

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

R. GONZÁLEZ^{1,4,*}, D. RAMOS², D. BLANCO², A. FERNÁNDEZ-GONZÁLEZ³, J. L. VIESCA^{2,4}, M. HADFIELD⁴, A. HERNÁNDEZ BATTEZ^{2,4}

¹ Department of Marine Science and Technology, University of Oviedo, Asturias 33203, Spain

² Department of Construction and Manufacturing Engineering, University of Oviedo, Asturias 33203, Spain

³ Department of Physical and Analytical Chemistry, University of Oviedo, Asturias 33006, Spain

⁴ Department of Design and Engineering, Bournemouth University, Poole BH12 5BB, UK

Received: 29 December 2017 / Revised: 07 May 2018 / Accepted: 14 July 2018

© The author(s) 2018. This article is published with open access at Springerlink.com

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-

* Corresponding author: R. GONZÁLEZ, E-mail: gonzalezruben@uniovi.es

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 ($\varnothing 6.0$ mm, $Ra \leq 0.05$ μm , 58–66 HRC) and AISI 52100 steel disks ($\varnothing 10$ mm, 3 mm thick, $Ra \leq 0.02$ 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.

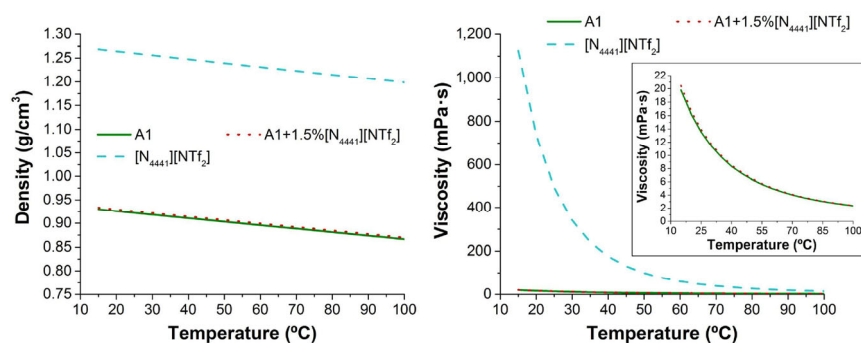


Fig. 1 Density and viscosity versus temperature for the lubricant samples.

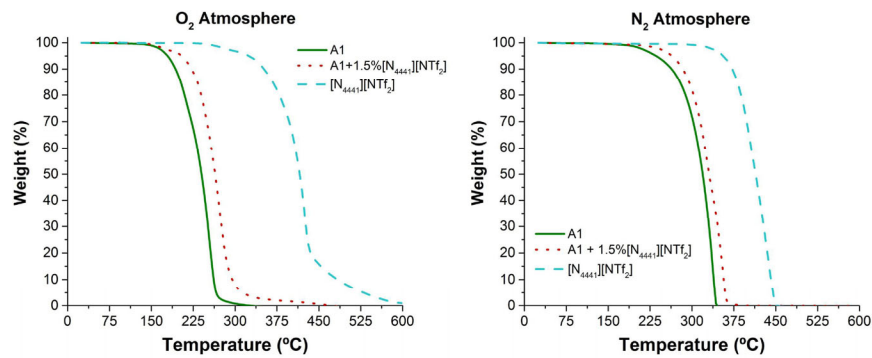


Fig. 2 Thermogravimetric characteristics of the lubricant samples under oxygen and nitrogen atmospheres.

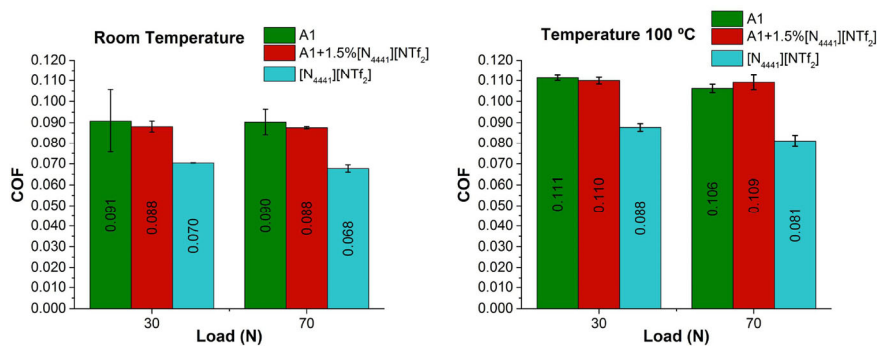


Fig. 3 Friction coefficient from tribological tests made at RT and 100 °C.

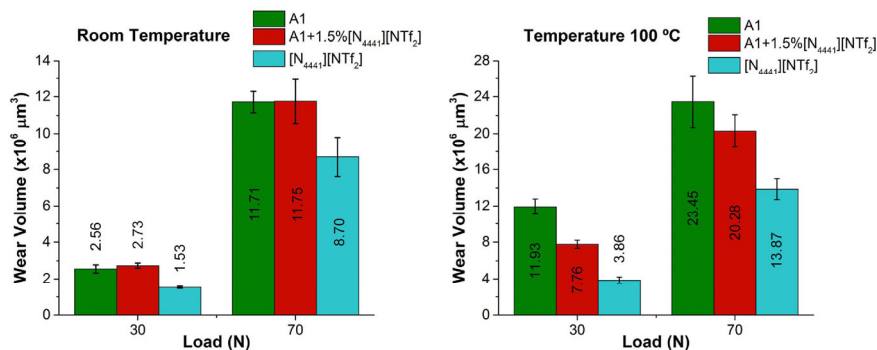


Fig. 4 Wear volume on the disk after tests made at RT and 100 °C.

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

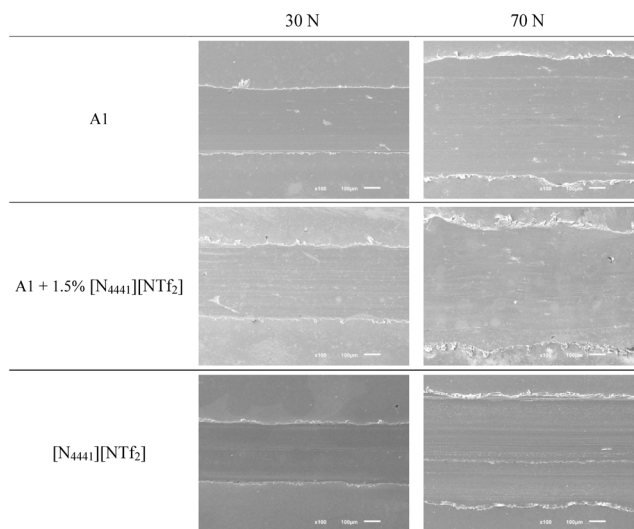


Fig. 5 SEM images from the wear scar of test made at room temperature.

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 O₂ 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 [NTf₂] 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.

Acknowledgments

The authors thank to the Foundation for the Promotion in Asturias of the Applied Scientific Research and Technology (FICYT) and the Ministry of Economy and Competitiveness (Spain) for supporting this work in the framework of the research projects Lubrication and Surface Technology (GRUPIN14-023) and STARLUBE (DPI2013-48348-C2-1-R). Rubén González made part of this work during a research stay at Bournemouth University (UK).

Open Access: The articles published in this journal are distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- [1] Ye C F, Liu W M, Chen Y X, Yu L G. Room-temperature ionic liquids: A novel versatile lubricant. *Chem Commun (Camb)* (21): 2244–2245 (2001)
- [2] Bermúdez M D, Jiménez A E, Sanes J, Carrión F J. Ionic liquids as advanced lubricant fluids. *Molecules* **14**(8): 2888–2908 (2009)
- [3] Minami I. Ionic liquids in tribology. *Molecules* **14**(6): 2286–2305 (2009)
- [4] Somers A E, Howlett P C, MacFarlane D R, Forsyth M. A review of ionic liquid lubricants. *Lubricants* **1**(1): 3–21 (2013)
- [5] Zhou Y, Qu J. Ionic liquids as lubricant additives: A review. *ACS Appl Mater Interfaces* **9**(4): 3209–3222 (2017)
- [6] Avilés M D, Saurín N, Sanes J, Carrión F J, Bermúdez M D. Ionanocarbon lubricants. The combination of ionic liquids and carbon nanophases in tribology. *Lubricants* **5**(2): 14 (2017)
- [7] Huang G W, Yu Q L, Ma Z F, Cai M R, Liu W M. Probing the lubricating mechanism of oil-soluble ionic liquids additives. *Tribol Int* **107**: 152–162 (2017)
- [8] Xiao H P. Ionic liquid lubricants: Basics and applications. *Tribol Trans* **60**(1): 20–30 (2017)
- [9] González R, Bartolomé M, Blanco D, Viesca J L, Fernández-González A, Hernández Battez A. Effectiveness of phosphonium cation-based ionic liquids as lubricant additive. *Tribol Int* **98**: 82–93 (2016)
- [10] Hernández Battez A, González R, Viesca J L, Fernández-González A, Hadfield M. Lubrication of PVD coatings with ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate. *Tribol Int* **58**: 71–78 (2013)
- [11] Viesca J L, García A, Hernández Battez A, González R, Monge R, Fernández-González A, Hadfield M. FAP⁻ anion ionic liquids used in the lubrication of a steel-steel contact. *Tribol Lett* **52**(3): 431–437 (2013)
- [12] Qu J, Luo H M, Chi M F, Ma C, Blau P J, Dai S, Viola M B. Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive. *Tribol Int* **71**: 88–97 (2014)
- [13] Monge R, González R, Hernández Battez A, Fernández-González A, Viesca J L, García A, Hadfield M. Ionic liquids as an additive in fully formulated wind turbine gearbox oils. *Wear* **328–329**: 50–63 (2015)
- [14] Fernandes C M C G, Hernández Battez A, González R, Monge R, Viesca J L, García A, Martins R C, Seabra J H O. Torque loss and wear of FZG gears lubricated with wind turbine gear oils using an ionic liquid as additive. *Tribol Int* **90**: 306–314 (2015)
- [15] Anand M, Hadfield M, Viesca J L, Thomas B, Hernández Battez A, Austen S. Ionic liquids as tribological performance improving additive for in-service and used fully-formulated diesel engine lubricants. *Wear* **334–335**: 67–74 (2015)
- [16] Pejaković V, Tomastik C, Kalin M. Influence of concentration and anion alkyl chain length on tribological properties of imidazolium sulfate ionic liquids as additives to glycerol in steel–steel contact lubrication. *Tribol Int* **97**: 234–243 (2016)
- [17] Zhu L L, Zhao Q, Wu X H, Zhao G Q, Wang X B. A novel phosphate ionic liquid plays dual role in synthetic ester oil: From synthetic catalyst to anti-wear additive. *Tribol Int* **97**: 192–199 (2016)
- [18] Otero I, López E R, Reichelt M, Villanueva M, Salgado J, Fernández J. Ionic liquids based on phosphonium cations as neat lubricants or lubricant additives for a steel/steel contact. *ACS Appl Mater Interfaces* **6**(15): 13115–13128 (2014)
- [19] Khemchandani B, Somers A, Howlett P, Jaiswal A K, Sayanna E, Forsyth M. A biocompatible ionic liquid as an antiwear additive for biodegradable lubricants. *Tribol Int* **77**: 171–177 (2014)
- [20] Fernández Rico J E, Hernández Battez A, García Cuervo D. Wear prevention characteristics of binary oil mixtures. *Wear* **253**(7–8): 827–831 (2002)

- [21] Cambiella A, Benito J M, Pazos C, Coca J, Hernández A, Fernández J E. Formulation of emulsifiable cutting fluids and extreme pressure behaviour. *J Mater Process Technol* **184**(1–3): 139–145 (2007)
- [22] Fernández-González A, Mallada M T, Viesca J L, González R, Badía R, Hernández-Battez A. Corrosion activity and solubility in polar oils of three bis(trifluoromethylsulfonyl) imide / bis(trifluoromethylsulfonyl) amide ([NTF₂]) anion-based ionic liquids. *J Ind Eng Chem* **56**: 292–298 (2017)
- [23] Mangolini F, Rossi A, Spencer N D. Influence of metallic and oxidized iron/steel on the reactivity of triphenyl phosphorothionate in oil solution. *Tribol Int* **44**(6): 670–683 (2011)
- [24] Minami I, Kita M, Kubo T, Nanao H, Mori S. The tribological properties of ionic liquids composed of trifluorotris(pentafluoroethyl) phosphate as a hydrophobic anion. *Tribol Lett* **30**(3): 215–223 (2008)
- [25] Mangolini F, Rossi A, Spencer N D. Tribochemistry of triphenyl phosphorothionate (TPPT) by in situ attenuated total reflection (ATR/FT-IR) tribometry. *J Phys Chem C* **116**(9): 5614–5627 (2012)
- [26] Wagner C D, Zlatko D A, Raymond R H. Use of the oxygen KLL Auger lines in identification of surface chemical states by electron spectroscopy for chemical analysis. *Anal Chem* **52**(9): 1445–1451 (1980)
- [27] NIST XPS database. <https://srdata.nist.gov/xps/>, 2018.



Rubén GONZÁLEZ. He received his B.S. degree in marine engineering in 2000 and obtained his PhD degree in 2007 from the University of Oviedo (Spain). From 2006 to 2010 he taught and researched at the Department of Mechanical and Civil Engineering of the University of Oviedo (Spain). Currently he is

associate professor at the Department of Nautical Science and Technology of the University of Oviedo (Spain). He is also senior visiting research fellow in Bournemouth University (United Kingdom) from 2009. His research areas cover coatings (thermal spray and laser cladding), and the use of ionic liquids and nanoparticles in lubricants.



Diego RAMOS. He received his bachelor degree in mechanical engineering in 2009 and his M.S. degree in industrial engineering in 2013 from University of León

(Spain). After then, in 2015, he started to work in the tribology field at University of Oviedo. He has been pursuing the PhD degree from 2016 to now at the same University, focused on the use of ionic liquids in the formulation of lubricants.



David BLANCO. He received his bachelor degree in chemical engineering in 2006 from University of Oviedo. After then, he started to work in the tribology field, obtaining his

PhD degree in tribology in 2011 from the same university. His main research objectives in recent years have been focused on the use of ionic liquids in the formulation of lubricants.



Alfonso FERNÁNDEZ-GONZÁLEZ. He received his bachelor degree in chemistry in 1997 and his master of science degree in chemistry in 1999, both in the Universidad de Oviedo. He got his PhD degree in chemistry in the Physical and

Analytical Chemistry Department of the same university. After that, he was post-doctoral researcher in Dresden (Germany), Madrid (Spain) and Kiev (Ukraine), and he is currently assistant lecturer in the Universidad de Oviedo. His research lines include XPS, FTIR spectroscopies and sensor development.



Jose L. VIESCA. He received his M.S. and PhD degrees in mining engineering from University of Vigo and University of Oviedo, Spain, in 2000 and 2007, respectively. Subsequently, he also obtained a degree in mechanical engineering

from the University of Salamanca and an MBA from the University of Oviedo. He joined the University of Oviedo from 2004 and his current position is an associate professor. He has been Director of Energy and Innovation of the state public company HUNOSA (Spain). His research interests include nanoparticles and ionic liquids as lubricant additives.



Mark HADFIELD. He is a professor within the Department of Design and Engineering with research theme responsibility of "Tribology and Design". He has been a member of staff at Bournemouth University since 1997 and a professor since 2001. Before this he was a lecturer at Brunel University from 1993 within the Mechanical Engineering Department. He has industrial experience

as a senior project engineer with AE Wellworthy Ltd (FEA). Mark has also worked at the Royal Aircraft Establishment in Farnborough working on FEA optimisation programs and at Marchant Filer and Dixon Consultant Design Engineers in Romsey. He completed the BEng degree in mechanical engineering at Brunel University in 1988. Mark completed a Science and Engineering Research Council PhD studentship also at Brunel University from 1990 to 1993.



Antolin HERNÁNDEZ BATTEZ. He received his B.S. degree in mechanical engineering from the University of Cienfuegos (Cuba) in 1996 and the Ph.D. degree from the University of Oviedo (Spain)

in 2002. He joined the University of Oviedo as a lecturer in 2001 and his current position is an associate professor. Since 2009 he is also a visiting research fellow at Bournemouth University (UK). His research areas cover the use of coatings, nanomaterials and ionic liquids in lubrication.