Lubrication properties of the ionic liquid dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide

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Abstract

The ionic liquid (IL) dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide was tested as neat lubricant and as additive (at 1 and 4 wt%) in a polar oil (diester). Tribological tests were performed using a reciprocating configuration for 90 minutes at 30 and 70 N, 10 Hz, 4 mm stroke length, and at room temperature and 100 ºC. Wear volume and surface-IL interaction were determined by confocal microscopy, SEM and XPS. The main findings were: neat ionic liquid showed the best tribological behavior; the IL-containing mixtures had similar behavior than the base oil at the lower load, meanwhile the mixture with 4 wt% of IL outperformed the antiwear behavior of the neat base oil at the higher load; surface-IL chemical interaction was found mainly at 100 ºC.

Keywords: ionic liquid, additive, friction, wear, polar oil

1. Introduction

The use of ionic liquids (ILs) as potential both lubricant base stock and additive has been studied since 2001 [1-6]. These compounds have excellent properties such as high polarity and thermal stability, low melting point and flammability, and large liquid range, which are desirable for lubrication. Studies using ILs as neat lubricant has been made in different tribological pairs: steel –aluminum [7-8], steel-cast iron [9], steel-steel [10-17], and also for coated materials [18-22]. However, the current high costs of the ILs lead the research studies to using them preferably as lubricant additive.

The use of ILs as lubricant additives have as main drawback the fact of their low solubility in common non-polar oils (mineral oils and polyalphaolefins). Numerous works used ILs at low concentrations mixed in non-polar oils without additional additives [9, 19-28]. Meanwhile, few studies have reported the use of ILs as additives in non-polar fully-formulated oils [29-31]. All the above-mentioned studies showed the improvement in tribological behavior (friction and/or wear reduction properties) with the use of IL as lubricant additive.

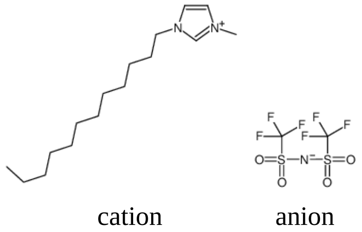
On the other hand, some works have used the ILs as lubricant additives in polar oils in order to avoid the above-mentioned low solubility in non-polar oils [32-48]. In these cases, improvement in tribological behavior were found, but the enhancement could be reduced due to the common polar nature of the base oil and the IL, which can lead to a competition between them for the metallic surface [48]. This effect is avoided when a mixture formed by a non-polar main component (base oil) and a polar secondary component (ester, IL, etc.) is used for lubricant purposes [49-50]. In order to gain deeper understanding in the use of ILs as neat lubricant and as lubricant additive in polar oils, this study deals with the use of an ionic liquid based on an imidazolium-derived cation and a [NTf$_2$]-derived anion.

2. Experimental details

2.1 Lubricant samples

The ionic liquid 1-dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide ([C12MIM][NTf$_2$]) was used as neat lubricant additive and as additive at concentration of 1 and 4 wt% in a biodegradable diester (polar oil), which has high hydrolytical and oxidative stability. The solubility of the [C12MIM][NTf$_2$] in this polar oil was determined by turbidimetry reaching at least 30 wt%. The ionic liquid (CAS Number: 404001-48-5, purity: 98 %) and the base oil were provided by Io-Li-Tec (Ionic Liquid Technologies GmbH) and CRODA S.A., respectively. Table 1 shows the main properties of the ionic liquid and the base oil.

Table 1. Material properties.

Ionic Liquid	
Chemical structure	**Empirical formulae**
	$C_{18}H_{31}F_6O_4N_3S_2$

Base Oil					
Name	**Oil type**	**Density 20ºC (g/cm^3)**	**Viscosity Index ASTM D 2270**	**Viscosity (mPa·s) ASTM D 445**	
				40ºC	**100ºC**
Priolube 1936 (coded as A2)	Petrochemical diester	0.91	139	26	5.3

The density and viscosity of the base oil, the ionic liquid and the mixtures were measured between 15 and 100 ºC by using a Stabinger Viscometer SVM3001. In addition, thermal analysis of the ionic liquid, the base oil and the mixtures were made under dry oxygen and nitrogen atmospheres (50 ml/min) in a thermogravimetric analyzer. The samples (10.8–20.5 mg) were used without any previous treatment and dynamic tests were performed from 25 to 600 °C at heating rate of 10 °C/min. The Mettler-Toledo

STARe version software was used for obtaining the onset temperature (T_{onset}), which is the intersection of the tangent of the decomposition curve (weight versus temperature) and the baseline weight.

The corrosion activity of the ionic liquid was measured during 20 days at both room temperature and 100 ºC on different surfaces (steel, CrN, ZrN and TiN) in a previous work [52]. Corrosion was only detected at room temperature on the steel, CrN and TiN surfaces, which was related to the presence of water as one of the impurities in the ionic liquid.

2.2. Friction and wear tests

The tribological tests were performed at least three times in a reciprocating ball-on-disk configuration (Bruker UMT-3) for 90 minutes, at 10 Hz and stroke length of 4 mm. The loads used were 30 and 70 N (corresponding to medium contact pressures of 1.37 and 1.82 GPa, respectively). 4 ml was used as lubricant sample volume for tests made with the base oil and the IL-containing mixtures and 25 μL for tests made with the neat IL. Tests were performed at both room temperature (RT) and 100 ºC. As upper specimen were used AISI 52100 chrome steel balls with diameter of 6.0 mm, roughness of Ra ≤ 0.05 µm and hardness of 58-66 HRC. On the other hand, as lower specimen were used AISI 52100 steel disks with the following properties: 3 mm thick, 10 mm diameter, roughness of Ra ≤ 0.02 μm, and hardness of 190-210 HV_{30}.

Coefficient of friction (COF) was recorded across the tests and a confocal microscope (Leica DCM 3D) was used for measuring wear volume (material losses below surface) on the disk's surface. Before and after tribological tests, and before wear volume measurements, the specimens were cleaned with heptane in an ultrasonic bath for 5 minutes, then rinsed in ethanol and dried in air.

2.3. Worn surface characterization

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used in order to study the wear mechanism and chemical interaction of the lubricant samples with the disk´s surface. X-Ray photoelectron spectroscopy was carried out with a SPECS spectrometer equipped with a Phoibos 150 hemispherical energy analyzer. Samples were excited with a monochromatic X-Ray source (1.5×1 mm^2; Al anode K_{α}=1486.7 eV) and medium area mode in the electromagnetic lenses was used. Peak shift due to charge effects was compensated when necessary considering the adventitious carbon peak at 284.6 eV.

3. Results and discussion

3.1. Density, viscosity and thermal characteristics of the lubricant samples

Density and viscosity of the neat samples (ionic liquid and base oil) and the mixtures are shown in Fig. 1. Viscosity values of the mixtures were similar to the ones of the base oil, which lead to conclude that the tribological behavior of the mixtures are close related to the chemical interaction of the ionic liquid with surface rather than their rheological properties. On the other hand, the viscosity of the ionic liquid is much more higher than that of the base oil and the mixtures at room temperature (RT) and that difference decreases sharply with temperature increase.

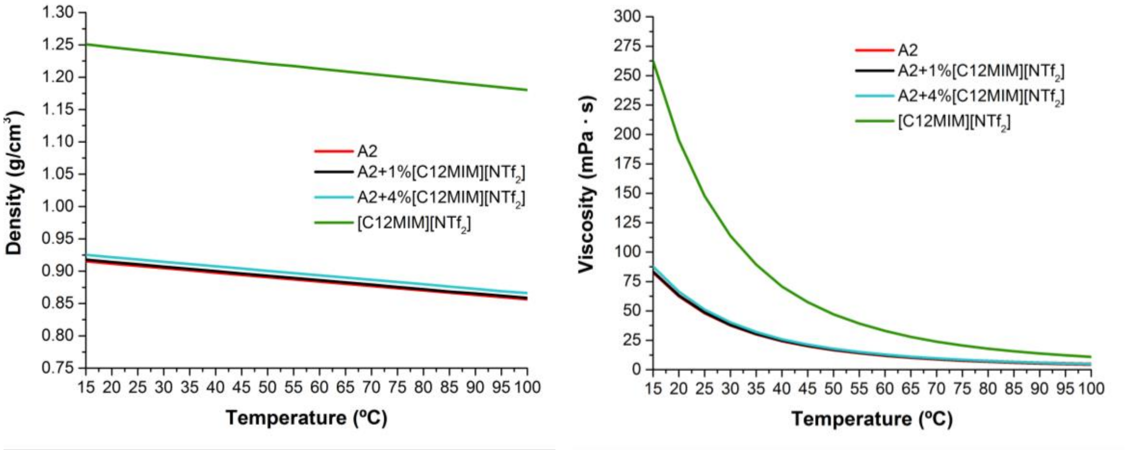


Fig. 1. Density and dynamic viscosity of the lubricant samples.

Fig. 2 shows the thermogravimetric curves of the lubricant samples under reactive (oxygen) and inert (nitrogen) atmospheres. All the lubricant samples showed an onset decomposition temperature above 240 and 300 ºC for reactive and inert atmospheres, respectively. The neat ionic liquid showed better thermal stability than the neat base oil and the mixtures; the slight mass loss above found in the ionic liquid sample under both atmospheres are related with the impurities present, including water. Both mixtures had a very similar thermal behavior irrespective the ionic liquid concentration but slightly better than the neat base oil.

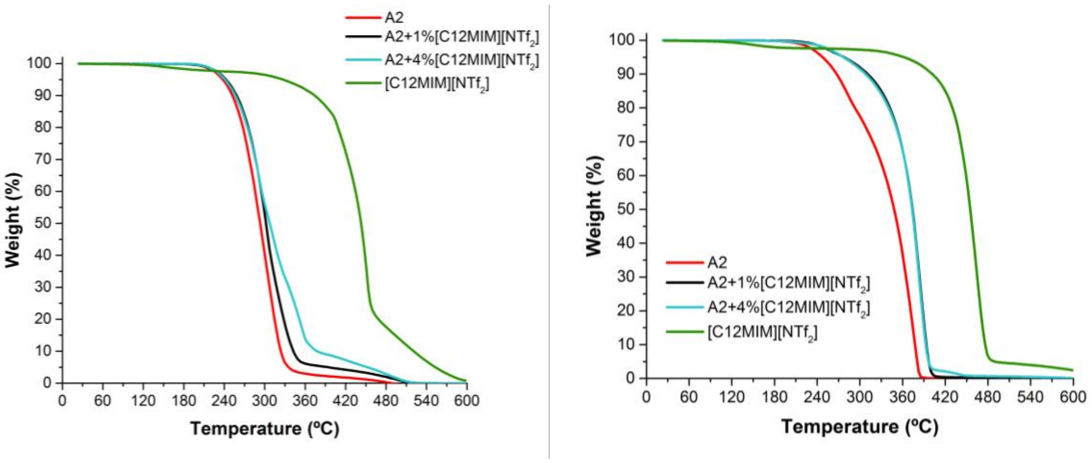


Fig. 2. Thermogravimetric analysis (TGA) of the lubricant samples under oxygen (left) and nitrogen (right) atmospheres.

3.2 Friction and wear tests

The friction results of the experiments showed that in general the use of the ionic liquid as additive hardly changed the coefficient of friction obtained with the neat base oil, Fig. 3. Although the neat base oil and mixtures exhibited similar friction values under both loads, these values increased with temperature raise, which can be related with viscosity decrease. The lubrication with neat ionic liquid resulted in the lowest friction values at both temperatures and loads.

Fig. 4 shows the evolution of the friction coefficient versus time of the most representative test (the nearest to the average friction value) of the three made for each lubricant sample. The neat ionic liquid not only showed the lowest average friction values but also had lower friction values than the ones of the other lubricant samples during the entire test duration. The mixture with the highest ionic liquid content (4 wt%) also displayed a slightly lower friction values than both the neat base oil and the mixture containing 1 wt% of ionic liquid under the harder test condition (100 ºC and 70 N). The increase in friction coefficient of the neat ionic liquid after 1800 s showed in Fig. 5b corresponds with one of the common shapes of friction-time curves described by P.J. Blau [53], which can be caused by several different phenomena.

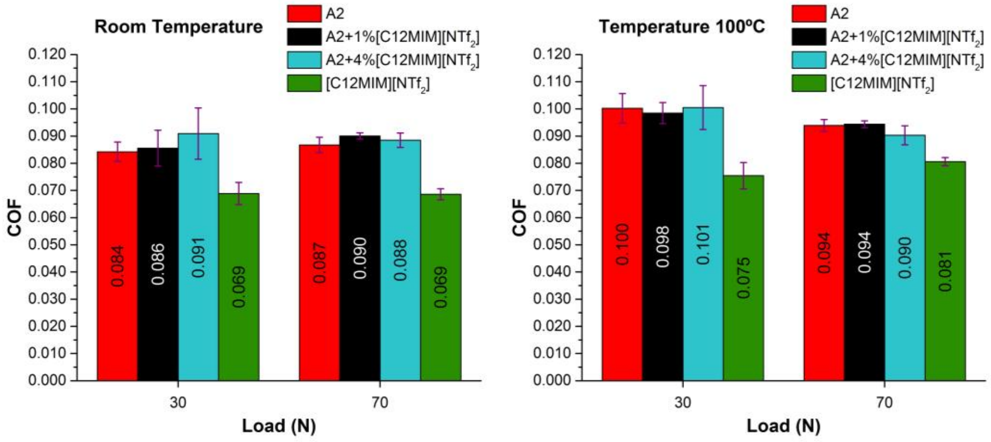


Fig. 3. Average coefficient of friction during tribological tests.

Regarding wear behavior of these lubricant samples, as expected wear increased with both load and temperature (Fig. 5). However, wear results showed more severe differences as a function of lubricant, load and temperature than the friction measurements. Under the milder test conditions of load and temperature (30 N and RT) the mixtures had similar wear behavior to the neat base oil, meanwhile the use of neat ionic liquid resulted in the lowest wear volume. At 100 ºC and 30 N-load, the mixtures improved slightly the antiwear behavior of the neat base oil, while the neat ionic liquid showed again the best antiwear results.

On the other hand, at 70 N-load and RT the mixtures, as well as the neat ionic liquid, reduced wear with regard to the neat base oil. However, only the mixture containing 4 wt% and the neat ionic liquid outperformed the neat base oil at 70 N-load and 100 ºC, meanwhile the mixture containing 1 wt% of ionic liquid had similar wear result than the base oil. According to friction results and the analysis of the wear scars, it can be assumed that tests were performed under mixed/boundary lubrication regimes.

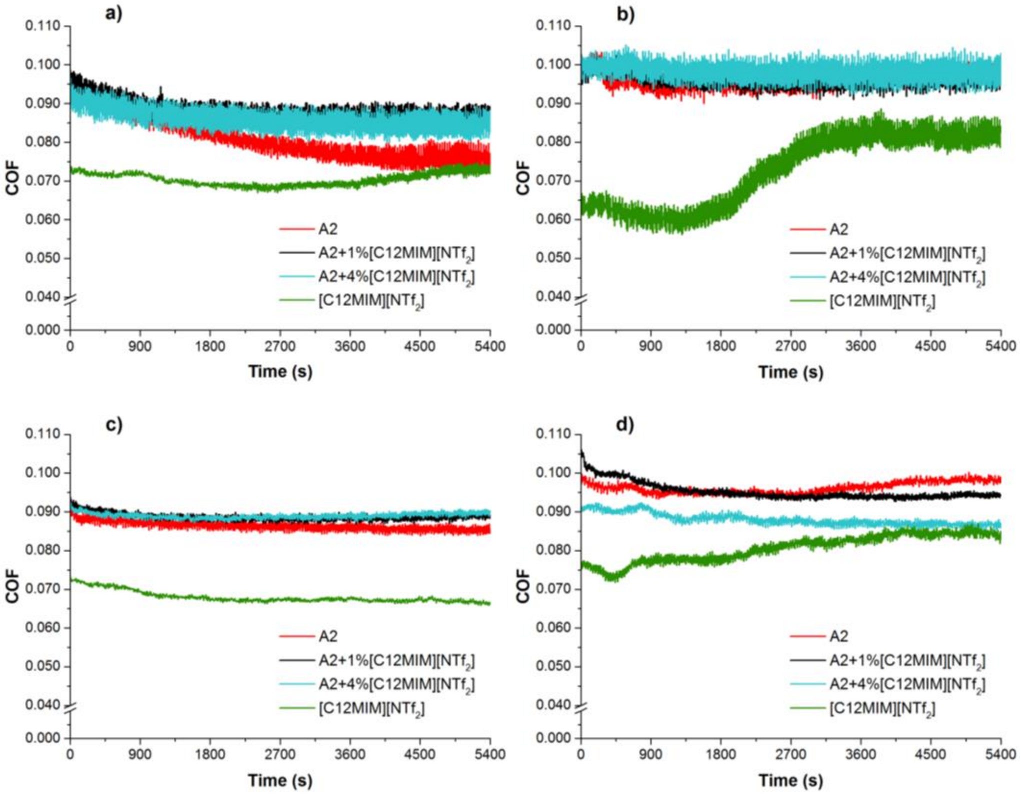


Fig. 4. Evolution of coefficient of friction with time for tests closest to the average COF values: a) RT and 30 N, b) 100 ºC and 30 N, c) RT and 70 N, d) 100 ºC and 70 N.

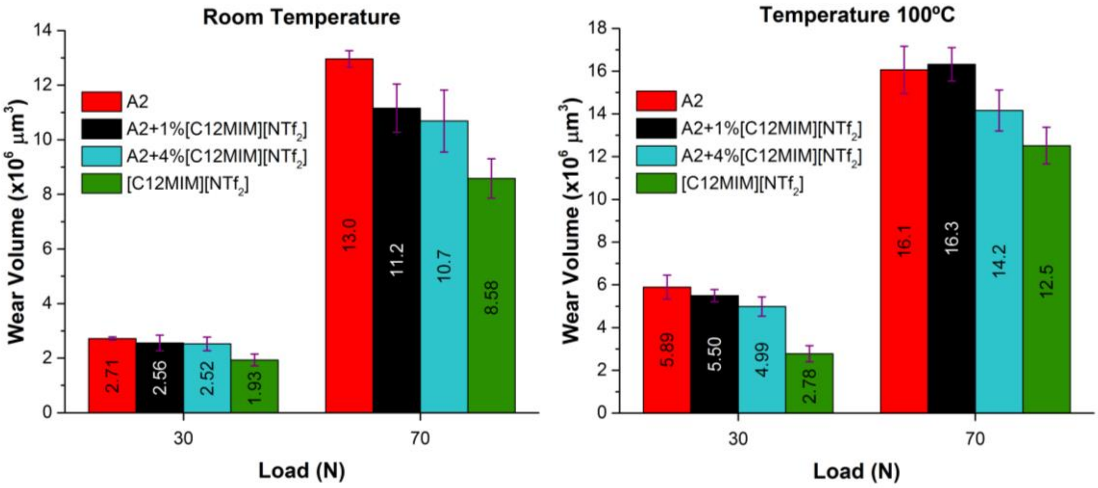
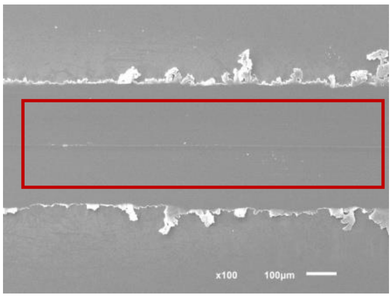
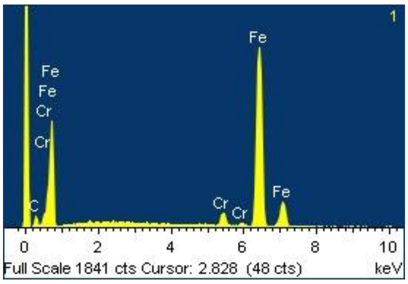
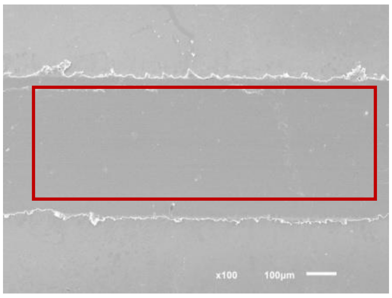
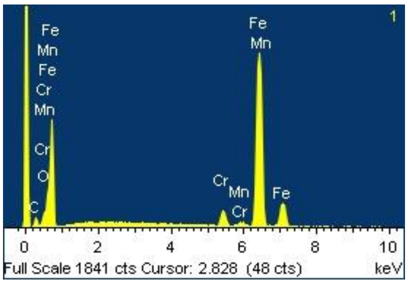
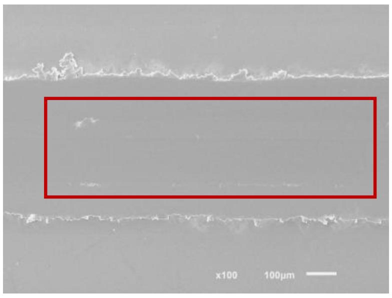
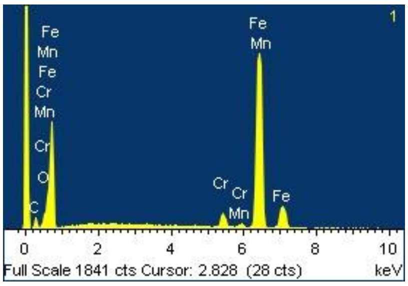


Fig. 5. Average wear volume after tribological tests.

3.3. Worn surface characterization

The worn surface on the disk was analysed by SEM and EDS after tribological tests. At room temperature and 30 N-load the wear scar obtained with the lubrication of the neat base oil (A2) showed a very smooth surface with evidence of plastic deformation at the edges of the wear scar (Fig. 6); however, material transfer was not detected between both specimens. The IL-containing mixtures also showed smooth wear scar with less plastic deformation. Tests lubricated with base oil or IL-containing mixtures showed adhesive wear. On the other hand, the worn surface from the test lubricated with neat IL presented grooves in the sliding direction, which are typical of abrasive wear. Despite the good anti-wear performance showed by the neat IL, the abrasive wear behavior could be related to the smaller amount of lubricant used in that test (25 µl), which hinders the evacuation of wear debris and provokes their entrapment in the contact, in comparison with tests lubricated with the neat base oil or the IL-containing mixtures (4 ml). On the other hand, the tests made at RT and 70 N-load (Fig. 7) exhibited the same wear mechanisms and bigger wear scar than the tests at RT and 30 N-load, but less plastic deformation was found at the edges of the wear scar. The EDS analysis showed that in all tests made at RT only the chemical elements from the steel were detected, Figs. 6-7.

A2		
A2 + 1 % [C12MIM][NTf$_2$]		
A2 + 4 % [C12MIM][NTf$_2$]		

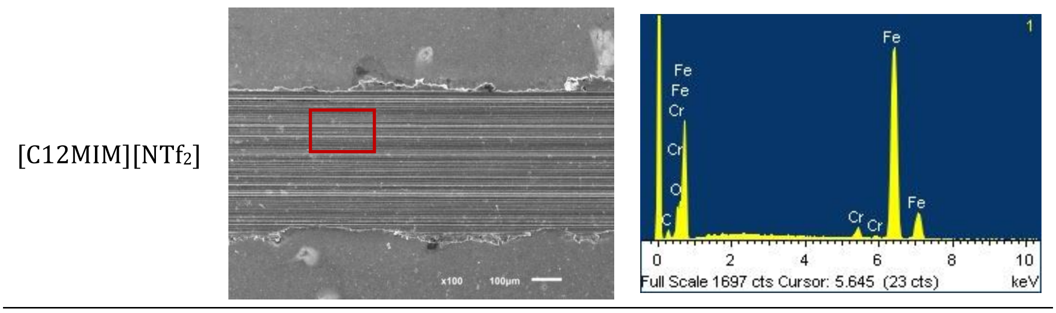


Fig. 6. SEM images and EDS (from marked zone) taken after tests made at 30 N and RT.

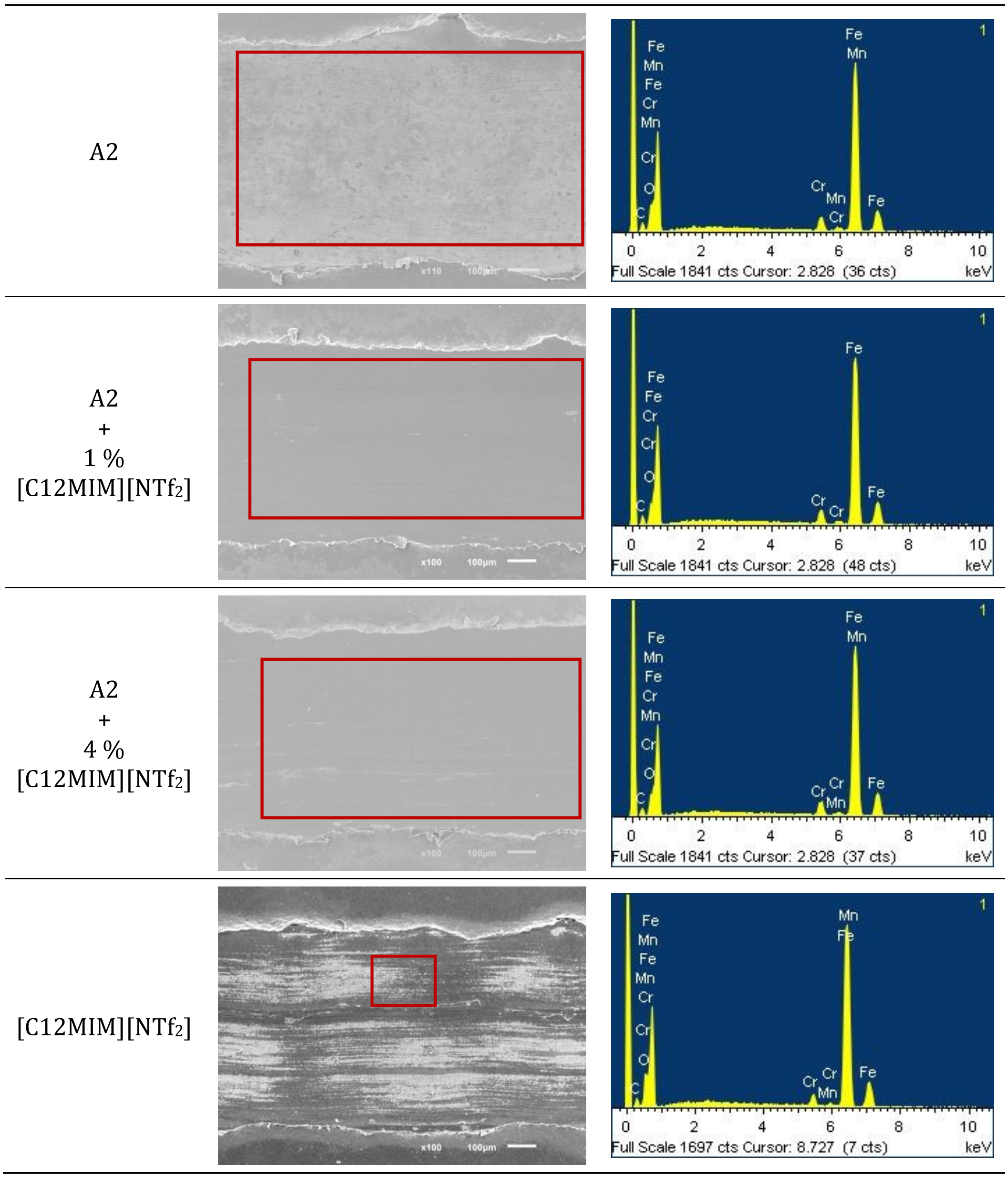


Fig. 7. SEM images and EDS (from marked zone) taken after tests made at 70 N and RT.

At the higher temperature (100 ºC), the wear results were clearly much more severe, even at the lower load (30 N), with also adhesive wear and plastic deformation at the edges of the wear scar for tests made with neat base oil and IL-containing mixtures, Fig. 8. Under this test condition (30 N and 100 ºC) the worn surface from the test lubricated with neat ionic liquid also showed abrasive wear. With regard to the chemical elements detected with EDS, only the elements present in the steel were found when the neat base oil and the mixtures were used as lubricant. However, sulphur was also detected on the worn surface when the neat ionic liquid was used in the lubrication.

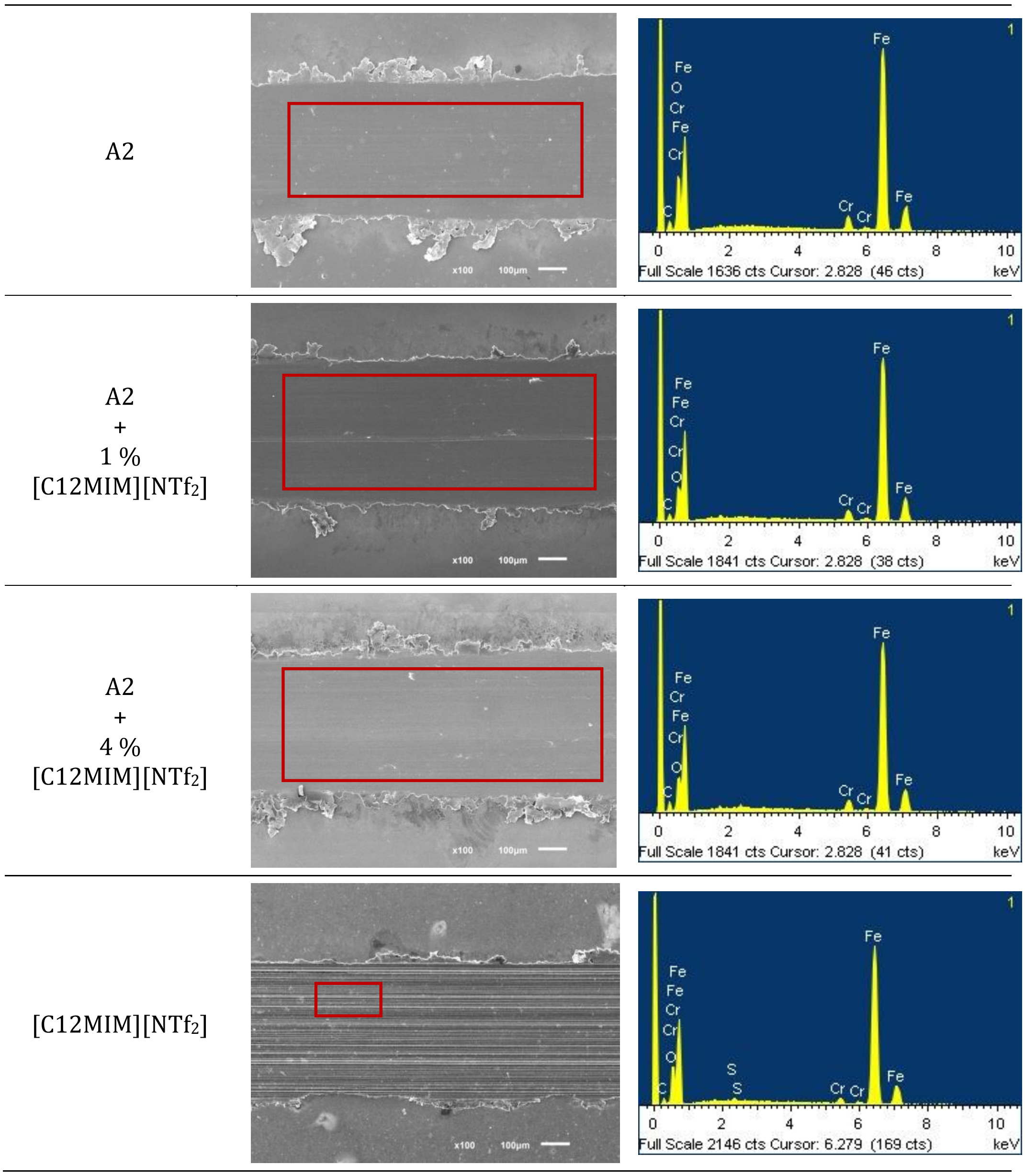


Fig. 8. SEM images and EDS (from marked zone) taken after tests made at 30 N and 100 ºC.

In addition, bigger wear scar and similar wear mechanisms to that found at 30 N were ascertained when the load of 70 N was used at 100 ºC, Fig. 9. In this case, sulphur was also encountered on the worn surface tested with neat IL during the EDS analysis, while on the surface lubricated with the neat base oil and the IL-containing mixtures only the chemical elements from the steel were detected.

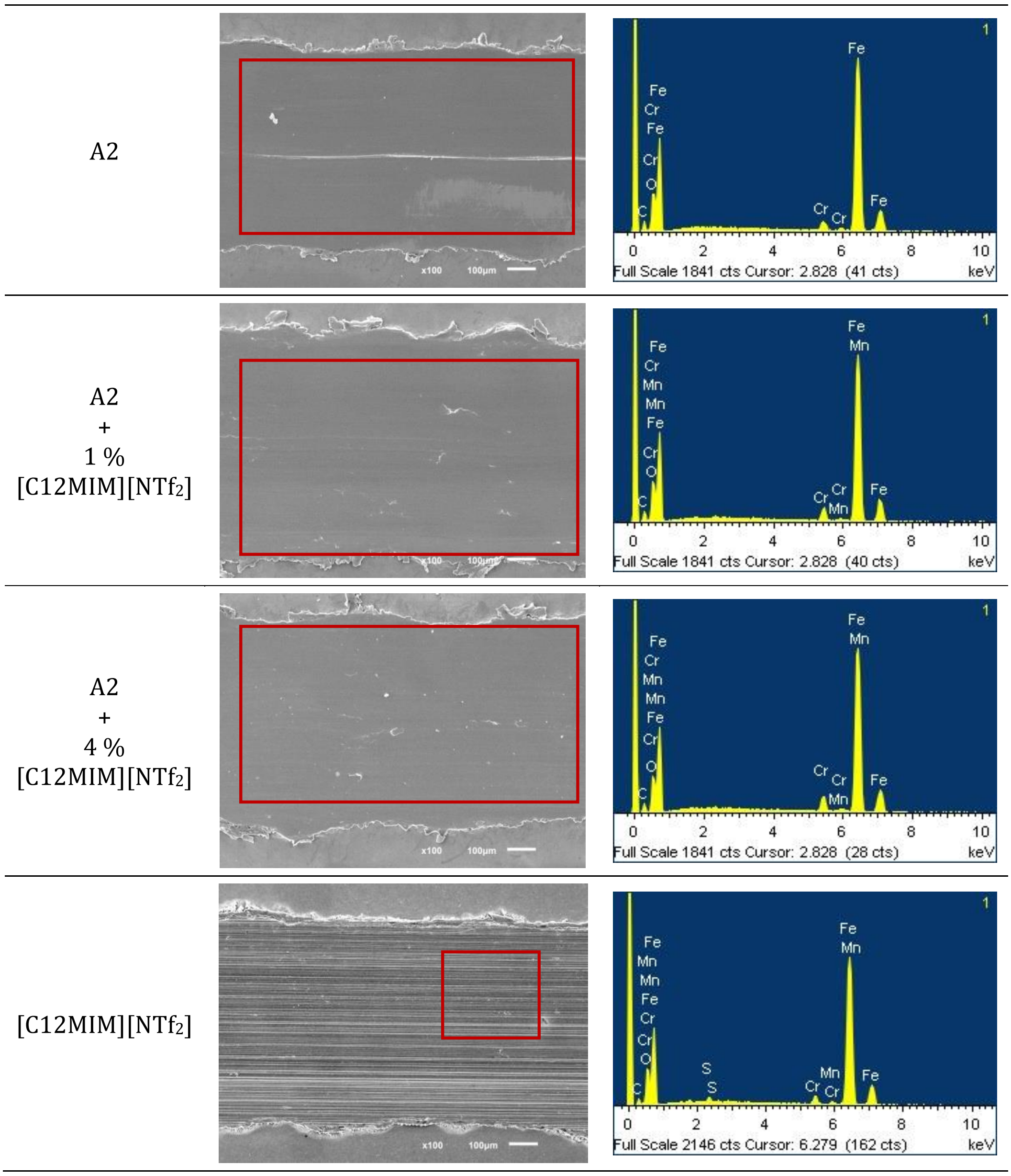


Fig. 9. SEM images and EDS (from marked zone) taken after tests made at 70 N and 100 ºC.

The XPS analysis of the worn surface revealed that there are no differences in the chemical states of iron among different samples at room temperature, regardless of the load or lubricant. Three different peaks could be found, a first one around 707.5 eV, fitted with a Gaussian-lorentzian 70:30 product modified by an exponential blend with k=0.65 which can be assigned to Fe^0; a second one at 710.8 eV fitted with a Gaussian-lorentzian 70:30 product modified by an exponential blend with k=1.5 assignable to Fe(III) and a third one around 712.8 eV fitted with a Gaussian-lorentzian 70:30 product assumed to be iron oxihydroxydes (FeOOH). The assignations and the selection of curve shapes were done according to the research of Mangolini [54] and Mayer [55].

For tests made at RT, the Fe(0):Fe(III):FeOOH ratio keeps at 35:50:15 without significant differences (Table 2). However, the same analysis carried out for the samples assayed at 100 ºC revealed a higher Fe(III)/FeOOH ratio for both samples with neat ionic liquid, what can be correlated with the better wear behavior of these samples compared to the other lubricant samples at the same temperature [29]. However, this ratio might be influenced by the presence of other chemical species. In fact, there is an apparent contradiction regarding the wear behavior between the Fe(III)/FeOOH ratio of the neat IL at RT and 100 ºC, which is explained by the presence of iron fluorides at higher temperatures which are not present at room temperature.

Table 2. Fe2p3/2 band analysis of XPS spectra.

Load	**A2**	**4% [C12MIM][NTf$_2$]**	**[C12MIM][NTf$_2$]**
Room temperature			
30 N	707.5 eV (37%) 710.8 eV (50%) 712.7 eV (13%)	707.4 eV (37%) 710.8 eV (50%) 712.7 eV (13%)	707.4 eV (37%) 710.8 eV (50%) 712.7 eV (13%)
70 N	707.5 eV (33%) 710.9 eV (54%) 712.9 eV (13%)	707.5 eV (36%) 710.8 eV (52%) 712.9 eV (12%)	707.5 eV (35%) 710.9 eV (53%) 712.9 eV (12%)
100 ºC			
30 N	707.5 eV (33%) 710.8 eV (54%) 712.9 eV (13%)	707.5 eV (29%) 710.9 eV (55%) 712.8 eV (16%)	707.5 eV (25%) 710.9 eV (62%) 712.8 eV (14%)
70 N	707.6 eV (32%) 710.8 eV (54%) 712.8 eV (13%)	707.5 eV (35%) 710.8 eV (51%) 712.7 eV (14%)	707.6 eV (20%) 711.0 eV (66%) 712.9 eV (14%)

In addition, fluorine was only analyzed in the IL-containing samples because the base oil does not contain that element. Fig. 10 shows the F/Fe ratio for both the mixture with the highest IL concentration and the neat IL samples. It seems clear that the interaction between iron and fluorine is mostly negligible at the lower load, whereas it becomes higher only for the neat IL sample as the load increases. These results confirm that higher load, temperature and/or IL concentration are key points for the chemical interaction of the ionic liquid with surface, contributing to tribofilm formation and both friction and wear reduction. Furthermore, the extremely low value of F/Fe ratio obtained at 30 N and RT for both lubricant samples means that the amount of fluorine in this case is not relevant. However, this F/Fe ratio becomes huge at 70 N with neat IL (especially at 100 ºC), indicating chemical interaction between the metal surface and the anion of the ionic liquid. Besides, it is interesting to state that at room temperature fluorine was detected as a single peak (between 688.9 eV and 689.5 eV) assignable to NTf_2 on the surface [56] regardless of the load or lubricant sample. In addition, both fluorine-containing samples showed two peaks at 100 ºC: a first one around 689 eV and a second one near 685 eV (Table 3). It is obvious that the higher one comes from NTf_2 on the surface, but the position of the lower one is consistent with the existence of iron fluorides according to the research of Kasrai [57].

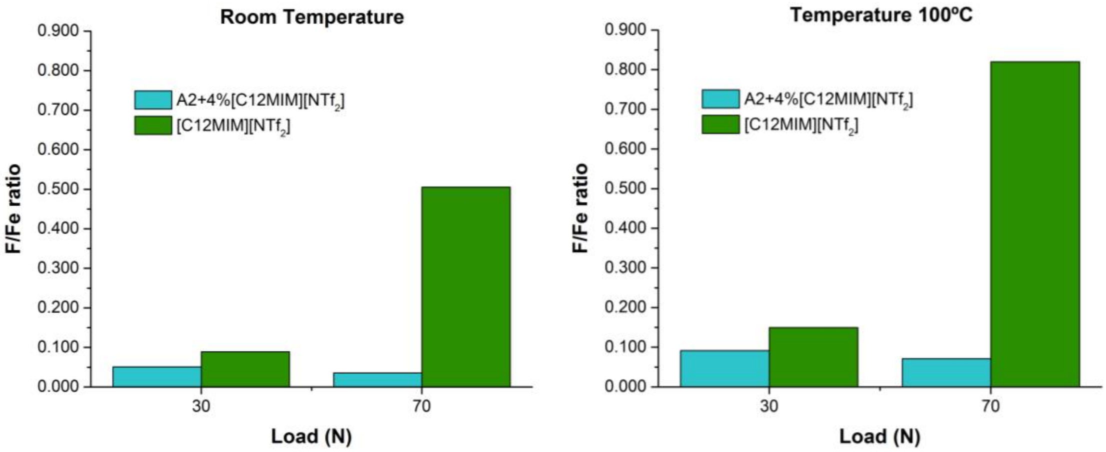


Fig. 10. F1s / Fe2p3/2 area ratio for XPS analysis.

Table 3. Position and area percentage of the F1s peak in XPS analysis.

Load	**4% [C12MIM][NTf2]**	**[C12MIM][NTf2]**
Room temperature		
30 N	689.1 eV	689.2 eV
70 N	688.9 eV	689.3 eV
Temperature 100 ºC		
30 N	689.3 eV (45%)	689.0 eV (60%)
	685.2 eV (53%)	685.0 eV (40%)
70 N	689.3 eV (55%)	689.3 eV (90%)
	684.9 eV (45%)	685.0 eV (10%)

4. Conclusions

The use of an $[NTf_2]$ anion-based IL as neat lubricant and as additive to a polar oil at two concentrations (1 and 4 wt%) was studied in this work. From the results obtained the following conclusions can be drawn:

- The neat base oil and the two mixtures used showed similar friction values probably due to similar rheological properties. Meanwhile, the neat ionic liquid showed clear lower friction values mainly influenced by its chemical interaction with surface.

- The neat ionic liquid showed the best antiwear behavior at 30 N-load and at both temperatures (RT and 100 ºC). On the contrary, the neat base oil and the IL-containing mixtures had similar antiwear behavior.
- At the higher load (70 N) both the neat ionic liquid and the mixture containing 4 wt% of IL showed in general better antiwear properties with regard the neat base oil, but the neat IL continued showing the best antiwear behavior.
- The SEM analysis of the worn surface showed adhesive wear in the tests lubricated with the neat base oil and the IL-containing mixtures, meanwhile abrasive wear was found in the tests lubricated with the neat IL. The EDS analysis only detected the elements present in the steel, except in the tests with neat ionic liquid at 100 ºC, where sulphur was also detected.
- The XPS analysis exhibited a slight chemical interaction between the ionic liquid and the surface (presence of the non-reacted [NTf_2]) during tests made at room temperature. On the contrary, assays at higher temperature also revealed chemical interaction between the fluorine from NTf_2 and the metal surface. The wear behavior is related both to the Fe(III)/FeOOH ratio and to the presence of iron fluorides.

Acknowledgments

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Lubrication properties of the ionic liquid dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide

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Abstract

The ionic liquid (IL) dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide was tested as neat lubricant and as additive (at 1 and 4 wt%) in a polar oil (diester). Tribological tests were performed using a reciprocating configuration for 90 minutes at 30 and 70 N, 10 Hz, 4 mm stroke length, and at room temperature and 100 ºC. Wear volume and surface-IL interaction were determined by confocal microscopy, SEM and XPS. The main findings were: neat ionic liquid showed the best tribological behavior; the IL-containing mixtures had similar behavior than the base oil at the lower load, meanwhile the mixture with 4 wt% of IL outperformed the antiwear behavior of the neat base oil at the higher load; surface-IL chemical interaction was found mainly at 100 ºC.

Keywords: ionic liquid, additive, friction, wear, polar oil

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1. Introduction

The use of ionic liquids (ILs) as potential both lubricant base stock and additive has been studied since 2001 [1-6]. These compounds have excellent properties such as high polarity and thermal stability, low melting point and flammability, and large liquid range, which are desirable for lubrication. Studies using ILs as neat lubricant has been made in different tribological pairs: steel –aluminum [7-8], steel-cast iron [9], steel-steel [10-17], and also for coated materials [18-22]. However, the current high costs of the ILs lead the research studies to using them preferably as lubricant additive.

The use of ILs as lubricant additives have as main drawback the fact of their low solubility in common non-polar oils (mineral oils and polyalphaolefins). Numerous works used ILs at low concentrations mixed in non-polar oils without additional additives [9, 19-28]. Meanwhile, few studies have reported the use of ILs as additives in non-polar fully-formulated oils [29-31]. All the above-mentioned studies showed the improvement in tribological behavior (friction and/or wear reduction properties) with the use of IL as lubricant additive.

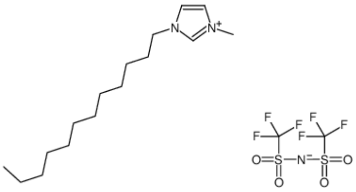
On the other hand, some works have used the ILs as lubricant additives in polar oils in order to avoid the above-mentioned low solubility in non-polar oils [32-48]. In these cases, improvement in tribological behavior were found, but the enhancement could be reduced due to the common polar nature of the base oil and the IL, which can lead to a competition between them for the metallic surface [48]. This effect is avoided when a mixture formed by a non-polar main component (base oil) and a polar secondary component (ester, IL, etc.) is used for lubricant purposes [49-50]. In order to gain deeper understanding in the use of ILs as neat lubricant and as lubricant additive in polar oils, this study deals with the use of an ionic liquid based on an imidazolium-derived cation and a [NTf_2]-derived anion.

2. Experimental details

2.1 Lubricant samples

The ionic liquid 1-dodecyl-3 methylimidazolium bis(trifluoromethylsulfonyl)imide ([C12MIM][NTf_2]) was used as neat lubricant additive and as additive at concentration of 1 and 4 wt% in a biodegradable diester (polar oil), which has high hydrolytical and oxidative stability. The solubility of the [C12MIM][NTf_2] in this polar oil was determined by turbidimetry reaching at least 30 wt%. The ionic liquid (CAS Number: 404001-48-5, purity: 98 %) and the base oil were provided by Io-Li-Tec (Ionic Liquid Technologies GmbH) and CRODA S.A., respectively. Table 1 shows the main properties of the ionic liquid and the base oil.

Table 1. Material properties.

Ionic Liquid	
Chemical structure	**Empirical formulae**
 cation anion	$C_{18}H_{31}F_6O_4N_3S_2$

Base Oil					
Name	**Oil type**	**Density 20ºC (g/cm^3)**	**Viscosity Index ASTM D 2270**	**Viscosity (mPa·s) ASTM D 445**	
				40ºC	**100ºC**
Priolube 1936 (coded as A2)	Petrochemical diester	0.91	139	26	5.3

The density and viscosity of the base oil, the ionic liquid and the mixtures were measured between 15 and 100 ºC by using a Stabinger Viscometer SVM3001. In addition, thermal analysis of the ionic liquid, the base oil and the mixtures were made under dry oxygen and nitrogen atmospheres (50 ml/min) in a thermogravimetric analyzer. The samples (10.8–20.5 mg) were used without any previous treatment and dynamic tests were performed from 25 to 600 °C at heating rate of 10 °C/min. The Mettler-Toledo

STARe version software was used for obtaining the onset temperature (T_{onset}), which is the intersection of the tangent of the decomposition curve (weight versus temperature) and the baseline weight.

The corrosion activity of the ionic liquid was measured during 20 days at both room temperature and 100 ºC on different surfaces (steel, CrN, ZrN and TiN) in a previous work [52]. Corrosion was only detected at room temperature on the steel, CrN and TiN surfaces, which was related to the presence of water as one of the impurities in the ionic liquid.

2.2. Friction and wear tests

The tribological tests were performed at least three times in a reciprocating ball-on-disk configuration (Bruker UMT-3) for 90 minutes, at 10 Hz and stroke length of 4 mm. The loads used were 30 and 70 N (corresponding to medium contact pressures of 1.37 and 1.82 GPa, respectively). 4 ml was used as lubricant sample volume for tests made with the base oil and the IL-containing mixtures and 25 μL for tests made with the neat IL. Tests were performed at both room temperature (RT) and 100 ºC. As upper specimen were used AISI 52100 chrome steel balls with diameter of 6.0 mm, roughness of Ra ≤ 0.05 µm and hardness of 58-66 HRC. On the other hand, as lower specimen were used AISI 52100 steel disks with the following properties: 3 mm thick, 10 mm diameter, roughness of Ra ≤ 0.02 µm, and hardness of 190-210 HV_{30}.

Coefficient of friction (COF) was recorded across the tests and a confocal microscope (Leica DCM 3D) was used for measuring wear volume (material losses below surface) on the disk's surface. Before and after tribological tests, and before wear volume measurements, the specimens were cleaned with heptane in an ultrasonic bath for 5 minutes, then rinsed in ethanol and dried in air.

2.3. Worn surface characterization

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used in order to study the wear mechanism and chemical interaction of the lubricant samples with the disk´s surface. X-Ray photoelectron spectroscopy was carried out with a SPECS spectrometer equipped with a Phoibos 150 hemispherical energy analyzer. Samples were excited with a monochromatic X-Ray source (1.5×1 mm^2; Al anode K_α=1486.7 eV) and medium area mode in the electromagnetic lenses was used. Peak shift due to charge effects was compensated when necessary considering the adventitious carbon peak at 284.6 eV.

3. Results and discussion

3.1. Density, viscosity and thermal characteristics of the lubricant samples

Density and viscosity of the neat samples (ionic liquid and base oil) and the mixtures are shown in Fig. 1. Viscosity values of the mixtures were similar to the ones of the base oil, which lead to conclude that the tribological behavior of the mixtures are close related to the chemical interaction of the ionic liquid with surface rather than their rheological properties. On the other hand, the viscosity of the ionic liquid is much more higher than that of the base oil and the mixtures at room temperature (RT) and that difference decreases sharply with temperature increase.

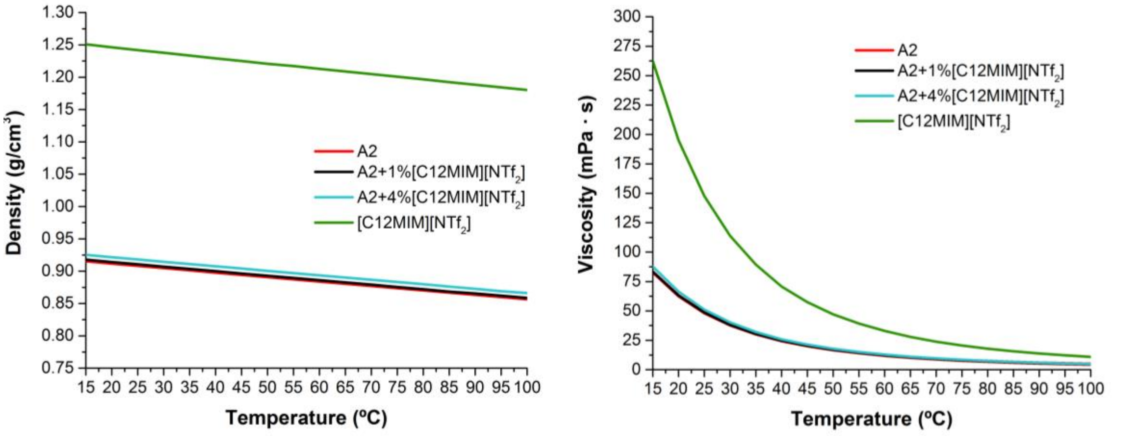


Fig. 1. Density and dynamic viscosity of the lubricant samples.

Fig. 2 shows the thermogravimetric curves of the lubricant samples under reactive (oxygen) and inert (nitrogen) atmospheres. All the lubricant samples showed an onset decomposition temperature above 240 and 300 ºC for reactive and inert atmospheres, respectively. The neat ionic liquid showed better thermal stability than the neat base oil and the mixtures; the slight mass loss above found in the ionic liquid sample under both atmospheres are related with the impurities present, including water. Both mixtures had a very similar thermal behavior irrespective the ionic liquid concentration but slightly better than the neat base oil.

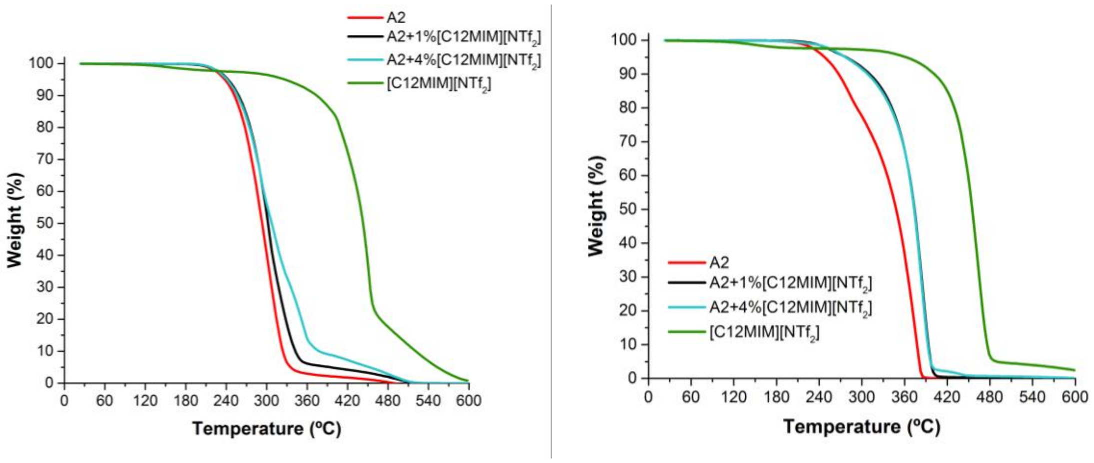


Fig. 2. Thermogravimetric analysis (TGA) of the lubricant samples under oxygen (left) and nitrogen (right) atmospheres.

3.2 Friction and wear tests

The friction results of the experiments showed that in general the use of the ionic liquid as additive hardly changed the coefficient of friction obtained with the neat base oil, Fig. 3. Although the neat base oil and mixtures exhibited similar friction values under both loads, these values increased with temperature raise, which can be related with viscosity decrease. The lubrication with neat ionic liquid resulted in the lowest friction values at both temperatures and loads.

Fig. 4 shows the evolution of the friction coefficient versus time of the most representative test (the nearest to the average friction value) of the three made for each lubricant sample. The neat ionic liquid not only showed the lowest average friction values but also had lower friction values than the ones of the other lubricant samples during the entire test duration. The mixture with the highest ionic liquid content (4 wt%) also displayed a slightly lower friction values than both the neat base oil and the mixture containing 1 wt% of ionic liquid under the harder test condition (100 ºC and 70 N). The increase in friction coefficient of the neat ionic liquid after 1800 s showed in Fig. 5b corresponds with one of the common shapes of friction-time curves described by P.J. Blau [53], which can be caused by several different phenomena.

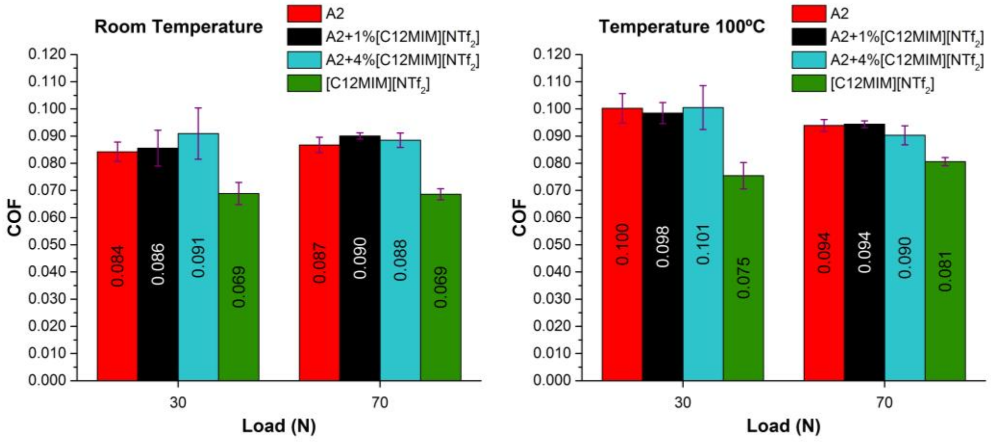


Fig. 3. Average coefficient of friction during tribological tests.

Regarding wear behavior of these lubricant samples, as expected wear increased with both load and temperature (Fig. 5). However, wear results showed more severe differences as a function of lubricant, load and temperature than the friction measurements. Under the milder test conditions of load and temperature (30 N and RT) the mixtures had similar wear behavior to the neat base oil, meanwhile the use of neat ionic liquid resulted in the lowest wear volume. At 100 ºC and 30 N-load, the mixtures improved slightly the antiwear behavior of the neat base oil, while the neat ionic liquid showed again the best antiwear results.

On the other hand, at 70 N-load and RT the mixtures, as well as the neat ionic liquid, reduced wear with regard to the neat base oil. However, only the mixture containing 4 wt% and the neat ionic liquid outperformed the neat base oil at 70 N-load and 100 ºC, meanwhile the mixture containing 1 wt% of ionic liquid had similar wear result than the base oil. According to friction results and the analysis of the wear scars, it can be assumed that tests were performed under mixed/boundary lubrication regimes.

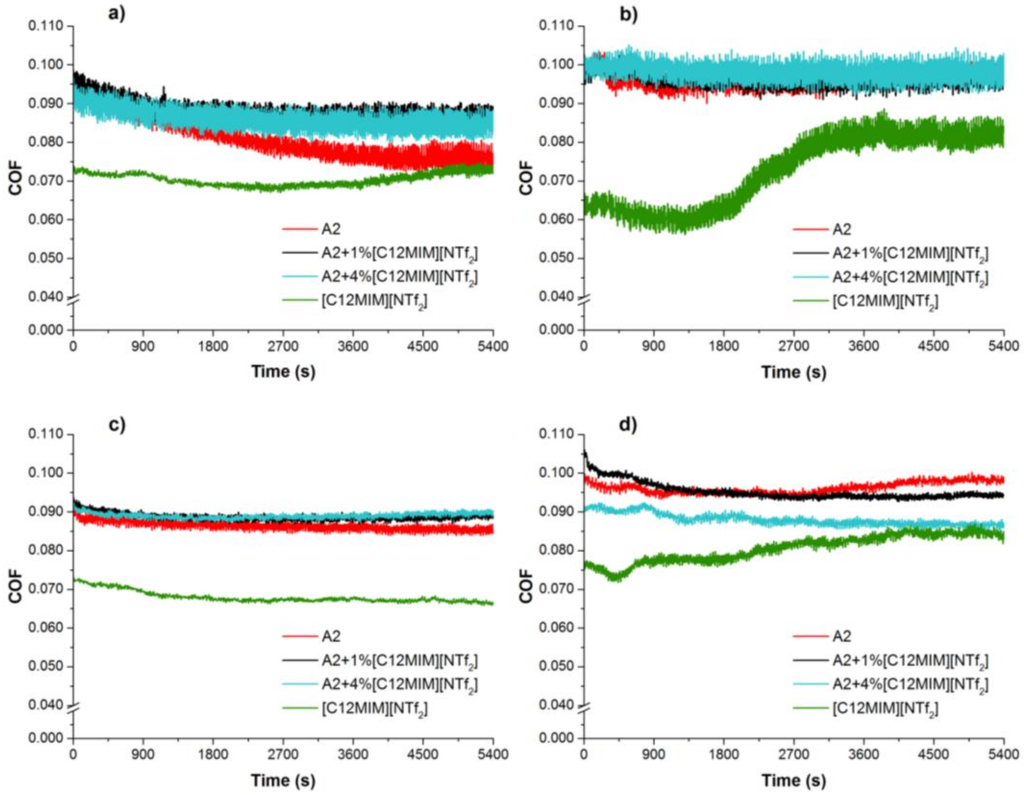


Fig. 4. Evolution of coefficient of friction with time for tests closest to the average COF values: a) RT and 30 N, b) 100 ºC and 30 N, c) RT and 70 N, d) 100 ºC and 70 N.

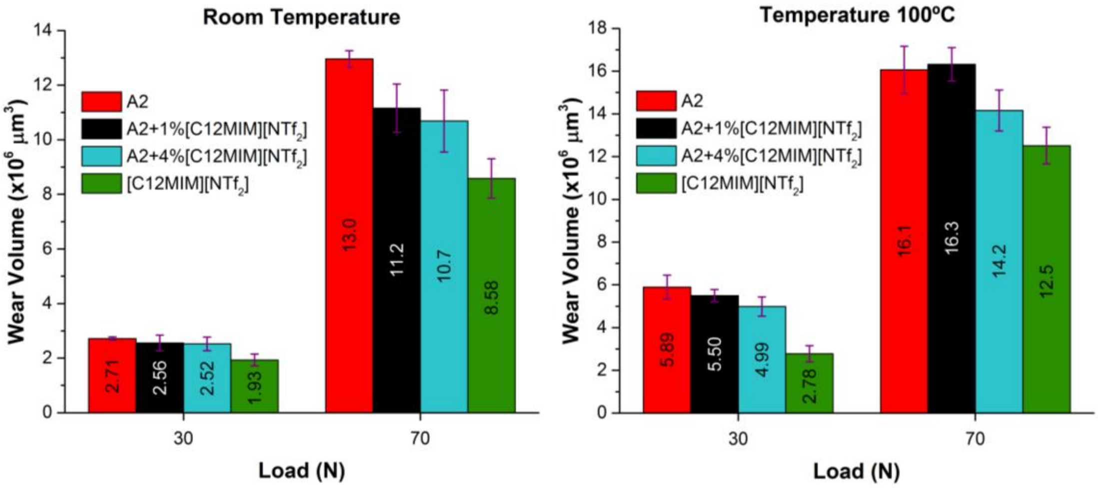
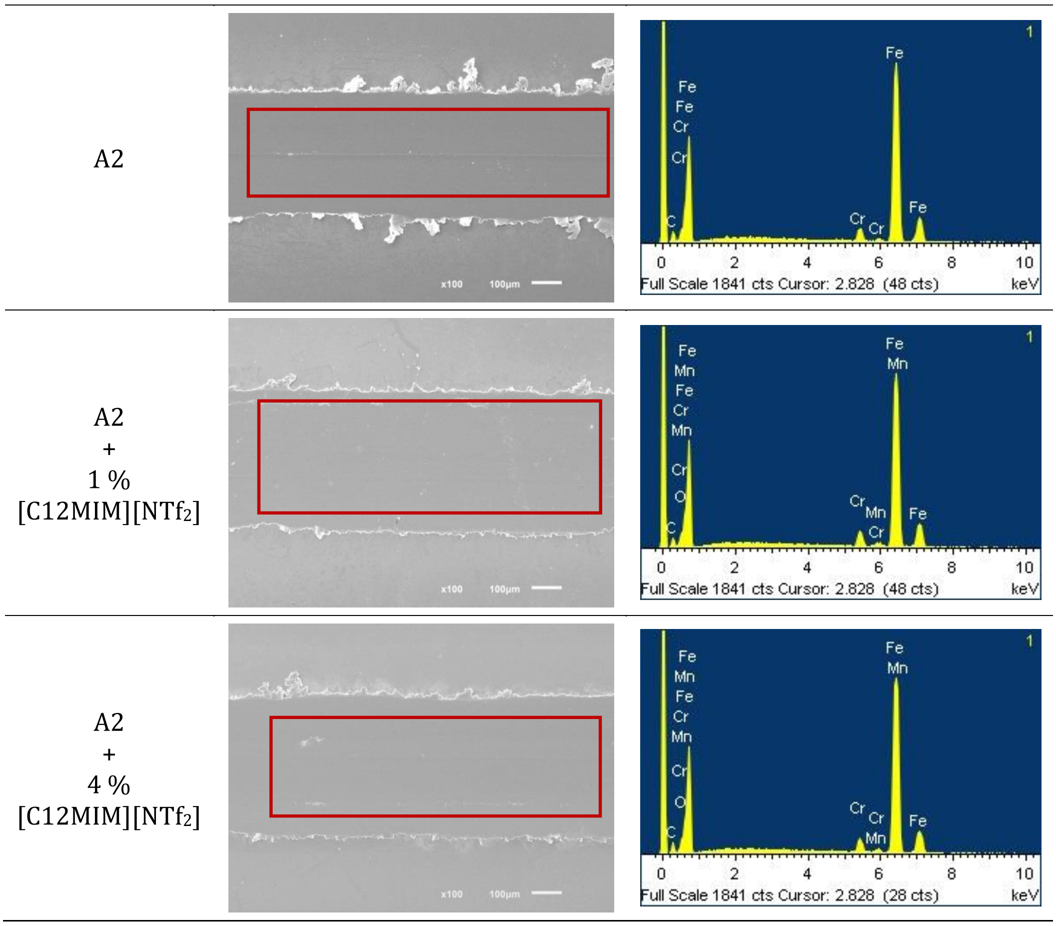


Fig. 5. Average wear volume after tribological tests.

3.3. *Worn surface characterization*

The worn surface on the disk was analysed by SEM and EDS after tribological tests. At room temperature and 30 N-load the wear scar obtained with the lubrication of the neat base oil (A2) showed a very smooth surface with evidence of plastic deformation at the edges of the wear scar (Fig. 6); however, material transfer was not detected between both specimens. The IL-containing mixtures also showed smooth wear scar with less plastic deformation. Tests lubricated with base oil or IL-containing mixtures showed adhesive wear. On the other hand, the worn surface from the test lubricated with neat IL presented grooves in the sliding direction, which are typical of abrasive wear. Despite the good anti-wear performance showed by the neat IL, the abrasive wear behavior could be related to the smaller amount of lubricant used in that test (25 µl), which hinders the evacuation of wear debris and provokes their entrapment in the contact, in comparison with tests lubricated with the neat base oil or the IL-containing mixtures (4 ml). On the other hand, the tests made at RT and 70 N-load (Fig. 7) exhibited the same wear mechanisms and bigger wear scar than the tests at RT and 30 N-load, but less plastic deformation was found at the edges of the wear scar. The EDS analysis showed that in all tests made at RT only the chemical elements from the steel were detected, Figs. 6-7.



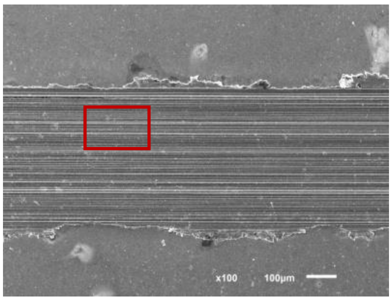
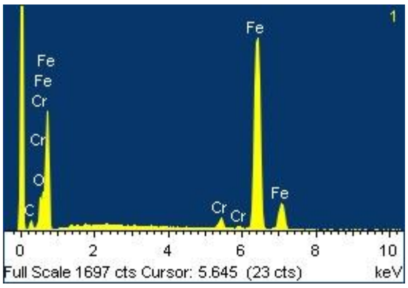
[C12MIM][NTf$_2$]		

Fig. 6. SEM images and EDS (from marked zone) taken after tests made at 30 N and RT.

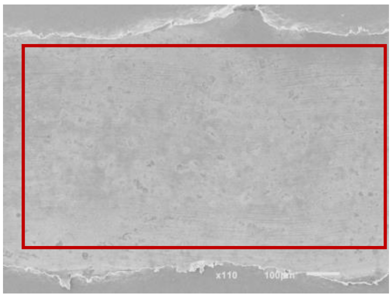
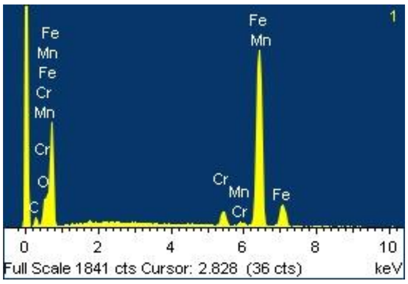
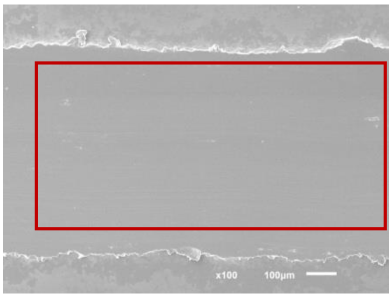
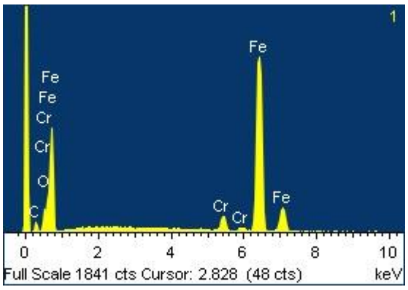
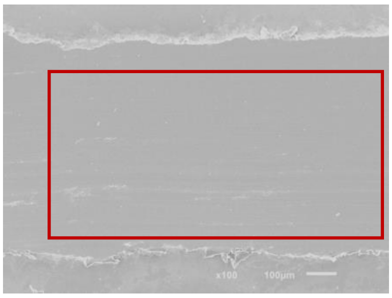
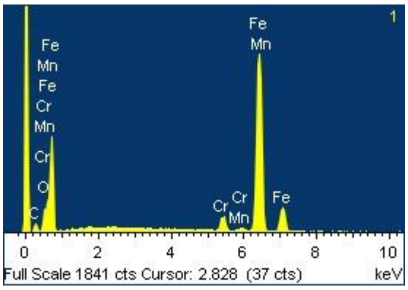
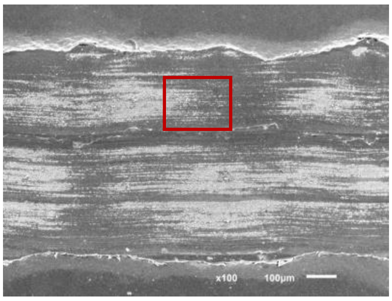
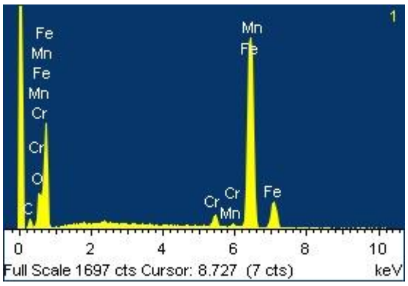
A2		
A2 + 1 % [C12MIM][NTf$_2$]		
A2 + 4 % [C12MIM][NTf$_2$]		
[C12MIM][NTf$_2$]		

Fig. 7. SEM images and EDS (from marked zone) taken after tests made at 70 N and RT.

At the higher temperature (100 °C), the wear results were clearly much more severe, even at the lower load (30 N), with also adhesive wear and plastic deformation at the edges of the wear scar for tests made with neat base oil and IL-containing mixtures, Fig. 8. Under this test condition (30 N and 100 ºC) the worn surface from the test lubricated with neat ionic liquid also showed abrasive wear. With regard to the chemical elements detected with EDS, only the elements present in the steel were found when the neat base oil and the mixtures were used as lubricant. However, sulphur was also detected on the worn surface when the neat ionic liquid was used in the lubrication.

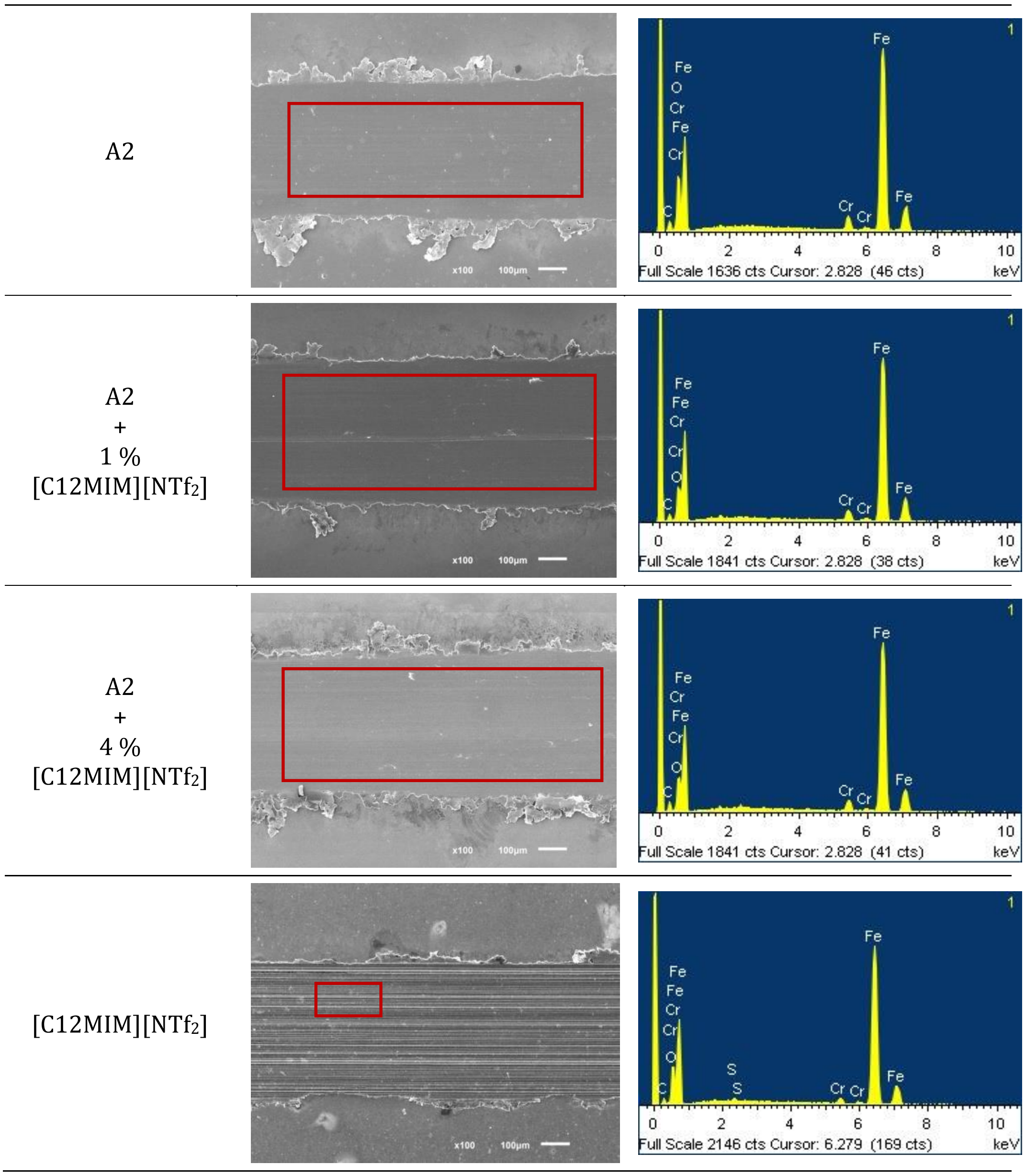


Fig. 8. SEM images and EDS (from marked zone) taken after tests made at 30 N and 100 ºC.

In addition, bigger wear scar and similar wear mechanisms to that found at 30 N were ascertained when the load of 70 N was used at 100 ºC, Fig. 9. In this case, sulphur was also encountered on the worn surface tested with neat IL during the EDS analysis, while on the surface lubricated with the neat base oil and the IL-containing mixtures only the chemical elements from the steel were detected.

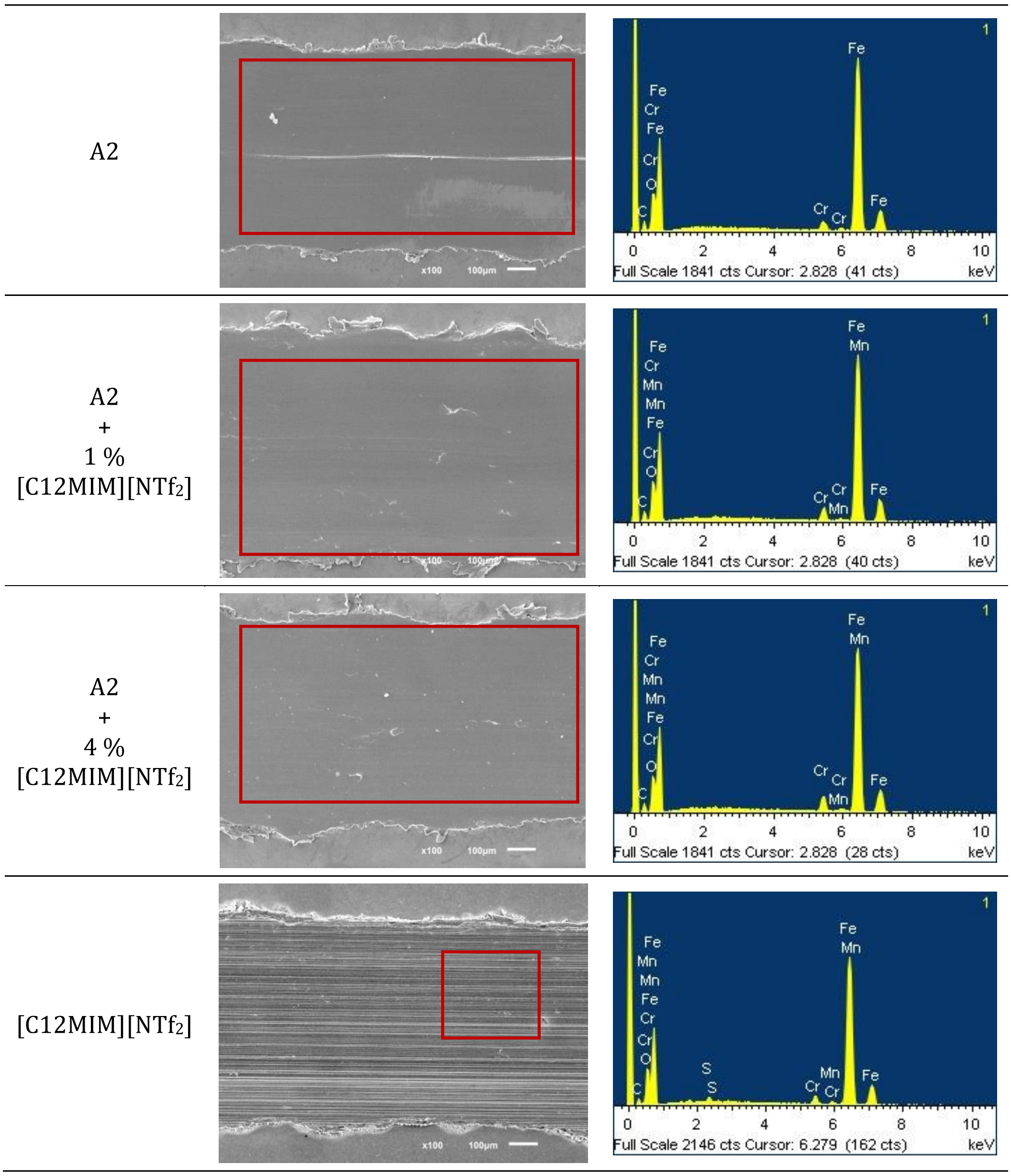


Fig. 9. SEM images and EDS (from marked zone) taken after tests made at 70 N and 100 ºC.

The XPS analysis of the worn surface revealed that there are no differences in the chemical states of iron among different samples at room temperature, regardless of the load or lubricant. Three different peaks could be found, a first one around 707.5 eV, fitted with a Gaussian-lorentzian 70:30 product modified by an exponential blend with k=0.65 which can be assigned to Fe^0; a second one at 710.8 eV fitted with a Gaussian-lorentzian 70:30 product modified by an exponential blend with k=1.5 assignable to Fe(III) and a third one around 712.8 eV fitted with a Gaussian-lorentzian 70:30 product assumed to be iron oxihydroxydes (FeOOH). The assignations and the selection of curve shapes were done according to the research of Mangolini [54] and Mayer [55].

For tests made at RT, the Fe(0):Fe(III):FeOOH ratio keeps at 35:50:15 without significant differences (Table 2). However, the same analysis carried out for the samples assayed at 100 ºC revealed a higher Fe(III)/FeOOH ratio for both samples with neat ionic liquid, what can be correlated with the better wear behavior of these samples compared to the other lubricant samples at the same temperature [29]. However, this ratio might be influenced by the presence of other chemical species. In fact, there is an apparent contradiction regarding the wear behavior between the Fe(III)/FeOOH ratio of the neat IL at RT and 100 ºC, which is explained by the presence of iron fluorides at higher temperatures which are not present at room temperature.

Table 2. Fe2p3/2 band analysis of XPS spectra.

Load	**A2**	**4% [C12MIM][NTf$_2$]**	**[C12MIM][NTf$_2$]**
		Room temperature	
30 N	707.5 eV (37%) 710.8 eV (50%) 712.7 eV (13%)	707.4 eV (37%) 710.8 eV (50%) 712.7 eV (13%)	707.4 eV (37%) 710.8 eV (50%) 712.7 eV (13%)
70 N	707.5 eV (33%) 710.9 eV (54%) 712.9 eV (13%)	707.5 eV (36%) 710.8 eV (52%) 712.9 eV (12%)	707.5 eV (35%) 710.9 eV (53%) 712.9 eV (12%)
		100 ºC	
30 N	707.5 eV (33%) 710.8 eV (54%) 712.9 eV (13%)	707.5 eV (29%) 710.9 eV (55%) 712.8 eV (16%)	707.5 eV (25%) 710.9 eV (62%) 712.8 eV (14%)
70 N	707.6 eV (32%) 710.8 eV (54%) 712.8 eV (13%)	707.5 eV (35%) 710.8 eV (51%) 712.7 eV (14%)	707.6 eV (20%) 711.0 eV (66%) 712.9 eV (14%)

In addition, fluorine was only analyzed in the IL-containing samples because the base oil does not contain that element. Fig. 10 shows the F/Fe ratio for both the mixture with the highest IL concentration and the neat IL samples. It seems clear that the interaction between iron and fluorine is mostly negligible at the lower load, whereas it becomes higher only for the neat IL sample as the load increases. These results confirm that higher load, temperature and/or IL concentration are key points for the chemical interaction of the ionic liquid with surface, contributing to tribofilm formation and both friction and wear reduction. Furthermore, the extremely low value of F/Fe ratio obtained at 30 N and RT for both lubricant samples means that the amount of fluorine in this case is not relevant. However, this F/Fe ratio becomes huge at 70 N with neat IL (especially at 100 ºC), indicating chemical interaction between the metal surface and the anion of the ionic liquid. Besides, it is interesting to state that at room temperature fluorine was detected as a single peak (between 688.9 eV and 689.5 eV) assignable to NTf_2 on the surface [56] regardless of the load or lubricant sample. In addition, both fluorine-containing samples showed two peaks at 100 ºC: a first one around 689 eV and a second one near 685 eV (Table 3). It is obvious that the higher one comes from NTf_2 on the surface, but the position of the lower one is consistent with the existence of iron fluorides according to the research of Kasrai [57].

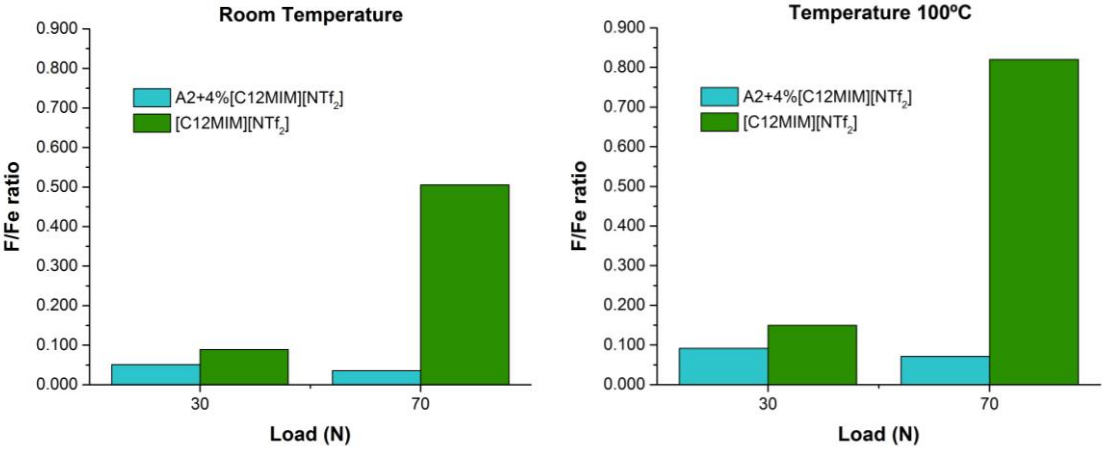


Fig. 10. F1s / Fe2p3/2 area ratio for XPS analysis.

Table 3. Position and area percentage of the F1s peak in XPS analysis.

Load	4% [C12MIM][NTf_2]	[C12MIM][NTf_2]
Room temperature		
30 N	689.1 eV	689.2 eV
70 N	688.9 eV	689.3 eV
Temperature 100 ºC		
30 N	689.3 eV (45%)	689.0 eV (60%)
	685.2 eV (53%)	685.0 eV (40%)
70 N	689.3 eV (55%)	689.3 eV (90%)
	684.9 eV (45%)	685.0 eV (10%)

4. Conclusions

The use of an [NTf_2] anion-based IL as neat lubricant and as additive to a polar oil at two concentrations (1 and 4 wt%) was studied in this work. From the results obtained the following conclusions can be drawn:

- The neat base oil and the two mixtures used showed similar friction values probably due to similar rheological properties. Meanwhile, the neat ionic liquid showed clear lower friction values mainly influenced by its chemical interaction with surface.

- The neat ionic liquid showed the best antiwear behavior at 30 N-load and at both temperatures (RT and 100 ºC). On the contrary, the neat base oil and the IL-containing mixtures had similar antiwear behavior.
- At the higher load (70 N) both the neat ionic liquid and the mixture containing 4 wt% of IL showed in general better antiwear properties with regard the neat base oil, but the neat IL continued showing the best antiwear behavior.
- The SEM analysis of the worn surface showed adhesive wear in the tests lubricated with the neat base oil and the IL-containing mixtures, meanwhile abrasive wear was found in the tests lubricated with the neat IL. The EDS analysis only detected the elements present in the steel, except in the tests with neat ionic liquid at 100 ºC, where sulphur was also detected.
- The XPS analysis exhibited a slight chemical interaction between the ionic liquid and the surface (presence of the non-reacted [NTf_2]) during tests made at room temperature. On the contrary, assays at higher temperature also revealed chemical interaction between the fluorine from NTf_2 and the metal surface. The wear behavior is related both to the Fe(III)/FeOOH ratio and to the presence of iron fluorides.

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