

Two phosphonium cation-based ionic liquids as lubricant additive to a polyalphaolefin base oil

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Abstract

This paper studies the tribological performance of two phosphonium cation-based ionic liquids: trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][iC_8)_2PO_2]$) and trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}][BEHP]$), as lubricant additive at 1 wt% to a polyalphaolefin. A comparison of their tribological behavior was made to that of one type of zinc dialkyldithiophosphate (ZDDP). Stribeck curve tests were made in a Mini Traction Machine (MTM) tribometer at entrainment speeds ranging from 2000 to 10 mm/s, 30 N-load, slide-to-roll ratio (SRR) of 50%, and temperatures of 40, 60, 80 and 100 °C. Tribofilm formation tests were also conducted in the MTM at 100 °C, load of 50 N, entrainment speed of 150 mm/s, SRR of 50%, and duration of 60 min. Additionally, reciprocating 60-min wear tests at 60 N-load, frequency of 15 Hz, stroke length of 4 mm and temperature of ... were performed with IL-containing mixtures at 0.5 and 1 wt%. Coefficient of friction was recorded during the tests, and wear on the discs surface was measured using confocal microscopy. SEM and EDS were also used for studying the lubricant-surface interactions after these tests. Lubricants including $[P_{6,6,6,14}][iC_8)_2PO_2]$ exhibited better tribological performance than $[P_{6,6,6,14}][BEHP]$ ones and close to the ZDDP results. SEM images of worn surfaces exhibited evidence of plastic deformation and adhesive wear and EDS analysis showed that only active elements (P, S, Zn) were detected for mixtures containing ZDDP. XPS analysis indicated a different lubrication mechanism of the blends with ionic liquids compared with the ZDDP ones.

Keywords: phosphonium cation-based ionic liquids; additive; friction; wear; ZDDP

1 Introduction

Friction, wear and lubrication (tribology problems) continue being a major challenge for industry, especially in fields such as aerospace, electronics and computers, where a lot of efforts are still necessary for optimizing practical applications. Nowadays, lubrication is a key factor to achieve friction and wear reductions, and then contribute to decrease energy consumption and emissions, which are important benefits for society. In order to accomplish the goal of reducing friction and wear through lubrication, it is very important the use of specific additives in lubricant formulation.

Ionic liquids are a current research topic in lubrication as possible additive to be used in order to prevent direct metal/metal contacts and consequently damages on the surfaces [1–4]. One ionic liquid is a salt which melts below 100 °C [5] much of them are liquids at room temperature and then are called “room temperature

ionic liquid” (RTIL) [6]. The first paper about the use of ionic liquids in lubrication was published in 2001 [7]. These substances have remarkable properties for lubrication such as large liquid range, low volatility and flammability and high thermal stability [3,8–12]. Despite of the fact that these substances have shown great performance as neat lubricants [13–24], their current relatively high cost is still a drawback. Therefore, the utilization of ILs as a lubricant additive should reduce the cost implications without losing the benefits of chemical interaction with surfaces, which can provoke friction and/or wear reductions [25].

On the other hand, the ionic character of these substances means that most of them are not capable of blending with neutral hydrocarbon oils (mineral oils and polyalphaolefins), which result in forming oil-IL emulsions with limited stability or mixtures with very low concentration of ionic liquid [24,26–30]. This inherent low solubility in non-polar substances leads to use the ionic liquids as additive in polar base oils (e.g. esters) [29,31–33]. However, phosphonium cation-based ionic liquids have shown excellent friction and wear reduction results when they were used as oil additive even in non-polar oils, showing also a good solubility [19,29,42,34–41]. The tribological improvement of using polar substances as additive in non-polar oils was proved by some authors in the past [43–45] and that approach can be used again with ionic liquids.

Despite of the fact that some researches have been focused on the tribological behavior of phosphonium cation-based ionic liquids as lubricant additive in different material pairs, no works dealt with the effectiveness of using that cation combined with phosphinate and phosphate anions as lubricant additive in a synthetic base oil for a steel-steel contact. This work deals with the use of the trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][iC_8)_2PO_2]$) and trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}][BEHP]$) ionic liquids as additive in a polyalphaolefin. Two blends of this base oil and ZDDP were used as comparison samples and in all cases the IL and ZDDP concentrations took into account different engine oil specifications (PC-11, ILSAC GF-5 and ILSAC GF-6) that recommend a phosphorus concentration under 800 ppm [46].

2 Experimental details

2.1 Ionic liquids and base oil

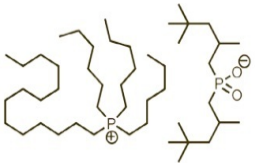
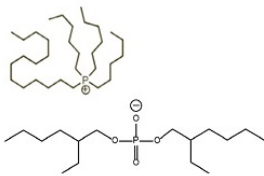
The phosphonium cation-based ionic liquids: trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][iC_8)_2PO_2]$) and trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}][BEHP]$), were supplied by Io-Li-Tec (Ionic Liquid Technologies GmbH) and used in this work

as lubricant additive to a polyalphaolefin (PAO 4) provided by Repsol S.A. A traditional lubricant additive, like zinc dialkyldithiophosphate (ZDDP), was used for comparison purposes. Table 1 exhibits the properties of all these lubricant compounds. Description and chemical structure of the $[P_{6,6,6,14}][(iC8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$ ionic liquids are shown in Table 2.

Table 1 Properties of the lubricant samples.

Lubricant samples	Density (g/cm ³) a 20 °C ASTM D 4052	Kinematic viscosity (mm ² /s)		Viscosity Index ASTM D 2270
		ASTM D 445		
		40 °C	100 °C	
PAO 4	0.815	16.89	3.89	
ZDDP	1.200	658.66	14.47	-
$[P_{6,6,6,14}][(iC8)_2PO_2]$	0.889	528.93	55.06	169
$[P_{6,6,6,14}][BEHP]$	0.915	528.05	59.00	181

Table 2 Description and chemical structure of the $[P_{6,6,6,14}][(iC8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$.

IUPAC name (CAS number)	Empirical formula	Purity (%)	Molecular weight	Chemical structure
Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate (465527-59-7)	C ₄₈ H ₁₀₂ O ₂ P ₂	95	773.27	
Trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate (1092655-30-5)	C ₄₈ H ₁₀₂ O ₄ P ₂	98	805.29	

The corrosion character of the $[P_{6,6,6,14}][(iC8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$ ionic liquids was studied in a previous work [13]. No corrosion activity for both ionic liquids was detected on the surface of AISI 52100 steel discs after tests made at room temperature.

A Mettler Toledo TGA/SDTA851 thermogravimetric analyzer (TGA) was used in order to determine the decomposition temperatures of the ionic liquids and the base oil. Dynamic tests were made from room temperature to approximately 600 °C at 10 °C/min heating rate in both oxygen and nitrogen atmospheres with a flow rate of 50 mL/min.

One of the key aspects in the use of ILs as additive in lubricants is their solubility in the base oil. The solubility of the $[P_{6,6,6,14}][iC_8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$ ionic liquids in PAO 4 was tested following a methodology similar to that used by Otero et al. [44]: a Labonet VX 100 Vortex was employed to mix 2mL of base oil and 1mL of IL in order to obtain a homogeneous suspension that guaranteed the saturation of the IL in the base oil. Later, a Thermo Scientific Heraeus Labofuge 200 centrifuge was employed to centrifuge the blend for five minutes at 5300 rpm. The densest phase was removed, and the base oil (the less dense phase) was analyzed by ICP-MS after being decanted and digested in a microwave oven (65% HNO₃: 25% H₂O 7:1), diluting the residue as necessary. The results of the solubility tests showed an ionic liquid concentration in the base oil around 22 and 16 wt% for $[P_{6,6,6,14}][iC_8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$, respectively.

Taking into account the above solubility results, PAO4-IL mixtures containing 0.5 and 1 wt% of IL were prepared. These IL concentrations corresponded with a phosphorus concentration of 350 and 700 ppm for $[P_{6,6,6,14}][iC_8)_2PO_2]$ and 358.5 and 717 ppm for $[P_{6,6,6,14}][BEHP]$. PAO-ZDDP mixtures with concentrations of ZDDP of 0.4 and 0.8 wt% (corresponding to 351.5 and 703 ppm of phosphorus) were also prepared to be used as reference lubricant samples.

Density and dynamic viscosity of the above samples at atmospheric pressure in a range of 20 to 100 °C were measured according to ASTM D7042 using a Stabinger SVM3001 viscometer.

2.2 Tribological tests

In order to study friction and tribofilm formation in a steel-steel contact, two different rolling-sliding tribological tests were carried out in a Mini Traction Machine tribometer with spacer layer image mapping (MTM2 3DSLIM -PCS Instruments-). In both cases, the pure PAO 4 and the PAO4-IL mixtures with the highest phosphorus concentration were tested using a configuration formed by a 19.05 mm-diameter AISI 52100 steel ball ($R_a \approx 0.01\mu m$) and a 46 mm-diameter AISI 52100 steel disc ($R_a \approx 0.01\mu m$). The ball is loaded against the face of the disc and the ball and disc are driven independently to create a mixed rolling/sliding contact under the presence on 10 mL of lubricant.

Firstly, experiments for evaluating the lubricant behavior under different lubrication regimes (Stribeck curve) were performed. The test conditions used for these experiments were: 30 N-load (corresponding to a maximum contact pressure of 0.95 GPa), slide-to-roll ratio (SRR) of 50%, mean entrainment speeds ranging from 2000 to 10 mm/s (steps of 100 mm/s from 2000 to 100 mm/s, and steps of 10 mm/s from 100

to 10 mm/s), and temperatures of 40, 60, 80 and 100 °C were developed. Traction coefficient and electrical contact resistance (ECR) between the ball and the disc were measured during tests.

Secondly, the thickness of the tribofilm formed on the ball surface during an specific test was measured with in situ spacer layer interferometry as described in [47]. Tests were conducted at a lubricant temperature of 100 °C, load of 50 N (corresponding to a maximum contact pressure of 1.13 GPa), mean entrainment speed of 150 mm/s, SRR of 50%, and duration of 60 min.

Finally, accelerate wear tests were performed for all mixtures and the pure base oil using a Bruker UMT-3 tribometer with a reciprocating ball-on-plate configuration. As upper specimen (ball) were used AISI 52100 chrome steel balls with diameter of 6.0 mm ($R_a \leq 0.05 \mu\text{m}$) and hardness of 58-66 HRC). On the other hand, as lower specimen (disk) were employed 3 mm-thick and 10 mm-diameter AISI 52100 steel disks ($R_a \leq 0.02 \mu\text{m}$) with hardness of 190-210 HV₃₀. 60-min tests at a load of 60 N (corresponding to maximum contact pressure of 1.91 GPa), a frequency of 15 Hz and stroke length of 4 mm in the presence of 4 mL of the corresponding lubricant sample were made. Coefficient of friction was measured during tests and each lubricant sample was tested at least three times under this test condition. All tests were carried out at room temperature and a relative humidity ranging 20-40%.

In all cases, the specimens used in the tribological tests were ultrasonically cleaned with heptane for 10 min, rinsed in ethanol and dried in hot air.

2.3 Surface Characterization

The wear depth on the disc surface was measured after the 60-min tests using a confocal microscope (Leica DCM 3D). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were also used in order to study the wear mechanism and the lubricant-surface chemical interactions after the 60-min tests. 20 kV of acceleration voltage was selected to do the SEM-EDS analysis.

XPS analysis through monochromatized Al K-alpha x-ray radiation were developed using a photoelectron spectrometer (SPECS) with a hemispherical energy analyser (type Phoibos). A single survey spectrum with energy pass 90 eV and energy step 1 eV was taken for every sample. Likewise, high-resolution spectra were taken with 30 eV energy pass and 0.1 eV energy step. Signal-to-noise ratio of the element in the sample determined the number of scans for high-resolution spectra.

3 Results and discussion

3.1 Physicochemical properties

Thermogravimetric analysis (TGA) of some phosphonium cation-based ionic liquids, including the $[P_{6,6,6,14}][(iC8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$ ones, was previously reported in [13]. Fig. 1 compares TGA curves of both ionic liquids and the base oil (PAO 4) under both oxygen and nitrogen atmospheres. The base oil exhibited similar thermal behavior under both atmospheres. However, a rapid degradation under oxygen atmosphere (more reactive), with the onset of degradation at a temperature of about 240 °C, can be observed. On the other hand, a more gradual degradation, starting at about 247 °C, was observed under an inert (nitrogen) atmosphere.

Both ionic liquids exhibited higher degradation temperatures than the base oil, specially under nitrogen atmosphere where their resistance to the pyrolysis process has great influence. Two steps degradation curve were observed for the $[P_{6,6,6,14}][BEHP]$ IL, probably due to the more reactive phosphate anion type [48].

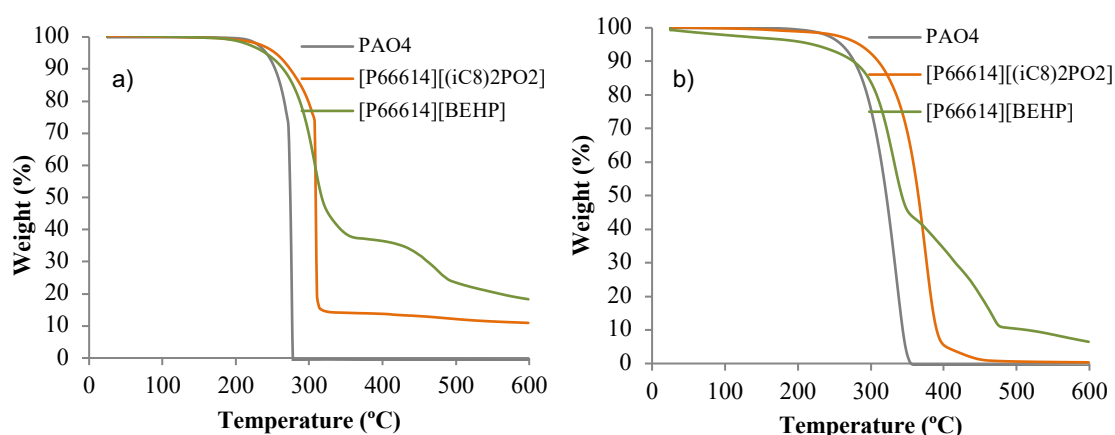


Fig. 1 Thermogravimetric analysis under: (a) O₂ atmosphere, (b) N₂ atmosphere.

The use of both studied ILs as additive only causes a slight increase in density and viscosity values in comparison with that of the pure base oil. Table 3 shows the viscosity changes with the additive concentration in all cases.

Table 3 Density and viscosity of lubricant samples.

Lubricant	Density (g/cm ³)* 20 °C	Viscosity (mm ² /s)*				
		20 °C	40 °C	60 °C	80 °C	100 °C
PAO 4	0.8153	36.802	16.891	9.244	5.723	3.892
PAO 4 + 0.5% $[P_{6,6,6,14}][iC8)_2PO_2]$	0.8157	37.112	17.006	9.292	5.733	3.902
PAO 4 + 1% $[P_{6,6,6,14}][iC8)_2PO_2]$	0.8162	37.410	17.118	9.336	5.765	3.855
PAO 4 + 0.5% $[P_{6,6,6,14}][BEHP]$	0.8159	37.242	17.007	9.313	5.785	3.990
PAO 4 + 1% $[P_{6,6,6,14}][BEHP]$	0.8162	37.413	17.168	9.320	5.746	3.893
PAO 4 + 0.4% ZDDP	0.8164	36.883	16.922	9.246	5.721	3.889
PAO 4 + 0.8% ZDDP	0.8174	37.004	16.953	9.263	5.723	3.887

* Measured in an SVM 3001 Stabinger Viscometer

3.2 Tribological tests

Both the traction coefficient and ECR versus mean entrainment speed at different temperatures were measured for pure PAO 4 and the mixtures with the maximum phosphorous concentration described in section 2.1. Fig. 2 shows the temperature dependence of the traction coefficient. For all lubricant samples tested, the higher the temperature the lower the traction coefficient in the zone of hydrodynamic lubrication regime due to reduction in the lubricant viscosity and then in the lubricant film thickness. On the other hand, the traction coefficient increased sharply at increasing temperatures in the zone of mixed lubrication regime, where contact between surfaces take place. With regard to the ECR behavior, as expected a decrease in ECR values leads to higher friction due to the increase in the asperities contact in both mixed and boundary lubrication regimes. Test lubricated with PAO 4 + 1% [P_{6,6,6,14}][BEHP] exhibits traction coefficient results very similar than those obtained for pure PAO 4. However, the addition of 1% [P_{6,6,6,14}][(iC8)₂PO₂] to the base oil causes the elastohydrodynamic regimen to be reached at higher speeds, especially at the higher temperatures studied. The same behavior can be observed in the tests lubricated with PAO 4 + 0.8% ZDDP.

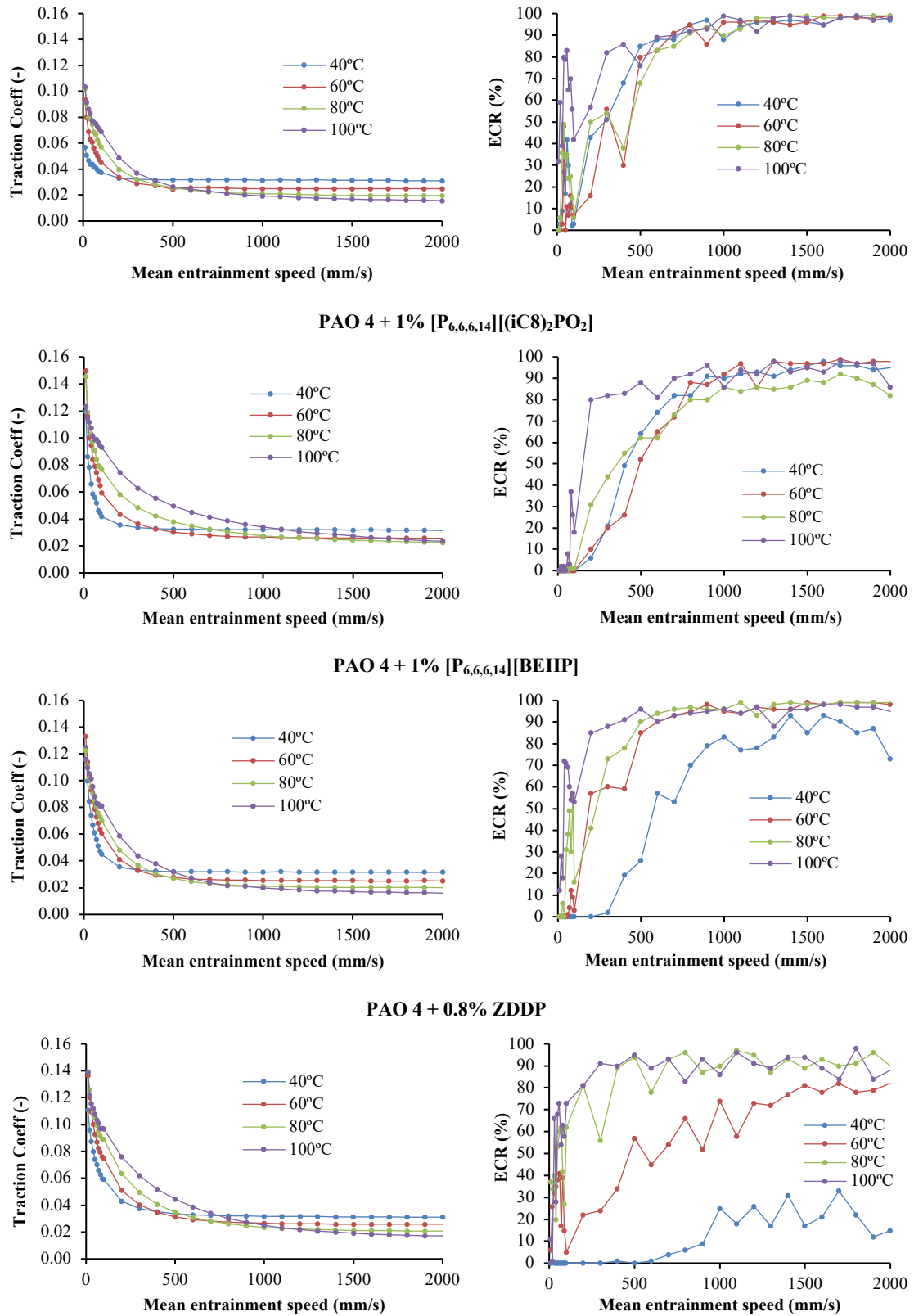


Fig. 2 Traction coefficient (Stribeck curves) and electrical contact resistance (ECR) during tests at different temperatures.

Fig. 3 shows the thickness of the tribofilm formed on the ball for tests made with both ILs compared with the one from the ZDDP-containing mixture. As can be observed, lubricant with [P_{6,6,6,14}][(iC8)₂PO₂] as

additive exhibited a rapid tribofilm formation compared with PAO 4 + 1% [P_{6,6,6,14}][BEHP], which showed lower tribofilm thickness values, probably due to a less capacity to interact with the surface. On the other hand, the PAO 4 + 0.8% ZDDP mixture showed the biggest final film thickness despite of its lower growing rate in comparison with the mixture of PAO 4 + [P_{6,6,6,14}][(iC8)₂PO₂].

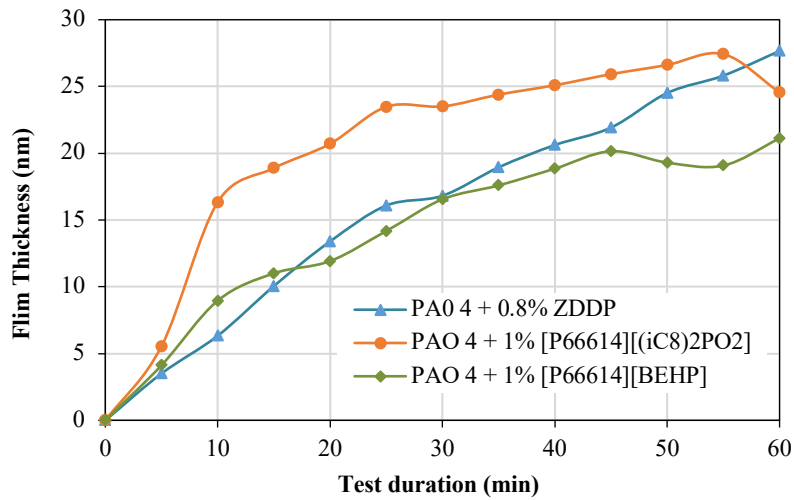


Fig. 3 Tribofilm thickness formed on the ball's surface.

The above-mentioned tribofilm formation results are in concordance with the obtained interference images (Fig. 4). As can be observed, a color change from blue to brown can be observed at the contact as the tribofilm thickness increases with time. The mixtures containing [P_{6,6,6,14}][(iC8)₂PO₂] and ZDDP showed a significant tribofilm build up almost from the test beginning; meanwhile, the [P_{6,6,6,14}][BEHP]-containing mixture showed a weaker tribofilm formation.

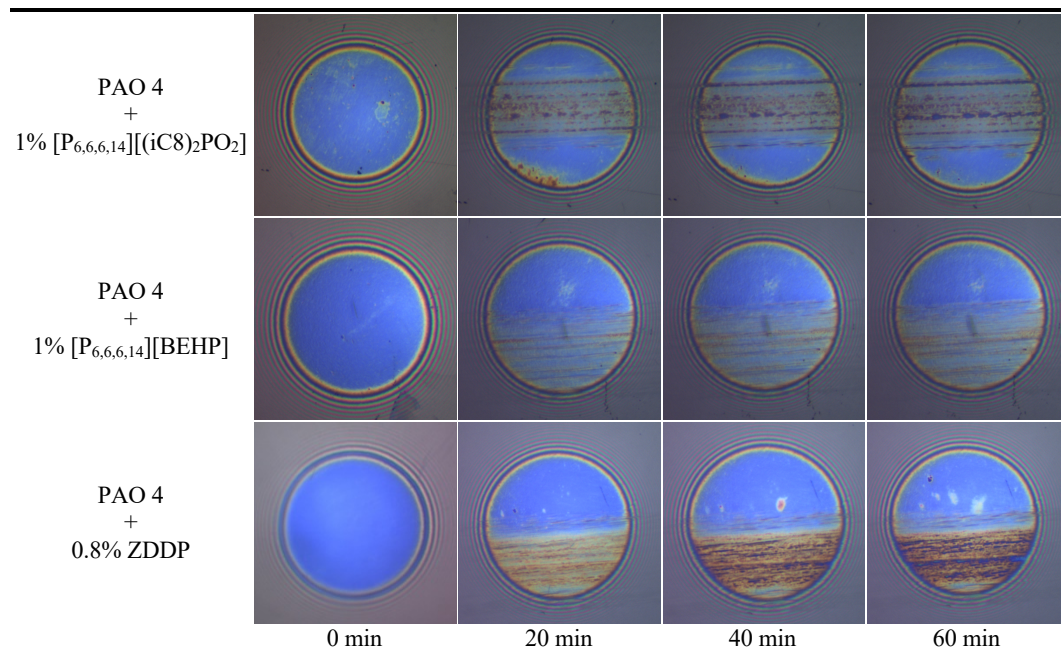


Fig. 4 Interference images of film formation on the ball's surface at 0, 20, 40 and 60 min.

Fig. 5. shows friction coefficient versus testing time during tests made with the base oil and the mixtures with the lowest concentration of ionic liquids and ZDDP (0.5 and 0.4 %wt., respectively) in the 60-min tribological tests. As can be observed, all mixtures presented lower friction coefficient than the base oil, but ZDDP-containing blend clearly showed a better behavior. In addition, wear volume measured on the lower specimen after tests is also displayed in Fig. 5. Both ionic liquids led to an important wear reduction compared to the base oil, especially the $[P_{6,6,6,14}][[(iC8)_2PO_2]$ IL, which reduced wear similarly to ZDDP. This is a remarkable result taking into account the well-known antiwear performance of this traditional antiwear additive.

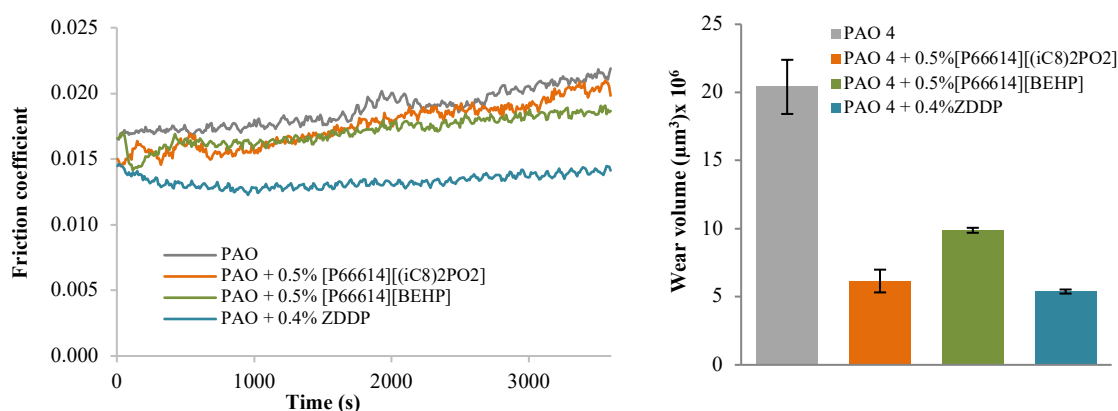


Fig. 5 Friction coefficient and mean wear volume in the 60-min tests lubricated with the base oil and the blends with the lowest concentration.

Friction values recorded in the 60-min tests made with the highest additive concentration shows that both ILs significantly reduce friction coefficient compared to the neat PAO 4 (Fig. 6) and have similar friction reduction behavior than the mixture containing ZDDP. However, higher ZDDP concentration led to higher friction coefficient, while higher IL concentration led to lower friction coefficient. With regard to the antiwear behavior (Fig. 6), a remarkable wear reduction was observed when 1 %wt. of both ILs was used as additive, showing the $[P_{6,6,6,14}][[(iC8)_2PO_2]$ IL the lowest wear values, close to the ones of the mixture containing 0.8 %wt. of ZDDP. The above tribological behavior agree with previous results obtained for both ILs used as additive to a mineral oil, where the $[P_{6,6,6,14}][[(iC8)_2PO_2]$ ionic liquid exhibited the best tribological behavior [42].

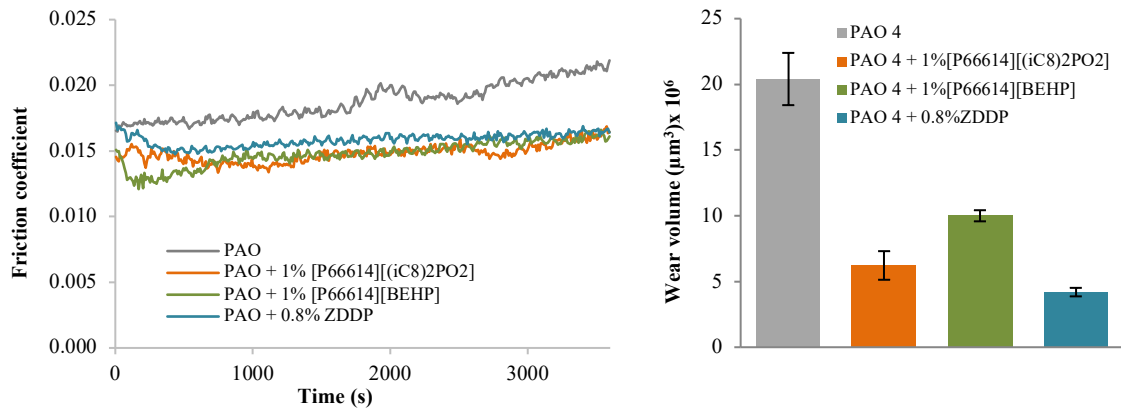
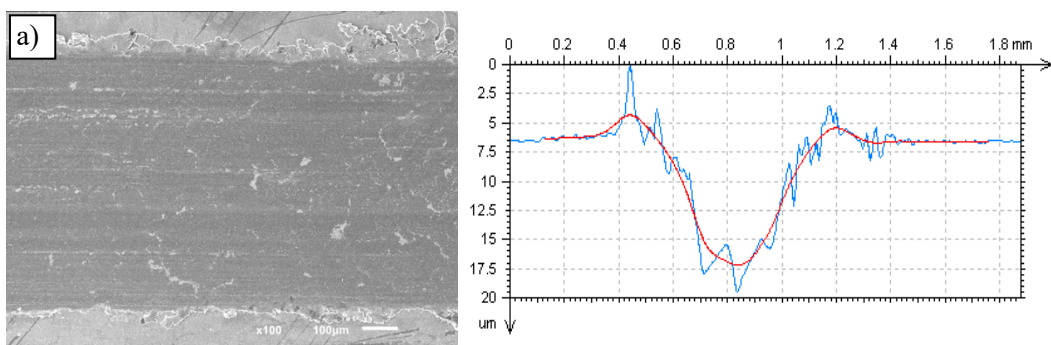
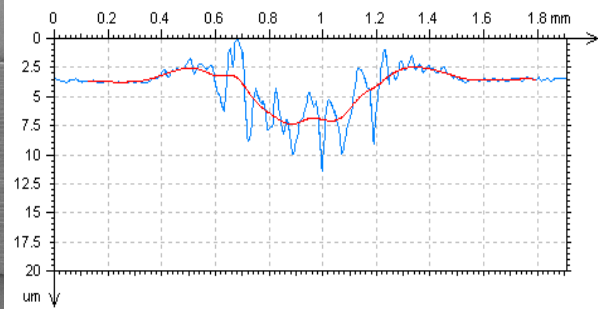
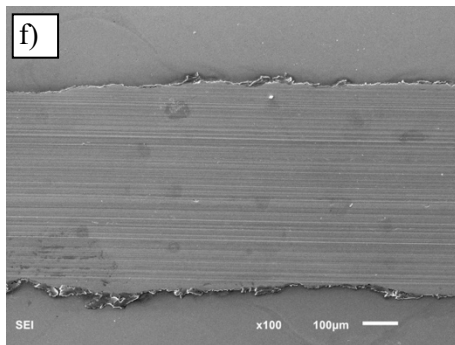
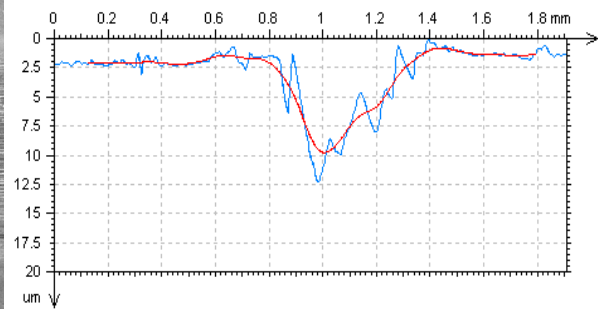
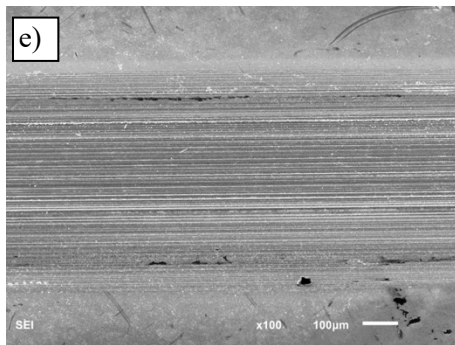
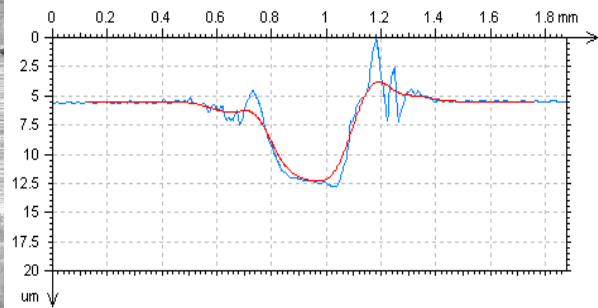
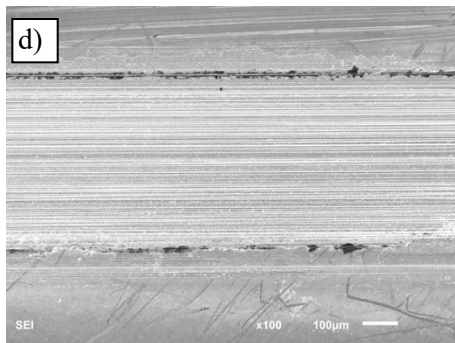
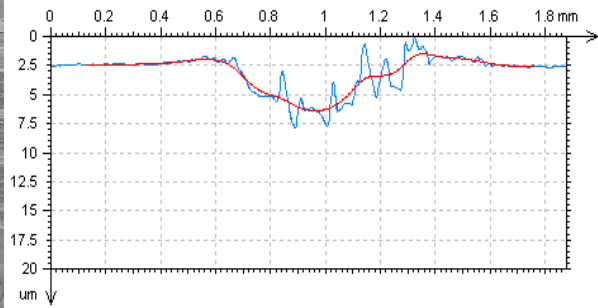
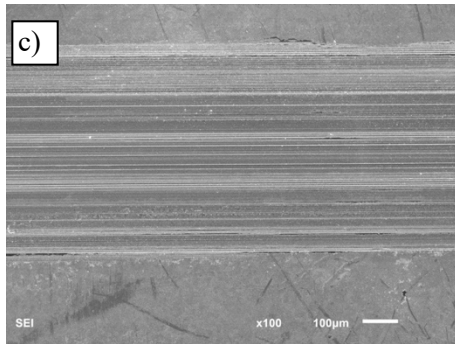
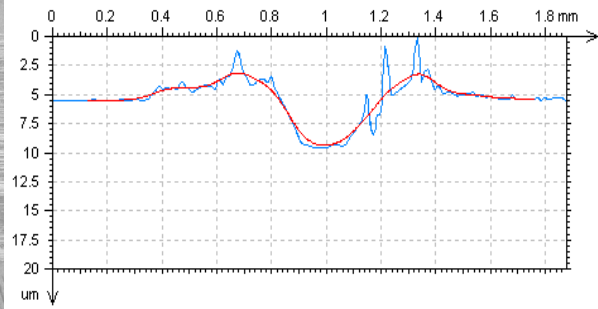
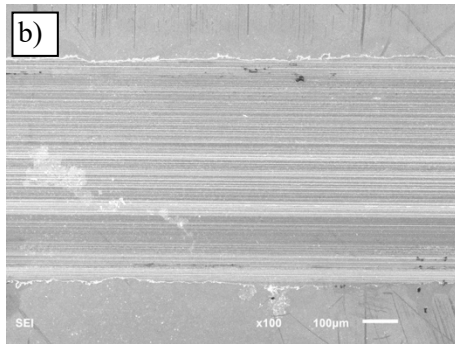


Fig. 6 Friction coefficient and mean wear volume in the 60-min tests lubricated with the base oil and the blends with de highest concentrations.

3.1. Surface characterization

Worn surfaces of the 60-min tests were examined by using SEM/EDS and confocal microscopy. Fig. 7 shows SEM images and waviness and roughness of a transversal profile of the wear scar after tests lubricated with pure PAO 4 and all the blends containing $[\text{P}_{6,6,6,14}][(\text{iC}8)_2\text{PO}_2]$, $[\text{P}_{6,6,6,14}][\text{BEHP}]$ and ZDDP. SEM images showed evidence of plastic deformation in all the worn surfaces, with a deep well-defined scar with high roughness ($R_a \approx 3\mu\text{m}$) and a predominant adhesive wear as a result of the tests lubricated with pure PAO 4 (Fig. 6a). The use of both ILs as additives provoked less surface damage (Figs. 6b, 6c, 6d and 6e) with a smaller wear scar and a roughness below $1.9\mu\text{m}$ R_a in all cases, especially when $[\text{P}_{6,6,6,14}][(\text{iC}8)_2\text{PO}_2]$ IL was employed (Fig. 6b and 6c). However, grooves in the sliding direction can be observed in the wear surface lubricated with IL-containing mixtures, which indicates abrasive wear.





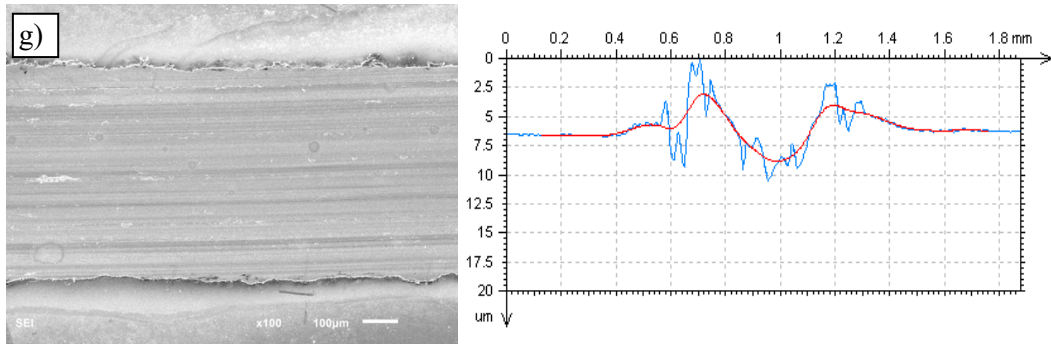


Fig. 7 Worn surfaces: SEM images and waveness and roughness of a transversal profile from tests with: (a) neat PAO 4, (b) PAO 4 + 0.5% $[P_{6,6,6,14}][[(iC8)_2PO_2]$, (c) PAO 4 + 1% $[P_{6,6,6,14}][[(iC8)_2PO_2]$, (d) PAO 4 + 0.5% $[P_{6,6,6,14}][BEHP]$, (e) PAO 4 + 1% $[P_{6,6,6,14}][BEHP]$, (f) PAO 4 + 0.4% ZDDP, (g) PAO 4 + 0.8% ZDDP.

The EDS spectra (Table 5) showed that for the PAO 4 and the ionic liquid samples the chemical elements found on the worn surface were those present in the steel, while phosphorus, sulphur and zinc were only detected for mixtures with ZDDP.

Table 5 Results obtained from EDS analysis after 60-min tribological tests.

Sample	C (% wt.)	O (% wt.)	P (% wt.)	S (% wt.)	Zn (% wt.)	Cr (% wt.)	Fe (% wt.)
PAO 4	8.43	11.52	-	-	-	2.68	77.37
PAO 4 + 0.5% $[P_{6,6,6,14}][[(iC8)_2PO_2]$	8.44	9.88	-	-	-	2.39	79.29
PAO 4 + 1% $[P_{6,6,6,14}][[(iC8)_2PO_2]$	7.15	9.30	-	-	-	2.10	81.45
PAO 4 + 0.5% $[P_{6,6,6,14}][BEHP]$	6.15	14.65	-	-	-	1.74	76.40
PAO 4 + 1% $[P_{6,6,6,14}][BEHP]$	6.24	9.43	-	-	-	2.00	82.34
PAO4 + 0.4% ZDDP	8.38	6.16	0.66	1.71	1.20	2.35	79.54
PAO4 + 0.8% ZDDP	5.52	7.29	0.78	1.85	1.40	2.20	80.96

From XPS analysis, $Fe_{2p3/2}$ was fitted using three different curves described as Gaussian-lorentzian product 70:30 with the same fwhm value. However, and according to the work of Mangolini and Mayer [49,50], curve centered around 707.5 eV and assignable as Fe(0), was modified with an exponential blend with $k=0.65$; curve centered around 711.0 eV and assignable to Fe(III), was modified with an exponential blend with $k=1.5$; curves centered around 713.0 eV is assumed to be FeOOH. Fig. 8 shows that samples containing $[P_{6,6,6,14}][[(iC8)_2PO_2]$ or $[P_{6,6,6,14}][BEHP]$ have a higher amount of Fe(III) and a lower amount of Fe(0) than samples with ZDDP or neat base oil. Furthermore, the Fe(III) is higher in samples lubricated with $[P_{6,6,6,14}][BEHP]$ which, in fact, turned out to be the less effective lubricant. Samples lubricated with $[P_{6,6,6,14}][[(iC8)_2PO_2]$ shows also a higher amount of Fe(III) than the other samples, but it is much closer to ZDDP or PAO than $[P_{6,6,6,14}][BEHP]$. This agrees with the tribological properties of $[P_{6,6,6,14}][[(iC8)_2PO_2]$, working better than $[P_{6,6,6,14}][BEHP]$ and similarly to ZDDP.

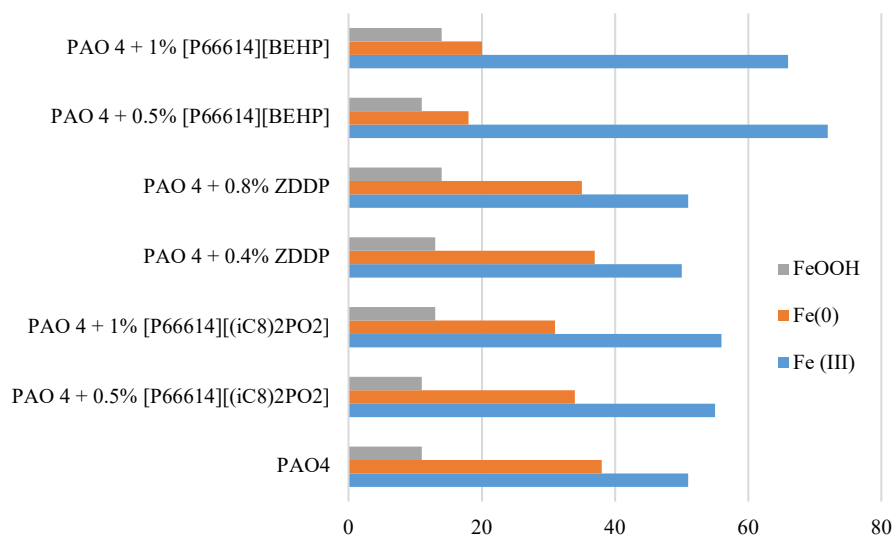


Fig. 8 Relative content in iron.

However, ZDDP samples show the presence of Zn with a Zn2p_{3/2} peak at about 1023 eV, which is commonly assigned to ZnO [42,51]. Furthermore, despite of the fact that the ionic liquid contains phosphorus, two P2p doublets can be detected in samples with ZDDP (Fig. 9), the first one at 134.0 and 135.0 eV and the second one at 140.5 and 141.5 eV, whereas only one appears in the samples with [P_{6,6,6,14}][(iC8)₂PO₂] at 133.9 and 134.9 eV (Fig. 10) or [P_{6,6,6,14}][BEHP] at 133.8 and 135.0 eV (Fig. 11). The common doublet (at 134 and 135 eV) can be interpreted as the presence of phosphates [52], whereas the highest one is usually detected in samples containing ZDDP [53].

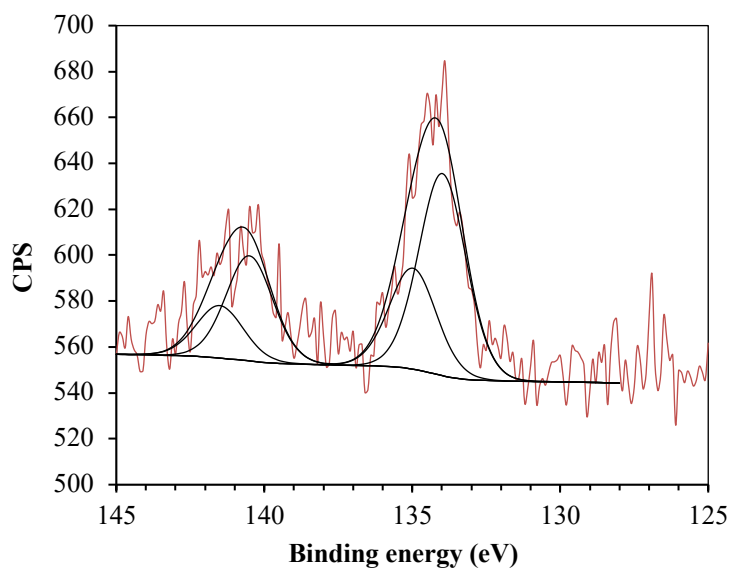


Fig. 9 XPS P2p spectrum for PAO 4 + 0.4% ZDDP sample.

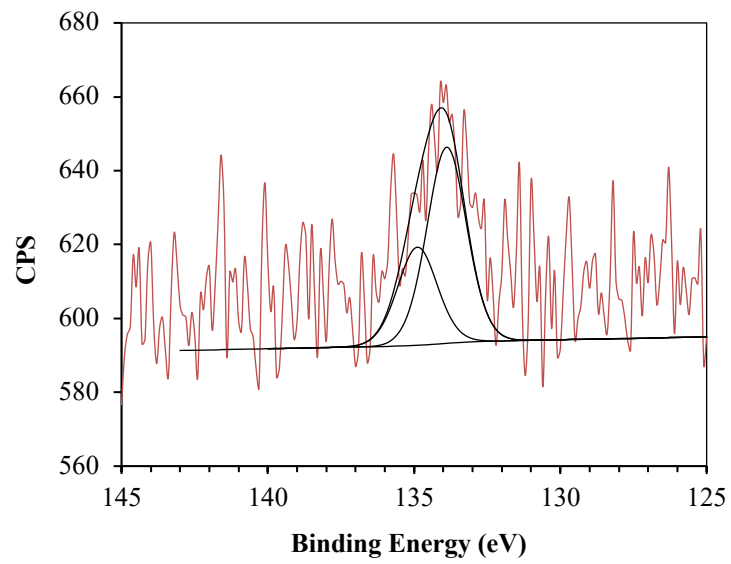


Fig. 10 XPS P2p spectrum for PAO 4 + 0.5% [P_{6,6,6,14}][(iC8)₂PO₂] sample.

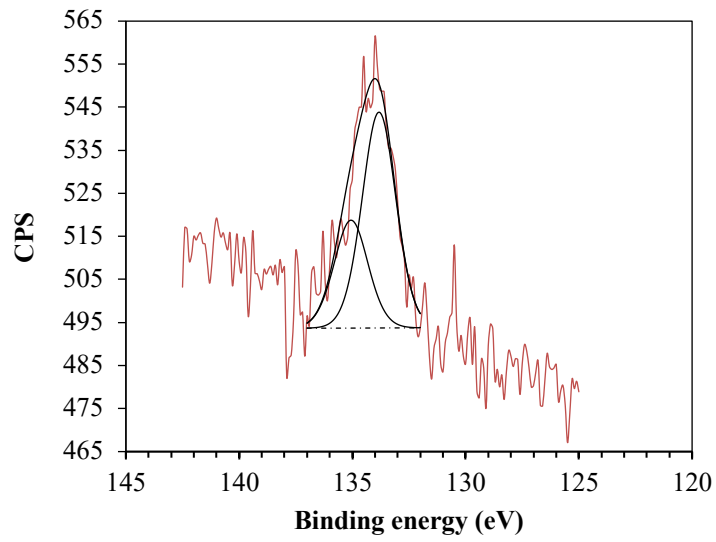


Fig. 11 XPS P2p spectrum for PAO 4 + 0.5% [P_{6,6,6,14}][BEHP] sample.

4. Conclusions

The traction behavior, tribofilm formation, friction and wear behavior of the trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate ($[P_{6,6,6,14}][(iC8)_2PO_2]$) and trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}][BEHP]$) phosphonium cation-based ionic liquids, used as lubricant additive to a polyalphaolefin (PAO 4), were studied. Two mixtures containing zinc dialkyldithiophosphate (ZDDP), with similar phosphorous concentration to that of the IL-containing mixtures, were used as comparison samples. The following main conclusions can be drawn from this work:

- The thermogravimetric analysis showed that the $[P_{6,6,6,14}][(iC8)_2PO_2]$ and $[P_{6,6,6,14}][BEHP]$ ionic liquids have higher degradation temperatures than pure PAO 4.
- The use of both liquids as an additive to the base oil did not increase density and viscosity, so the tribological behavior could be attributed to the adsorption of the ionic liquid on the surface.
- The mixture containing $[P_{6,6,6,14}][BEHP]$ showed similar traction behavior than pure PAO 4; however, the $[P_{6,6,6,14}][(iC8)_2PO_2]$ had a similar behavior than the ZDDP-containing mixture.
- PAO 4 + $[P_{6,6,6,14}][(iC8)_2PO_2]$ lubricant seems to be more reactive than the blend with $[P_{6,6,6,14}][BEHP]$, exhibiting a faster tribofilm formation, with a similar final thickness to that registered for the ZDDP-containing mixture.
- The 60-min tests showed that the use of the mixtures with IL resulted in lower coefficient of friction than that of the base oil, especially at the maximum IL concentration studied, when similar values to that of the ZDDP were obtained.
- The IL-containing mixtures showed significant wear reduction properties compared to that of the pure base oil, being the mixture with $[P_{6,6,6,14}][(iC8)_2PO_2]$ the one that showed the biggest wear reduction. This result agrees with the results of the traction coefficient and tribofilm thickness tests.
- Wear mechanisms observed in the wear scar were adhesive wear and plastic deformation in the test lubricated with pure base oil (PAO 4) and abrasive wear in the tests lubricated with the IL-containing mixtures.

- After friction and wear tests, the EDS analysis only found the chemical elements of the steel in the wear scar when pure base oil and the II-containing mixtures were used as lubricant, while Phosphorous, Sulphur and Zinc were found for the ZDDP-containing mixture.
- The use of the ionic liquids and ZDDP as additive leads to forming phosphates on the wear scar, but the ZDDP also acts via Zn incorporation.

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