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SHORT COMMUNICATION

Tribological performance of tributylmethylammonium bis(trifluoromethylsulfonyl)amide as neat lubricant and as an additive in a polar oil

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Abstract: The ionic liquid (IL) tributylmethylammonium bis(trifluoromethylsulfonyl)amide ([N_{4441}][NTf_2]) was used as neat lubricant and as an additive (1.5 wt%) in a polar oil to study its friction and wear reducing properties. Tribological tests were completed for 90 minutes at room temperature and 100 °C in a reciprocating configuration at loads of 30 and 70 N, 10 Hz-frequency, and 4 mm stroke length. Wear volume was measured by confocal microscopy and the surface-IL interaction determined by XPS. The main findings were that neat IL showed the best tribological behavior; the IL-containing mixture behaved similar to the base oil regarding friction, however outperformed the antiwear behavior of the base oil under higher temperature; surface-IL chemical interaction was found mainly at 100 °C.

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

1 Introduction

The ionic liquids (ILs) as a potential component (basestock and/or additive) in a lubricant formulation has been studied since 2001 [1–8]. Despite all their excellent properties for lubrication (large liquid range, high thermal stability and polarity, and low flammability and melting point), the ILs have the problem of low solubility in non-polar compounds (mineral oils and polyalphaolefins) usually used in lubricant formulation. Most of the studies on use of ILs as an additive have been completed with nonpolar-neat and fully formulated oils [9–15], and only a few works worked with polar base oils [13-16]. The former situation is related with previous studies [20, 21], where a binary mixture formed by a non-polar base oil and a polar additive was used for lubricant purposes, avoiding the possible competition of both compounds for the metallic surfaces.

Due to the use of polar base oils for different applications and the expected better solubility of the ILs in these base oils, it is important not only the study of ILs as an additive but also as a neat lubricant or basestock in order to compare their friction and wear reduction with other ILs. This current research considers the antifriction and antiwear performance of a [NTf_2] anion-based IL as neat lubricant and as an additive in a polar oil.

2 Experimental details

2.1 Lubricant samples

The ionic liquid tributylmethylammonium bis(trifluoro-

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methylsulfonyl)amide ($[N_{4441}][NTf_2]$), supplied by Io-Li-Tec (Ionic Liquid Technologies GmbH) and whose chemical formulae is $C_{15}H_{30}F_6O_4N_2S_2$ and with 99% of purity, was used as a pure lubricant and as an additive at 1.5 wt% in a hydrolytically stable and readily biodegradable diester oil (coded as A1). This concentration was the maximum value found in solubility tests previously made [22]. A Stabinger Viscometer SVM3001 was used for density and viscosity measurements of the lubricant samples (base oil, ionic liquid and the mixture) at temperatures ranging from 15–100 °C. Thermogravimetric analysis (TGA) was made for all lubricant samples under reactive (oxygen) and inert (nitrogen) atmospheres (50 mL/min) at temperatures ranging from 25–600 °C and heating rate of 10 °C/min.

2.2 Tribological tests and surface characterization

Friction and wear tests were performed using a ball-on-disk reciprocating rig with AISI 52100 chrome steel balls (∅6.0 mm, Ra ≤ 0.05 μm, 58–66 HRC) and AISI 52100 steel disks (∅10 mm, 3 mm thick, Ra ≤ 0.02 μm, 190–210 HV_{30}). Normal load is applied using a closed-loop servomechanism, and normal load and friction force are measured with strain-gages. Test conditions were: 90 min-duration, stroke length of 4 mm, 10 Hz-frequency, loads of 30 and 70 N (medium contact pressures of 1.37 and 1.82 GPa, respectively) at room temperature (RT) and 100 °C. Tests with neat base oil and mixture used 4 ml as lubricant volume, while tests with neat IL used 25 μL.

Test specimens were cleaned in an ultrasonic bath with heptane for 5 minutes, rinsed in ethanol later and dried in hot air. After the tribological tests, wear volume on the disks was determined using confocal microscopy. Three tests were conducted for each lubricant sample, and the average value and the standard deviation for friction coefficient and wear volume was determined. X-Ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were used for chemical interaction measurements on the disk's surface, respectively.

3 Results and discussions

The density and viscosity measurements of the IL-containing mixture showed that the addition of the IL at 1.5 wt% hardly changed these properties in comparison to that of the base oil (Fig. 1). This result suggests that the tribological behavior of the mixture can be explained by the influence of the chemical composition of the IL instead of its rheological properties. Figure 2 shows thermal characteristics of the lubricants samples and as expected the neat IL has the highest thermal stability with temperatures of thermal degradation (T_{onset}) of 304 °C (oxygen atmosphere) and 360 °C (nitrogen atmosphere). On the other hand, the base oil showed T_{onset} values of 179 and 223 °C under oxygen and nitrogen atmospheres, respectively, and the T_{onset} of the mixture were 205 and 258 °C.

Figure 3 shows the friction reducing behavior of the mixture and the neat IL in comparison with the neat base oil. The mixture had similar mean friction values as the base oil at both RT and 100 °C, meanwhile the IL presented the best antifriction result. This behavior was also found on the wear reducing properties of the mixture and the neat IL at RT (Fig. 4). But the mixture showed better antiwear behavior than the base oil at 100 °C, although the neat IL demonstrated the best results.

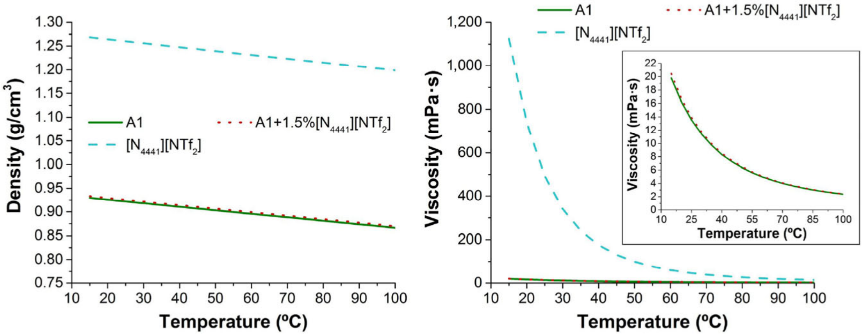

Fig. 1 Density and viscosity versus temperature for the lubricant samples.

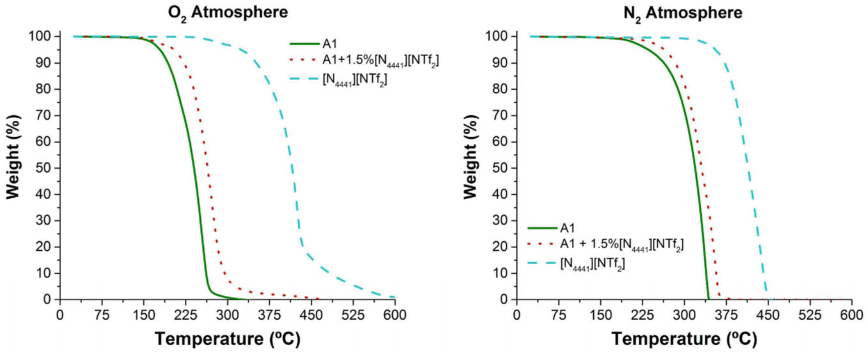

Fig. 2 Thermogravimetric characteristics of the lubricant samples under oxygen and nitrogen atmospheres.

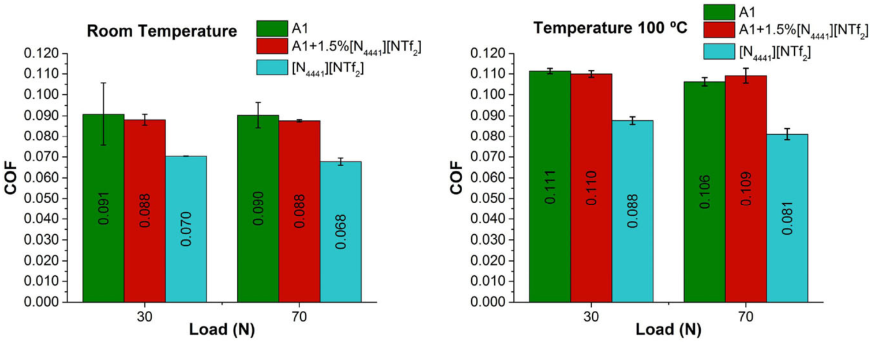

Fig. 3 Friction coefficient from tribological tests made at RT and 100 °C.

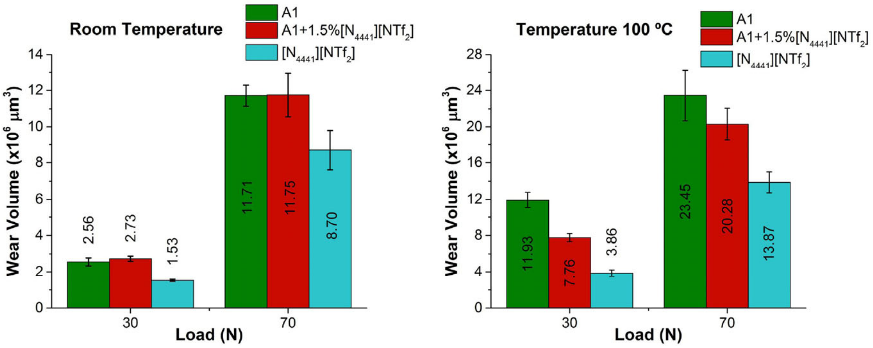

Fig. 4 Wear volume on the disk after tests made at RT and 100 °C.

Figure 5 shows SEM images of the wear scar after the tribological tests made with all the lubricant samples at room temperature. It can be observed that the samples lubricated with the mixture and the base oil exhibited similar appearance, while the surfaces tested with neat IL present a smoother wear scar and less material displacement at its borders for the both studied loads. Similar results can be observed in the test at 100 °C according with tribological behavior, where neat IL had the best friction and antiwear performance. In addition, the EDS spectra showed that for all the lubricants and test conditions, the only chemical elements found on the worn surface were those present in the steel.

Table 1 shows XPS results. According to the work of Mangolini et al. [23], iron spectra peaks around 711, 713 and 708 eV were assigned to Fe (III), FeOOH and Fe (0), respectively. Similar results were obtained for all the tests conditions. Only the sample lubricated with neat IL at 100 °C showed a slight decrease in the Fe (0) content and an equivalent increase in the Fe (III).

At RT the presence of fluorine is only clear with neat IL. Two peaks were detected at 689.3 eV (80% total fluorine) assignable to NTf_2 residues [24], and at

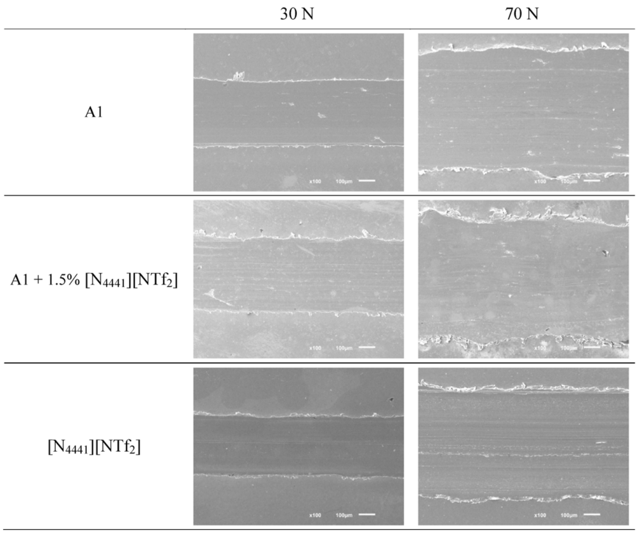

Fig. 5 SEM images from the wear scar of test made at room temperature.

685.1 eV belonging to Fe–F interactions [25], which indicate a low-extent IL-surface reaction. For neat IL the same peaks were also detected at 100 °C, but the peak at 685.1 eV (Fe–F) represents the 70% of the total fluorine. Furthermore, sample lubricated with the mixture at 100 °C shows a weaker peak at 685.0 eV, indicating also a IL-surface interaction generating Fe–F.

These results demonstrate that higher temperature promotes the chemical interaction between the IL and the surface, modifying its tribological performance.

On the other hand, the behavior of O1s was very similar in all the samples, showing three peaks at 530.5 eV, 532.2 eV and 533.5 eV. These bands are very hard to assign, since there are many possibilities for these positions. Taking into account the position of the peak and the fact of being the least contribution to the O1s envelope, the peak at 533 eV belongs probably to water [26]. The assignation of the other two peaks is unclear, because peaks around 530 eV can be assignable to metal oxides, but also to O_2 adsorbed on certain metals or some long-chain ethers [27]. Likewise, the oxygen in some long-chain esters as well as the oxygen in some organic complexes of iron appears around 532 eV. It is probably that there is a combination of different compounds difficult to identify without further experimentation [27].

4 Conclusions

A [NTf_2] anion-based IL was used as neat lubricant and as an additive in a polar oil and the main conclusions are: neat IL showed better tribological behavior under all testing conditions than the neat base oil and the IL-containing mixture; the addition of the IL hardly changed friction with regard to the neat

Table 1 Positions in eV of the photoelectron peaks of iron and fluorine. In brackets the relative amount of this species with respect to the total amount of the element.

Iron					
Room temperature			100 °C		
A1	1.5% IL	[N_{4441}][NTf_2]	A1	1.5% IL	[N_{4441}][NTf_2]
710.8 (49%)	710.9 (53%)	710.8 (54%)	710.8 (52%)	710.7 (51%)	711.0 (68%)
712.6 (14%)	712.8 (14%)	712.8 (14%)	712.7 (13%)	712.6 (14%)	713.0 (13%)
707.5 (37%)	707.6 (33%)	707.5 (32%)	707.5 (35%)	707.5 (35%)	707.6 (19%)
Fluorine					
Room temperature			100 °C		
A1	1.5% IL	[N_{4441}][NTf_2]	A1	1.5% IL	[N_{4441}][NTf_2]
—	—	689.3 (80%)	—	—	689.1 (31%)
—	—	685.1 (20%)	—	685.0 (100%)	685.1 (69%)
Oxygen					
Room temperature			100 °C		
A1	1.5% IL	[N_{4441}][NTf_2]	A1	1.5% IL	[N_{4441}][NTf_2]
530.5 (49%)	530.6 (50%)	530.5 (53%)	530.4 (48%)	530.5 (51%)	530.5 (50%)
532.2 (41%)	532.3 (38%)	532.0 (35%)	532.0 (40%)	532.1 (38%)	532.0 (40%)
533.7 (10%)	533.6 (12%)	533.3 (12%)	533.4 (12%)	533.4 (11%)	533.3 (11%)

base oil but decreased wear at higher temperature; and the antiwear behavior at higher temperature was related to reaction of active elements of the IL with the steel surface.

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