

# Ionic liquids as a neat lubricant applied to steel-steel contacts

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## Abstract

This paper studies the use of 3 ionic liquids ([NEMM]MOE][FAP], [BMP][FAP] and [BMP][NTf<sub>2</sub>]) as neat lubricant within steel-steel contact conditions. Tribological tests (at 40 and 100°C) were conducted in a HFRR tribometer and hence a complementary study was developed using a MTM tribometer. The wear surface on the discs was measured after the HFRR tests by confocal microscopy and also analyzed by SEM and XPS. The [BMP][NTf<sub>2</sub>] showed the lowest friction coefficient in the MTM and HFRR tests at 40°C but at 100°C its tribological behavior worsened due to its lowest viscosity. Similar results were found for wear behavior. Both antifriction and antiwear results were related to the tribofilms formation from the ECR and XPS measurements.

*Keywords:* ionic liquids, lubrication, wear, friction coefficient

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## 1. Introduction

Since 2001 several papers have been published that investigate the potential use of ionic liquids (ILs) for lubrication. Most of this work has been focused on using ILs as base stock or as a pure lubricant [1].

Ionic liquids have some high performance properties for lubrication such as non-flammability, non-volatility, high ionic conductivity, high thermo-oxidative stability and miscibility with organic compounds [2- 4]. Due to the high temperature properties of the ionic liquids, they can be used as a pure lubricant under severe tribological conditions for which conventional lubricants do not perform well [5- 7].

In addition, the advantages of using ILs as additives and their interaction with the wear surfaces have been studied by numerous authors [2,8,9]. Most of the early researches in the use of IL as lubricants has been focused on the use of PF<sub>6</sub> and BF<sub>4</sub> imidazolium salts [10,11]. However, the presence of these anions can produce unfavorable chemical reactions of the IL with water and lead to the formation of hydrogen fluoride, which can damage tribology systems [12]. For these reasons, several authors are focused on the research with hydrophobic ILs. Among the hydrophobic ILs can be found those based on the anions bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>] and tris(pentafluoroethyl)trifluorophosphate [FAP]. These ILs combine their higher hydrophobicity with their excellent hydrolytic stability [13]. Taking into account that fact, Gonzalez *et al.* studied the use of the ionic liquid 1-Butyl-1-methylpyrrolidinium

1 tris(pentafluoroethyl)trifluorophosphate ([BMP][FAP]) as neat lubricant and as additive in the lubrication  
2 of conventional PVD coatings (CrN, TiN and DLC) [14]. Blanco *et al.* used ethyl-dimethyl-2-  
3 methoxyethylammoniumtris(pentafluoroethyl)trifluorophosphate ([NEMM)MOE][FAP]) as base oil  
4 additive in the lubrication of TiN and CrN PVD coatings [15,16]  
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6 The tribological behaviour of ionic liquids as neat lubricants or as additives has been evaluated for  
7 different types of contact, with steel-steel being the most studied case [17- 21]. Now, this paper studies  
8 the use of three ionic liquids based on the [FAP] and [NTf<sub>2</sub>] anions as neat lubricant applied to steel-  
9 steel contacts.  
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## 18 **2. Experimental details**

19 The properties of the ionic liquids used as lubricants in this study are listed in Table 1. The viscosity of  
20 the ionic liquid at high shear rates ( $10^6$ - $10^7$  s<sup>-1</sup>) and temperatures of 70 and 100°C was measured using an  
21 Ultra Shear Viscometer (PCS Instruments, UK), because of typical shear rates in the boundary lubrication  
22 regime reach values greater than  $10^6$  s<sup>-1</sup>. The tribological tests conducted using the high frequency  
23 reciprocating rig (HFRR) (PCS Instruments, UK) considered the typical specimens: AISI 52100 steel  
24 balls (with 6.0 mm diameter, 58-66 HRC of hardness and less than 0.05 µm of roughness) and softer AISI  
25 52100 steel discs (190-210 HV<sub>30</sub> and roughness of less than 0.02 µm). The HFRR is a reciprocating  
26 friction and wear test machine which provides reliable assessment of the tribological behavior of  
27 lubricants and additives under a wide range of load, stroke length, frequency and temperature values.  
28 Such experiments were developed at a normal load of 7.85 N (corresponding to a maximum contact  
29 pressure of 1.31 GPa) under fully flooded lubrication, a stroke length of 2 mm, a frequency of 25 Hz, and  
30 duration of 60 minutes (corresponding to a sliding distance of 360 m). The ionic liquid temperature was  
31 controlled and these experiments were conducted at temperatures of 40 and 100°C. Friction force and  
32 electrical contact resistance (ECR) in order to determine the tribofilms formation on the wear surfaces  
33 were measured during the tribological tests. Each tribological test was repeated at least three times. The  
34 wear scar volume on the disc surface was measured after each test using confocal microscopy  
35 methodology. Tested surfaces were also analyzed by SEM and XPS in order to determine their chemical  
36 composition and the dominant wear mechanism.  
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38 Before the experiments using the HFRR tribometer, the ionic liquids were tested in a Mini Traction  
39 Machine (MTM) from PCS Instruments Ltd. in order to obtain their tribological behaviour under different  
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1 contact conditions. The MTM is a tribometer with a ball-on-disc configuration where the antifriction and  
2 antiwear properties of lubricants and additives can be tested under variable load, speed and temperature  
3 conditions. Both the disc and the ball are driven independently providing slide-roll ratios (SRR) from 0%  
4 (pure rolling) to 200% (pure sliding). Such tests were performed at room temperatures using 0.25 ml of  
5 ionic liquid in the contact between the ball (AISI 52100, 18 mm. diameter,  $R_a < 0.01 \mu\text{m}$ ) and the disc  
6 (AISI 52100, 46 mm. diameter,  $R_a < 0.01 \mu\text{m}$ ), at normal load of 50 N (corresponding to a maximum  
7 contact pressure of 1.13 GPa), at sliding-rolling ratio of 50%, and rolling speed from 3 to 200 mm/s.  
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### 16 **3. Results and discussion**

17 The results obtained from the experiments conducted using the MTM at room temperature, Fig. 1,  
18 showed clearly that under favorable contact conditions (higher rolling speed in this case) the  
19 [BMP][NTf<sub>2</sub>] ionic liquid performs better. However, its tribological behaviour become worse more  
20 rapidly than the FAP-based ionic liquids when the rolling speed decreases. This tribological behaviour is  
21 related not only to the balance of formation/destruction of the tribofilms on the wear scar surface but also  
22 to the rheological behavior of the ionic liquids. It is noted that [BMP][NTf<sub>2</sub>] ionic liquid has lower  
23 viscosity than the other ionic liquids for both tested temperatures, Fig. 2.  
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32 The results of the experiments conducted at 40°C using the HFRR machine showed that the lowest  
33 friction coefficient values was reached with the [BMP][NTf<sub>2</sub>] ionic liquid, while the FAP-based ionic  
34 liquids presented similar friction coefficient values being slightly better the [BMP][FAP], shown as Fig.  
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43 Some tribological changes were detected during tests made at 100°C, Fig. 4. Now, the tribofilms  
44 formation in the tests with [BMP][NTf<sub>2</sub>] was almost null and hence the increase in the friction coefficient.  
45 The FAP-based ionic liquids with similar tribofilms formation showed close friction coefficient values.  
46 This change with temperature for the tribological behavior of the [BMP][NTf<sub>2</sub>] was analysed more in  
47 detail using the XPS technique.  
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52 Fig. 5 shows the average friction coefficient of all testing conditions performed in the HFRR machine. In  
53 general the friction coefficient rises with temperature. It is of interest to note the sharply increase of  
54 friction coefficient showed by [BMP][NTf<sub>2</sub>] from 40 to 100°C.  
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1 Figs. 6, 7 and 8 show the wear behavior found in the tests at both temperatures. It can be observed that  
2 wear increase sharply with temperature. At 40°C the wear results for ionic liquids with the same cation,  
3 [BMP][FAP] and [BMP][NTf<sub>2</sub>] were similar (Figs. 6 and 8) and lower than the [(NEMM)MOE][FAP]  
4 values but the SEM image of the base of the wear track show identical wear behavior in all cases. At  
5 100°C the situation changed and the [BMP][NTf<sub>2</sub>] ionic liquid showed poor wear behavior not only in  
6 quantity but also showing abrasive wear which can be observed in the SEM images, Figs. 7-8.  
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8 X-Ray photoelectron analysis was performed using a Phoibos hemispherical detector MDA5 from  
9 SPECS, using Mg x-ray radiation (1253.6 eV) at 13 kV and 200 W. High resolution measurements were  
10 recorded at constant pass energy 30 eV with an energy step 0.1 eV. Spatial resolution was achieved using  
11 a 2.5 mm iris between the sample and the detector. Pressure in the analysis chamber was kept below  
12 5·10<sup>-9</sup> mbar during the measurements. Analysis of the spectra was recorded using CasaXPS software as  
13 well as fitting software developed by the authors. Calibration of spectra was performed using the peak of  
14 adventitious C1s at 284.6 eV.  
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16 In Fig. 9 can be seen that samples lubricated with [(NEMM)MOE][FAP] at 40°C presents two XPS F1s  
17 bands inside the wear scar, one assignable to [FAP<sup>-</sup>] anion at 688.6 eV (47%) and a second one at 687.5  
18 eV (53%) related to fluoride-metal interaction due to chemical reaction between the ionic liquid and the  
19 surface [14]. When the sample is analysed outside the wear scar, only the peak corresponding to [FAP<sup>-</sup>]  
20 can be observed, as there is no chemical reaction between the ionic liquid and the surface (tribofilm). The  
21 situation remains very similar when the test temperature increased to 100°C both inside the wear scar with  
22 two F1s peaks at 687.5 eV (56%, fluoride-metal) and 688.6 eV (44%, [FAP<sup>-</sup>]), and outside the wear scar  
23 with a single peak at 688.0 eV belonging to unreacted [FAP<sup>-</sup>], see Fig. 10 and Table 2.  
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25 The sample lubricated with [BMP][FAP] behaves very similarly to that with [(NEMM)MOE][FAP]. At  
26 40°C, F1s photoelectron band inside the wear scar can be splitted into a [FAP<sup>-</sup>] band at 688.5 eV (85%)  
27 and a F-metal interaction band at 686.6 eV (15%) whereas outside the wear scar only the [FAP<sup>-</sup>] F1s  
28 photoelectron band can be observed at 688.2 eV. When temperature increased to 100°C the situation is  
29 practically the same than at 40°C: two bands inside the wear scar ([FAP<sup>-</sup>] at 688.6 eV, 80%, and fluorine-  
30 metal interaction at 687.0 eV, 20%) but only [FAP<sup>-</sup>] was found in the analysis of the outer part of the  
31 wear scar (688.4 eV) (Table 2).  
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33 Samples lubricated with [BMP][NTf<sub>2</sub>] do not show qualitative differences at 40°C or 100°C in F1s  
34 photoelectron bands. F1s band appears between 689.0 eV and 689.2 eV in any case (both temperatures,  
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1 inside and outside, Fig.11, Table 2), matching the F1s band of the [NTf<sub>2</sub><sup>-</sup>] anion as described by Bovio et  
2 al. [22].

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4 The presence of neat [BMP][NTf<sub>2</sub>] can be also detected inside and outside the wear scar at both 40°C and  
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6 100°C analysing the N1s photoelectron band. Pyrrolidinium based ionic liquids shows two N1s bands at  
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8 399.5 eV from the [NTf<sub>2</sub><sup>-</sup>] anion and at 403 eV from the pyrrolidinium cation [23] which are clearly seen  
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10 in our case as reflected in Fig. 12.

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12 Nevertheless, O1s band shows an interesting behaviour in these samples. Three different O1s bands can  
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14 be detected at 40°C inside the wear scar: 529.8 eV (assignable to Fe<sub>2</sub>O<sub>3</sub>, [24]), 532.8 eV (from the [NTf<sub>2</sub><sup>-</sup>]  
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16 anion according to [22-23]) and 531.2 eV which probably arises from the tribofilm. Only two of these  
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18 bands are present in the outer part of the wear scar (530.1 eV from Fe<sub>2</sub>O<sub>3</sub> and 532.7 eV from the ionic  
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20 liquid), although the band at 531.9 eV due to the tribofilm is not present, as there is no tribofilm outside  
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22 the wear scar (Fig. 13, Table 3).

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24 When the test is performed at 100°C, the situation in the outer part is very similar (O1s bands at 530.5 eV  
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26 and 532.8 eV from iron oxides and neat [NTf<sub>2</sub><sup>-</sup>]) although inside the wear scar only neat ionic liquid can  
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28 be detected at 532.8 eV (Fig. 14, Table 3), confirming the inexistence of tribofilm as suggested by ECR  
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30 measurements. According to the previously shown results, the tribofilm in the lubrication with  
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32 [BMP][NTf<sub>2</sub>] at 40°C does not seem to involve the anion as it happened with [BMP][FAP], but the ionic  
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34 liquid seems to somehow induce the formation of the tribofilm while remaining chemically unaltered.  
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36 [BMP][NTf<sub>2</sub>] at 100°C does not create a tribofilm on the surface, thus increasing the friction coefficient.  
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38 The presence of iron oxides was confirmed by checking the Fe2p3/2 photoelectron band inside the wear  
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40 scar. Every sample shows a band between 709.9 and 710.4 eV assignable to iron oxides [24] with the  
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42 single exception of [BMP][NTf<sub>2</sub>] at 100°C.

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44 Further XPS analysis concerning P and S elements was also carried out. As reflected in the following  
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46 tables 4 and 5, [(NEMM)(MOE)][FAP] shows a clear P2p peak both at 40°C and 100°C around 133.6  
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48 which is a typical value for phosphates [25]. The behaviour of [BMP][FAP] is very similar, although the  
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50 intensity of the P2p peaks is lower. However, the intensity of P2p in the case of [BMP][NTf<sub>2</sub>] is  
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52 negligible.

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54 Analysis of S2p peak reveals a band at 169.3 eV (FWHM 2.8 eV) for [(NEMM)(MOE)][FAP] at 40°C  
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56 which is almost the same than for [(NEMM)(MOE)][FAP] at 100°C (169.6 eV (FWHM 2.5 eV)) which is  
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58 near the iron (III) sulfate band at 168.9 eV [24,25]. The situation is the same for [BMP][NTf<sub>2</sub>] with peaks  
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at 169.2 eV (FWHM 2.5 eV) at 40°C and 169.2 eV (FWHM 2.8 eV) at 100°C suggesting also the presence of iron (III) sulfate. However, the intensity of S2p peak is very low in the case of [BMP][FAP] with a noisy peak at 169.4 eV (FWHM 2.4 eV) at 40°C which disappears when increasing the temperature at 100°C suggesting the disappearance of the iron (III) sulfate in the tribolayer.

#### 4. Conclusions

This paper studied the use of ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ionic liquids as neat lubricants within steel-steel contact.

Results show that [BMP][NTf<sub>2</sub>] ionic liquid exhibited the minimum friction coefficient for the HFRR tests conducted at 40°C and for MTM tests. For the two ionic liquids with the same [FAP] anion, the [BMP][FAP] showed the better anti-friction performance for all the tests made, according with previous author's results related to these two ionic liquids ([BMP][FAP] and [(NEMM)MOE][FAP]) in the lubrication of PVD coatings. Nevertheless, [BMP][NTf<sub>2</sub>] showed the highest friction coefficient in the HFRR tests made at 100°C according with its lowest viscosity value at this temperature.

Wear results exhibited similar behavior, showing the surfaces lubricated with [BMP][NTf<sub>2</sub>] as the lowest wear volume for the tests made at 40°C. However with the increasing temperature this ionic liquid worsened its anti-wear performance showing the higher wear track with an important surface damage. Wear volume measured after tests made with [BMP][FAP] and [(NEMM)MOE][FAP] were similar, although the former showed a slightly higher anti-wear behavior.

XPS confirmed the presence of tribofilms in samples lubricated with [BMP][FAP] or [(NEMM)MOE][FAP] both at 40°C and 100°C whereas only neat ionic liquid without interaction with the surface could be detected inside the wear scar of sample lubricated with [BMP][NTf<sub>2</sub>] at 100°C, thus confirming the evidences obtained through ECR.

#### Acknowledgements

The authors are grateful to the FICYT (the Foundation for the promotion in Asturias of the Applied Scientific Research and Technology) for supporting the research stay of the first author at Imperial College London (UK) and the Spanish Ministry of Science and Innovation for also supporting this paper within the framework of the Research Project WINDTRIB (DPI2010-18166). They also thank the

1 Ministry of Education, Culture and Sport for funding, within the program "*José Castillejo*", the research  
2 stay of José Luis Viesca at Bournemouth University. In addition, we would like to thank the Unit for  
3  
4 Molecular Spectroscopy and XPS from the Scientific-Technical Services of the University of Oviedo.  
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## 8 **References**

- 9  
10 [1] Qu J, Bansal DG, Yu B, Howe, JY, Luo H, Dai S, et al. Antiwear Performance and Mechanism of an  
11 Oil-Miscible Ionic Liquid as a Lubricant Additive. ACS Appl. Mater. Interfaces 2012;4:997–1002.  
12  
13 [2] Minami I. Ionic Liquids in Tribology. Molecules 2009;14:2286-305.  
14  
15 [3] Jimenez AE, Bermudez MD. Imidazolium ionic liquids as additives of the synthetic ester propylene  
16 glycol dioleate in aluminium–steel lubrication. Wear 2008;265:787-98.  
17  
18 [4] Zhou F, Liang Y, Liu W. Ionic liquid lubricants: designed chemistry for engineering applications,  
19 Chemical Society Reviews 2009;28: 2590-9.  
20  
21 [5] Bermúdez MD, Jiménez AE, Sanes J, Carrión, FJ. Ionic Liquids as Advanced Lubricant Fluids.  
22 Molecules 2009;14:2888-908.  
23  
24 [6] Yao M, Fan M, Liang Y, Zhou F, Xia Y. Imidazolium hexafluorophosphate ionic liquids as high  
25 temperature lubricants for steel-steel contacts. Wear 2010;268:67-71.  
26  
27 [7] Jiménez AE, Bermúdez MD, Iglesias P. Lubrication of Inconel 600 with ionic liquids at high  
28 temperature. Tribol Int 2009;42:1744-51.  
29  
30 [8] Liu W, Liang Y, Zhou F. Ionic liquid lubricants: designed chemistry for engineering applications.  
31 Chem Soc Rev 2009;38:2590-9.  
32  
33 [9] Jimenez AE, Bermudez MD, Carrion FJ, Martinez-Nicolas G. Room temperature ionic liquids as  
34 lubricant additives in steel-aluminium contacts: Influence of sliding velocity, normal load and  
35 temperature. Wear 2006;261:347-59.  
36  
37 [10] Battez AH, González R, Viesca JL, Blanco D, Asedegbega E, Osorio A. Tribological behavior of  
38 two imidazolium ionic liquids as lubricant additives for steel/steel contacts. Wear 2009;266:1224-8.  
39  
40 [11] Viesca JL, Battez AH, González R, Torres Pérez A, Reddyhoff T, Spikes HA. Assessing boundary  
41 film formation of lubricant additived with 1-hexyl-3-methylimidazolium tetrafluoroborate using  
42 ECR as qualitative indicator. Wear 2010;269:112-7.  
43  
44 [12] Torimoto T, Tsuda T, Okazaki K, Kuwabata S. New Frontiers in Materials Science Opened by Ionic  
45 Liquids. Adv Mater 2010; 22:1196–221.  
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- [13] Gaciño FM, Regueira T, Lugo L, Comuñas MJP, Fernández F. Influence of Molecular Structure on Densities and Viscosities of Several Ionic Liquids. *J Chem Eng Data* 2011;56:4984–99.
- [14] Gonzalez R, Hernandez Battez A, Blanco D, Viesca JL, Fernández-González A. Lubrication of TiN, CrN and DLC PVD coatings with 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate. *Tribol Lett* 2010;40:269–77.
- [15] Blanco D, Viesca JL, Hernandez Battez A, Gonzalez R, Fernández-González A. Lubrication of CrN Coating With Ethyl-Dimethyl-2-Methoxyethylammonium Tris(pentafluoroethyl)Trifluorophosphate Ionic Liquid as Additive to PAO 6. *Tribol Lett* 2011;41:295-302.
- [16] Blanco D, Gonzalez R, Hernandez Battez A, Viesca JL, Fernández-González A. Use of ethyl-dimethyl-2-methoxyethylammoniumtris(pentafluoroethyl)trifluorophosphate as base oil additive in the lubrication of TiN PVD coating. *Tribol Int* 2011;44:645-50.
- [17] Liu W, Ye C, Gong Q, Wang H, Wang P. Tribological performance of room-temperature ionic liquids as lubricant. *Tribol Lett* 2002;13:81-5.
- [18] Lu Q, Wang H, Ye C, Liu W, Xue Q. Room temperature ionic liquid 1-ethyl-3-hexylimidazoliumbis(trifluoromethylsulfonyl)-imide as lubricant for steel/steel contact. *Tribol Int* 2004;37:547-52.
- [19] Sanes J, Carrion FJ, Bermudez MD, Martinez-Nicolas G. Ionic liquids as lubricants of polystyrene and polyamide 6-steel contacts. Preparation and properties of new polymer-ionic liquid dispersions. *Tribol Lett* 2006;21:121-33.
- [20] Yao M, Liang Y, Xia Y, Zhou F. Bisimidazolium Ionic Liquids as the High-Performance Antiwear Additives in Poly (ethylene glycol) for Steel-Steel Contacts. *ACS Appl Mater Interfaces* 2009;1:467-71.
- [21] Palacio M, Bhushan B. A Review of Ionic Liquids for Green Molecular Lubrication in Nanotechnology. *Tribol Lett* 2010; 40:247–68.
- [22] Bovio S, Podesta A, Lenardi C, Milani P. Evidence of Extended Solidlike Layering in [Bmim][NTf2] Ionic Liquid Thin Films at Room-Temperature. *J Phys Chem B* 2009;113:6600-3.
- [23] Shuang M, Hurisso BB, Lovelock KRJ, Licence P. Does the influence of substituents impact upon the surface composition of pyrrolidinium-based ionic liquids? An angle resolved XPS study. *Phys Chem Chem Phys* 2012;14:5229–38.



[24] Wagner CD, Riggs WM, Davis LE, Moulder JF. Handbook of X-Ray Photoelectron Spectroscopy.  
1st ed. Eden Prairie: Perkin-Elmer Corporation; 1979.

[25] Mangolini F, Rossi A, Spencer N D. Chemical Reactivity of Triphenyl Phosphorothionate (TPPT)  
with Iron: An ATR/FT-IR and XPS Investigation. J. Phys. Chem. C 2011;115(4):1339-54.

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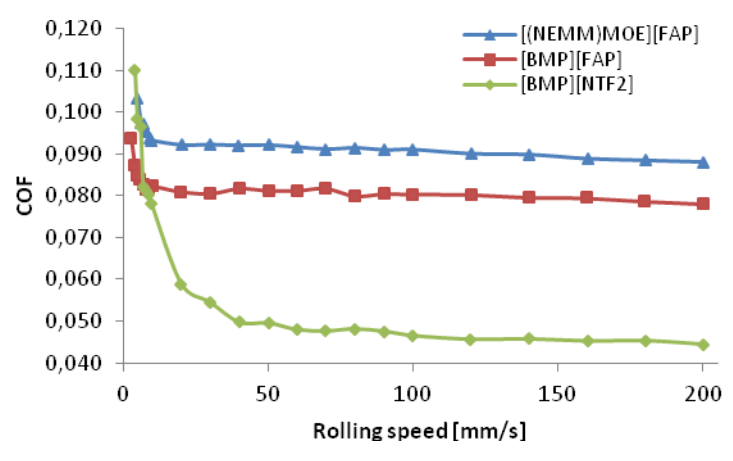


Fig. 1. Stribeck curves obtained at the MTM at normal load of 50N and 50% of SRR.

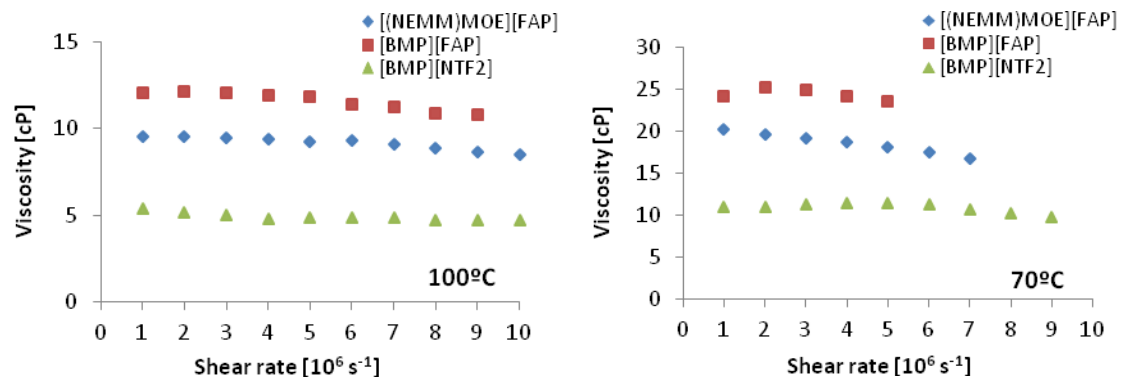


Fig. 2. Viscosity of IL's measured at high shear rates.

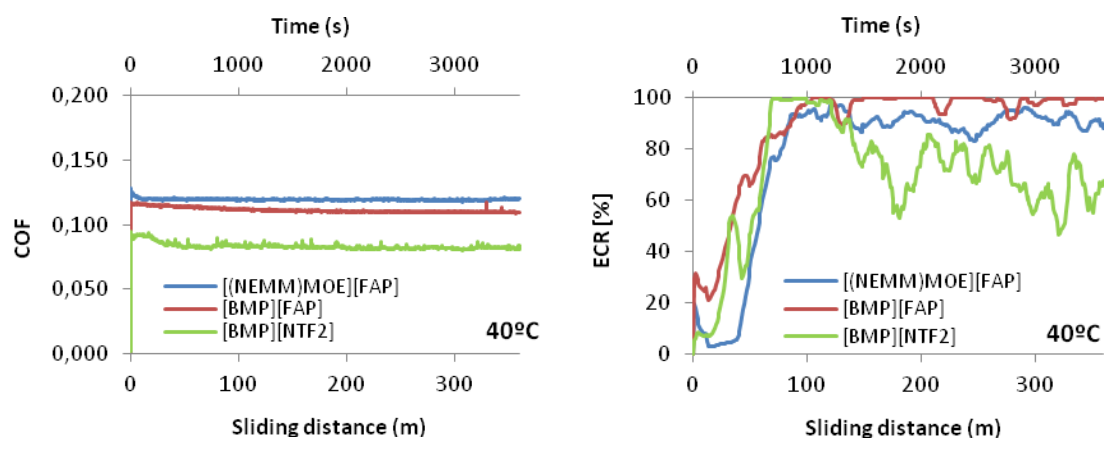


Fig. 3. Friction and ECR behavior for tests at 40°C.

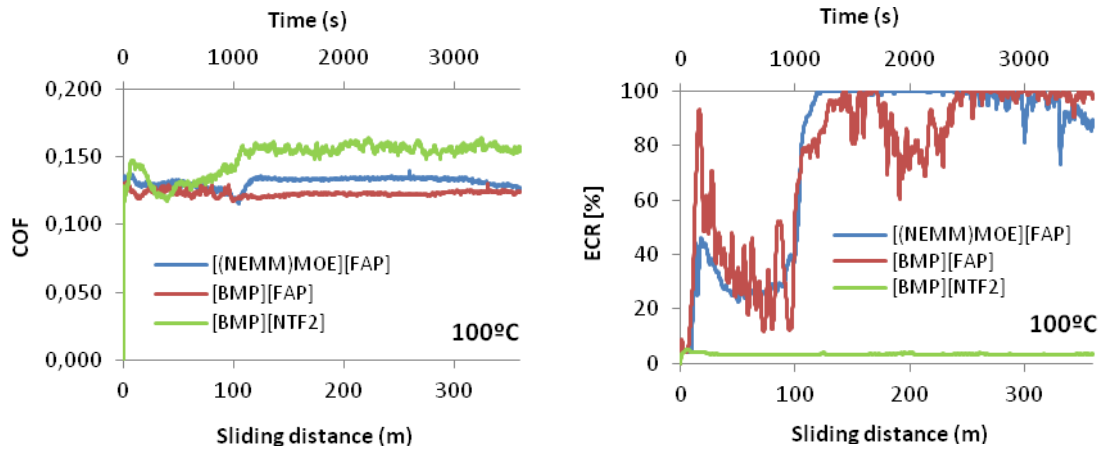


Fig. 4. Friction and ECR behavior for tests at 100°C.

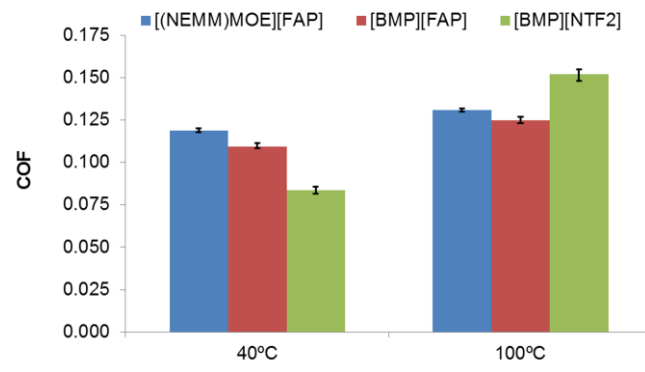


Fig. 5. Average friction coefficient from the reciprocating wear tests made in the HFRR machine.

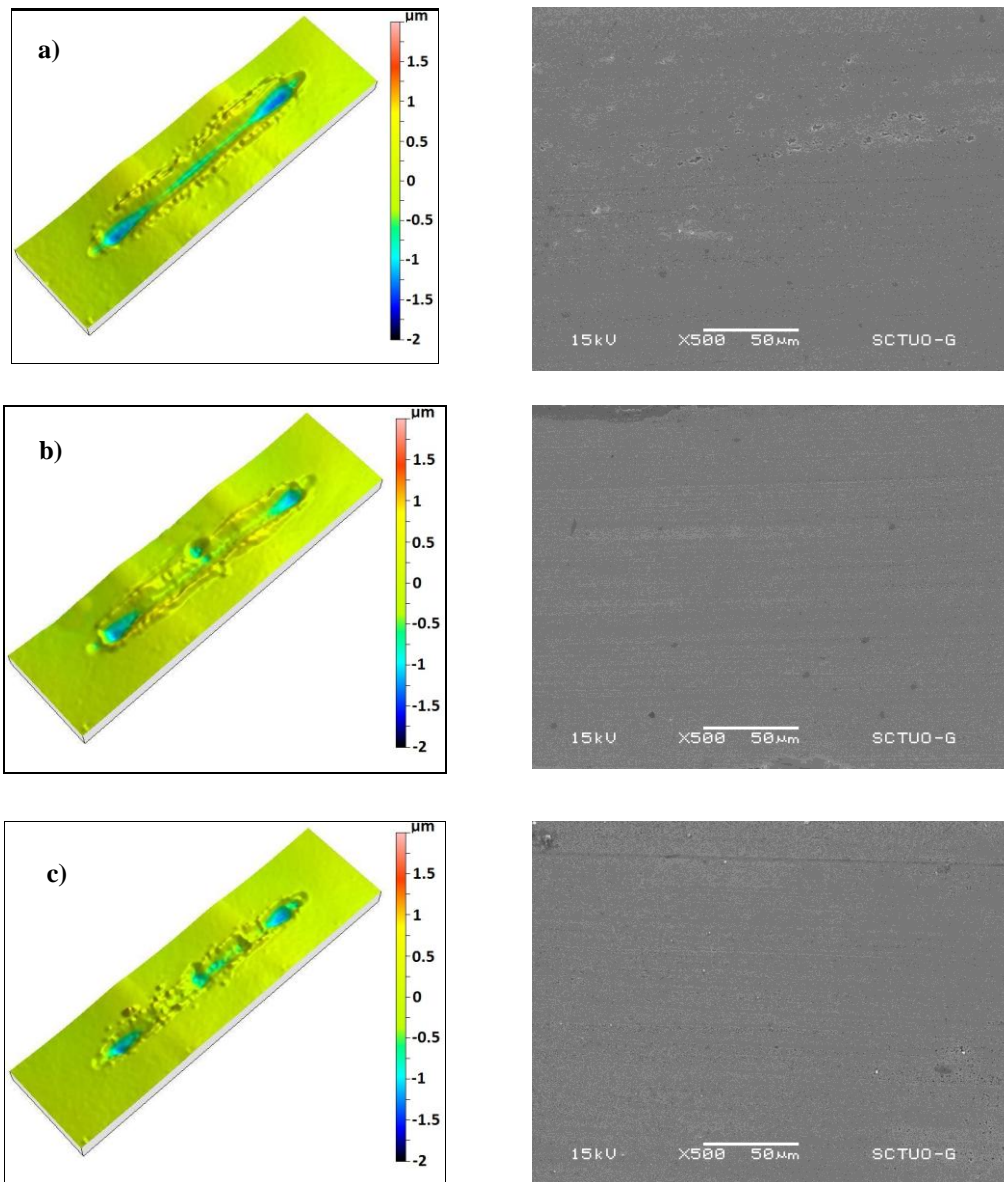


Fig. 6. 3D confocal reconstruction of wear track and SEM image of the bottom of wear track for test at 40°C. a) [(NEMM)MOE][FAP]; b) [BMP][FAP]; c) [BMP][NTf<sub>2</sub>]

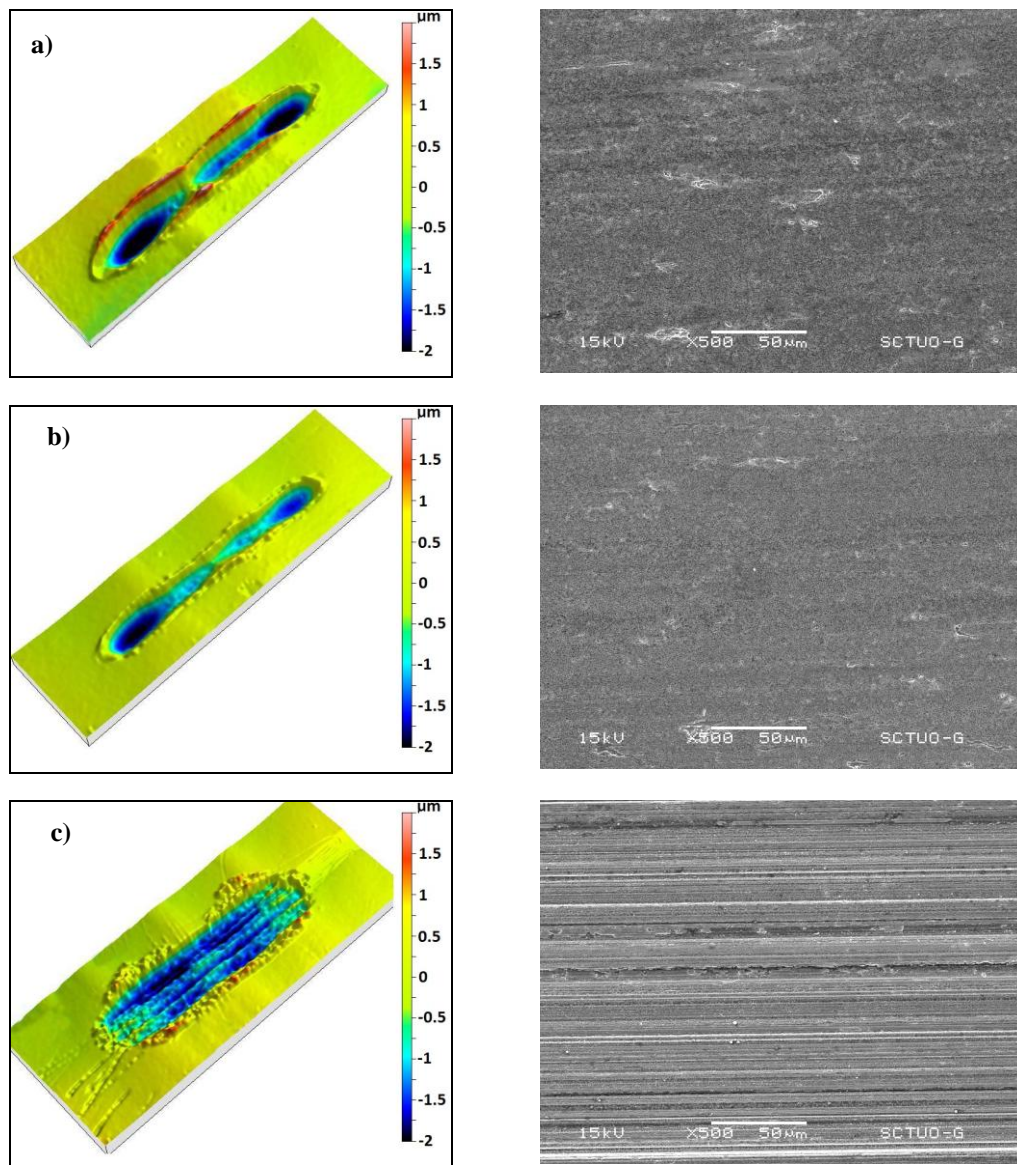


Fig. 7. 3D confocal reconstruction of wear track and SEM image of the bottom of wear track for test at 100°C. a) [(NEMM)MOE][FAP]; b) [BMP][FAP]; c) [BMP][NTf<sub>2</sub>]



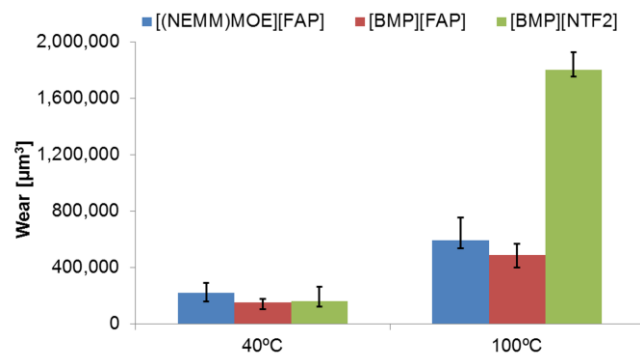


Fig. 8. Average wear volume.

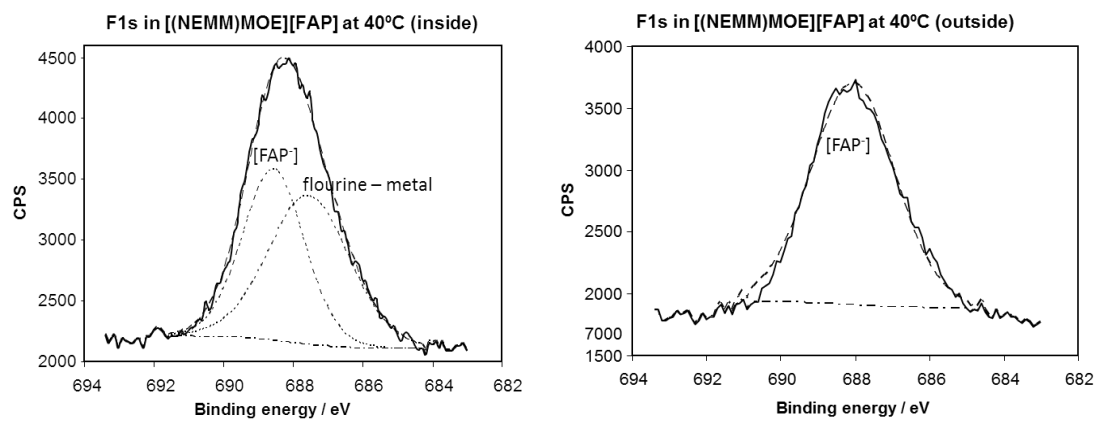


Fig. 9. F1s XPS spectra for [(NEMM)MOE][FAP] at 40°C (inside and outside the wear scar).

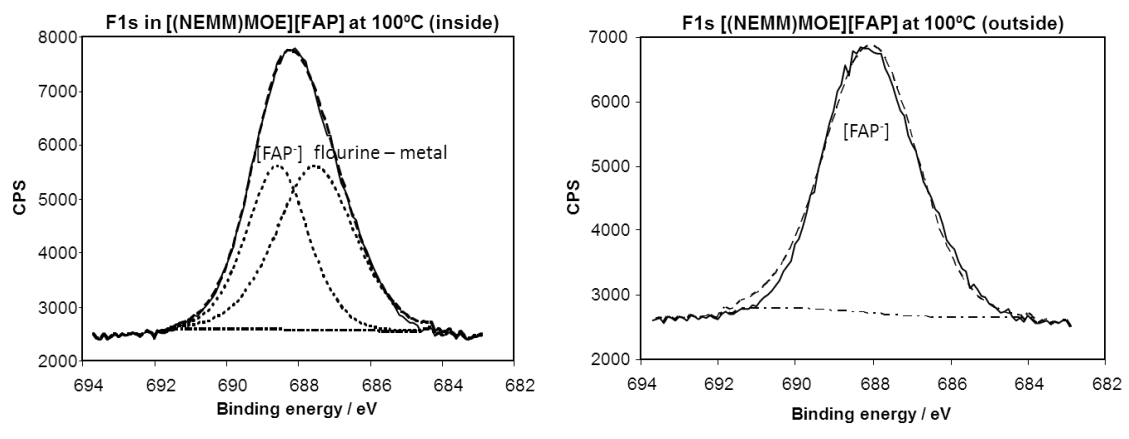


Fig. 10. F1s XPS spectra for [(NEMM)MOE][FAP] at 100°C (inside and outside the wear scar).

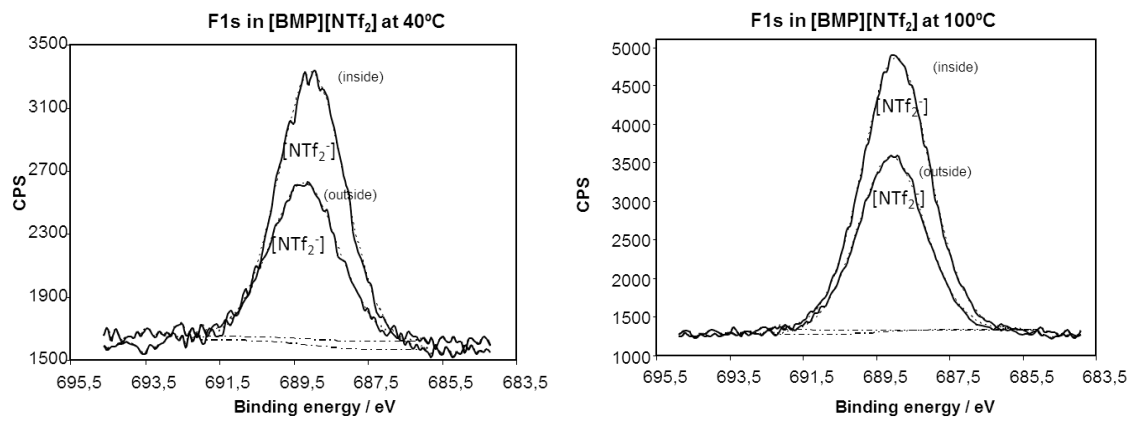


Fig. 11. F1s XPS spectra for [BMP][NTf<sub>2</sub>] at 40°C and 100°C (outside and inside the wear scar).

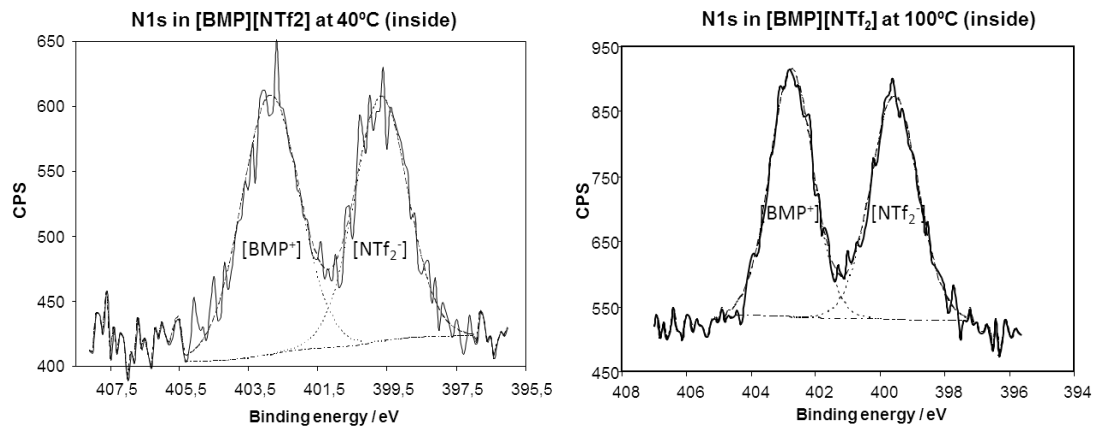


Fig. 12. N1s XPS spectra for [BMP][NTf<sub>2</sub>] at 40°C and 100°C (inside the wear scar).

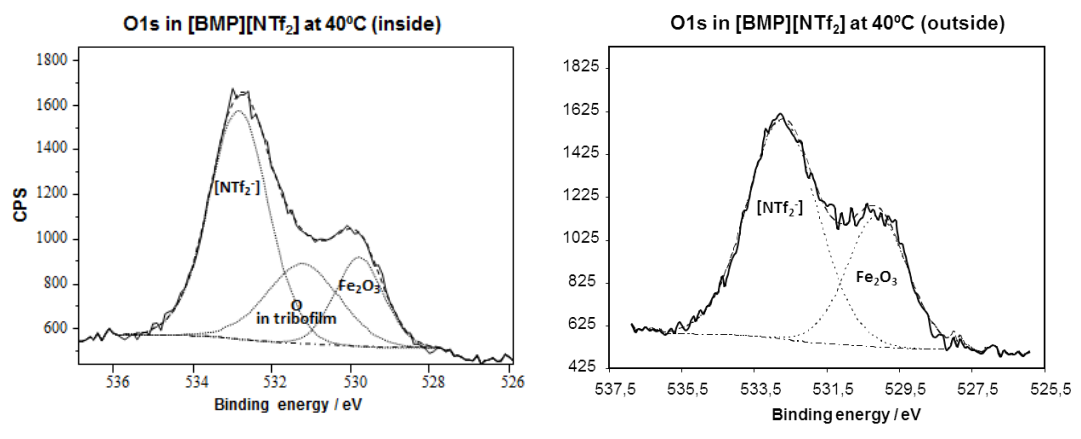


Fig. 13. O1s XPS spectra for [BMP][NTf<sub>2</sub>] at 40°C (inside and outside the wear scar).

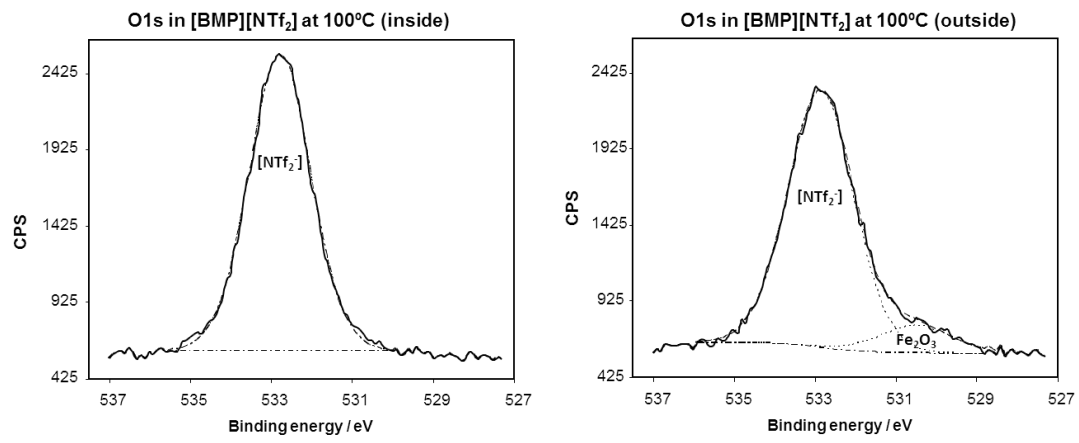


Fig. 14. O1s XPS spectra for [BMP][NTf<sub>2</sub>] at 100°C (inside and outside the wear scar).

Table 1. Ionic liquids properties.

Ionic Liquids		IUPAC name	Purity (%)	Water content (ppm)	Viscosity (mm <sup>2</sup> /s)*		Viscosity Index*
Cation	Anion				40°C	100°C	
[(NEMM)MOE]	[FAP]	ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate	>99	<100 (Karl Fisher)	38.652	6.550	123
[BMP]	[FAP]	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	>99	<1 %	58.758	8.538	118
[BMP]	[NTf <sub>2</sub> ]	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	>99	<100 (Karl Fisher)	28.826	6.228	174

\* Measured in a SVM 3000 Stabinger Viscometer (ASTM D7042, D2270)

### Chemical structure

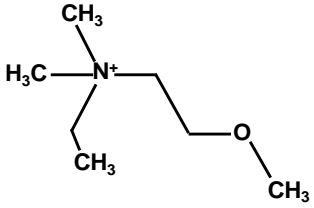
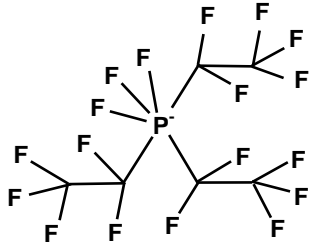
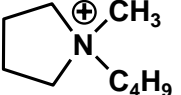
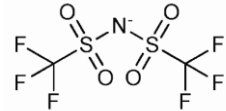
Cations	Anions
$(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OCH}_3)\text{N}^+$  [(NEMM)MOE]	$\text{F}_3(\text{C}_2\text{F}_5)_3\text{P}^-$  [FAP]
$\text{C}_9\text{H}_{20}\text{N}^+$  [BMP]	$(\text{CF}_3\text{SO}_2)_2\text{N}^-$  [NTf <sub>2</sub> ]



Table 2. F1s photoelectron band. FWHM is given in brackets.

<b>F1s (inside)</b>	<b>[(NEMM)(MOE)][FAP]</b>	<b>[BMP][FAP]</b>	<b>[BMP][NTf<sub>2</sub>]</b>
<b>40°C</b>	688.6 (2.1) eV 47%	688.5 (2.4) eV 85%	689.0 (2.1) eV
	687.5 (2.7) eV 53%	686.6 (2.1) eV 15%	
<b>100°C</b>	687.5 (2.5) eV 56%	688.6 (2.2) eV 80%	689.0 (2.1) eV
	688.6 (2.0) eV 44%	687.0 (1.9) eV 20%	

<b>F1s (outside)</b>	<b>[(NEMM)(MOE)][FAP]</b>	<b>[BMP][FAP]</b>	<b>[BMP][NTf<sub>2</sub>]</b>
<b>40°C</b>	688.0 (2.6) eV	688.2 (2.7) eV	689.2 (2.2) eV
<b>100°C</b>	688.0 (2.8) eV	688.4 (2.8) eV	689.1 (2.1) eV

Table 3. O1s photoelectron band. FWHM is given in brackets.

<b>O1s (inside)</b>	<b>[(NEMM)(MOE)][FAP]</b>	<b>[BMP][FAP]</b>	<b>[BMP][NTf<sub>2</sub>]</b>
<b>40°C</b>	531.6 (2.9) eV 68%	531.7 (2.7) eV 62%	532.8 (1.8) eV 57%
	529.8 (1.5) eV 32%	529.9 (1.6) eV 38%	531.2 (2.1) eV 25% 529.8 (1.4) eV 18 %
<b>100°C</b>	532.4 (2.9) eV 62%	531.4 (3.1) eV 75%	532.8 (1.8) eV
	530.0 (1.8) eV 38%	529.7 (1.4) eV 25%	
<b>O1s (outside)</b>	<b>[(NEMM)(MOE)][FAP]</b>	<b>[BMP][FAP]</b>	<b>[BMP][NTf<sub>2</sub>]</b>
<b>40°C</b>	532.3 (2.3) eV 60%	531.9 (2.3) eV 55%	532.7 (2.2) eV 66%
	530.1 (1.8) eV 40%	529.9 (1.7) eV 45%	530.1 (1.9) eV 34%
<b>100°C</b>	532.2 (2.8) eV 60%	531.9 (2.8) eV 68%	532.8 (1.9) eV 90%
	530.0 (1.8) eV 40%	529.9 (1.6) eV 32%	530.5 (2.1) eV 10%

Table 4. P2p photoelectron band. FWHM is given in brackets.

<b>P2p (inside)</b>	<b>[(NEMM)(MOE)][FAP]</b>	<b>[BMP][FAP]</b>	<b>[BMP][NTf<sub>2</sub>]</b>
<b>40°C</b>	133.5 (2.1) eV	133.8 (2.2) eV	Undetectable
<b>100°C</b>	133.6 (2.1) eV	133.4 (2.3) eV	Undetectable

Table 5. S2p photoelectron band. FWHM is given in brackets.

S2p (inside)	[(NEMM)(MOE)][FAP]	[BMP][FAP]	[BMP][NTf <sub>2</sub> ]
40°C	169.3 (2.8) eV	169.4 (2.4) eV	169.2 (2.5) eV
100°C	169.6 (2.5) eV	Undetectable	169.2 (2.8) eV