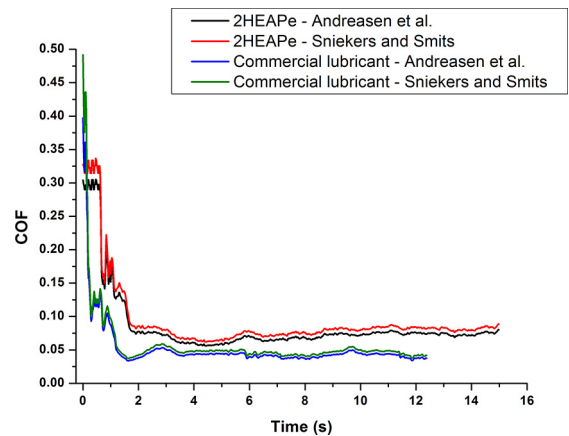


Figure 12. Coefficient of friction obtained by the Andreasen et al. and Sniekers and Smits equations.

The results obtained for 2HEAPE and for the commercial lubricant agree with those found in the ball-on-plate tests, where these lubricant fluids presented similar results regarding wear rates. However, with 2HEAPE displayed higher coefficient of friction for aluminum plate-steel ball contacts. Besides, using these liquids as lubricant fluids in BUT left no scars in the steel die, fact that also took place when tested with the steel ball (Figure 7).

The roughness values (Table 5) showed that no important modification on the strip surface took place, since values are almost the same considering average and standard deviations. However, the slight decrease in the roughness value caused by the use of the lubricant fluids revealed the presence of plastic deformation of the strip surface when slid on the dye surface. It is explained by the fact of the aluminum ductility; aluminum can deform plastically when in contact with a material with higher strength. It also suggested that the asperities and surface imperfections could have been in

Table 4. Average coefficient of friction values obtained using Equations 1 and 4.

Lubricant fluid	Eq. Snickers and Smits ⁵⁹	Eq. Andreassen et al. ⁵⁸
2HEAPe	0.084 ± 0.007	0.076 ± 0.006
Commercial lubricant	0.054 ± 0.002	0.049 ± 0.002

Table 5. Roughness (Ra) values for the strip.

Lubricant fluid	Roughness – Ra (µm)
As received	0.56 ± 0.022
2HEAPe	0.51 ± 0.038
Commercial lubricant	0.54 ± 0.040

contact using both 2HEAPe and the commercial lubricant, thus, it yielded a slight polishing of the aluminum surface.

The natural wear mechanism of both the studied contacts corresponded to adhesion, with formation of third body that also produced wear. The use of the tested lubricants reduced the adhesive wear, evidenced by the reduction of the transferred material from the metal to the ball, but promoted abrasion and plastic deformation.

System 2HEAPe yielded low coefficient of friction for both the tests, given the carboxylate, hydroxyl and protonated amino groups that promoted strong metal-organic surface interaction and, in consequence, boundary lubrication. Despite these structural characteristics are also present in 2HEAF PIL, this one has only one carbon atom inside the anion chain; meanwhile, 2HEAPe has five carbons in the anion chain. Also, this chain is completely linear, without branches. Hence, this 2HEAPe longer anion chain was capable of stress dissipation, which reduced the coefficient of friction, as well as heteroatoms, capable of interacting with the metals^{16,19,20,60-62}, which aided to maintain the tribofilm in place along the experiment. 2HEAF, the PIL with the simplest structure and one carbon in the anion chain, could not reduce adhesion and yielded coefficient of friction similar as in the absence of lubricant in the ball-on-plate test, reflected in the impossibility to deform the aluminum 1100 as expected for the BUT test and in the stress concentration that provoked the rupture. It was the opposite for the 2HEAPe whose longer anion chain avoided adhesion, developed a uniform film and successfully allowed the strip deformation.

Comparing PILs, the best lubrication performance corresponded to the PIL with the longest anion chain. The commercial lubricant is composed mainly by linear chains whose function is stress dissipation. Also there were ester and carboxylic groups inside, as observed in the structural characterization, and they promoted anchoring onto the surface^{16,19,20,60-62}. Those structures are in agreement with the wettability results, since the longer the linear chains the bigger the area where they can place and interact on the metallic surface and anticipate good lubrication performance²⁰. The presence of heteroatoms in the structure of the lubricant fluids was important to improve the lubrication, since these atoms could become anchoring points that enhance the film formation

and stability observed in the coefficient of friction plots and values obtained by ball-on-plate and BUT tests, as well as in the torque behavior in the interface strip-die in the BUT assay.

Another important consideration is viscosity. It is granted that a highly viscous fluid will be the best lubricant in most of the cases, to promote the formation of a thick fluid layer that separates the contacting surfaces. However, in this work, viscosity was not the only main parameter for the lubricant, since the most viscous fluid, i.e., 2HEAPe did not yield the minimum coefficient of friction; meanwhile the intermediate viscosity value belonging to the commercial lubricant induced the minimum coefficient of friction achieved, despite they both had similar wear rates. Hitherto, it is possible to state that, for a lubricant fluid, a compromise between the rheological properties, the structure and the interaction with the working materials are necessary. It explains why both 2HEAPe and the commercial lubricant allowed to conduct the BUT tests successfully and with similar results. Other authors also observed similar performances between imidazolium-based ionic liquids and conventional cutting fluids for micro-milling application³⁰. In addition, an advantage of using protic ionic liquids as simple as the ones used in this work is their biodegradability and low ecotoxicity, compared to oils and ionic liquids with more complex structures, which eases their disposal^{32,33}.

4. Conclusion

(1) The anion chain length was the determining factor in the performance of the 2-hydroxyethylammonium-based protic ionic liquids: the longer the anion chain the lower coefficient of friction, for the studied conditions. The PIL 2HEAPe promoted lower COF than 2HEAF.

(2) Despite the 2HEAPe promoted significant COF and worn volume decrease vs. the dry condition, the COF was higher than the commercial lubricant. However, they both presented a similar wear rate, which made 2HEAPe performance satisfactory in comparison with the commercial lubricant for aluminum-steel contacts.

(3) After the wear tests, the PILs structural integrity was not affected; meanwhile the commercial lubricant suffered oxidation that could harm its long-term lubrication performance and contribute to the corrosion of the metallic plate. The PIL 2HEAPe showed an important capability for wear reduction, similar to that of the commercial lubricant, with the advantage of possible future recovering for reuse, given its chemical stability.

(4) Bending under tension evidenced that 2HEAPE showed a performance similar to that of the commercial lubricant and displayed the PIL potential to be used in metal forming applications. Tribofilms with 2HEAPE and the commercial lubricant were stable and yielded similar torque and force values. With these fluids, COF typical of mixed lubrication regime was developed.

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6. References

- Santos D, Costa F, Franceschi E, Santos A, Dariva C, Mattedi S. Synthesis and physico-chemical properties of two protic ionic liquids based on stearate anion. *Fluid Phase Equilibria*. 2014;376:132-140.
- Alvarez VH, Mattedi S, Aznar M. Isobaric (vapor+liquid) equilibria of 1-ethyl-3-methylimidazolium ethylsulfate plus (propionaldehyde or valeraldehyde): Experimental data and prediction. *The Journal of Chemical Thermodynamics*. 2011;43(6):895-900.
- Alvarez VH, Mattedi S, Martin-Pastor M, Aznar M, Iglesias M. Thermophysical properties of binary mixtures of {ionic liquid 2-hydroxy ethylammonium acetate + (water, methanol, or ethanol)}. *The Journal of Chemical Thermodynamics*. 2011;43(7):997-1010.
- Álvarez VH, Dosil N, Gonzalez-Cabaleiro R, Mattedi S, Martin-Pastor M, Iglesias M, et al. Brønsted Ionic Liquids for Sustainable Processes: Synthesis and Physical Properties. *Journal of Chemical & Engineering Data*. 2010;55(2):625-632.
- Mattedi S, Carvalho PJ, Coutinho JAP, Alvarez VH, Iglesias M. High pressure CO₂ solubility in N-methyl-2-hydroxyethylammonium protic ionic liquids. *The Journal of Supercritical Fluids*. 2011;56(3):224-230.
- Ortega Vega MR, Kunst SR, Torres Da Silva JA, Mattedi S, Malfatti CdeF. Influence of anion chain length of protic ionic liquids on the corrosion resistance of API X70 steel. *Corrosion Engineering, Science and Technology*. 2015;50(7):547-558.
- de Souza RL, de Faria EL, Figueiredo RT, Freitas LdosS, Iglesias M, Mattedi S, et al. Protic ionic liquid as additive on lipase immobilization using silica sol-gel. *Enzyme and Microbial Technology*. 2013;52(3):141-150.
- Ye C, Liu W, Chen Y, Yu L. Room-temperature ionic liquids: a novel versatile lubricant. *Chemical Communications*. 2001;(21):2244-2245.
- Liu W, Ye C, Gong Q, Wang H, Wang P. Tribological Performance of Room-Temperature Ionic Liquids as Lubricant. *Tribology Letters*. 2002;13(2):81-85.
- Jiménez AE, Bermúdez MD. Ionic liquids as lubricants for steel-aluminum contacts at low and elevated temperatures. *Tribology Letters*. 2007;26(1):53-60.
- Zhou F, Liang Y, Liu W. Ionic liquid lubricants: designed chemistry for engineering applications. *Chemical Society Reviews*. 2009;38(9):2590-2599.
- Somers AE, Howlett PC, MacFarlane DR, Forsyth M. A Review of Ionic Liquid Lubricants. *Lubricants*. 2013;1(1):3-21.
- Minami I. Ionic Liquids in Tribology. *Molecules*. 2009;14(6):2286-2305.
- Barnhill WC, Qu J, Luo H, Meyer HM 3rd, Ma C, Chi M, et al. Phosphonium-Organophosphate Ionic Liquids as Lubricant Additives: Effects of Cation Structure on Physicochemical and Tribological Characteristics. *ACS Applied Materials & Interfaces*. 2014;6(24):22585-22593.
- Hernández Battez A, Bartolomé M, Blanco D, Viesca JL, Fernández-González A, González R. Phosphonium cation-based ionic liquids as neat lubricants: Physicochemical and tribological performance. *Tribology International*. 2016;95:118-131.
- Kondo H. Protic Ionic Liquids with Ammonium Salts as Lubricants for Magnetic Thin Film Media. *Tribology Letters*. 2008;31(3):211-218.
- Jiménez AE, Bermúdez MD. Ionic Liquids as Lubricants of Titanium-Steel Contact. *Tribology Letters*. 2009;33(2):111-126.
- Jiménez AE, Bermúdez MD. Ionic Liquids as Lubricants of Titanium-Steel Contact. Part 2: Friction, Wear and Surface Interactions at High Temperature. *Tribology Letters*. 2010;37(2):431-443.
- Espinosa T, Sanes J, Jiménez AE, Bermúdez MD. Surface interactions, corrosion processes and lubricating performance of protic and aprotic ionic liquids with OFHC copper. *Applied Surface Science*. 2013;273:578-597.
- Espinosa T, Sanes J, Jiménez AE, Bermúdez MD. Protic ammonium carboxylate ionic liquid lubricants of OFHC copper. *Wear*. 2013;303(1-2):495-509.
- Schedin E. Control of friction in sheet metal forming can result in more stable production. *Materials & Design*. 1993;14(2):127-129.
- Folle LF. *Estudo do coeficiente de atrito para processos de estampagem*. [Doctorate Thesis]. Porto Alegre: Universidade Federal do Rio Grande do Sul (UFRGS); 2012.
- Wang W, Zhao Y, Wang Z, Hua M, Wei X. A study on variable friction model in sheet metal forming with advanced high strength steels. *Tribology International*. 2016;93(Part A):17-28.
- Liu XQ, Zhou F, Liang YM, Liu WM. Tribological performance of phosphonium based ionic liquids for an aluminum-on-steel system and opinions on lubrication mechanism. *Wear*. 2006;261(10):1174-1179.
- Mu Z, Zhou F, Zhang S, Liang Y, Liu W. Effect of the functional groups in ionic liquid molecules on the friction and wear behavior of aluminum alloy in lubricated aluminum-on-steel contact. *Tribology International*. 2005;38(8):725-731.
- Iglesias P, Bermúdez MD, Carrión FJ, Martínez-Nicolás G. Friction and wear of aluminium-steel contacts lubricated with ordered fluids-neutral and ionic liquid crystals as oil additives. *Wear*. 2004;256(3-4):386-392.
- Jiménez AE, Bermúdez MD, Carrión FJ, Martínez-Nicolás G. Room temperature ionic liquids as lubricant additives in steel-aluminum contacts: Influence of sliding velocity, normal load and temperature. *Wear*. 2006;261(3-4):347-359.

28. Jiménez AE, Bermúdez MD. Imidazolium ionic liquids as additives of the synthetic ester propylene glycol dioleate in aluminium-steel lubrication. *Wear*. 2008;265(5-6):787-798.
29. Sharma AK, Tiwari AK, Dixit AR. Effects of Minimum Quantity Lubrication (MQL) in machining processes using conventional and nanofluid based cutting fluids: A comprehensive review. *Journal of Cleaner Production*. 2016;127:1-18.
30. Pham MQ, Yoon HS, Khare V, Ahn SH. Evaluation of ionic liquids as lubricants in micro milling - process capability and sustainability. *Journal of Cleaner Production*. 2014;76:167-173.
31. Álvarez VH, Mattedi S, Martín-Pastor M, Aznar M, Iglesias M. Synthesis and thermophysical properties of two new protic long-chain ionic liquids with the oleate anion. *Fluid Phase Equilibria*. 2010;299(1):42-50.
32. Peric B, Sierra J, Martí E, Cruañas R, Garau MA. A comparative study of the terrestrial ecotoxicity of selected protic and aprotic ionic liquids. *Chemosphere*. 2014;108:418-425.
33. Peric B, Martí E, Sierra J, Cruañas R, Iglesias M, Garau MA. Terrestrial ecotoxicity of short aliphatic protic ionic liquids. *Environmental Toxicology and Chemistry*. 2011;30(12):2802-2809.
34. Zhang QB, Hua YX. Corrosion inhibition of aluminum in hydrochloric acid solution by alkylimidazolium ionic liquids. *Materials Chemistry and Physics*. 2010;119(1-2):57-64.
35. Iglesias M, Torres A, Gonzalez-Olmos R, Salvatierra D. Effect of temperature on mixing thermodynamics of a new ionic liquid: {2-Hydroxy ethylammonium formate (2-HEAF)+short hydroxylic solvents}. *The Journal of Chemical Thermodynamics*. 2008;40(1):119-133.
36. Sicaire AG, Vian M, Fine F, Joffre F, Carré P, Tostain S, et al. Alternative Bio-Based Solvents for Extraction of Fat and Oils: Solubility Prediction, Global Yield, Extraction Kinetics, Chemical Composition and Cost of Manufacturing. *International Journal of Molecular Sciences*. 2015;16(4):8430-8453.
37. Bicak N. A new ionic liquid: 2-hydroxy ethylammonium formate. *Journal of Molecular Liquids*. 2005;116(1):15-18.
38. Stuart B. Organic Molecules. In: Stuart B. *Infrared Spectroscopy: Fundamentals and Applications*. Chichester: John Wiley & Sons; 2004. p. 71-93.
39. Solomons TWG, Fryhle CB. *Organic Chemistry*. 10th ed. Hoboken: John Wiley & Sons; 2011.
40. Kurnia KA, Wilfred CD, Murugesan T. Thermophysical properties of hydroxyl ammonium ionic liquids. *The Journal of Chemical Thermodynamics*. 2009;41(4):517-521.
41. Talavera-Prieto NMC, Ferreira AGM, Simões PN, Carvalho PJ, Mattedi S, Coutinho JAP. Thermophysical characterization of N-methyl-2-hydroxyethylammonium carboxylate ionic liquids. *The Journal of Chemical Thermodynamics*. 2014;68:221-234.
42. Stachowiak GW, Batchelor AW. *Engineering Tribology*. 3rd Ed. Oxford: Butterworth Heinemann; 2005. 832 p.
43. Freitas SVD, e Silva FA, Pastoriza-Gallego MJ, Piñeiro MM, Lima AS, Coutinho JAP. Measurement and Prediction of Densities of Vegetable Oils at Pressures up to 45 MPa. *Journal of Chemical & Engineering Data*. 2013;58(11):3046-3053.
44. Sefiane K, Skilling J, MacGillivray J. Contact line motion and dynamic wetting of nanofluid solutions. *Advances in Colloid and Interface Science*. 2008;138(2):101-120.
45. ManojKumar K, Ghosh A. Assessment of cooling-lubrication and wettability characteristics of nano-engineered sunflower oil as cutting fluid and its impact on SQCL grinding performance. *Journal of Materials Processing Technology*. 2016;237:55-64.
46. Blanco D, Viesca JL, Mallada MT, Ramajo B, González R, Battez AH. Wettability and corrosion of [NTf₂] anion-based ionic liquids on steel and PVD (TiN, CrN, ZrN) coatings. *Surface and Coatings Technology*. 2016;302:13-21.
47. Kalin M, Polajnar M. The correlation between the surface energy, the contact angle and the spreading parameter, and their relevance for the wetting behaviour of DLC with lubricating oils. *Tribology International*. 2013;66:225-233.
48. Fildes JM, Meyers SJ, Mulligan CP, Kilaparti R. Evaluation of the wear and abrasion resistance of hard coatings by ball-on-three-disk test methods—A case study. *Wear*. 2013;302(1-2):1040-1049.
49. Bhushan B. *Introduction to Tribology*. Hoboken: John Wiley & Sons; 2013. 738 p.
50. Menezes PL, Nosonovsky M, Ingole SP, Kailas SV, Lovell MR. *Tribology for Scientists and Engineers. From Basics to Advanced Concepts*. New York: Springer Science+Business Media; 2013.
51. Komanduri R, Shaw MC. Galling wear of materials at high speed sliding contact. *Wear*. 1975;33(2):283-292.
52. Bhushan B. *Principles and Applications of Tribology*. Hoboken: John Wiley & Sons; 1999. 1048 p.
53. Trezona RI, Hutchings IM. Three-body abrasive wear testing of soft materials. *Wear*. 1999;233-235:209-221.
54. Fox NJ, Stachowiak GW. Vegetable oil-based lubricants—A review of oxidation. *Tribology International*. 2007;40(7):1035-1046.
55. Adhvaryu A, Erhan SZ, Liu ZS, Perez JM. Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochemica Acta*. 2000;364(1-2):87-97.
56. Brook JHT, Matthews JB. Iron and copper as catalysts in the oxidation of hydrocarbon lubricating oils. *Discussions on the Faraday Society*. 1951;10(10):298-307.
57. Ma B, Liu ZG, Jiang Z, Wu X, Diao K, Wan M. Prediction of forming limit in DP590 steel sheet forming: An extended fracture criterion. *Materials & Design*. 2016;96:401-408.
58. Andreasen JL, Olsson DD, Chodnikiewicz K, Bay N. Bending Under Tension Test with Direct Friction Measurement. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture*. 2006;220(1):73-80.
59. Sniekers RJJM, Smits HAA. Experimental set-up and data processing of the radial strip-drawing friction test. *Journal of Materials Processing Technology*. 1997;66(1-3):216-223.

60. Cavalcante IM, Rocha NR de C, Maier ME, de Lima APD, Andrade Neto DM, de Brito DHA, et al. Synthesis and characterization of new esters of oleic acid and glycerol analogues as potential lubricants. *Industrial Crops and Products*. 2014;62:453-459.
61. Espinosa T, Jiménez M, Sanes J, Jiménez AE, Iglesias M, Bermúdez MD. Ultra-Low Friction with a Protic Ionic Liquid Boundary Film at the Water-Lubricated Sapphire-Stainless Steel Interface. *Tribology Letters*. 2014;53(1):1-9.
62. Kondo Y, Yagi S, Koyama T, Tsuboi R, Sasaki S. Lubricity and corrosiveness of ionic liquids for steel-on-steel sliding contacts. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*. 2012;226(11):991-1006.

Supplementary Material

The following online material is available for this article: Nuclear Magnetic Resonance (NMR).