

# FAP-anion ionic liquids used in the lubrication of a steel-steel contact

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## Abstract

This study compares the tribological behavior of two ionic liquids ([BMP][FAP] and [(NEMM)MOE][FAP]) used as oil additive for the lubrication of a steel-steel contact. Friction and wear experiments were performed using a HFRR test machine. Friction coefficient and electrical contact resistance (ECR) were measured during the tests and the wear surface was analysed by confocal microscopy and XPS. The tribological results showed that both ionic liquids used as additive decrease friction and wear but the [BMP][FAP] had a better performance than the [(NEMM)MOE][FAP] due to its higher reactivity with the steel.

**Keywords:** FAP-based ionic liquids, additives, lubricants, friction, wear.

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## 1. Introduction

In recent years many efforts have been made in order to study the advantages of ionic liquids (ILs) as lubricants or additives [1]. The possible use of ionic liquids in lubrication is due to mainly their high thermal stabilities, wide range of viscosities (50-1500 mm<sup>2</sup>/s at 23°C), non-flammability, negligible volatility and controlled miscibility with organic compounds. On the other hand, ionic liquids with a huge range of properties can be obtained by changing the cation/anion combinations [2-3]. Therefore, ILs due to their tribological behavior, which are better than the one of synthetic, mineral or engine oils (frequently used in lubricated contacts), are a feasible alternative to substitute traditional additives or lubricants [4].

Among the several combinations of anionic and cationic moiety that have been considered, the tris(pentafluoroethyl)trifluorophosphate (FAP) has begun to be used in the formulation of ionic liquids [5]. The hydrolytic stability and hydrophobic character of FAP make this anion a good election to be used in lubrication.

González et al. [6] studied the use of the 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ionic liquid, [BMP][FAP], as 1 wt% additive to a PAO 6 (polyalphaolefin) and as pure lubricant in the lubrication of three coatings (CrN, DLC and TiN) obtained by the PVD technique. The wear and friction tests made showed that [BMP][FAP] used as additive only slightly decrease friction in comparison with the results of the pure base oil. However, the [BMP][FAP]

as pure lubricant significantly decreased the friction coefficient with regard to the base oil and the mixture showing similar friction values for all the coatings. The surface analysis performed after the tribological tests showed that the FAP- anion reacted up to 80% with TiN and DLC surface but the reaction did not occur with the CrN coating.

Blanco et al. [7] tested the ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate ionic liquid, [(NEMM)MOE][FAP], also as 1 wt% additive to a PAO 6 for the lubrication of a CrN PVD coating. The tribological behavior of the mixture of PAO 6 and [(NEMM)MOE][FAP] was compared to the traditional ZDDP added to the base oil in similar concentration. In this case both additives greatly improved the antiwear and antifriction properties of the base oil although ZDDP had the best performance. The [(NEMM)MOE][FAP] ionic liquid was also tested as 1 wt% additive in the lubrication of TiN coating using again PAO 6 as base oil [8]. The use of the ionic liquid as additive also improved the tribological behavior with regard to the use of the pure base oil in the lubrication of this coating. On the other hand, Hernández Battez et al. [9] compared the use of the [(NEMM)MOE][FAP] ionic liquid as neat lubricant and as additive (also PAO 6 was used as base oil) in the lubrication of CrN, TiN and DLC coatings obtained by PVD. In general, the ionic liquid showed a slight antifriction performance for all coatings when it was used as an additive in comparison with the behavior of the pure base oil. However, when the ionic liquid was used as neat lubricant a significant friction and wear reduction was obtained.

In this present study, the ionic liquids, ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate, [(NEMM)MOE][FAP], and 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, [BMP][FAP], have been considered. A proportion of 2 and 4 wt% additives to a mineral hydrocracking oil (M2) for a steel-steel contact have been studied.

## 2. Experimental details

Mineral Hydrocracked Oil (M2) used as base lubricant was kindly provided by Repsol, S.A. with a density of 0.838 g/cm<sup>3</sup> (ASTM D4052), a kinematic viscosity of 32.89 and 5.96 mm<sup>2</sup>/s (ASTM D445) at 40 and 100°C, respectively, and a viscosity index of 127 (ASTM D2270). The ionic liquids used in this study (Table 1) were commercially available from Merck (Germany). Before the tribological tests the ionic liquids were separately mixed with the base oil at concentrations of 2 and 4 wt% using an ultrasonic probe for 5 minutes at 400 W and 50% of amplitude assuring that the temperature of the samples did not

reach 60°C. The stability of the mixtures was measured by light backscattering at room temperature during 2 hours with data acquisition every 10 minutes. During the 2 hours test the blend remained practically constant and no creaming phenomena was found. This results guarantee that the blend is homogeneous during the tribological tests.

Reciprocating ball-on-disc wear tests were performed on a HFRR (a microprocessor-controlled reciprocating friction and wear test system) machine from PCS Instruments using a load of 1.0 kg. (corresponding to a maximum contact pressure of 1.42 GPa), temperature of 100°C, stroke length of 1 mm, frequency of 30 Hz and test duration of 60 minutes. In the tribological tests 6.0 mm diameter AISI 52100 steel balls with a surface finish (Ra) of less than 0.05 µm and a hardness of 58-66 HRC and discs of AISI 52100 steel with a hardness of 190-210 HV and a surface finish (Ra) of less than 0.02 µm were used as specimens. Before tribological tests all specimens were cleaned ultrasonically with toluene and propinol for 5 min and dried with hot air. Three tests were undertaken for each lubricant sample in order to give mean values of friction coefficient. The electrical contact resistance (ECR) was measured during all tests for monitoring tribofilm formation.

After tribological test the specimens were cleaned by rinsing in propinol and air drying. Post tribological experiment steps also included the wear volume determination by using a Leica DCM 3D confocal microscope and worn surface analysis by XPS (X-ray photoelectron spectroscopy). XPS measurements were taken under ultra-high vacuum conditions ( $\leq 5 \cdot 10^{-9}$  mbar) using the K $\alpha$  Mg (1253.6 eV) at 200 W and 13 kV. A Phoibos Hemispherical Energy Analyzer Series MDA5 was used to measure kinetic energy from the electrons in a constant pass energy mode. High resolution spectra were taken using 30 eV as pass energy and 0.1 eV as step size energy; a 2.5 mm diameter iris between detector and sample was used to select the desired zone of the sample (inner part of the wear scar). The position of the C1s band of the spurious carbon was used to check whether the spectrometer should be calibrated using a low energy electron flood gun.

High resolution spectra of both Iron (at 2p<sub>3/2</sub> band) and Fluorine (at 1s band) were taken in every sample. Fe was selected as it is the main component of the steel of the sample, whereas fluorine was selected on the basis of being the most abundant atom in the common anion of both ionic liquids (FAP) and also on previous experience of the authors [6]. On the other hand, phosphorus was analysed in order to check the presence of phosphates.

1 The analysis of the high resolution XPS spectra was performed using CasaXPS software. Curve fitting  
2 was carried out using a Shirley-type baseline [10] and pseudovoigt curves (Product Gaussian (70%)-  
3 Lorentzian (30%)). Levenberg-Marquardt algorithm was selected as optimization procedure.  
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5 Supplementary analysis using Simplex method was also performed with software developed by the  
6 authors.  
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### 10 11 **3. Results and discussions**

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13 The friction coefficient results from the tribological tests are shown in Fig. 1. In general, the addition of  
14 both ionic liquids to the base oil (M2) decrease friction in comparison with the friction results of the neat  
15 base oil. For both ionic liquids the highest friction reduction was obtained when the IL content was 4  
16 wt%. However, the [BMP][FAP] ionic liquid showed improved tribological behaviour as an oil additive  
17 than [(NEMM)MOE][FAP].  
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20 The evolution of the friction coefficient during the tribological tests using the pure base oil and the  
21 mixtures with the [(NEMM)MOE][FAP] is observed as Fig. 2. The friction behavior can be clearly  
22 related to the formation of tribofilm on worn surfaces which change the electrical contact resistance  
23 (ECR) values. For the pure base oil the ECR is approximately zero and this corresponds to the highest  
24 friction coefficient. On the other hand, when the ionic liquid was added to the base oil the ECR values  
25 changed from zero and lower friction coefficient was observed for higher ECR values. The mixtures with  
26 4 wt% of ionic liquid had the highest ECR results and then the lowest friction coefficient.  
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29 Fig. 3 shows the friction evolution of the tests made using the [BMP][FAP]. In this case the result is quite  
30 similar to the [(NEMM)MOE][FAP] one. The highest and stable ECR values showed by the mixture with  
31 4 wt% of ionic liquid also contributed to obtain the lowest and stable friction coefficient. However, it is  
32 important to point out the fact that the [BMP][FAP] reacted more quickly with the wear surfaces  
33 (tribofilm formation) and showed higher ECR values than the [(NEMM)MOE][FAP]. The influences of  
34 the ionic liquid used as additives on the tribofilm formation and the improvement of antifricition and  
35 antiwear behaviour have been studied in depth recently by Qu et al. [11].  
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38 This study also showed the antiwear properties of these ionic liquids used as additives, Fig. 4. Both used  
39 ionic liquids concentration (2 and 4 wt%) decreased wear, but the higher concentration showed better  
40 results. Similar to friction results, [BMP][FAP] improved the antiwear performance of the base oil more  
41 than the [(NEMM)MOE][FAP] one. Fig. 5 shows the 2D image of the wear scar on the lower specimen  
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(disc) and it can be observed the best antiwear performance of [BMP][FAP] with regard to the [(NEMM)MOE][FAP] and also how the 4 wt% concentration is more effective than the 2 wt% one.

The variation on the concentration of [(NEMM)MOE] seems not to have a strong effect on the surface from the chemical point of view. The iron on the surface at both concentrations (2 and 4 wt%) has a very similar behaviour, with a strong main peak from iron (III) oxide at 710.8-710.9 eV [12-13] and a smaller peak at 712.6 belonging to  $\text{FePO}_4$  [14]. Fluorine-Iron interactions can be appreciated in the 2 wt% [(NEMM)MOE][FAP] samples with a peak at 714.1 eV [12] too (Fig. 6). Fluorine content in the surface is low in both cases, although it is lower in the 4 wt% [(NEMM)MOE][FAP] samples (Fig.7). Curve fitting for fluorine shows two different species: the most abundant coming from FAP-anion (688.5 eV, 289.2 eV [5-6]) and a smaller band at 684.6–684.7 eV from the Fe–F interactions [12]. Phosphorus in both samples shows a peak at 133.7–133.8 eV coming from  $\text{FePO}_4$  [15]. These results are summarized in Table 2.

Lubrication with [BMP][FAP] at 2 wt% concentration behaves very similarly to that with [(NEMM)MOE][FAP].  $\text{Fe}2p_{3/2}$  band appears at 710.8 eV, being due to iron (III) oxide with a small contribution at 712.8 eV arising from  $\text{FePO}_4$  (Fig. 8). Fluorine concentration is too low, so Fe-F interactions are masked by  $\text{FePO}_4$  and  $\text{Fe}_2\text{O}_3$ . Even so, two different peaks at 684.5 and 690.5 eV can be detected for F1s. These bands are assignable to metallic fluorides and FAP-anion respectively. The presence of  $\text{FePO}_4$  is confirmed checking the high resolution  $\text{P}2p$  XPS spectrum, showing a band at 133.5 eV assignable to iron (III) phosphate. When the concentration of the ionic liquid is increased to 4 wt%, the main difference is a stronger presence of fluorine on the surface, which can be appreciated also in the  $\text{Fe}2p$  band (with a very small component at 714.3 eV) together with the bands of  $\text{Fe}_2\text{O}_3$  and  $\text{FePO}_4$  (Fig. 9). The high resolution analysis of the F1s band indicates a similar situation to that from the 2 wt% [BMP][FAP] sample, with 50% of fluorine as Fe-F and 50% as unreacted FAP-anion. As in the previous cases, the presence of phosphate can be easily checked by analysing the  $\text{P}2p$  band, finding a peak at 133.6 eV. These results are summarized in Table 3.

In general the tribological behavior (antifriction and antiwear properties) of [BMP][FAP] was better than the [(NEMM)MOE][FAP] one. These improved results are related with the higher decomposition of the  $\text{FAP}^-$  anion and the reaction of fluorine with the wear surface. Similar results were obtained when these ionic liquids were tested as additives in the lubrication of two PVD coatings (TiN and DLC) [6,9,16]. With these two coatings, more than the 60% of fluorine (F) of the [BMP][FAP] ionic liquid was bound to

metals inside the wear scar, while the rest of fluorine remained as FAP- anion. On the other hand, the tribological behavior of the [(NEMM)MOE][FAP] was better than the [BMP][FAP] one in the lubrication of a CrN coating [6,9] because the former also reacted much more with the surface than the latter.

#### 4. Conclusions

The use of [(NEMM)MOE][FAP] and [BMP][FAP] ionic liquids as additives to a mineral hydrocracked oil (base oil) was studied in this work. Mixtures of the base oil with 2 and 4 wt% of ionic liquid was tribologically tested and the worn surface was measured by confocal microscopy and analyzed by XPS. The main results showed that both ionic liquids have antifriction and antiwear properties when they are used as additives. The [BMP][FAP] showed better tribological behavior than the [(NEMM)MOE][FAP] one. In both cases, higher content of ionic liquid in the mixture resulted in higher friction and wear reduction. The friction behavior of the mixtures was related to the tribofilm formation and this fact was evaluated by measuring the electrical contact resistance (ECR). As expected, higher ECR values resulted in lower friction and wear.

The wear results were similar to the friction ones, being the mixtures with 4 wt% of ionic liquid the best in both cases. The XPS analysis showed that the ionic liquid reacted with surfaces forming both phosphates- and fluorine-iron compounds, but not at 100%, remaining certain percentage of FAP-anion. The mixture with 4 wt% of [BMP][FAP] reacted with the surface much more than the other mixtures, leading to the highest overall friction and wear reduction.

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Table 1. Ionic liquids properties (provided by the supplier).

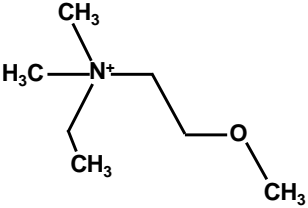
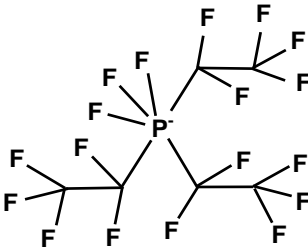
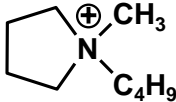
Ionic Liquids		IUPAC name	Purity (%)	Water content	Viscosity (cP)
Cation	Anion				
[(NEMM)MOE]	[FAP]	ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate	>99	<100 ppm (Karl Fisher)	178
[BMP]	[FAP]	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	>99	<1 % (Karl Fisher)	292
Chemical structure					
Cations			Anion		
$(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OCH}_3)\text{N}^+$			$\text{F}_3(\text{C}_2\text{F}_5)_3\text{P}^-$		
					
[(NEMM)MOE]			[FAP]		
$\text{C}_9\text{H}_{20}\text{N}^+$					
					
[BMP]					

Table 2. XPS results for samples lubricated with [(NEMM)MOE][FAP] at 2 and 4 wt%.

	M2 + 2% [(NEMM)MOE][FAP]	M2 + 4% [(NEMM)MOE][FAP]
Fe2p3/2	710.9 eV, 84%, Fe <sub>2</sub> O <sub>3</sub>	
	712.6 eV, 12%, FePO <sub>4</sub>	710.8 eV, 73%, Fe <sub>2</sub> O <sub>3</sub>
	714.4 eV, 4%, Fe – F	712.6, 27%, FePO <sub>4</sub>
	( $\chi^2=0.5190$ )	( $\chi^2=0.7473$ )
F1s	684.6 eV, 20%, Fe - F	684.7 eV, 23%, Fe -F
	688.5 eV, 80%, [FAP <sup>-</sup> ]	689.2 eV, 77%, [FAP <sup>-</sup> ]
	( $\chi^2=0.5294$ )	( $\chi^2=0.4139$ )
P2p	133.7 eV, 100%, FePO <sub>4</sub>	133.8 eV, 100%, FePO <sub>4</sub>
	( $\chi^2=0.9680$ )	( $\chi^2=0.5512$ )

Table 3. XPS results for samples lubricated with [BMP][FAP] at 2 and 4wt%.

	M2 + 2% [BMP][FAP]	M2 + 4% [BMP][FAP]
Fe2p3/2	710.8 eV, 90%, Fe <sub>2</sub> O <sub>3</sub>	710.8 eV, 77%, Fe <sub>2</sub> O <sub>3</sub>
	712.8 eV, 10%, FePO <sub>4</sub> ( $\chi^2=0.5272$ )	712.6 eV, 20%, FePO <sub>4</sub> 714.3 eV, 3%, Fe – F ( $\chi^2=0.7440$ )
F1s	684.5 eV, 40%, Fe – F	684.4 eV, 50%, Fe – F
	690.5 eV, 60%, [FAP] <sup>-</sup> ( $\chi^2=1.0681$ )	688.5 eV, 50%, [FAP] <sup>-</sup> ( $\chi^2=0.3747$ )
P2p	133.5 eV, 100%, FePO <sub>4</sub> ( $\chi^2=0.4250$ )	133.6 eV, 100%, FePO <sub>4</sub> ( $\chi^2=0.5658$ )

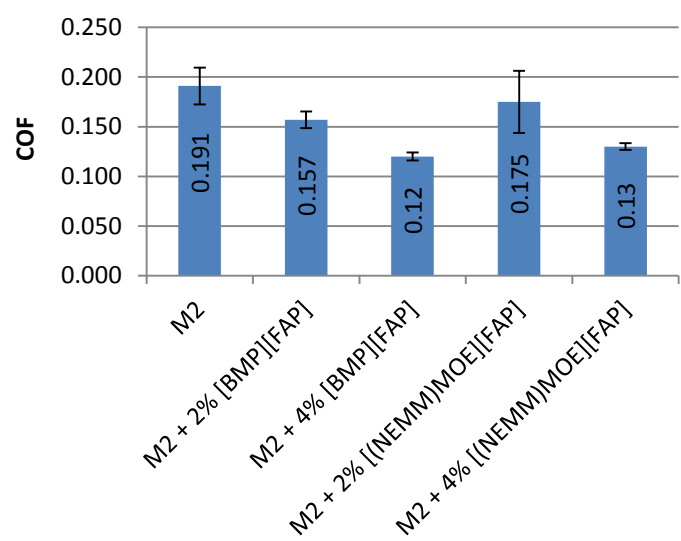


Fig. 1. Average friction coefficient.

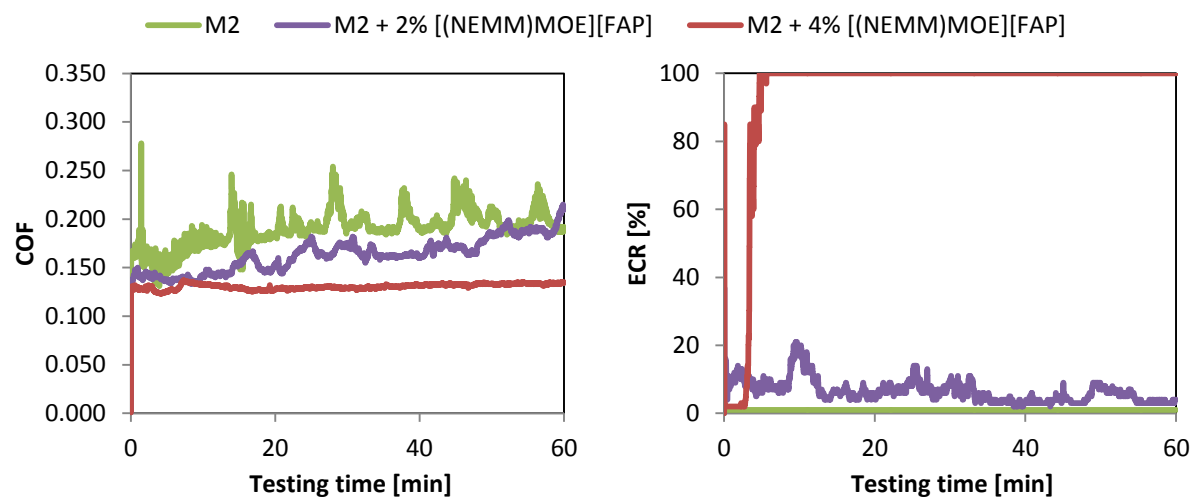


Fig. 2. Friction and ECR behaviour for [(NEMM)MOE][FAP].

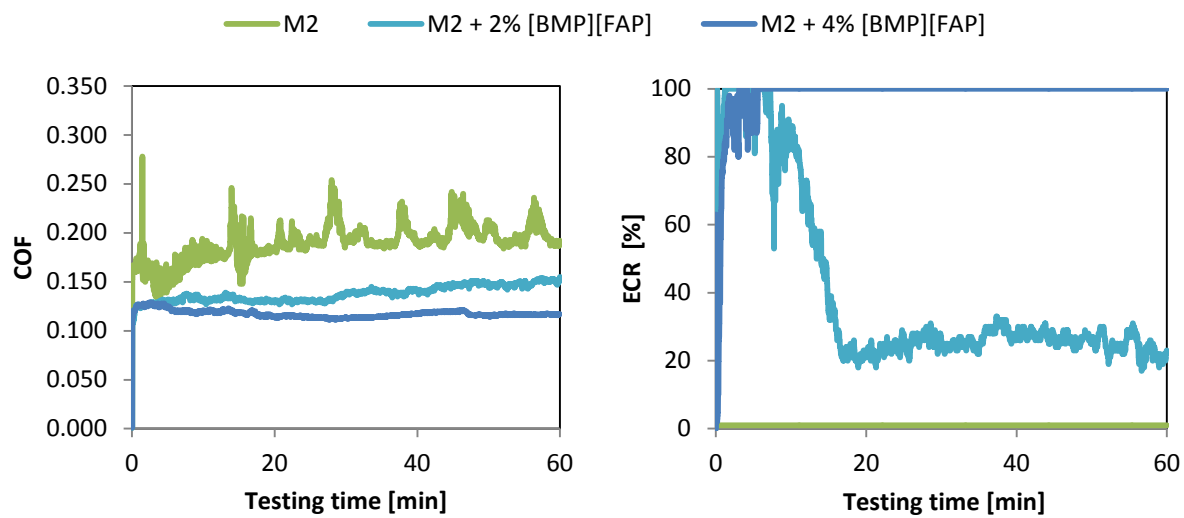


Fig. 3. Friction and ECR behaviour for [BMP][FAP].

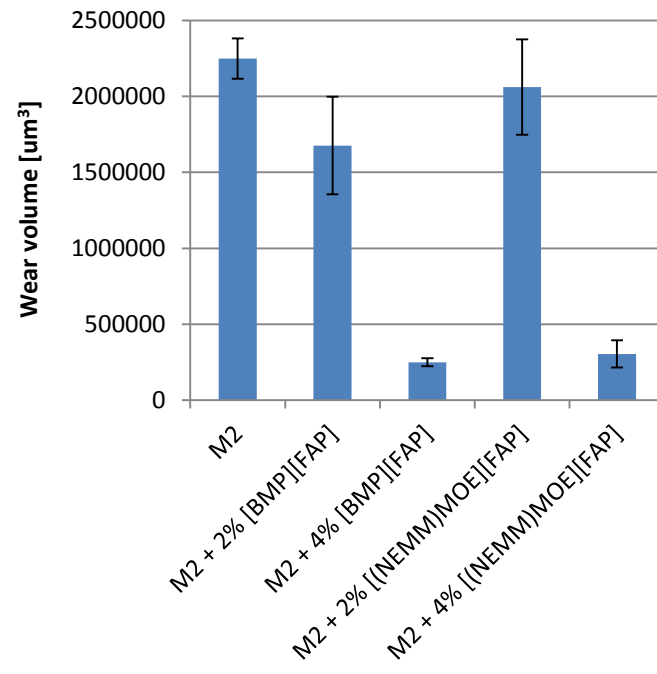


Fig. 4. Average wear volume.

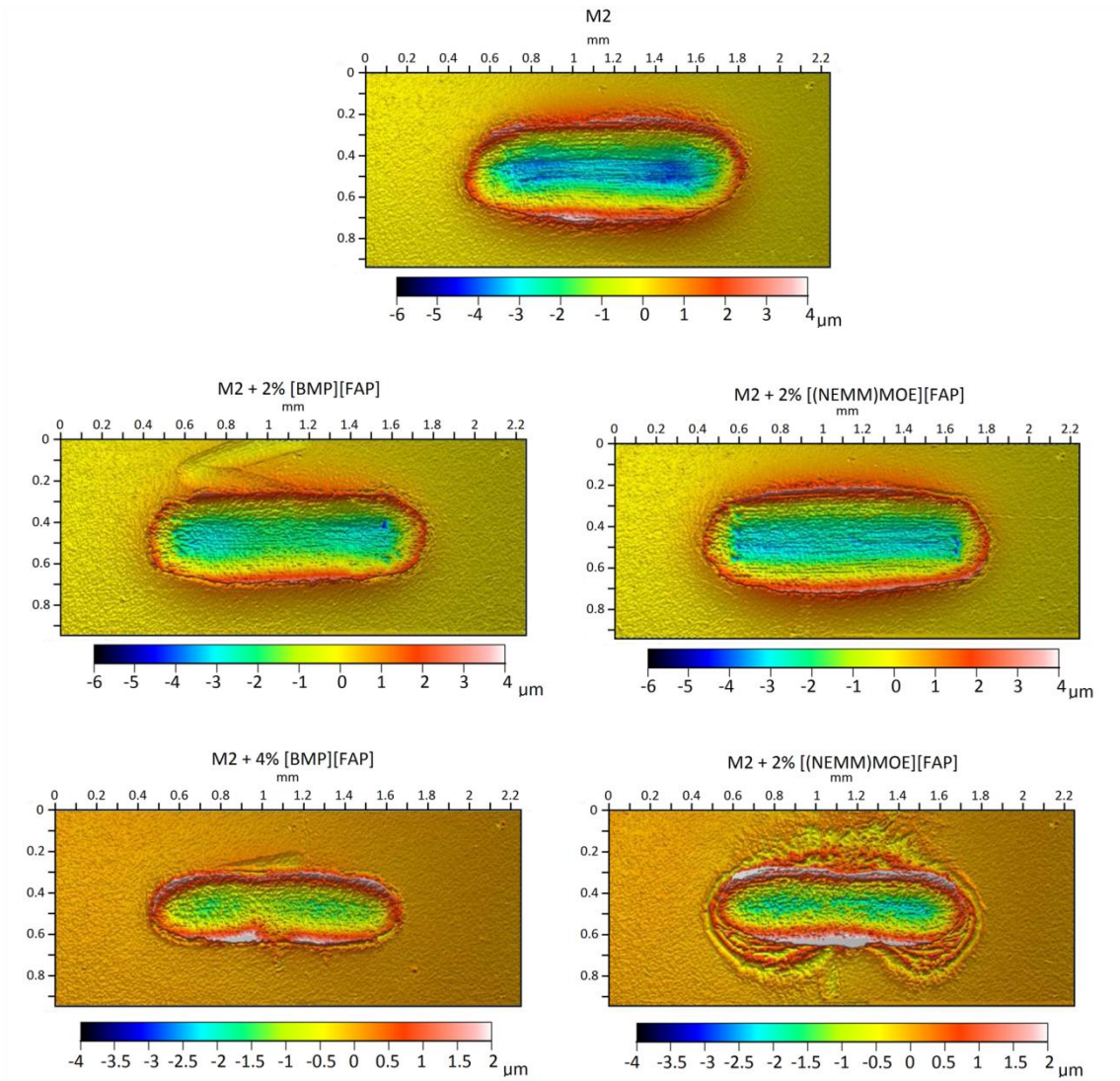


Fig. 5. 2D wear scar on the lower specimen (disc).



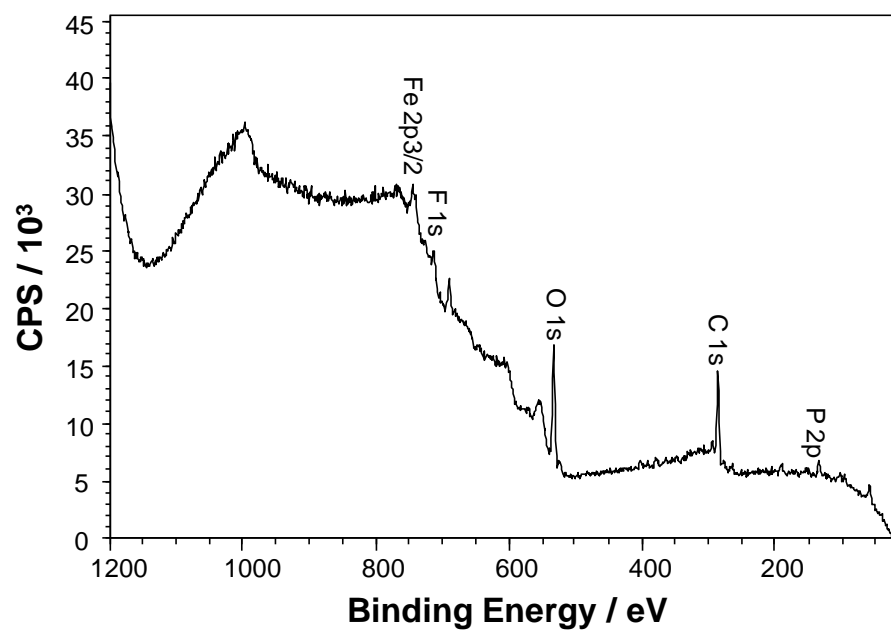


Fig. 6. Survey spectrum of M2 + 2wt% [(NEMM)MOE][FAP].

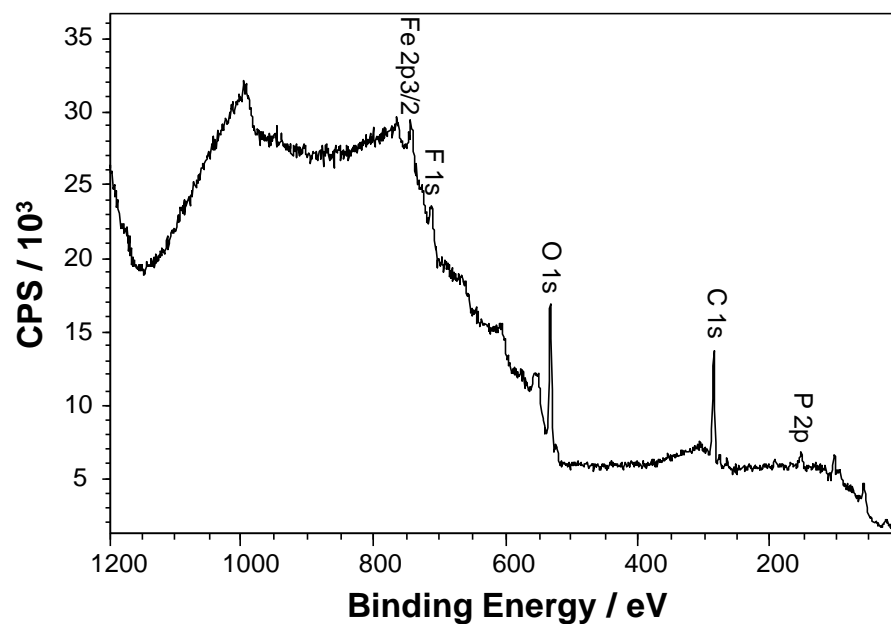


Fig. 7. Survey spectrum of M2 + 4wt% [(NEMM)MOE][FAP].

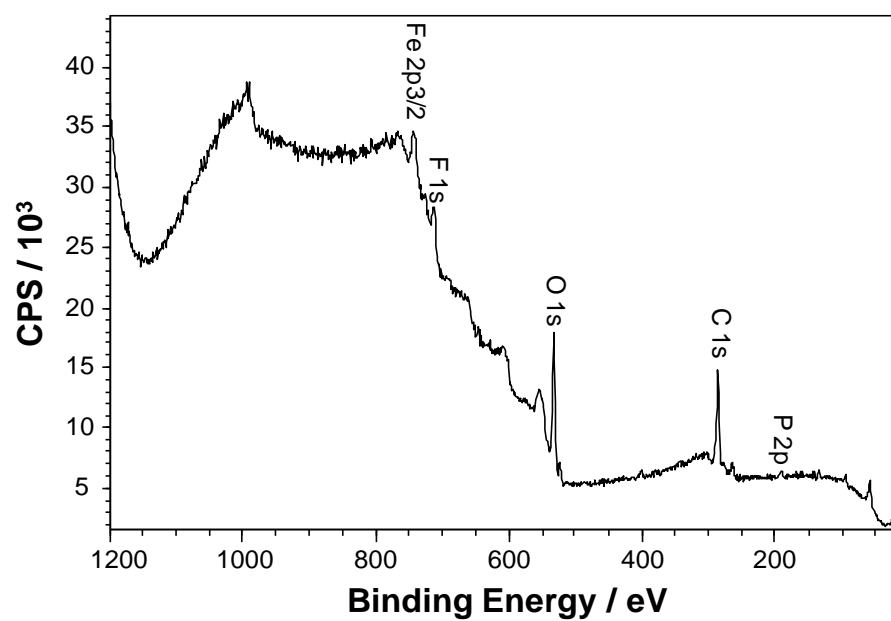


Fig. 8. Survey spectrum of M2 + 2wt% [BMP][FAP].

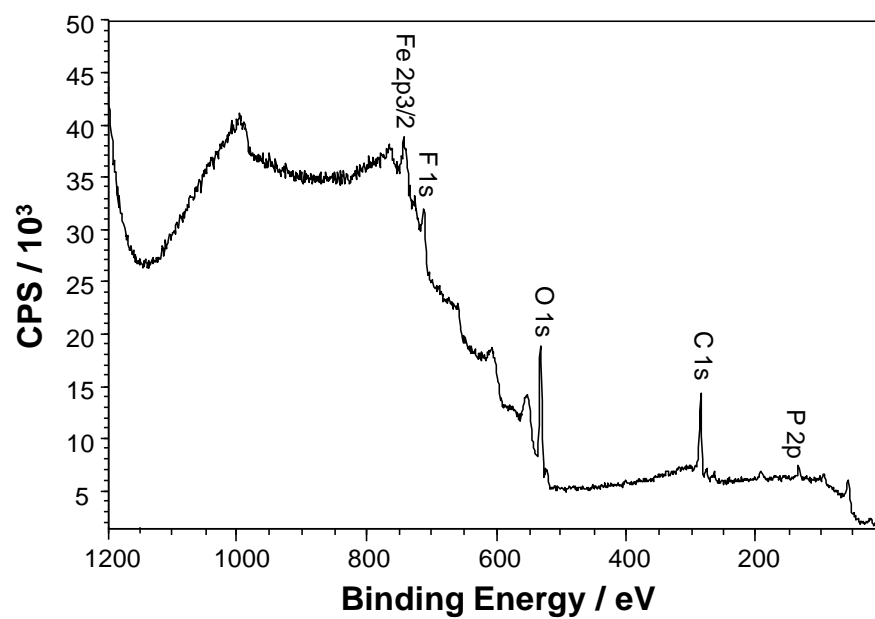


Fig. 9. Survey spectrum of M2 + 4wt% [BMP][FAP].