Tribological Effectiveness of Graphene Oxide and Ionic Liquids in PAG Oil: Could Absorbed Water Play Beneficial Role?

Prof. Vincenzo D'AGOSTINO, Dr. Mario PISATURO, Dr. Claudia CIRILLO, Prof. Dr. Maria SARNO, Prof. Dr. Adolfo SENATORE

Department of Industrial Engineering, NANO_MATES Research Centre, University of Salerno, Fisciano, Italy, {dagostino, mpisaturo, clcirillo, msarno, a.senatore}@unisa.it

Abstract: The polyalkylene glycol (PAG) lubricants are widely used as gear, bearing and compressor oils. Indeed, the base PAG oil can be used as additive in engine oil or transmission oil as well as compressor lubricant in refrigerant systems. They are designed to provide outstanding benefits in terms of efficiency, long oil life, and equipment protection. These fully synthetic lubricants were developed for use under operating conditions beyond the capabilities of other synthetic lubricants and mineral oils. Their low pour points ensure excellent low-temperature fluidity. On the other hand the main disadvantage of the PAG oils is the marked hygroscopicity, i.e. they absorb and bind moisture from the ambient air. In this paper the results from tribological testing of PAG oil featuring 46 cSt at 40°C with solid (graphene oxide) and liquid (ionic liquids) additives are proposed. Moreover, in this study the influence of the absorbed moisture from ambient air has been taken into account. Preliminary experiments with ball-on-flat setup by using reciprocatory tribometer have been carried out on the base oil PAG 46 blended with 1-Ethyl-3-methylimidazolium acetate or graphene oxide, alternatively. In this way the influence of each additive has been investigated. Based on this information the aim of this research is to test the hybrid formulations and to verify potential improvements on anti-friction and anti-wear PAG 46 behaviour in broad range of lubrication regimes. The experimental tests have been carried out by using rotational disc tribometer in ball-on-disc configuration. Additional experiments after samples exposure to ambient air and ensuing moisture absorption were executed. The results highlight that in most cases the absorbed moisture do not introduce detrimental effects on the tribological performances of the tested oil samples. Rather, water content reduces wear of the sliding steel surfaces in the whole testing spectrum and in many cases the frictional dissipation.

Keywords: Nanosized friction modifiers, tribological testing, graphene oxide, ionic liquid, water absorption, Stribeck graphs.

1. Introduction

Friction and wear are the two major causes for energy and material losses in tribological conjunctions of mechanical systems. Lubrication is principal focus to improve energy efficiency and mechanical durability. In addition, in order to minimize wear not only the lubricant film needs to be kept thick enough to prevent any contact between the surfaces, but also friction has to be reduced so as to obtain an efficiency as high as possible; pressure peaks must be not large to avoid sub-surface stresses and, thus, pitting fatigue [1].

The properties of lonic Liquids (ILs) at room-temperature make them excellent lubricants [2-4]. Their pertinent physico-chemical characteristics [5-7] include their negligible volatility, nonflammability, high thermal stability and high thermal conductivity, low melting point, and broad liquid range. In addition, ionic liquids are highly polar and miscible with water and with number of organic solvents (aromatic, heterocyclic compounds, etc.) [1]. The ILs' viscosity can be modified by selecting different lengths of the nonpolar alkyl side chain of the cation or different type of anion [8]. Indeed, the intrinsic properties of ILs could likely avoid the use of some additives [9], such as: (1) detergents because ILs act as solvents, (2) anti-oxidants due to ILs' high thermal stability, (3) several anti-wear additives such as zinc butyl and octyl dithiophosphate (ZDDP) due to the formability of surface boundary films, although for several cases due to the corrosion, additives could be needed [10-11]. Moreover literature results, [4,5,12,13], proved that pure ionic liquids even without any additives deliver low friction coefficients and wear. Ionic liquids exhibit superior tribological behaviour because of their polar structure. They can be easily adsorbed on the sliding surfaces of frictional pairs. Consequently, an effective boundary film can reduce friction and wear. Ionic liquids have comparable heat characteristics to current thermal fluids [1].

Finally, in [14,15], the Authors analysed the connection between the voltage effect on the structure of the IL layers and their lubricating properties.

On the other hand, in the field of tribological applications, nanoparticles as additives in base oil have been extensively investigated. These studies refer to synthesis and preparation of nanoscale particles and their tribological properties and friction reduction mechanisms. It has been generally found that when the nanoparticles were added to base oil, the extreme pressure property and load-carrying capacity were improved and friction coefficient was decreased.

Nanocarbon materials have received great attention by tribology researchers in the last three decades, due to high load-bearing capacity, low surface energy, high chemical stability, weak intermolecular, and strong intramolecular bonding [16-18]. The lubrication mechanism of the carbon nanoparticles has not been yet completely understood, but their properties as frictional media are definitely based on structural modification. They present the same main advantage that nanoparticles made on metal dichalcogenides: they are efficient even at room temperature. The comprehension of their action at the interfaces of frictional conjunction and the tailored functionalization will certainly aim at improving their excellent performance in this field.

As well known, graphene has recently enjoyed extensive attention because of its excellent properties, such as high thermal conductivity, high Young's modulus, large specific surface area, electromagnetic interference shielding, electrical conductivity. Recent studies focused on mechanical features of joints underline considerable increase in tensile strength with favourable effect probably due to the cumulative effects of intermolecular interactions between the graphene and resin networks [19]. From the tribological point of view, Huang et al. [20] investigated the properties of graphite nanosheets obtained by ball milling of natural flake graphite, in oil. They found that the frictional behaviour and anti-wear ability of the lubricating oil were improved when graphite nanosheets and dispersant were added to the paraffin oil at the optimal concentration. Lin et al. [21] suggested that functionalizing the graphene platelets with proper modifier is an effective way to enhance the additive dispersion.

This paper aims at investigating the tribological performance of Graphene Oxide (GO) and ionic liquid as friction modifiers in polyalkylene glycol (PAG) base oil. As well known, the base PAG oil can be used as additive in engine or transmission lubricants whereas it's the preferred compressor lubricant in refrigerant systems [22-24]. The behaviour of PAG oil with additives in the latter field is one of the targets of this research, as some reference reports of generally adverse effects [25]. Although refrigerant systems are categorized as closed systems, the absorption of moisture/humidity is inevitable due to permeation through barrier hoses [22]. For this reason additional test campaigns on the influence of water content in oil should be carried out. In the present analysis, tribological tests have been performed through ball-on-disc tribometer. The Wear Scar Diameter (WSD) after steady-state tests has been selected as wear parameter for samples comparison.

The results provide useful data about the influence of graphene oxide, ionic liquid and water on the friction coefficient and wear parameter.

2. Lubricant samples and methods

2.1 Materials

The experimental tests were carried out by using both the pure PAG 46 and the PAG 46 with IL and GO as friction modifiers. In particular, the GO nanosheets were prepared by modified Hummer method [26]. The oxidation of graphite particles were obtained from Lonza [26,27] to graphitic oxide accomplished with water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. The entire process requires less than two hours for completion at temperatures below 45°C. With the aid of further sonication step, the oxidized graphite layers were exfoliated from each other. Then 30% H_2O_2 was added to the suspension to eliminate the excess MnO_{4}^{-4} . The desired products were rinsed with deionized water. The remaining salt impurities were eliminated with resinous anion and cation exchangers. The dry form of graphitic oxide was obtained by centrifugation followed by dehydration at 40°C [28]. Such synthesis process was entirely developed at Laboratories of Dept. of Industrial Engineering/Nano_Mates Research Centre at University of Salerno. The ionic liquid used as additive for the PAG base oil is the 1-Ethyl-3-

methylimidazolium acetate. Such halogen-free ionic liquids turned out as potential alternatives to fluorinated ionic liquids for lubrication and proved their liquid/metal surface interactions mainly dominated by the anion with formation of layers as tribochemical reaction mechanism with friction benefits [29].

For each oil sample sonication (Hielsher UP 400s) of 30 min followed by mixing with Silverson L5M homogenizer for 30 min has been carried out. Moreover, before each tribological test stirring of 30 min at 13.000 rpm with IKA T25 digital ULTRA-TURRAX® has been performed.

No dispersant agent has been blended with base oil and additives of the lubricant formulations under test. In this analysis three 350 ml oil samples have been tested; Tab. 1 reports the concentration of the additives for each sample.

OIL SAMPLE	BASE OIL	IL [w.t.%]	GO [w.t.%]
1		-	-
2	PAG 46	2.0	0.1
3		2.0	0.5

TABLE 1: Tested oil samples

2.2 Friction test – Stribeck curve

The experimental tests were carried out by using rotational disc WAZAU TRM100 tribometer in ball-on-disc configuration. This tribometer setup allows applying different tribopair parameters, which is desirable in order to study the different regimes in the Stribeck curve, i.e., boundary, mixed and elastohydrodynamic lubrication conditions. The normal force was applied on the mating surfaces by lever system and could be varied in the range of 0–100 N. The spinning shaft was driven by brushless motor with speed variable up to 3000 rpm. The measurement of the normal force was performed through force sensor arranged between the load lever and the lower specimen holder. The lubricant average temperature has been controlled through NiCr-Ni-thermocouple in the oil reservoir and an electric resistance. The investigated contact type was composed of an upper rotating X155CrVMo12-1 steel disc of hardness 60 HRC, roughness of Ra=0.5 μ m and 105 mm in diameter. lower X39Cr13 steel ball, 57±3 HRC, grade 100, 8 mm diameter was completely immersed in temperature-controlled 350 ml lubricant bath. An average contact pressure of 1.50 GPa, corresponding to normal load of 70 N, was applied at the ball/disc interface.

A speed-sweep test at constant load on wide speed range has been designed to cover broad operating conditions with the purpose of minimizing the modification of the tribopair steel surfaces in order to get frictional results in comparable surface topography conditions. For this reason, the time extension of the tests was limited to 24 min. The disc speed rose up to 2.0 m/s in the first 4 min and dropped to zero in the following 4 min. This speed pattern was repeated three times. The tests were performed for two different temperatures, i.e., 25°C and 80°C. These two temperatures have been chosen to get useful results both for engine and gearbox applications as well as for compressor in refrigerant plants.

The current design of this experiment allowed to cover slow-to-high speed range and to obtain complete Stribeck frictional graph. Another advantage of this setting was the high reproducibility of the friction coefficient (CoF) in several ramps and the good averaging-out of the noise-level. Also, since the sliding acceleration was very low along each speed ramp there was no relevant fluid inertial phenomena and transducers dynamic effects, i.e., each "CoF vs. speed" curve was obtained in quasi-steady state condition.

The measured data are presented according to the Stribeck curves representation, i.e., friction coefficient vs. sliding speed. The friction coefficient is the average value calculated by considering each ramp as single test. Standard deviation calculations are also depicted on the plots in the form of error bar.

2.3 Friction and wear in steady-state tests

Long running frictional tests of 1-hour have been performed to analyse the influence of the nanoparticles on wear behaviour of the steel ball/disc pair. For this test, constant values for average contact pressure, temperature and speed were 1.50 GPa, 25°C and 80°C, 5.0 mm/s and 0.50 m/s, respectively, resulting in four combinations. After each test the wear scar diameter has been measured with Sensofar PLu-neox 3D optical profiler.

3. Results

3.1 Screening tests

Preliminary experiments were carried out on the same base oil PAG 46 blended with 1-Ethyl-3methylimidazolium acetate or graphene oxide, alternatively. The selected lubrication regime was boundary. The tests have been performed with ball-on-flat setup on Ducom TR-BIO-282 reciprocatory tribometer: the stroke of 3 mm and the frequency of 5 Hz led to maximum sliding speed equal to 94 mm/s. According to the Figure 1, the friction measurement in 1-hour sliding test by testing the four samples displayed in the graph label exhibited similar results. Hence, no sensible gain achievable through addition of ILs or GO dispersion appeared in such testing conditions.



Fig. 1. Friction coefficient vs. time

Nevertheless, the analysis of the in-line values of the electric contact resistance (ECR) could lead at least to partial understanding of the concurrent phenomena taking place at sliding interfaces, Figure 2.



Fig. 2. Electric contact resistance (ECR) vs. time

As observed in previous papers, e.g. [30], the formation of tribolayer due to material transfer from lubricant carbon based nanoadditive to metal surface yields out rapid increment of ECR along with CoF reducing. The result is even marked by increasing the nanoparticles concentration. Hence, an inverse correlation between CoF and ECR could be stated when nanocarbon materials are used as friction modifiers. The Figure 2 shows trend inversion in the case of ILs blending with base oil, as the lower the CoF, the lower the ECR. This result would confirm the different lubrication mechanism at the metal sliding interface. By assuming as common target the lowering of frictional loss at sliding interface, the material transfer from solid nanoadditive dispersed in the lubricant and ensuing lower shear stress and prevention of direct contact between metal interfaces [28] is replaced by the lubricity property of ILs in the pure-liquid blending formulation [14].

These same four samples exhibited in steady sliding speed conditions at 5.0 mm/s and 100 mm/s: optimal anti-wear behaviour by adding 0.1 w.t.% GO with decrease of wear parameter equal to 14% and 18%, respectively; reduced CoF by ILs blending at 5 w.t.% up to 11% and 22%, respectively.

Based on the above discussion, in this research the Authors aimed at testing the hybrid formulations to verify potential improvements from both the concurrent interfacial effects to improve anti-friction and anti-wear PAG 46 behaviour in broad range of lubrication regimes.

3.2 Influence of graphene oxide and ionic liquid additives

3.2.1 Friction test – Stribeck curve

The Figure 3 shows the Stribeck curves for all oil samples at 25° C (a) and 80° C (b) before that they have been exposed to the ambient air. It is worth noting that at lower temperature for all graphs it is possible recognize well-developed minimum, that is considered the transition from mixed lubrication regime to EHL regime for increasing speed [31]. This frontier divides the region with concurrent phenomena of solid-to-solid contacts, adhesion and interaction between friction modifier additives and steel surface (mixed lubrication) from the other with predominant viscous stress and elastic deformation of the tribopair surfaces (EHL). The oil sample 2, i.e. PAG 46 with 2.0% w.t. IL and GO at 0.1% w.t. (red line), shows the lower friction coefficient. Moreover, it exhibits minimum at sliding speed of 1 m/s. In all cases the minimum falls in the sliding speed range 0.67 – 1 m/s. The reduction of the friction coefficient for the sample 2 as compared to the other samples is on average of 14%.



Fig. 3. Stribeck curves at 25°C (a) and 80°C (b).

The lower oil viscosity at higher temperature results in transition between mixed and EHL regime at higher sliding speed. Indeed, only the boundary and the mixed lubrication regimes are prevailing in Figure 3 (b). In contrast to the results at 25°C, at higher temperature the pure PAG 46 oil exhibits friction coefficient slightly higher than other samples for sliding speeds lower than 0.7 m/s. Beyond this value the oil samples 2 and 3 display friction coefficient slightly higher than the pure base oil.

ISSN 1453 – 7303 "HIDRAULICA" (No. 2/2016) Magazine of Hydraulics, Pneumatics, Tribology, Ecology, Sensorics, Mechatronics

3.2.2 Friction in steady-state tests

In this section the friction coefficients measured in steady-state condition are reported. At 25°C and 5 mm/s, Figure 4 (a), the base oil PAG 46 displays higher friction coefficient than samples with solid and liquid additives; average data +17%. Moreover, for all oil samples with ILs/GO additives the measured friction coefficient is confined in more narrow range. It is worth noting that under these test conditions the best results were exhibited by the oil sample 2. In Figure 4 (c) the results with oil bath at 80°C and sliding speed of 5 mm/s are plotted. The measured friction coefficient for the base PAG 46 exhibits stable and constant behaviour. On the other hand, the oil samples with additives show variable friction coefficient which tends to stable value. This value is approximately the same of the pristine PAG 46. In any case the lower friction coefficient was measured for the oil sample with the higher concentration of graphene oxide (magenta line). Figure 4 (b) and (d) show the results at 25°C and 80°C in mixed lubrication regime, i.e. sliding speed of 0.5 m/s. In such a lubrication regime at low temperature, the oil sample 1 exhibits friction coefficient which slightly increases during the first 400 s and it attains to stable value. Instead, for the oil samples with additives the measured friction coefficients decrease in the first part of the test, reaching stable value. The lower friction coefficient was observed for the oil sample 2 which has the higher loading of graphene oxide (red line). Moreover, by comparing the Figures 4 (b) and (d) it is worth noting that the measured friction coefficients at 80°C are higher than values measured at 25°C.



Fig. 4. Steady-state tests at 25°C (a)-(b) and 80°C (c)-(d).

3.3 Influence of water content

As explained in the introduction section, each sample has been exposed for two months in open air in protected from light ambient. In this way, the influence of the moisture absorption could be investigated from the tribological point of view. Such analysis has twofold purpose: the proof of lubricant performance through lifetime without changing it, as in car or industrial refrigerator systems; the investigation about water capability to promote surface chemical reactions beneficial to friction reduction [32]. After two months weight increment of about 0.2% has been observed for each oil sample. The tab. 2 reports the water content and the labels of the samples after water absorption. The "B" label refers to the same samples of the tab. 1 ("A" labelled) after the ambient air exposure. The fifth column provides the water content in ppm. Even though the sample have been for long time in ambient air, all the samples exhibited weak hygroscopicity by comparing the present data with literature ones [22]. This behaviour can be mainly addressed to the double end capped chemical structure of the tested PAG 46 oil.

OIL SAMPLE	BASE OIL	IL [w.t.%]	GO [w.t.%]	WATER CONTENT [ppm]
1 A	PAG 46	-	-	-
1 B		-	-	2060
2 A		2.0	0.1	-
2 B		2.0	0.1	1885
3 A		2.0	0.5	-
3 B		2.0	0.5	1833

TABLE 2: Oil samples after ambient air exposure

3.3.1 Friction test – Stribeck curve

The Figures 5 show the hygroscopicity effect on friction coefficient displayed by the Stribeck curves at 25°C and 80°C. In particular, at 25°C the PAG 46 which absorbed moisture from the ambient air (case B) doesn't exhibit minimum in the analysed speed range. Indeed, the friction coefficient significantly decreases with the sliding speed. On the other hand, the same figure highlights that at sliding speed lower than 0.40 m/s the friction coefficient is lower for PAG 46 case A. Also at 80°C the water contained in PAG oil results in lower friction coefficient at higher sliding speed. However, in this case at lower sliding speed the friction coefficient exhibits the same behaviour in both cases.



Fig. 5. Stribeck curves at 25°C (a) and 80°C (b) – oil sample 1: case A (before water absorption), case B (after water absorption).

In Figure 6, the results obtained by testing the oil sample 2 are presented. As for the previous sample, at 25°C the oil which absorbed moisture from ambient air (case B) doesn't exhibit minimum in the whole speed range. At 80°C the water absorbed by the sample results in lower

friction coefficient at higher sliding speed, whereas at lower sliding speed the friction coefficient exhibits the same behaviour in both cases.



Fig. 6. Stribeck curves at 25° C (a) and 80° C (b) – oil sample 2: case A (before water absorption), case B (after water absorption).

Finally, in Figure 7 the results for the oil sample 3 are presented. In this case, at 25°C the oil sample which absorbed moisture from ambient air (case B) exhibits minimum around 1.40 m/s. Moreover, both at 25°C and at 80°C the water bound in oil results in reduction of the friction coefficient in the whole analysed speed range.



Fig. 7. Stribeck curves at 25° C (a) and 80° C (b) – oil sample 3: case A (before water absorption), case B (after water absorption).

3.3.2 Friction in steady-state tests

In this section the friction coefficients measured in steady-state condition are described. In Figure 8 the friction coefficient vs. time both at 25°C, sliding speed 5 mm/s (a) and 0.5 m/s (b) and 80°C, sliding speed 5 mm/s (c) and 0.5 m/s (d), for the pure PAG 46 is showed. It is worth noting that only at 25°C and sliding speed 5 mm/s, i.e. graph (a), an increment of the friction coefficient, on average of 8%, in the oil which has absorbed moisture (case B) has been observed. Instead, in all others tests carried out on pure PAG 46 have highlighted reduction of the friction coefficient, on average from 8 to 25%.



Fig. 8. Steady-state tests at 25°C (a)-(b) and 80°C (c)-(d) – oil sample 1: case A (before water absorption), case B (after water absorption).

In Figure 9, the friction coefficient vs. time both at 25°C, sliding speed 5 mm/s (a) and 0.5 m/s (b) and 80°C, sliding speed 5 mm/s (c) and 0.5 m/s (d), for the PAG46 with 2.0w.t.% IL and GO at 0.1w.t.% is shown. For this oil sample the results are conflicting. In fact, at lower temperature both in boundary lubrication regime and mixed lubrication regime the water absorption results in higher friction coefficient, + 35% and +10%, respectively. On the other hand, at 80°C in both lubrication regimes lower friction coefficient has been observed in the oil sample with water content. In particular, in boundary regime the average reduction is about 10% whereas in mixed regime it attains 40%.





Fig. 9. Steady-state tests at 25°C (a)-(b) and 80°C (c)-(d) – oil sample 2: case A (before water absorption), case B (after water absorption).

Finally, in Figure 10 the friction coefficient vs. time both at 25°C, sliding speed 5 mm/s (a) and 0.5 m/s (b) and 80°C, sliding speed 5 mm/s (c) and 0.5 m/s (d), for the PAG46 with 2.0w.t.% IL and GO at 0.5w.t.% is showed. For this oil sample the differences between the two cases, A and B, are more evident in boundary lubrication regime. Conversely, in mixed lubrication regime only small differences could be noticed.



Fig. 10. Steady-state tests at 25°C (a)-(b) and 80°C (c)-(d) – oil sample 3: case A (before water absorption), case B (after water absorption).

3.4 Wear parameter in steady-state tests

As explained before, at the end of 1-hour steady state tests, the worn surface of the steel ball has been measured with Sensofar PLu-neox 3D optical profiler to acquire the wear scar diameter (WSD). In Figure 11 typical 3D surface image is reported.



Fig. 11. Steel ball specimen and wear scar on its top side.

Smaller wear scar diameters have been observed at the end of steady tests carried out with lubricant samples whit water content, table 3, both in boundary regime, sliding speed of 5 10^{-3} m/s and mixed regime, sliding speed of 5 10^{-1} m/s. These results confirms the analysis in [32], whose Authors explain that in boundary lubrication condition the presence of air and water in polar lubricants promote surface chemical reactions with ensuing friction and wear reduction.

SAMPLE	v [m/s]	WSD at 25°C [µm]	WSD At 80°C [µm]
1 A	5 10 ⁻³	340	290
1 B		270	280
1 A	5 10 ⁻¹	590	470
1 B		300	280
2 A	5 10 ⁻³	320	470
2 B		270	330
2 A	5 10 ⁻¹	630	450
2 B		310	320
3 A	5 10 ⁻³	350	500
3 B		276	285
3 A	5 10⁻¹	650	530
3 B		400	450

	Wear	Scar	Diameter	(MSD)
IADLE J.	vveai	Scar	Diameter	(000)

4. Discussion

Previous studies about the reduction of frictional losses obtained by nanoparticles as friction modifiers additive finds several physical explanations: rolling-sliding motions coupled to flexibility behaviour, nanoadditive exfoliation and material transfer to metal surface to form the so called "tribofilm" or "tribolayer", electronic effects in tribological interfaces, surface roughness reduction or "mending", sliding on lower shear stress layers with reduced direct contact between metal surfaces [28,33,34]. The results of the present research confirm the sensible reduction of friction coefficient in boundary and mixed lubrication regime in the region of high contact pressure provided by the dispersion of GO. However, low stability of GO dispersion was observed at the end of tests at 80°C; i.e. settlement tendency due to low viscosity of the base oil. Hence, the concentration of GO at inlet side of lubricated wedge is actually lower than the expected theoretical data. Unfortunately, the inclusion of ionic liquid in the lubricant formulations under test did not provide an improvement of GO dispersion stability, as possible side-effect benefit.

ISSN 1453 – 7303 "HIDRAULICA" (No. 2/2016) Magazine of Hydraulics, Pneumatics, Tribology, Ecology, Sensorics, Mechatronics

The anti-wear action performed by the tested formulations was generally weak. Apart from couple of outliers, the selected wear parameter generally fell for both GO/ILs based formulations in the uncertainty range of the PAG 46 data with weak tendency to increase with the additives loading, regardless their nature, solid or liquid one. On the other hand, the water absorption results in clear improvement of the anti-wear action, as confirmed from wear parameter measurements. The water content enables friction coefficient reduction in the whole range of sliding speed of the tests, as displayed by the Stribeck graphs. Nevertheless, steady state tests provided less straight results with detrimental role of adsorbed water in some test at 25°C. The latter point needs deepening in future researches.

5. Conclusions

The tribological performance of graphene oxide (GO) and ionic liquids (ILs) as friction modifiers in polyalkylene glycol (PAG) base oil have been measured in the region of high contact pressure, 1.50 GPa, in boundary lubrication regime and mixed regime as well. Lubricant samples with different concentration of ILs and GO have been tested by way of tribometer setups. The experiments were carried out through sweep-speed tests to achieve the Stribeck curves for each sample as well as in steady-state condition to capture the friction coefficient evolution resultant from tribopair surfaces modification. The results confirm the reduction of friction coefficient provided by GO dispersion, although certain settlement tendency of such solid additive appeared, especially at higher lubricant temperature. The inclusion of ionic liquid allows enhancing of frictional behaviour at higher temperature by compensating the reduced GO action in such operating conditions. About anti-wear properties the tested formulations before moisture exposure showed weak protection. On the other hand, experimental tests on the influence of water content in oil have highlighted improvements of the anti-wear action in the entire testing spectrum and reduction of the friction coefficient in many cases.

Forthcoming experimental analysis will focus on the stability improvement of the colloidal suspension through tailored dispersant agent as well as the role of water content at different temperature levels.

Acknowledgement

This research was partially funded by the program "Legge Regionale 28/03/2002 N. 5 - Regione Campania, Bando 2007"- Research project name: "Indagini sperimentali su accoppiamenti meccanici in presenza di lubrificanti innovativi additivati con nanoparticelle basso impatto ambientale/Experimental investigations on mechanical pairs with innovative lubricant based on environment-friendly nanoparticles additives".

References

- [1] A. S. Pensado, M. J. P. Comuñas, and J. Fernández, 'The Pressure–Viscosity Coefficient of Several Ionic Liquids', Tribol. Lett., vol. 31, no. 2, pp. 107–118, Aug. 2008.
- [2] W. Liu, C. Ye, Q. Gong, H. Wang, and P. Wang, 'Tribological performance of room-temperature ionic liquids as lubricant', Tribol. Lett., vol. 13, no. 2, pp. 81–85, 2002.
- [3] Q. Lu, H. Wang, C. Ye, W. Liu, and Q. Xue, 'Room temperature ionic liquid 1-ethyl-3hexylimidazolium- bis(trifluoromethylsulfonyl)-imide as lubricant for steel-steel contact', Tribol. Int., vol. 37, no. 7, pp. 547–552, 2004.
- [4] C. Ye, W. Liu, Y. Chen, and L. Yu, 'Room-temperature ionic liquids novel versatile lubricant', Chem. Commun., no. 21, pp. 2244–2245, Oct. 2001.
- [5] A.-E. Jiménez and M.-D. Bermúdez, 'lonic liquids as lubricants for steel–aluminum contacts at low and elevated temperatures', Tribol. Lett., vol. 26, no. 1, pp. 53–60, Feb. 2007.
- [6] A. E. Jiménez, M. D. Bermúdez, F. J. Carrión, and G. Martínez-Nicolás, 'Room temperature ionic liquids as lubricant additives in steel–aluminium contacts: Influence of sliding velocity, normal load and temperature', Wear, vol. 261, no. 3–4, pp. 347–359, Aug. 2006.
- [7] H. Kamimura, T. Kubo, I. Minami, and S. Mori, 'Effect and mechanism of additives for ionic liquids as new lubricants', Tribol. Int., vol. 40, no. 4, pp. 620–625, 2007.
- [8] J. N. A. Canongia Lopes and A. A. H. Pádua, 'Nanostructural Organization in Ionic Liquids', J. Phys. Chem. B, vol. 110, no. 7, pp. 3330–3335, Feb. 2006.
- [9] J. Qu, J. J. Truhan, S. Dai, H. Luo, and P. J. Blau, 'Ionic liquids with ammonium cations as lubricants

or additives', Tribol. Lett., vol. 22, no. 3, pp. 207-214, 2006.

- [10] I. Minami, N. Watanabe, H. Nanao, S. Mori, K. Fukumoto, and H. Ohno, 'Improvement in the tribological properties of imidazolium-derived ionic liquids by additive technology', J. Synth. Lubr., vol. 25, no. 2, pp. 45–55, Apr. 2008.
- [11] M. Uerdingen, C. Treber, M. Balser, G. Schmitt, and C. Werner, 'Corrosion behaviour of ionic liquids', Green Chem., vol. 7, no. 5, p. 321, 2005.
- [12] H. Wang, Q. Lu, C. Ye, W. Liu, and Z. Cui, 'Friction and wear behaviors of ionic liquid of alkylimidazolium hexafluorophosphates as lubricants for steel/steel contact', Wear, vol. 256, no. 1–2, pp. 44–48, Jan. 2004.
- [13] L. J. Weng, X. Q. Liu, Y. M. Liang, and Q. J. Xue, 'Effect of tetraalkylphosphonium based ionic liquids as lubricants on the tribological performance of steel-on-steel system', Tribol. Lett., vol. 26, no. 1, pp. 11–17, 2007.
- [14] O. Y. Fajardo, F. Bresme, A. A. Kornyshev, and M. Urbakh, 'Electrotunable lubricity with ionic liquid nanoscale films.', Sci. Rep., vol. 5, p. 7698, 2015.
- [15] O. Y. Fajardo, F. Bresme, A. A. Kornyshev, and M. Urbakh, 'Electrotunable Friction with Ionic Liquid Lubricants: How Important Is the Molecular Structure of the Ions?', J. Phys. Chem. Lett., vol. 6, no. 20, pp. 3998–4004, 2015.
- [16] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, 'C60: Buckminsterfullerene', Nature, vol. 318, no. 6042, pp. 162–163, Nov. 1985.
- [17] K. Lee, Y. Hwang, S. Cheong, L. Kwon, S. Kim, and J. Lee, 'Performance evaluation of nanolubricants of fullerene nanoparticles in refrigeration mineral oil', Curr. Appl. Phys., vol. 9, no. 2 SUPPL., pp. e128–e131, 2009.
- [18] V. Chauveau, D. Mazuyer, F. Dassenoy, and J. Cayer-Barrioz, 'In Situ Film-Forming and Friction-Reduction Mechanisms for Carbon-Nanotube Dispersions in Lubrication', Tribol. Lett., vol. 47, no. 3, pp. 467–480, Sep. 2012.
- [19] L. Guadagno, M. Sarno, U. Vietri, M. Raimondo, C. Cirillo, and P. Ciambelli 'Graphene-based structural adhesive to enhance adhesion performance', RSC Adv., vol. 5, 27874-27886, 2015.
- [20] H. D. Huang, J. P. Tu, L. P. Gan, and C. Z. Li, 'An investigation on tribological properties of graphite nanosheets as oil additive', Wear, vol. 261, no. 2, pp. 140–144, Jul. 2006.
- [21] J. Lin, L. Wang, and G. Chen, 'Modification of Graphene Platelets and their Tribological Properties as Lubricant Additive', Tribol. Lett., vol. 41, no. 1, pp. 209–215, Jan. 2011.
- [22] Y. Kawaguchi, M. Kaneko, and M. Takagi, 'The Performance of End Capped PAG as Refrigeration Oil for HFC134a', in International Compressor Engineering Conference, 1998, pp. 267–273.
- [23] M. Woydt, I.-S. Rhee, and S. W. Dean, 'Polyalkylene Glycols as Next Generation Engine Oils', J. ASTM Int., vol. 8, no. 6, p. 103368, 2011.
- [24] J. Thoen, D. Zweifel, and M. Woydt, 'Potential for polyalkylene glycols in automotive engine oil applications', in Engine oil circulation system of internal combustion engines, 2009.
- [25] P. N. Ananthanarayanan, Refrigeration and Air Conditioning, Third. Tata McGraw-Hill Education, 2005.
- [26] J. William S. Hummers and R. E. Offeman, 'Preparation of Graphitic Oxide', J. Am. Chem. Soc, vol. 80, no. 1937, p. 1339, 1958.
- [27] -, 'The history of Lonza's graphite powders', Ind. Lubr. Tribol., vol. 27, no. 2, pp. 59–59, 1948.
- [28] M. Sarno, A. Senatore, C. Cirillo, V. Petrone, and P. Ciambelli, 'Oil Lubricant Tribological Behaviour Improvement Through Dispersion of Few Layer Graphene Oxide', J. Nanosci. Nanotechnol., vol. 14, no. 7, pp. 4960–4968, 2014.
- [29] MINILUBES Report Summary, available at URL: http://cordis.europa.eu/result/rcn/47466_en.html accessed on Sept. 17th, 2015.
- [30] V. Zin, F. Agresti, S. Barison, L. Colla, C. Pagura, and M. Fabrizio, 'Investigation on tribological properties of nanolubricants with carbon nano-horns as additives at different temperatures', in Proceedings of World Tribology Congress 2013, 2013, pp. 1–4.
- [31] M. Kalin, I. Velkavrh, and J. Vižintin, 'The Stribeck curve and lubrication design for non-fully wetted surfaces', Wear, vol. 267, no. 5–8, pp. 1232–1240, Jun. 2009.
- [32] W. H. Van Glabbeek, T. K. Sheiretov, and C. Cusano, 'The Effect of Dissolved Water on the Tribological Properties of Polyalkylene Glycol and Polyolester Oils', Report of ACRC Project 04 Compressor--Lubrication, Friction, and Wear, 1994.
- [33] L. Yadgarov, V. Petrone, R. Rosentsveig, Y. Feldman, R. Tenne, and A. Senatore, 'Tribological studies of rhenium doped fullerene-like MoS₂ nanoparticles in boundary, mixed and elastohydrodynamic lubrication conditions', Wear, vol. 297, no. 1–2, pp. 1103–1110, 2013.
- [34] C. Altavilla, M. Sarno, P. Ciambelli, A. Senatore, and V. Petrone, 'New "Chimie Douce" approach to the synthesis of hybrid nanosheets of MoS₂ on CNT and their anti-friction and anti-wear properties', Nanotechnology, vol. 24, no. 12, 2013.