

Phosphonium-based ionic liquids as additives in calcium/lithium greases

A. García Tuero^a, M. Bartolomé^b, D. Gonçalves^c, J.L. Viesca^{a,d}, A. Fernández-González^e, J.H.O. Seabra^f, A. Hernández Battez^{a,d,*}

^a Department of Construction and Manufacturing Engineering, University of Oviedo, Pedro Puig Adam, s/n, 33203 Gijón, Spain

^b Department of Marine Science and Technology, University of Oviedo, Blasco de Garay, s/n 33203, Gijón, Spain

^c INEGI, Universidade do Porto, Faculdade de Engenharia, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

^d Faculty of Science & Technology, Bournemouth University, Poole BH12 5BB, United Kingdom

^e Department of Physical and Analytical Chemistry, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain

^f FEUP, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:

Received 20 April 2021

Revised 31 May 2021

Accepted 8 June 2021

Available online 11 June 2021

Keywords:

Ionic liquids

Additives

Grease

Lubricated wear

ABSTRACT

This work studies the performance of three phosphonium-based ionic liquids ([P_{6,6,6,14}][BEHP], [P_{6,6,6,14}][TCM] and [P_{6,6,6,14}][DEC]) when used separately as additives on the thermal conductivity, thermal stability and tribological properties of two non-additised greases (a lithium-based and a calcium-based grease). The main results confirmed that the [P_{6,6,6,14}][TCM] improved the thermal stability of both greases. Only the mixtures G1 + 5% [P_{6,6,6,14}][BEHP] and G2 + 5% [P_{6,6,6,14}][TCM] showed a slight increase in thermal conductivity. In general, the addition of the ILs to the lithium-based grease increased the friction coefficient in both the four-ball tests and the reciprocating tests, while the friction coefficient decreased with the addition of the ILs to the calcium-based grease in the four-ball tests. The addition of the [P_{6,6,6,14}][BEHP] and [P_{6,6,6,14}][TCM] improved the antiwear behavior of the lithium-based grease under both tribological tests, whereas all the ionic liquids worsened the antiwear behavior of the calcium-based grease in the four-ball tests. The [P_{6,6,6,14}][BEHP] had the best antiwear behavior due to the higher interaction of phosphorous with the metal surface. A possible interference of the calcium thickener with the ionic liquid–metal surface interaction was found, resulting in lower antiwear behavior of the mixtures with the calcium-based grease.

© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Ionic liquids (ILs) have excellent characteristics that are important in a high-performance lubricant, such as high thermo-oxidative stability, ashless character, polarity, non-flammability and non-volatility. For this reason, these salts have been studied in the field of lubrication since 2001 [1–4]. The polarity and reactivity of ILs promote the formation of tribolayers by adsorption on the metal surfaces and lead to a reduction in friction and/or wear [5–7]. Due to the inherent polarity of the ILs, they are immiscible in non-polar hydrocarbon oils (Groups I, II and III) and therefore, most researchers have studied the behavior of ILs as additives in non-polar hydrocarbon oils as oil-IL emulsions [8,9] or using the ILs at very low concentrations (≤ 1 wt%) [10,11]. On the contrary, ILs have better compatibility with polar oils (e.g. esters, PEG, glycerol, etc.) [12–14]. Despite this, a new family of ILs with improved miscibility properties in non-polar hydrocarbon oils (mineral oils

and PAOs) was found [15]. These ILs are based on quaternary phosphonium cations and the number of studies into their use as lubricant additives have increased in recent years, due to the above-mentioned improved miscibility [16–22]. The miscibility of the phosphonium-based IL in non-polar oils was related to a cation size with alkyl chains from 6 carbons onwards and a total of carbons above 30 [18]. In general, the use of these phosphonium-based ILs as additives reduced friction and/or wear in both reciprocating and continuous motion.

Since 2010, the use of ILs as additives in greases has been the focus of many research groups. Most of these used synthetic oils (PAOs and PAG) as the base oil for the grease formulation, and the ILs used as additives in concentrations between 0.1 and 10 wt% were mainly based on imidazolium- and phosphonium-cations (Table 1). Cai et al. [23,24] used some ILs based on the imidazolium cation combined with hexafluorophosphate, tetrafluoroborate and bis(trifluoromethanesulfonyl)-imide anions as additives at 1 and 2 wt% in a polyurea-based grease. All the IL-containing greases promoted a considerable reduction in both friction and wear at a temperature higher than room temperature,

* Corresponding author.

E-mail address: ahernandez@uniovi.es (A. Hernández Battez).

Nomenclature

Acronyms

[BEHP] ⁻	bis(2-ethylhexyl)phosphate	[DMIM] ⁺	1-decyl-3-methylimidazolium
[TCM] ⁻	tricyanomethanide	[BTAMIM] ⁺	3-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-1-methyl-1H-imidazolium
[DEC] ⁻	decanoate	[AOT] ⁻	1,4-bis(2-ethylhexyl) sulfosuccinate
[P _{6,6,6,14}] ⁺	triethyltetradecylphosphonium	[BMB] ⁻	bis(mandelato)borate
[C ₁₄ mim] ⁺	1-tetradecyl-3-methylimidazolium	[BF ₄] ⁻	tetrafluoroborate
[C2OHHim] ⁺	1-(2-hydroxyethyl)-3-methylimidazolium	[BOB] ⁻	bis(oxalato)borate
[C2OHHim] ⁺	1-(2-hydroxyethyl)-3-hexylimidazolium	[BMPP] ⁻	bis-2,4,4-(trimethylpentyl)phosphinate
[P _{8,8,8,1}] ⁺	trioctylmethylphosphonium	[DCA] ⁻	Dicyanamide
[P _{8,8,8,10}] ⁺	trioctyldecylphosphonium	[NTF ₂] ⁻	bis(trifluoromethanesulfonyl)-imide
[P _{8,8,8,14}] ⁺	trioctyltetradecylphosphonium	[PF ₆] ⁻	hexafluorophosphate
[P _{8,8,8,p}] ⁺	trioctyl(3'-O, O'-diethylphosphinylpropyl)phosphonium	PAO	polyalphaolefin
[EMIM] ⁺	1-ethyl-3-methylimidazolium	PAG	poly(alkylene glycol)
[BMIM] ⁺	1-butyl-3-methylimidazolium	PEG	polyethylene glycol
[HMIM] ⁺	1-hexyl-3-methylimidazolium	PTFE	polytetrafluorethylene
[OMIM] ⁺	1-octyl-3-methylimidazolium	PILs	protic ionic liquids
		DTCs	dialkyldithiocarbamates

Table 1

Ionic liquids used as additives in greases (2010–2021).

Ionic liquids		Conc. (wt.%)	Greases		Ref.
Cation	Anion		Base oil	Thickener	
[BMIM] ⁺	[PF ₆] ⁻	1	N.P.	Polyurea	[23]
[HMIM] ⁺	[PF ₆] ⁻				
[OMIM] ⁺	[PF ₆] ⁻				
[DMIM] ⁺	[PF ₆] ⁻				
[HMIM] ⁺	[BF ₄] ⁻				
[BTAMIM] ⁺	[NTF ₂] ⁻	1, 2, 3, 4	N.P.	Polyurea	[24]
	[PF ₆] ⁻				
	[BF ₄] ⁻				
[BMIM] ⁺	[PF ₆] ⁻	0.1, 0.2, 0.3, 0.4	N.P.	Polyurea	[25]
	[BF ₄] ⁻				
3 compounds containing both PILs and DTCs groups		1, 2, 3, 4, 5	PAO 40	Lithium complex	[26]
[BMIM] ⁺	[PF ₆] ⁻	5	PAO 40	Organo-attapulgitite	[27]
[HMIM] ⁺	[PF ₆] ⁻			Organo-bentonite	
[OMIM] ⁺	[BF ₄] ⁻				
[C2OHHim] ⁺	[NTF ₂] ⁻	1, 2	N.P.	Calcium sulfonate	[28]
[C2OHHim] ⁺					
[EMIM] ⁺	[PF ₆] ⁻	8	PAG	PTFE	[29]
[P _{8,8,8,14}] ⁺	[BEHP] ⁻	5	PAO 10	Lithium complex	[30]
[P _{8,8,8,14}] ⁺	[AOT] ⁻				
[P _{8,8,8,p}] ⁺	[DEHP] ⁻				
[P _{8,8,8,14}] ⁺	[BEHP] ⁻	10	PAO 40	Polyurea	[31]
[P _{8,8,8,10}] ⁺					
[P _{8,8,8,1}] ⁺					
[P _{8,8,8,14}] ⁺	[BEHP] ⁻	3	PAO 10	Lithium complex	[32]
[C ₁₄ mim] ⁺					
[P _{6,6,6,14}] ⁺	[BMB] ⁻	2, 5, 10	PAO + Adipate ester	Polypropylene Lithium-complex	[33]
	[BOB] ⁻				
	[BMPP] ⁻				
	[DCA] ⁻				
[P _{6,6,6,14}] ⁺	[BEHP] ⁻	2, 5	Mineral oil	Lithium complex	[34]
	[TCM] ⁻			Anhydrous calcium	
	[DEC] ⁻				

N.P. = not provided

which was attributed to the good solubility, thermal stability and mobility of the ILs at high temperature. Cao et al. [25] found similar antifriction and antiwear results at room temperature when they used imidazolium-cation based ILs with hexafluorophosphate and tetrafluoroborate anions as additives at 0.1–0.4 wt% in a polyurea-based grease.

Zhao et al. [26] added a lithium grease with three novel compounds containing both PILs (protic ionic liquids with ammonium salts) and DTCs (dialkyldithiocarbamates) at concentrations ranging from 1 to 5 wt%, finding that these PILs can improve both friction

and wear reduction properties in combination with DTCs, the latter being used as additive (antiwear, extreme pressure, friction modifier and antioxidant) in lubricant formulation. Wang et al. [27] also used imidazolium-based ILs as additives at 5 wt% in attapulgitite- and bentonite-based greases. They concluded that the use of these ILs improved the tribological performance of the non-additised greases, probably because of the affinity of the thickener and the IL. Qiao et al. [28] studied the use of imidazolium-based ILs combined with molybdenum dialkyldithiocarbamate (MoDTC). This combination improved the friction reduction char-

Table 2
Description of the greases.

Designation	G1	G2
Base oil	Mineral oil	Mineral oil
Thickener	Lithium complex	Anhydrous Ca-soap
Base oil viscosity ($\text{mm}^2\cdot\text{s}^{-1}$) / 40 °C	200	176
Base oil viscosity ($\text{mm}^2\cdot\text{s}^{-1}$) / 100 °C	14.6	13.6
Worked penetration (1/10 mm) / 60 S	270	277
NLGI grade	2	2

acteristics of overbased calcium sulfonate complex greases, while the antiwear performance was hardly enhanced. Fan et al. [29] have also shown the tribological improvement (mainly in antiwear performance) of a grease (prepared from PAG as base fluid and PTFE as thickener) after additivation with an imidazolium-based IL.

Some phosphonium-based ILs have been used as additives at 2–10 wt% concentrations in greases prepared from different polyalphaolefins as the base oil and propylene, lithium or polyurea as thickener [30,31,32,33]. In general, the use of these ILs as additive enhanced the friction and wear reduction properties of the base greases by forming tribofilms containing iron oxides, iron fluoride and/or iron phosphate. Traction (friction) in rolling/sliding tests over a wide range of SRR (slide-to-roll ratio) was also studied for $[\text{P}_{6,6,6,14}][\text{BMB}]$ - and $[\text{P}_{6,6,6,14}][\text{BOB}]$ -containing greases resulting in lower traction values [33]. The rheological and tribological behavior of the ionic liquids used in this work ($[\text{P}_{6,6,6,14}][\text{BEHP}]$, $[\text{P}_{6,6,6,14}][\text{TCM}]$ and $[\text{P}_{6,6,6,14}][\text{DEC}]$) were reported in a previous study [34]. The addition of the ILs decreased some rheological properties of the base grease, such as viscosity and yield stress, but lowered the coefficient of friction (CoF) in the range of the entrainment speeds tested.

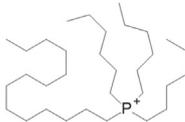
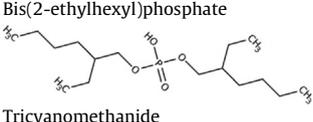
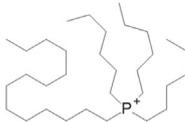
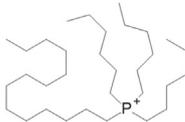
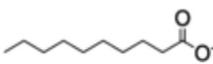
This work studies the use of three phosphonium ionic liquids as additives in two greases formulated from a mineral oil as base fluid and a lithium complex or an anhydrous calcium-soap as thickener. These (grease + IL) combinations have not been tested before under the testing conditions used here. The aim of the study is to find out the influence of these ionic liquids used as additives on the thermal stability, thermal conductivity and tribological properties of two lubricant greases.

2. Methodology

2.1. Greases and ionic liquids

The two non-additised greases used in this work were kindly provided by Axel Christiernsson International (Sweden). Table 2 shows the main properties of these greases. They were formulated using a mineral oil as base oil and the thickener was added at

Table 3
Chemical structure and empirical formula of the ionic liquids.

Ionic liquid	Cation	Anion
Trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate $[\text{P}_{6,6,6,14}][\text{BEHP}]$ Empirical formula: $\text{C}_{48}\text{H}_{102}\text{O}_4\text{P}_2$ Designation: IL1		Bis(2-ethylhexyl)phosphate 
Trihexyltetradecylphosphonium tricyanomethanide $[\text{P}_{6,6,6,14}][\text{TCM}]$ Empirical formula: $\text{C}_{36}\text{H}_{68}\text{N}_3\text{P}$ Designation: IL2		Tricyanomethanide 
Trihexyltetradecylphosphonium decanoate $[\text{P}_{6,6,6,14}][\text{DEC}]$ Empirical formula: $\text{C}_{42}\text{H}_{87}\text{PO}_2$ Designation: IL3		Decanoate 

8.6 wt% in the lithium complex-based grease (G1) and at 7.6 wt% in the anhydrous calcium-based grease (G2). IOLITEC GmbH provided the ionic liquids (Table 3) used as additives at concentrations of 2 and 5 wt%: trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate, $[\text{P}_{6,6,6,14}][\text{BEHP}]$ (designated as IL1); trihexyltetradecylphosphonium tricyanomethanide, $[\text{P}_{6,6,6,14}][\text{TCM}]$ (designated as IL2); and trihexyltetradecylphosphonium decanoate, $[\text{P}_{6,6,6,14}][\text{DEC}]$ (designated as IL3). A planetary centrifugal mixer (Kakuhunter SK-300 SII) was used to prepare the grease and the ionic liquid blends. The process included two mixing cycles of 5 min at 1600 rpm and a final degassing cycle of 2 min at 2200 rpm.

2.2. Thermal stability and thermal conductivity

The thermal stability of the blends and of the pure samples (both greases and ionic liquids) was tested with a DSC/SDT Q600 instrument (TA Instruments). A dynamic exploration was performed over a range from room temperature to 600 °C at a heating rate of 10 °C/min under an inert atmosphere (nitrogen at a flow rate of 100 mL/min).

The thermal conductivity was measured at room temperature (25 ± 1 °C), using the transient hot wire technique by means of a TEMPOS thermal conductivity meter (METER Environment) with the KS-3 sensor (accuracy of $\pm 10\%$ in the range of $0.2\text{--}2.00 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). A total of five measurements were made at room temperature.

2.3. Tribological tests

Two different tribological tests were used in this study. Firstly, four-ball tests according to the ASTM D2266 standard were performed as screening tests in order to select the IL-containing mixtures with better antiwear behavior. Those mixtures which led to a wear scar diameter reduction of at least 15% in the four-ball tests were selected for testing under another test configuration (reciprocating). The steel balls (AISI 52100, 12.7 mm-diameter, hardness of 65 HRC and surface roughness lower than $0.020 \mu\text{m Ra}$) used in the four-ball tests were cleaned in heptane for 10 min in an ultrasonic bath, rinsed in ethanol and dried in hot air before and after tests. The tests were run for 60 min at 1200 rpm with a load of 392 N (corresponding to a maximum contact pressure of 2.18 GPa). The grease temperature during the experiment was 75 °C (the pot temperature selected was 78 °C in order to reach the desired temperature in the grease sample). The coefficient of friction (CoF) was registered throughout the tests with a data acquisition frequency of 10 Hz and the average value was calculated using the whole extension of the obtained spectrum. The wear scar diameter (WSD) and wear volume were measured on the bottom three balls with a confocal microscope (Leica DCM 3D).

According to the results from the screening (four-ball) tests, the mixtures and the base grease selected were tested under a reciprocating

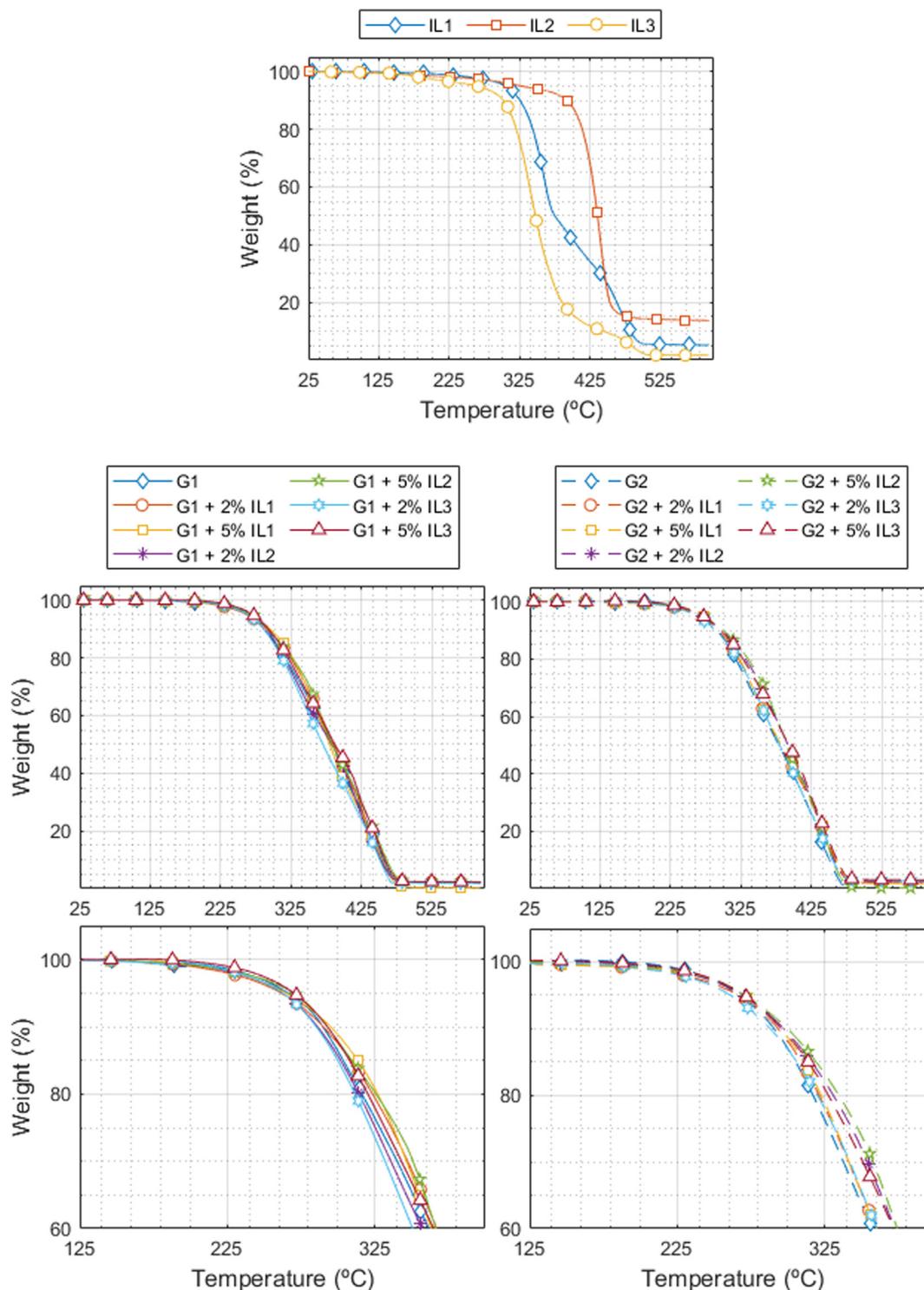


Fig. 1. Thermogravimetric analysis (TGA) of each grease and its mixtures with each IL.

cating ball-on-disc configuration in the same tribometer (CETR UMT-3) used in the four-ball tests. Both specimens (ball and disc) were manufactured from AISI 52,100 steel. The disc (10 mm-diameter) has a hardness of 190–210 HV₃₀ and surface roughness of 0.018 μm Ra, while the ball (6 mm-diameter) has a hardness of 58–66 HRC and a surface roughness of 0.05 μm Ra. The cleaning procedure of the specimens before and after the tests was the same as that used for the screening (four-ball) tests. The experiments

were run at a load of 60 N (corresponding to a maximum pressure of 2.59 GPa), a frequency of 25 Hz for 30 min, with a 1 mm stroke length and at 25 °C. The CoF was also recorded during the tests at a rate of 10 Hz and calculated using all the obtained data. The wear volume of the lower specimen (disc) was measured with a confocal microscope (Leica DCM 3D). Each reciprocating test was replicated at least two times using a fresh lubricant sample in order to achieve high repeatability.

Table 4
Decomposition onset temperature (T_{onset}) of the greases, ILs and their mixtures (expressed in °C).

Sample	Ionic liquids		
	IL1	IL2	IL3
G1 + 0% IL	281	281	281
G1 + 2% IL	298	281	280
G1 + 5% IL	303	312	279
G2 + 0% IL	291	291	291
G2 + 2% IL	287	306	290
G2 + 5% IL	291	315	291
100% IL	326	412	312

2.4. Surface characterization

The morphology and chemical composition of the worn surface was analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDX) after all tribological tests. A JEOL

Table 5
Thermal conductivity of each grease and its mixture with each IL (expressed in $W \cdot m^{-1} \cdot K^{-1}$).

Sample	Ionic liquids		
	IL1	IL2	IL3
G1 + 0% IL	0.153	0.153	0.153
G1 + 2% IL	0.162	0.144	0.132
G1 + 5% IL	0.183	0.145	0.158
G2 + 0% IL	0.142	0.142	0.142
G2 + 2% IL	0.154	0.148	0.126
G2 + 5% IL	0.149	0.164	0.130

JSM-5600 instrument operated at 20 kV using secondary electrons was used for this purpose.

X-ray photospectroscopy (XPS) was also used to explore the chemical elements formed on the worn surface after reciprocating tests. XPS analysis were carried out using a PHI VersaProbe II spectrometer with a monochromatic Al X-Ray source (1486.6 eV) at

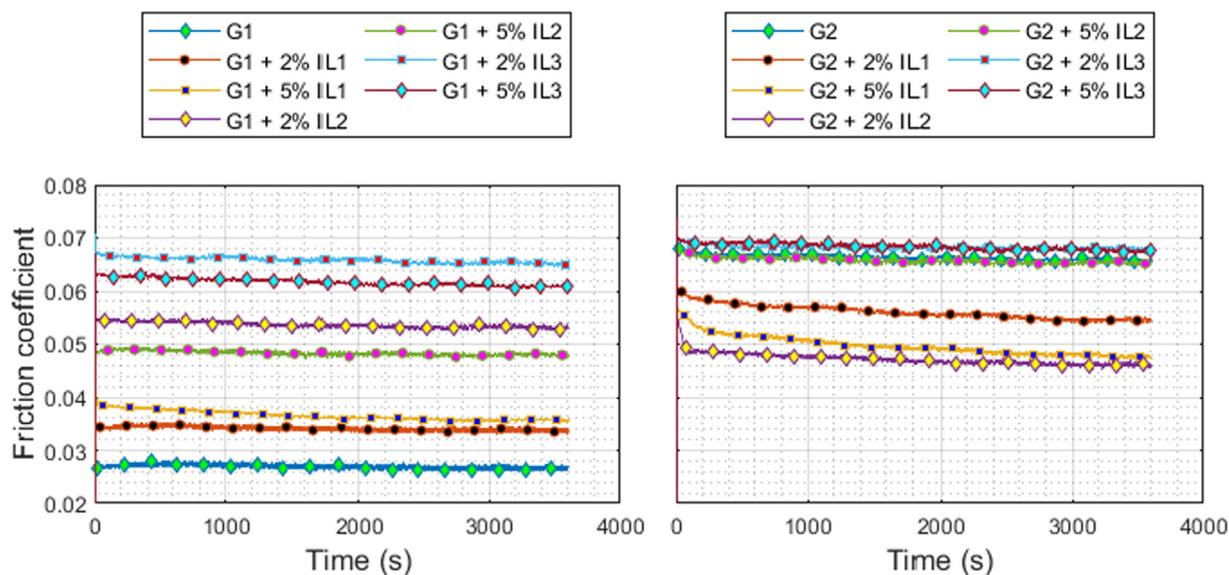


Fig. 2. Average friction coefficient of the four-ball tests.

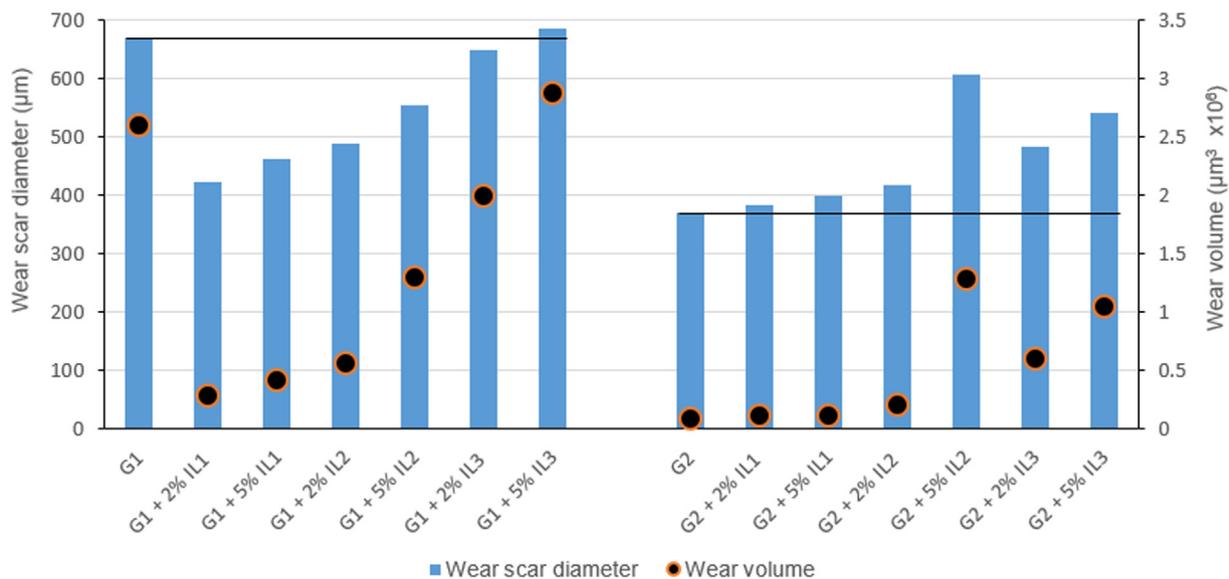


Fig. 3. Wear scar diameter and wear volume measured after 4-balls tests.

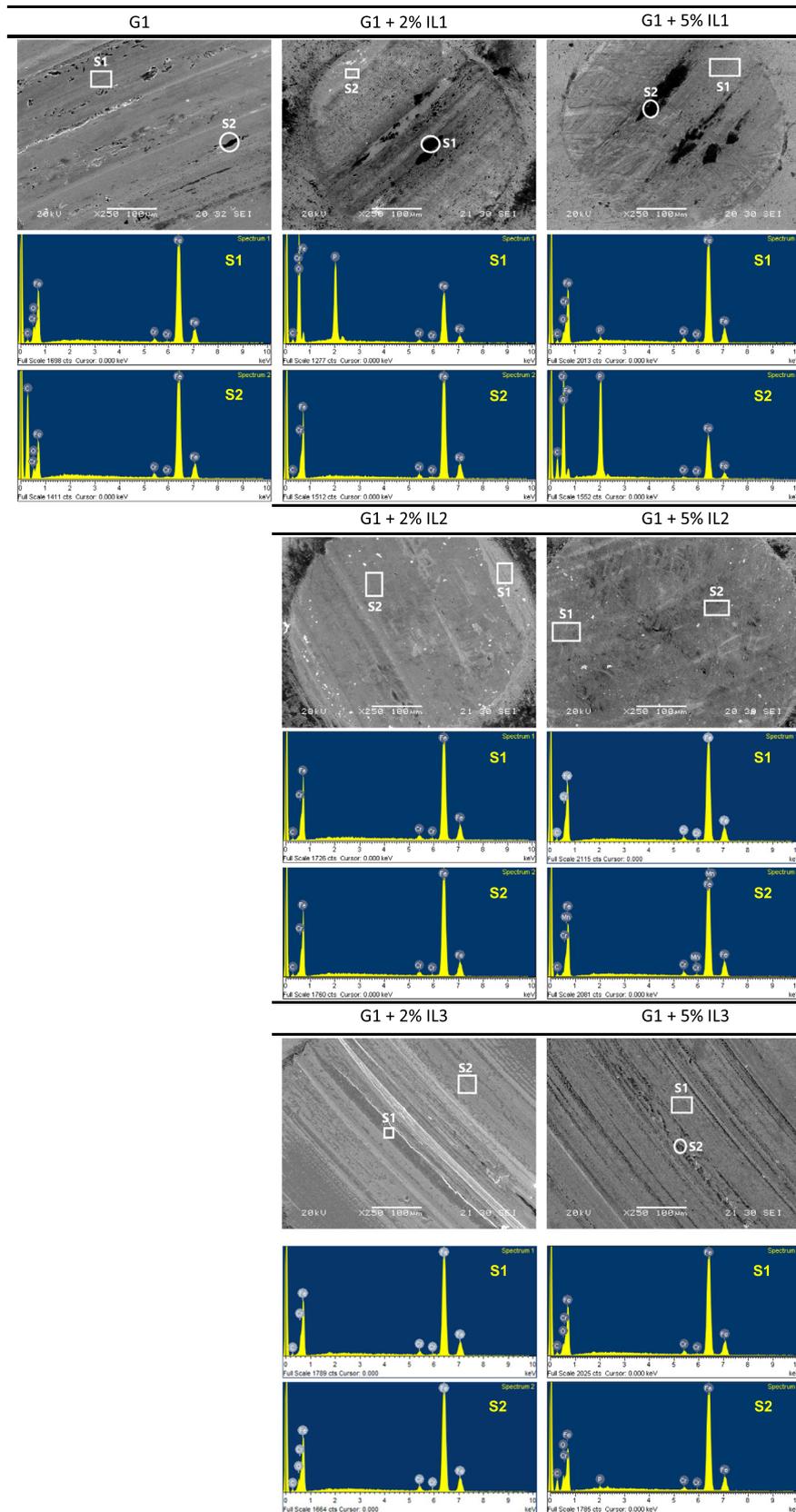


Fig. 4. SEM images and EDX of the worn surface after the four-ball tests conducted with G1 and G1 + ILs.

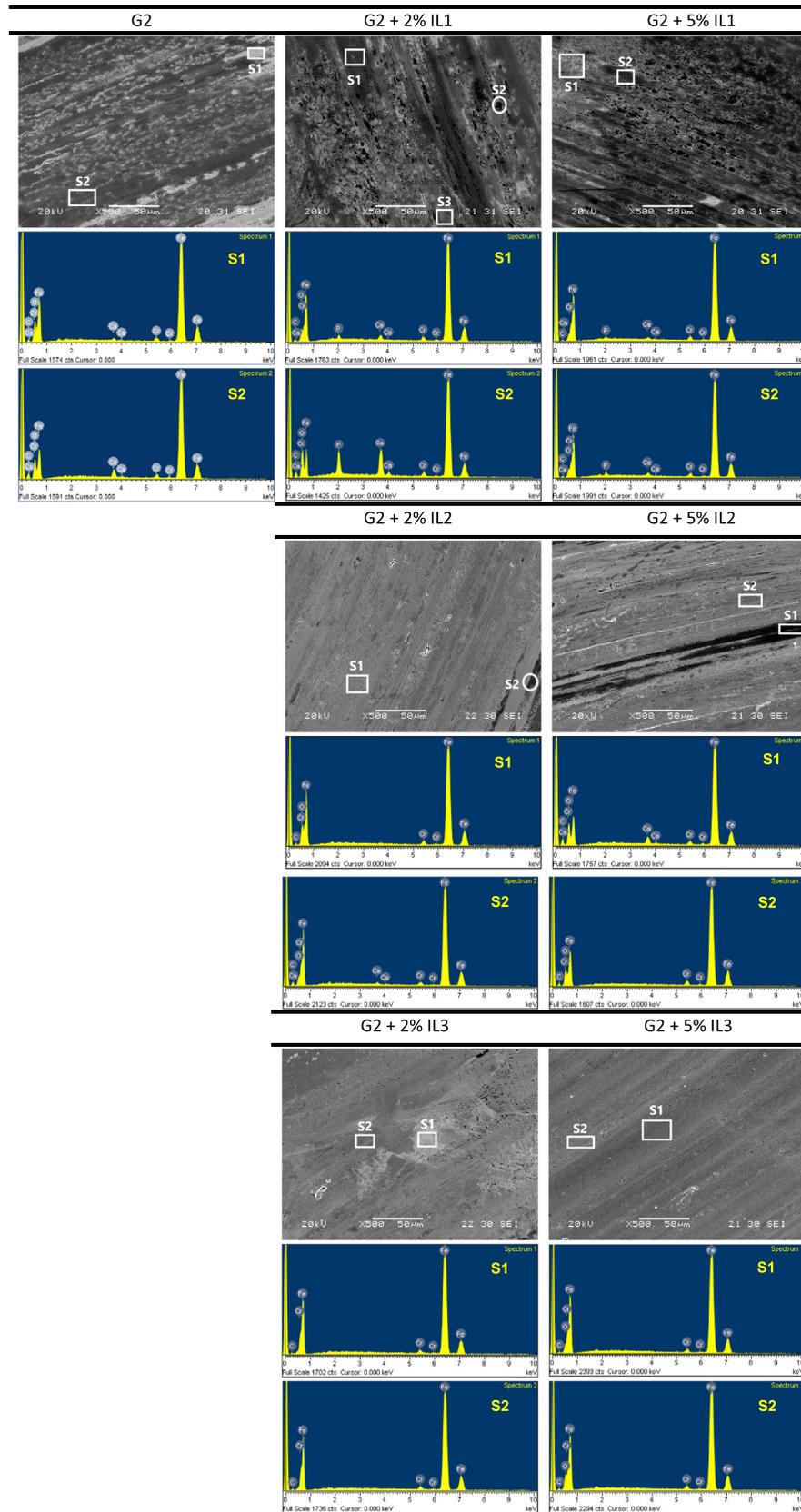


Fig. 5. SEM images and EDX of the worn surface after the four-ball tests conducted with G2 and G2 + ILs.

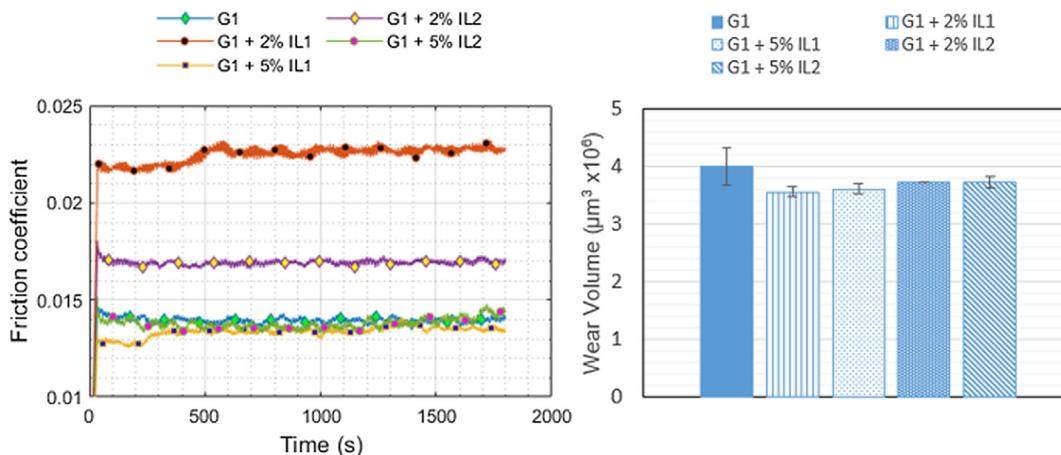


Fig. 6. Average friction coefficient and wear volume from the reciprocating tests.

4.8 W, using a 20 μm diameter spot focused inside the wear scar. Peak fit of high resolution spectra is performed using a Gaussian-Lorentzian (70:30) curve for FeO and FeOOH, the same curve with an exponential tail ($k = 0.65$) for Fe(O) and with an exponential tail ($k = 1.5$) for Fe_2O_3 .

3. Results and discussion

3.1. Thermal stability and thermal conductivity

The two greases, with and without ionic liquids, showed similar thermal stability (differences in mass loss below 5%) until the temperature reached around 300 $^\circ\text{C}$, Fig. 1. The higher degradation onset temperatures (T_{onset}), determined as the point of intersection of the starting-mass baseline and the tangent to the TGA curve at the point of maximum slope ($^\circ\text{C}$), were obtained with the use of IL2 as additive (Table 4). Both, the ionic liquids IL1 and IL2 improved the thermal stability of the lithium-based grease (G1), while this property for the calcium-based grease (G2) was only improved by the IL2. The improvement of the thermal stability with the addition of the ILs agrees with the comparatively higher thermal stability of the ILs (given by its decomposition onset temperature) with respect to that of the neat greases.

Table 5 shows the thermal conductivity of the base greases and their blends with the ILs. Taking into account the accuracy of the testing device, the two base greases have similar thermal conductivity and in general the addition of the ionic liquids barely changed the thermal conductivity of the greases. A slight increase in the thermal conductivity of the mixtures with respect to the base grease was found for the mixtures G1 + 5%IL1 and G2 + 5%IL2. These results indicated that the increase in thermal conductivity with the addition of an ionic liquid depends on both the ionic liquid and its concentration and the type of thickener used. Thermal conductivity influences the heat dissipation of the lubricant sample; however, no correlation of this property was found with the tribological behavior of the lubricant samples tested in this study.

3.2. Tribological tests and surface characterization

3.2.1. Four-ball tests and surface characterization

Fig. 2 shows the friction results from the four-ball tests. The addition of the ILs to the lithium-based grease (G1) increased the CoF. The lowest increase of CoF was obtained with the ionic liquid IL1 and the highest one with the IL3. On the other hand, the addition of the ILs to the calcium-based grease (G2) barely changed the CoF when the mixtures containing 5% of IL2 and 2 and 5% of IL3 were used. Meanwhile, the mixtures with 2% of IL2 and 2 and 5%

of IL1 showed lower CoF than the grease G2. In general, the friction values recorded for all tests correspond to a mixed lubrication regime, where friction is conditioned by both the lubricant viscosity and the asperities contact.

Fig. 3 shows the wear measurements from the four-ball tests. According to the ASTM D2266 standard, the wear scar diameter (WSD) should be reported, although it could also be useful to report the wear volume from the four-ball tests [35]. The WSD reported for the mixtures with the lithium-based grease (G1) decreased considerably in the case of those containing ionic liquids IL1 and IL2, with the reductions ranging from 36.4% (2 wt% of IL1) to 16.6% (5 wt% of IL2). On the other hand, the presence of IL3 in the mixture barely had any effect on the WSD. Regarding the wear volume, a reduction ranging from 88.8% (2 wt% of IL1) to 23.3% (2 wt% of IL3) is observed for lithium complex-based blends. As an exception, the wear volume measured for the mixture containing 5 wt% of IL3 was 10.5% higher than that of the neat grease. On the other hand, the use of the ILs as additives in the calcium-based grease (G2) increased both the wear scar diameter and wear volume. The changes in the WSD with the addition of the ILs were lower than those in wear volume, corresponding with the difference between a length- and a volume-based approach and demonstrating that wear volume is a better comparative parameter in four-ball tests, as reported in [35]. The rising wear found at higher concentration of IL was also reported by Zhou et al. [18]. They stated that improving tribological performance depends not only on the IL concentration but also on the IL chemistry and the tribosystem.

Figs. 4-5 show the SEM images of the worn surface from the four-ball tests. Typical plastic deformation zones with cavities were found on the worn surface, which suggest adhesive wear. The EDX analysis was performed to detect whether any chemical element from the greases was present on the surface. The chemical composition on these surfaces is mainly composed by the elements present in the steel. Lithium from the thickener in grease G1 is not detectable because SEM/EDX systems can only detect elements with atomic number $Z \geq 4$. On the contrary, calcium from the thickener was found on the worn surface, mainly when grease G2 was used in combination with IL1. Phosphorous from the IL1 was found when used in combination with grease G1, which can explain the higher wear reduction with this mixture. In addition, phosphorous was detected when IL1 was used as additive in grease G2, which could be caused by the presence of phosphorous in both the cation and the anion of the IL1, although wear reduction was not achieved in this case. The worse antiwear behavior of the mixtures with grease G2 could be due to competing formation and decomposition of the protective tribofilm resulting from the inter-

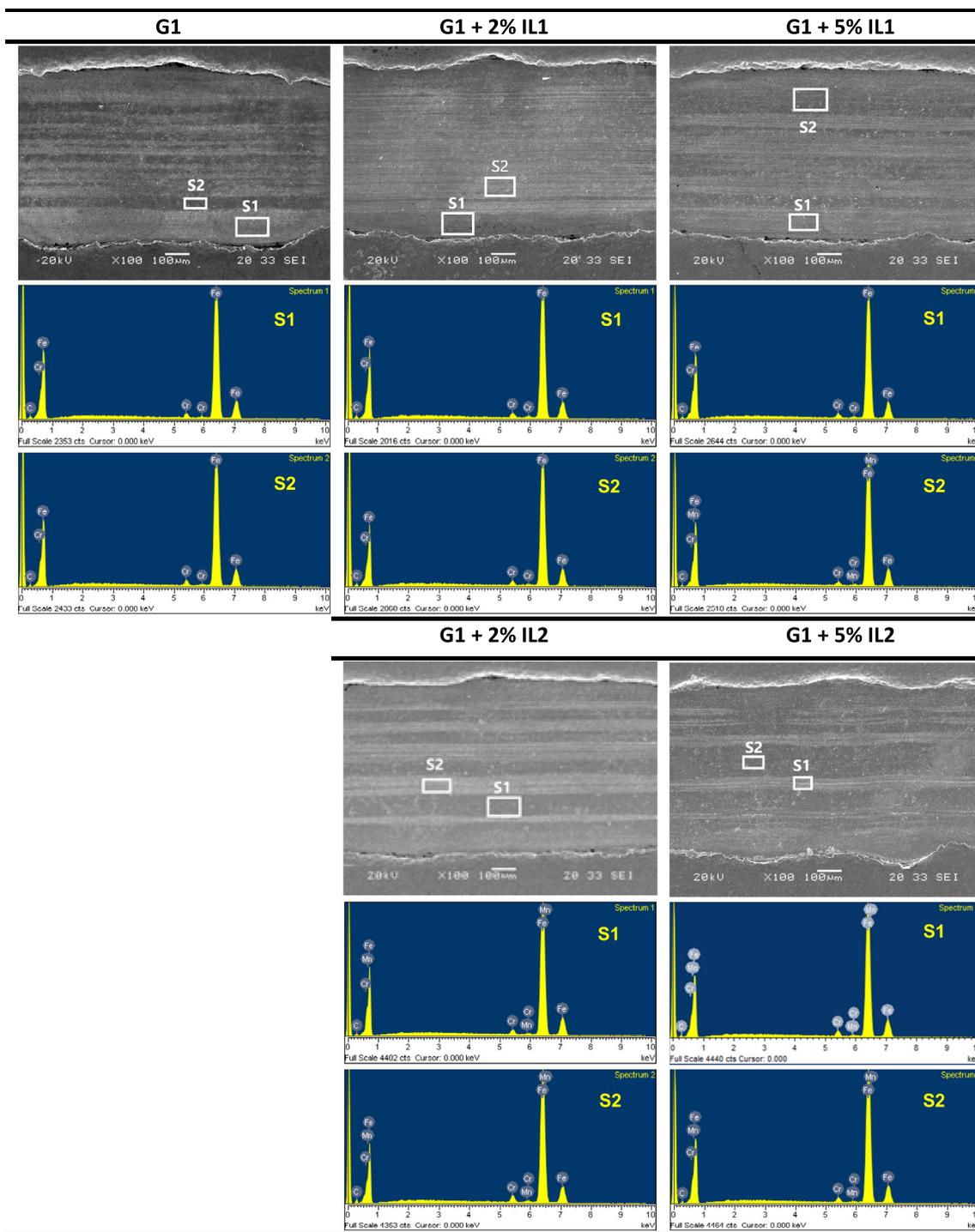


Fig. 7. SEM images and EDX analysis on the wear scar obtained after reciprocating tests with grease G1.

action between the ionic liquid or the thickener with the surface. In this case, the calcium thickener of grease G2 was much more heavily involved in the tribochemistry processes than was the lithium

Table 6
Surface composition (atomic %) on the wear scar.

Sample	C	O	P	Fe	N	Li
G1 + 2% IL1	48.7%	38.4%	1.0%	11.9%	—	—
G1 + 2% IL2	89.4%	8.4%	0.1%	1.3%	0.5%	—
G1 + 5% IL1	81.0%	16.0%	0.3%	2.7%	—	—
G1 + 5% IL2	95.8%	3.0%	0.1%	1.2%	0.0%	—

thickener of grease G1, as could be proved by the XPS analysis after the reciprocating tests (see section 3.2.2). The presence of the calcium from the thickener on the wear surface could interfere with the phosphorous reaction with the surface and impair the antiwear behavior. In addition, the low presence of phosphorous at the detection depth of the EDX technique (microns range) can be indicative of less phosphorous on the surface and a lower possibility of forming $FePO_4$, a well-known friction and wear reducing compound [30–32]. Phosphorous was not detected by EDX on the worn surface after tests with IL2- and IL3-containing mixtures, revealing that the phosphorous mainly comes from the anion.

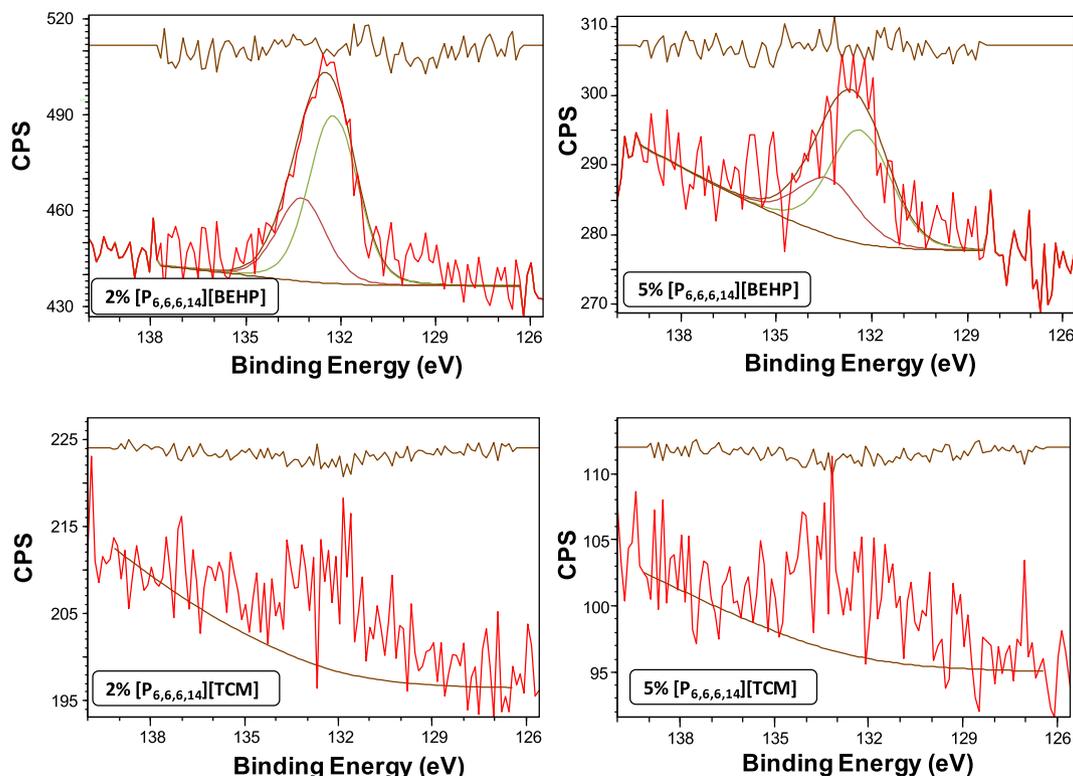


Fig. 8. P2p spectra for samples tested with the mixtures of G1 + IL1 and G1 + IL2.

3.2.2. Reciprocating tests and surface characterization

Taking into account the screening criteria used in the four ball tests, the mixtures of the grease G1 with IL1 and IL2 were selected for testing under reciprocating motion and mixed lubrication regime. The mixtures containing 2% of the ionic liquids showed higher CoF than the grease G1, while those containing 5% of the ionic liquids showed similar friction values to the grease G1, Fig. 6. On the other hand, the antiwear behavior of these lubricant samples showed that the addition of the IL1 resulted in a moderate and consistent reduction in wear.

The SEM analysis (Fig. 7) found adhesive wear and plastic deformation at the edge of the wear scar, and the EDX analysis only detected the elements from the steel. No elements from the ionic liquids were identified by EDX, including phosphorous. However, these elements might be adsorbed on the surface forming tribofilms, which can be detected by other detection techniques reliable in the nanometer scale (e.g. XPS).

Table 6 shows the surface composition on the wear scar after reciprocating tests as obtained in XPS analysis. Fig. 8 shows that the P2p signal is more evident in samples lubricated with the G1 + IL1 blends, the P2p being at a maximum at around 132.2 – 132.4 eV, which agrees with the position reported for phosphate by Wang and Wu [31]. This phosphate is likely to come from iron phosphate, which is responsible for the improved antiwear behavior of the mixtures. P2p fitting was performed, taking into account the 2p_{1/2}:2p_{3/2} doublet for every expected P peak. Fitting was carried out taking into account the 1:2 area ratio as well as a constant value of FWHM (Full Width at Half Maximum).

4. Conclusions

This study investigates the thermal stability, thermal conductivity and tribological behavior of two greases (a lithium-based grease or G1, and a calcium-based grease or G2) additised sepa-

rately with 3 ionic liquids: [P_{6,6,6,14}][BEHP] (IL1), [P_{6,6,6,14}][TCM] (IL2) and [P_{6,6,6,14}][DEC] (IL3). The main conclusions extracted from the experiments are:

- The [P_{6,6,6,14}][TCM] improved the thermal stability of both greases because of its higher thermal stability, while the [P_{6,6,6,14}][DEC] did not promote any change due to its lower thermal stability.
- Only the mixtures G1 + 5%[P_{6,6,6,14}][BEHP] and G2 + 5%[P_{6,6,6,14}][TCM] showed a slight increase in thermal conductivity, indicating that the improvement in this property in these mixtures depends on both the ionic liquid and its concentration and also the thickener used in the grease formulation.
- In general, the addition of the ILs to the lithium-based grease increased the friction coefficient in both the four-ball tests and the reciprocating tests, while the friction coefficient decreased with the addition of the ILs to the calcium-based grease in the four-ball tests.
- The addition of the [P_{6,6,6,14}][BEHP] and [P_{6,6,6,14}][TCM] improved the antiwear behavior of the lithium-based grease under both tribological tests, whereas all the ionic liquids worsened the antiwear behavior of the calcium-based grease in the four-ball tests.
- The stronger antiwear performance of [P_{6,6,6,14}][BEHP] as additive to the lithium-based grease is closely related to the iron phosphate found on the worn surface, mainly derived from the P-containing anion.
- Lower phosphorous interaction with the surface was found with the [P_{6,6,6,14}][TCM]- and [P_{6,6,6,14}][DEC]-containing blends at low temperature (reciprocating tests). Possible interference of the calcium thickener with phosphorous adsorption on, or the phosphorous reaction with, the surface was found for the calcium-based mixtures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the support for this work of the government of the Principality of Asturias (Spain) [grant number IDI/2018/000131] and the research stay [grant number: CAS19/00290] of Marlene Bartolomé at the Universidade do Porto (Portugal) financed by the Ministry of Science, Innovation and Universities (Spain). The authors would also like to thank Axel Christiernsson International AB for providing the greases used in this research.

References

- [1] C. Ye, W. Liu, Y. Chen, L.-Y. Yu, Room-temperature ionic liquids: a novel versatile lubricant, *Chem. Commun.* 21 (21) (2001) 2244–2245, <https://doi.org/10.1039/B106935G>.
- [2] F. Zhou, Y. Liang, W. Liu, Ionic liquid lubricants: designed chemistry for engineering applications, *Chem. Soc. Rev.* 38 (9) (2009) 2590–2599, <https://doi.org/10.1039/B817899M>.
- [3] I. Minami, Ionic liquids in tribology, *Molecules* 14 (6) (2009) 2286–2305, <https://doi.org/10.3390/molecules14062286>.
- [4] M.D. Bermúdez, A.E. Jiménez, J. Sanes, F.J. Carrión, Ionic liquids as advanced lubricant fluids, *Molecules* 14 (8) (2009) 2888–2908, <https://doi.org/10.3390/molecules14082888>.
- [5] J.L. Viesca, A. García, A. Hernández Battez, R. González, R. Monge, A. Fernández-González, M. Hadfield, FAP-anion ionic liquids used in the lubrication of a steel–steel contact, *Tribol Lett.* 52(3) (2013) 431–437, <https://doi.org/10.1007/s11249-013-0226-7>.
- [6] I. Otero, E.R. López, M. Reichelt, J. Fernández, Friction and anti-wear properties of two tris(pentafluoroethyl) trifluorophosphate ionic liquids as neat lubricants, *Tribol Int.* 70 (2014) 104–111, <https://doi.org/10.1016/j.triboint.2013.10.002>.
- [7] D. Blanco, A.H. Battez, J.L. Viesca, R. González, A. Fernández-González, Lubrication of CrN coating with ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate ionic liquid as additive to PAO 6, *Tribol Lett.* 41 (1) (2011) 295–302, <https://doi.org/10.1007/s11249-010-9714-1>.
- [8] J. Qu, J.J. Truhan, S. Dai, H. Luo, P.J. Blau, Ionic liquids with ammonium cations as lubricants or additives, *Tribol Lett.* 22 (3) (2006) 207–214, <https://doi.org/10.1007/s11249-006-9081-0>.
- [9] A.E. Somers, B. Khemchandani, P.C. Howlett, J. Sun, D.R. Macfarlane, M. Forsyth, Ionic liquids as antiwear additives in base oils: Influence of structure on miscibility and antiwear performance for steel on aluminum, *ACS Appl Mater Interfaces* 5(22) (2013) 11544–11553, <https://doi.org/10.1021/am4037614>.
- [10] A.E. Jiménez, M.D. Bermúdez, P. Iglesias, F.J. Carrión, G. Martínez-Nicolás, 1-N-alkyl-3-methylimidazolium ionic liquids as neat lubricants and lubricant additives in steel–aluminium contacts, *Wear* 260 (7–8) (2006) 766–782, <https://doi.org/10.1016/j.wear.2005.04.016>.
- [11] A.H. Battez, R. González, J.L. Viesca, D. Blanco, E. Asedegbea, A. Osorio, Tribological behaviour of two imidazolium ionic liquids as lubricant additives for steel/steel contacts, *Wear* 266 (11–12) (2009) 1224–1228, <https://doi.org/10.1016/j.wear.2009.03.043>.
- [12] M. Cai, Y. Liang, M. Yao, Y. Xia, F. Zhou, W. Liu, Imidazolium ionic liquids as antiwear and antioxidant additive in poly(ethylene glycol) for steel/steel contacts, *ACS Appl Mater Interfaces* 2 (3) (2010) 870–876, <https://doi.org/10.1021/am900847j>.
- [13] A.E. Jiménez, M.D. Bermúdez, Short alkyl chain imidazolium ionic liquid additives in lubrication of three aluminium alloys with synthetic ester oil, *Tribol – Mater Surf Interfaces* 6(3) (2012) 109–115, <https://doi.org/10.1179/1751584X12Y.0000000011>.
- [14] V. Pejaković, M. Kronberger, M. Kalin, Influence of temperature on tribological behaviour of ionic liquids as lubricants and lubricant additives, *Lubr Sci.* 26 (2) (2014) 107–115, <http://doi.wiley.com/10.1002/lis.1233>.
- [15] W.C. Barnhill, J. Qu, H. Luo, H.M. Meyer, C. Ma, M. Chi, B.L. Papke, Phosphonium-organophosphate ionic liquids as lubricant additives: effects of cation structure on physicochemical and tribological characteristics, *ACS Appl Mater Interfaces* 6 (24) (2014) 22585–22593, <https://doi.org/10.1021/am506702u>.
- [16] Y. Zhou, J. Dyck, T.W. Graham, H. Luo, D.N. Leonard, J. Qu, Ionic liquids composed of phosphonium cations and organophosphate, carboxylate, and sulfonate anions as lubricant antiwear additives, *Langmuir* 30 (44) (2014) 13301–13311, <https://doi.org/10.1021/la5032366>.
- [17] J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, M.B. Viola, Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive, *Tribol Int.* 71 (2014) 88–97, <https://doi.org/10.1016/j.triboint.2013.11.010>.
- [18] Y. Zhou, J. Qu, Ionic Liquids as Lubricant Additives: A Review, *ACS Appl. Mater. Interfaces* 9 (4) (2017) 3209–3222, <https://doi.org/10.1021/acsami.6b12489>.
- [19] R. González, M. Bartolomé, D. Blanco, J.L. Viesca, A. Fernández-González, A.H. Battez, Effectiveness of Phosphonium Cation-Based Ionic Liquids as Lubricant Additive, *Tribol. Int.* 98 (2016) 82–93, <https://doi.org/10.1016/j.triboint.2016.02.016>.
- [20] A. Hernández Battez, Carlos M.C.G. Fernandes, Ramiro C. Martins, M. Bartolomé, R. González, Jorge H.O. Seabra, Two phosphonium cation-based ionic liquids used as lubricant additive: Part I: Film thickness and friction characteristics, *Tribology International* 107 (2017) 233–239, <https://doi.org/10.1016/j.triboint.2016.10.048>.
- [21] A. Hernández Battez, Carlos M.C.G. Fernandes, Ramiro C. Martins, Beatriz M. Graça, M. Anand, D. Blanco, Jorge H.O. Seabra, Two phosphonium cation-based ionic liquids used as lubricant additive: Part II: Tribofilm analysis and friction torque loss in cylindrical roller thrust bearings at constant temperature, *Tribology International* 109 (2017) 496–504, <https://doi.org/10.1016/j.triboint.2017.01.020>.
- [22] R. González, J.L. Viesca, A. Hernández Battez, M. Hadfield, A. Fernández-González, M. Bartolomé, Two phosphonium cation-based ionic liquids as lubricant additive to a polyalphaolefin base oil, *Journal of Molecular Liquids* 293 (2019), <https://doi.org/10.1016/j.molliq.2019.11.1536>.
- [23] M. Cai, Z. Zhao, Y. Liang, F. Zhou, W. Liu, Alkyl Imidazolium Ionic Liquids as Friction Reduction and Anti-Wear Additive in Polyurea Grease for Steel/Steel Contacts, *Tribol. Lett.* 40 (2) (2010) 215–224, <https://doi.org/10.1007/s11249-010-9624-2>.
- [24] M. Cai, Y. Liang, F. Zhou, W. Liu, Tribological Properties of Novel Imidazolium Ionic Liquids Bearing Benzotriazole Group as the Antiwear/Anticorrosion Additive in Poly(ethylene glycol) and Polyurea Grease for Steel/Steel Contacts, *ACS Appl. Mater., Interfaces* 3 (2011) 4580–4592, <https://doi.org/10.1021/am200826b>.
- [25] Z. Cao, Y. Xia, C. Chen, Fabrication of novel ionic liquids-doped polyaniline as lubricant additive for anti-corrosion and tribological properties, *Tribol. Int.* 120 (2018) 446–454, <https://doi.org/10.1016/j.triboint.2018.01.009>.
- [26] Q. Zhao, G. Zhao, M. Zhang, X. Wang, W. Liu, Tribological Behavior of Protic Ionic Liquids with Dodecylamine Salts of Dialkylthiocarbamate as Additives in Lithium Complex Grease, *Tribol. Lett.* 48 (2) (2012) 133–144, <https://doi.org/10.1007/s11249-012-0011-z>.
- [27] Z. Wang, Y. Xia, Z. Liu, Comparative study of the tribological properties of ionic liquids as additives of the attapulgite and bentone greases, *Lubr. Sci.* 24 (4) (2012) 174–187, <https://doi.org/10.1002/lis.1173>.
- [28] P. Qiao, Y. Xia, X. Ge, Tribological properties of the overbased calcium sulfonate complex greases containing different lubricant additives, *Advanced Materials Research* 645 (2013) 133–136, <https://doi.org/10.4028/www.scientific.net/AMR.645.133>.
- [29] X. Fan, Y. Xia, L. Wang, J. Pu, T. Chen, H. Zhang, Study of the Conductivity and Tribological Performance of Ionic Liquid and Lithium Greases, *Tribol. Lett.* 53 (1) (2014) 281–291, <https://doi.org/10.1007/s11249-013-0266-z>.
- [30] Z. Wang, J. Chang, C. Cai, Tribological Performance of Phosphonium Ionic Liquids as Additives in Lithium Lubricating Grease, *Lubricants* 6 (1) (2018) 23, <https://doi.org/10.3390/lubricants6010023>.
- [31] Z. Wang, W. Wu, The tribological properties of the polyurea greases based on oil-miscible phosphonium-based ionic liquids, *Lubr. Sci.* 30 (1) (2018) 16–22, <https://doi.org/10.1002/lis.1391>.
- [32] Z. Wang, J. Chang, W. Wu, Synergistic effects of phosphate ionic liquids and octadecylamine-oleoyl sarcosinate as lubricating grease additives, *Lubr. Sci.* 31 (4) (2019) 127–136, <https://doi.org/10.1002/lis.1454>.
- [33] M. Ploss, Y. Tian, S. Yoshikawa, R. Westbroek, J. Leckner, S. Glavatskih, Tribological Performance of Non-halogenated Phosphonium Ionic Liquids as Additives to Polypropylene and Lithium-Complex Greases, *Tribol. Lett.* 68 (3) (2020) 1–13, <https://doi.org/10.1007/s11249-019-1240-1>.
- [34] M. Bartolomé, D. Gonçalves, A. García Tuero, R. González, A. Hernández Battez, J.H.O. Seabra, Greases additised with phosphonium-based ionic liquids - Part I: Rheology, lubricant film thickness and Stribeck curves, *Tribology International* 156 (2021), <https://doi.org/10.1016/j.triboint.2020.106851>.
- [35] A. Torres Pérez, A. Hernández Battez, G. García-Atance, J.L. Viesca, R. González, M. Hadfield, Use of optical profilometry in the ASTM D4172 standard, *Wear* 271(11–12) (2011) 2963–2967, <https://doi.org/10.1016/j.wear.2011.06.016>.