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Reduction of the Coefficient of Friction of Steel-Steel Tribological Contacts by Novel Graphene-Deep Eutectic Solvents (DESs) Lubricants

Ignacio Garcia *, Silvia Guerra, Juan de Damborenea and Ana Conde

Surface Engineering, Corrosion and Durability Department, National Centre for Metallurgical Research (CENIM-CSIC), Avda. Gregorio del Amo 8, E28040 Madrid, Spain; silvia.guerra@csic.es (S.G.); jdambo@cenim.csic.es (J.d.D.); a.conde@cenim.csic.es (A.C.)

* Correspondence: igarcia@cenim.csic.es

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Abstract: Deep eutectic ionic liquids (DES) possess similar properties to conventional ionic liquids (ILs). However, ILs cannot be considered as environmentally friendly compounds due to both its processing and synthesis, which could have significant polluting effects. On the contrary, deep eutectic solvents (DESs) can be biodegradable, non-toxic, and have a lower price than most ILs, making them potentially useful in a wide variety of advanced technological applications, such as tribology. On the other hand, graphene has recently been proposed as an extremely promising lubricant due to its combination of mechanical properties and chemical stability as well as its "green" character. In the present paper, graphene flakes (≈250 nm) have been used as an additive to DES composed of choline chloride (ChCl)-urea, ChCl-ethylene glycol, and ChCl-malic acid. According to the results, the addition of 1 wt% graphene reduces friction coefficient (COF) and, notably, prevents adhesive wear, reducing wear rate on steel-steel sliding contacts.

Keywords: carbon nanomaterials; graphene; friction and wear mechanisms; steel; deep eutectic solvents; ionic liquids

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1. Introduction

In 2001, the potential use of ionic liquids (ILs) as alternative high-performance synthetic lubricants was first reported [1]. ILs are salts with melting points lower than 100 °C that possess interesting features for lubricants, such as negligible volatility, non-flammability and high thermal stability [2]. Several reviews have described the friction coefficient (COF) and wear properties on various tribological pairs, including steel, aluminum, copper, titanium, Si, SiO_2, SiAlN and Si_3N_4 using imidazolium, phosphonium, pyridinium, and ammonium-based ILs combined with anions such as BF^{4-}, PF^{6-}, CF_3SO^{3-}, $(CF_3SO_2)_2N^-$, and $(C_2F_5)_3PF^{3-}$ [1,3–6]. ILs are also compatible with nanophase carbon additives, offering improved tribological performances that can be attributed to the synergy established between the ionic liquid fluid phase and the solid nanophase tribolayers [7]. Although ILs were initially considered as "green" compounds due to their negligible vapor pressure and inability to produce air pollution, their toxicity to aquatic organisms and their low degradability led to their removal from the category of green compounds [8]. Then, research focused new environmentally friendly ionic liquids [9]. A new class of ILs called deep eutectic ionic liquids (DES) were also proposed in 2001 by Abbot [10]. They are usually obtained by complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD) [11]. DES possess similar properties to conventional ILs, but a much lower toxicity and environmental impact [12–15]. A first study using choline chloride (ChCl)-based DES as lubricant was performed by Abbott et al. [16] for steel-on-steel and, more recently, for other metals and even carbon fiber PTFE composites [17,18]. These studies revealed that ChCl ILs provide lower COF than ordinary oil lubricants.

On the other hand, graphene is a prospective solid lubricant due to its ability to form a tribofilm that prevents the direct contact of the asperities of the surfaces in relative motion and, consequently, reducing friction and wear rate [19–21]. Literature has also reported the positive influence on steel, epoxy and ceramic tribo-contacts of the addition of graphene or graphene oxide, either mono or multilayer, into ionic liquid lubricants, i.e., different alkyl imidazolium ILs with trifluoromethylsulfonyl or fluoroborate anions [22–26].

In the present paper, mixtures of low toxicity DES with graphene additions are studied as lubricants for steel-steel sliding contacts. The tribological behavior was evaluated using the block-on-ring wear test configuration.

2. Materials and Methods

DES were prepared by the mixing of ChCl and the corresponding hydrogen bond donor at 80 °C under continuous stirring, until a homogeneous liquid was obtained. The nominal molar ratio of the mixture was 1:2 for ChCl-urea and ChCl-ethylene glycol (ChCl-EG) and 1:1 for ChCl-malic acid. Analytical-grade reactive choline chloride (>99%), ethylene glycol (99.8%) and malic acid (>99%) from Aldrich were used as received. Values of physical properties including viscosity, conductivity, density and surface tension have been taken from similar works reported previously in the literature. Table 1 shows the physical properties of the DES used in present study [11,27–29]. As can be seen, viscosity of ChCl-urea > EG > ChCl-malic, which can be attributed to the formation of stronger hydrogen bonds in deep eutectic solvents (DESs) with urea-based compounds.

Table 1. Physical properties of DESs.

Halide Salt	mp/°C	Hydrogen Bond Donor (HBD)	mp/°C	Salt:HBD (Molar Ratio)	Viscosity (cP)	Density (g/cm^3)	Conductivity (mS/cm^{-1})	DES T_f °C
ChCl	303	Urea	134	1:2	630–750	1.16	0.75	12
ChCl	303	Ethylene glycol	−12.9	1:2	36	1.06–1.10	7.61	-
ChCl	303	Malic acid	130	1:1	446	1.23	0.1–10	−56

Commercial synthetic oil based on poly-alpha-olefine, Synfluid PAO6 (Chevron Phillips Chemical Company LP, The Woodlands, TX, USA), was used as reference. The graphene flakes of nanosheets (Avanzare Innovacion Tecnologica S.L., Navarrete (La Rioja), Spain) with an average size of 250 nm were used. A detailed characterization of these nanosheets can be found elsewhere [21].

DES and PAO6 were modified by adding 1 wt% of multilayer graphene and subsequently sonicated for 1 h until a homogenous dispersion was formed. Mixtures were used immediately after sonication to prevent phase separation, mainly for the PAO6 oil.

Wear tests were conducted in a CETR-UMT-2 microtribometer (Bruker Nano Surfaces, San Jose, CA, USA) using a block-on-ring configuration according to the ASTM G77-05 standard test method. The wear-mass loss of the rings used as counterbody was estimated by weight using a precision scale of ± 0.1 mg. Tests were performed in ambient air at 22 °C and 50% relative humidity. The load applied was 120 N and the rotation speed of the ring was fixed to 480 rpm. The sliding distance for the tests with DES-based lubricants was up to 12,633 m to assess their stability. The block, the specimen, was an oil-hardening low-alloyed cold work steel (H-60 SAE O1 Steel, Rc 58-63, with dimensions 6.35 mm × 10.16 mm × 15.75 mm) commonly used in molds and tools manufacturing. The ring was alloyed steel S-10 SAE 4620 Steel (Rc 58-63) with dimension Ø 34.98 mm × 8.74 mm. Blocks and rings were provided by Falex (Sugar Grove, IL, USA). The mechanical properties of both steels are similar, hence, the effect of the new lubricant can be clearly appreciated. Figure 1 shows the tribometer, specimens used, and a sketch of the block-on-ring test geometry.

Figure 1. Tribometer and specimens used for the wear tests.

A small amount of lubricant to cover the surface was applied on the ring just before the test to ensure a boundary lubrication regime. No more lubricant was added during the tests. After the wear tests, blocks were cleaned with propanol and DI water and dried with warm air before inspection and measurement.

The width of the wear scars was measured by optical microscopy (Olympus GX 51 (Olympus Iberia S.A.U., L'Hospitalet de Llobregat, Spain) while surface characterization was carried out using a scanning electron microscope with field emission gun (FEG-SEM), Hitachi S 4800 J (Hitachi Ltd., Tokyo, Japan), also equipped with energy-dispersive X-ray spectroscopy (EDX) (Oxford Instruments NanoAnalysis, High Wycombe, UK).

3. Results and Discussion

Figure 2 shows the images of the wear scars of the blocks, taken by the optical microscope after testing with the different lubricants. Figure 2a–d corresponds to PAO6 and DES lubricants without graphene addition, and Figure 2e–h to such lubricants with graphene. Each lubricant presents a different behavior according to the size and morphology of the wear scar and the surrounding block surface, so the analysis of the wear tracks reveals that the wear mechanisms depend on the kind of lubricant used.

Figure 2a shows the scar formed after the wear test, lubricated with PAO6 oil, with just a smooth appearance. Figure 2b shows the scar of the block after being tested on ChCl-urea. It can be seen that the wear track is wider and deeper, quite homogeneous with some accumulation of worn material at the left side. The rest of the block surface appears quite clean, with no apparent defects. Nevertheless, it is worthwhile to remark that all the tests carried out with the lubricants based on DES experienced twice the sliding distance of those lubricated with PAO6 oil. Figure 2c shows the view of the block tested with the mixture of ChCl-malic acid. In this case, the scar was too large to be fully observed in the image at these magnifications. It can be observed that the width of the scar is irregular, showing deep scratches characteristic of an abrasive wear mechanism. It can be clearly seen that the surface does not appear neat, as in the previous cases, but has some darker areas that may be either traces of lubricant or accumulated wear particles. Figure 2d shows the block after the test in the mixture of ChCl-EG. The wear scar is very uniform and neat and slightly narrower than in the case of ChCl-urea. In this case, the marks made by the ring are quite regular, and no traces of fluid are visible at the edges of the wear scar.

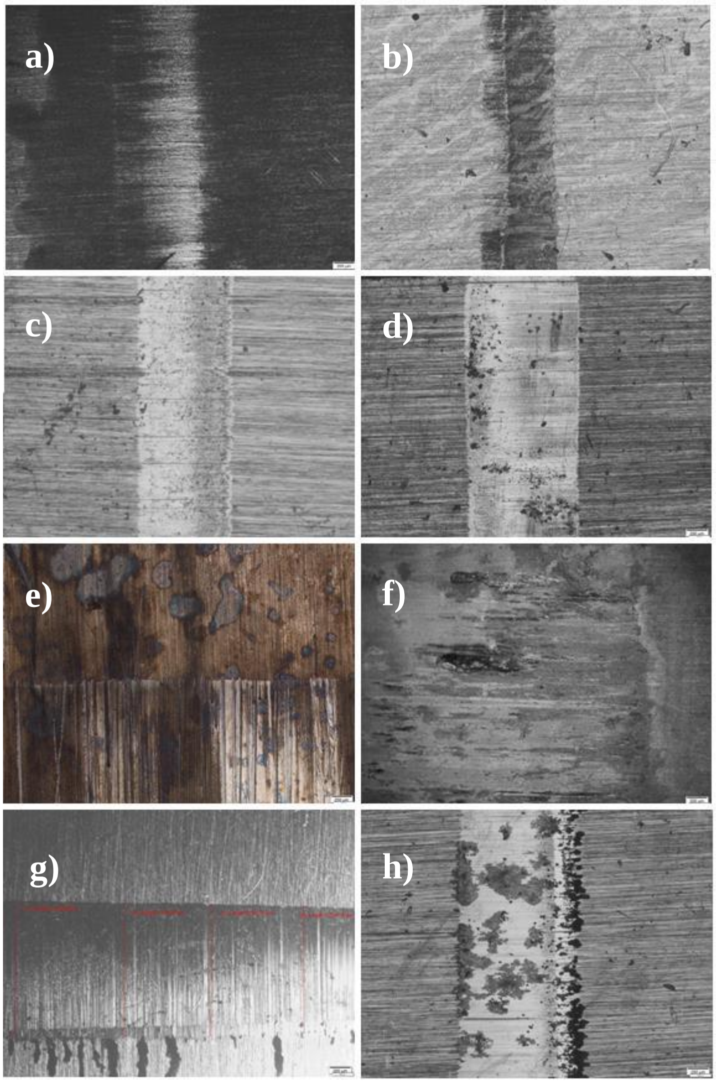

Figure 2. Optical microscope images (×500) of the wear scar in the blocks after tests with the different lubricating fluids: (**a**) PAO6, (**b**) PAO6 + graphene, (**c**) ChCl-urea, (**d**) ChCl-urea + graphene, (**e**) ChCl-malic ac., (**f**) ChCl-malic ac. + graphene, (**g**) ChCl-EG, (**h**) ChCl-EG + graphene.

Regarding the test performed with the graphene-added lubricants, Figure 2e shows the block tested with PAO6 oil with added graphene. In this case, the wear scar is smoother than that obtained after the test lubricated by PAO6, although slightly more irregular. In this case the volume worn appears to be lower. Figure 2f shows the scar corresponding to the test lubricated with ChCl-urea with graphene addition. As for the test performed with these DES without graphene, the scar is fairly well defined. However, some particles are observed at both sides. Figure 2g shows the scar corresponding to one of the blocks tested with ChCl- malic acid with added graphene. It can be observed that the scar is very rough and shows deep and irregular scratches. As in the non-graphene malic acid mixture, the surface of the block around the scar is severely damaged. Finally, Figure 2h shows the wear scar corresponding to the block tested with ChCl-EG with graphene. It can be seen that the scar is narrower than in Figure 2d, but it is also more regular. Traces of the lubricant used can be seen either inside the scar or at the edges of the scar.

A more in-depth examination performed by SEM shows remarkable differences in each case. For the conventional oil PAO6, Figure 3a, the surface of the wear scar produced in the block shows small voids containing lubricant residues. These small cavities are a consequence of the detachment of material due to either micro-bonding and subsequent breakage by the relative motion of the surfaces in contact or the nucleation and growth of micro-cracks in successive passes, i.e., pointing out to an adhesive wear mechanism.

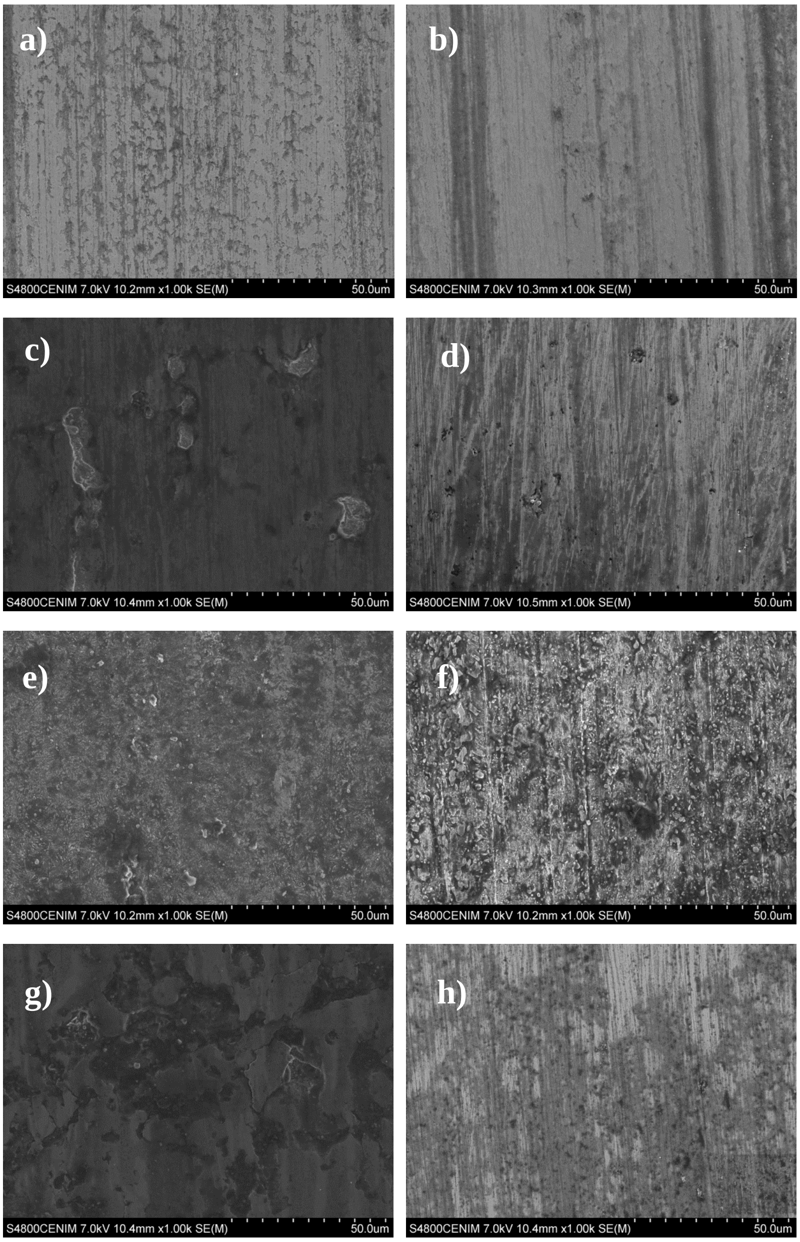

Figure 3. SEM images (×1000) of the wear scar in the blocks after tests with the different lubricating fluids: (**a**) PAO6, (**b**) PAO6 + graphene, (**c**) ChCl-urea, (**d**) ChCl-urea + graphene, (**e**) ChCl-malic ac., (**f**) ChCl-malic ac. + graphene, (**g**) ChCl-EG, (**h**) ChCl-EG + graphene.

The samples lubricated with ChCl-urea, Figure 3c and ChCl-EG, Figure 3g, showed a similar appearance to those lubricated with PAO6 despite larger cavities being observed. On the contrary, the appearance of the scar lubricated with ChCl-malic acid, Figure 3e, is very different. It shows a rough surface, the result of a severe corrosion attack. To the naked eye, dark brown corrosion products cover either the wear track or the entire block and the ring. This severe corrosion hinders the accurate measurement of the depth of the wear track because this IL has not been considered for the comparison in wear properties. Adverse results, the consequence of corrosion processes, have been previously reported when lubricating steels with some ionic liquids, so it is important to properly select the DES used as lubricant to avoid corrosion of the steel [30].

The addition of graphene apparently changed the mechanism from adhesion to abrasive wear in the case of PAO6 oil lubricated contacts. As can be seen in Figure 3b, the cavities almost disappear, and the wear scar appears less damaged. The image suggests a two-body abrasion mechanism, which is typical in metal-on-metal contact. This effect is even more pronounced for ChCl-urea, Figure 3d, and ChCl-EG, Figure 3h. These results suggest that the addition of graphene to these two lubricants prevents the formation and detachment of wear particles. This result is consistent with the lower COF values recorded for these lubricant systems, see Figure 4. Conversely, the addition of graphene into the ChCl-malic acid DES, Figure 3f, enhances the corrosion damage of the steel, making it even more difficult to estimate the wear rate.

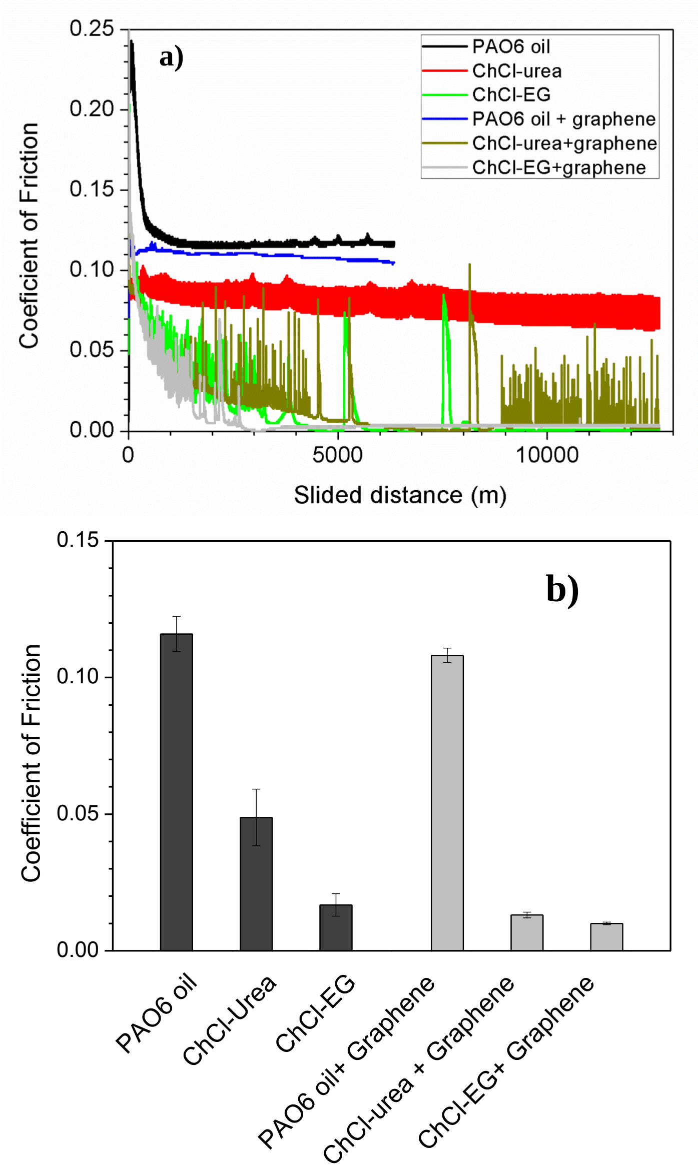

Figure 4. (**a**) Coefficient of friction recorder during the tests under different lubricating fluids, (**b**) Average coefficient of friction (three tests) for each lubricating fluid.

Figure 4a gathers the evolution of the COF corresponding to the reference oil PAO6 and DES, with and without graphene addition. The PAO6 oil shows an initial running-in period of about 800 m, where COF decreases from 0.25 to a stable value of 0.12. By adding 1 wt% graphene, the running-in stage notably reduces, and the COF ranges about 0.12 from the beginning. ChCl-EG without and with graphene addition and ChCl-urea + graphene show a longer running-in stage of about 4200 m, as well as scattered COF values that tend to zero. Conversely, the ChCl-urea shows a stable COF value of 0.01.

The mean COF value for each lubricant was estimated from the values recorded after the running-in period for the three tests performed, Figure 4b and Table 2. ChCl-EG reduces friction significantly in comparison with the conventional oil. Moreover, the addition of graphene leads to further decreases in COF for the ChCl-urea and ChCl-EG ILs. For the ChCl-EG, graphene addition virtually suppresses friction in steel-steel pairs, since COF is as low as 0.01. Conversely, the graphene addition to PAO6 hardly decreases friction, and the COF ranges about 0.11.

Table 2. Average and standard deviation (three tests) of the wear rates and coefficient of friction recorder during the tests under different lubricating fluids.

Lubricant	Wear Rate (10^{-8} mm^3/mN)	SD (10^{-8} mm^3/mN)	COF	SD
PAO6	1.5	0.2	0.116	0.006
ChCl-urea	4.9	1.1	0.05	0.01
ChCl-malic acid	1.3	0.9	0.024	0.004
ChCl-ethylene glycol	2.6	1.8	0.017	0.004
PAO6 + graphene	0.2	0.1	0.108	0.003
ChCl-urea + graphene	2.1	0.6	0.013	0.001
ChCl-malic acid + graphene	1.1	1.1	0.043	0.009
ChCl-ethylene glycol + graphene	2.2	0.2	0.010	0.005

The wear-mass loss of the rings was negligible, meanwhile, the steel blocks exhibit significant wear rate, Figure 5 and Table 2. Most of the DES-lubricated contacts show similar wear rate than PAO6 oil, except for ChCl-urea, which shows higher values. In general, graphene addition to the lubricants promotes further decrease in wear rate. However, in spite of the greater reduction in COF observed for ChCl-urea + graphene, the greater decrease in wear rate was described for PAO6 + graphene.

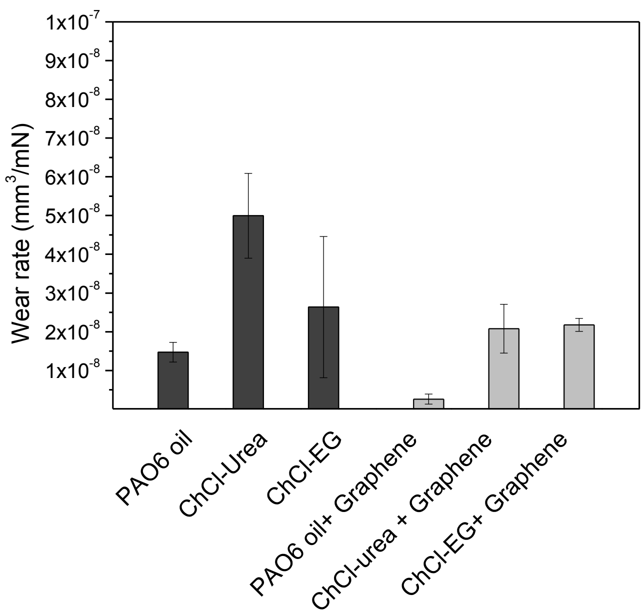

Figure 5. Average wear rate of the block (three tests) for each lubricating fluid.

It is likely that the significant improvements in friction found in this study are a consequence of the adsorption of the graphene sheets to the surfaces of the steel sliding parts behaving as protective coatings [31,32]. It is thought that the influence of graphene addition to lubricants on wear behavior is due to a greater trend to form a protective transfer film with increased mechanical strength and hardness, which limits the onset and growth of adhesive wear particles. The improved lubricating properties are, therefore, a consequence of the provision of graphene nanoplates between the friction surfaces, preventing the direct steel contact and providing low shear strength. Graphene, as a two-dimensional material, is easily sheared at the sliding contact interface and, therefore, provides low friction [19,33].

4. Conclusions

ChCl-EG + graphene combines good wear and friction properties, suggesting that these DES could be an attractive "green" lubricant alternative, since choline chloride and ethylene glycol are readily biodegradable and harmless to the environment.

The DES ChCl-urea and ChCl-EG show good lubrication properties with lower COF values and similar wear rates than PAO6 for steel-steel tribo-contact in a block-on-ring configuration. The addition of 1 wt% graphene reduces COF and notably prevents the adhesive wear mechanism, reducing thus the wear rate. ChCl-EG + graphene is a potential low-toxicity lubricant, with 10 times lower COF than an oil base + graphene.

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References

1. Ye, C.; Liu, W.; Chen, Y.; Yu, L. Room-temperature ionic liquids: A novel versatile lubricant. *Chem. Commun.* **2001**, 2244–2245. [CrossRef]
2. Armand, M.; Endres, F.; MacFarlane, D.R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629. [CrossRef]
3. Bermúdez, M.D.; Jiménez, A.E.; Sanes, J.; Carrión, F.J. Ionic liquids as advanced lubricant fluids. *Molecules* **2009**, *14*, 2888–2908. [CrossRef] [PubMed]
4. Minami, I. Ionic liquids in tribology. *Molecules* **2009**, *14*, 2286–2305. [CrossRef] [PubMed]
5. Palacio, M.; Bhushan, B. A Review of Ionic Liquids for Green Molecular Lubrication in Nanotechnology. *Tribol. Lett.* **2010**, *40*, 247–268. [CrossRef]
6. García, A.; González, R.; Hernández Battez, A.; Viesca, J.L.; Monge, R.; Fernández-González, A.; Hadfield, M. Ionic liquids as a neat lubricant applied to steel–steel contacts. *Tribol. Int.* **2014**, *72*, 42–50. [CrossRef]
7. 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* **2017**, *5*, 14. [CrossRef]
8. Cevasco, G.; Chiappe, C. Are ionic liquids a proper solution to current environmental challenges? *Green Chem.* **2014**, *16*, 2375–2385. [CrossRef]
9. Syahir, A.Z.; Zulkifli, N.W.M.; Masjuki, H.H.; Kalam, M.A.; Alabdulkarem, A.; Gulzar, M.; Khuong, L.S.; Harith, M.H. A review on bio-based lubricants and their applications. *J. Clean. Prod.* **2017**, *168*, 997–1016. [CrossRef]
10. Abbott, A.P.; Capper, G.; Davies, D.L.; Munro, H.L.; Rasheed, R.K.; Tambyrajah, V. Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. *Chem. Commun.* **2001**, 2010–2011. [CrossRef]
11. Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082. [CrossRef] [PubMed]
12. Haerens, K.; Matthijs, E.; Chmielarz, A.; Van der Bruggen, B. The use of ionic liquids based on choline chloride for metal deposition: A green alternative? *J. Environ. Manag.* **2009**, *90*, 3245–3252. [CrossRef] [PubMed]

13. Petkovic, M.; Ferguson, J.L.; Gunaratne, H.Q.N.; Ferreira, R.; Leitao, M.C.; Seddon, K.R.; Rebelo, L.P.N.; Pereira, C.S. Novel biocompatible cholinium-based ionic liquids-toxicity and biodegradability. *Green Chem.* **2010**, *12*, 643–649. [CrossRef]
14. Hayyan, M.; Hashim, M.A.; Hayyan, A.; Al-Saadi, M.A.; AlNashef, I.M.; Mirghani, M.E.S.; Saheed, O.K. Are deep eutectic solvents benign or toxic? *Chemosphere* **2013**, *90*, 2193–2195. [CrossRef] [PubMed]
15. Vanda, H.; Dai, Y.; Wilson, E.G.; Verpoorte, R.; Choi, Y.H. Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents. *Comptes Rendus Chimie* **2018**, *21*, 628–638. [CrossRef]
16. Lawes, S.D.A.; Hainsworth, S.V.; Blake, P.; Ryder, K.S.; Abbott, A.P. Lubrication of Steel/Steel Contacts by Choline Chloride Ionic Liquids. *Tribol. Lett.* **2010**, *37*, 103–110. [CrossRef]
17. Abbott, A.P.; Ahmed, E.I.; Harris, R.C.; Ryder, K.S. Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants. *Green Chem.* **2014**, *16*, 4156–4161. [CrossRef]
18. Shi, Y.J.; Mu, L.W.; Feng, X.; Lu, X.H. Friction and Wear Behavior of CF/PTFE Composites Lubricated by Choline Chloride Ionic Liquids. *Tribol. Lett.* **2013**, *49*, 413–420. [CrossRef]
19. Berman, D.; Erdemir, A.; Sumant, A.V. Graphene: A new emerging lubricant. *Mater. Today* **2014**, *17*, 31–42. [CrossRef]
20. Penkov, O.; Kim, H.J.; Kim, H.J.; Kim, D.E. Tribology of graphene: A review. *Int. J. Precis. Eng. Manuf.* **2014**, *15*, 577–585. [CrossRef]
21. Arenas, M.A.; Ahuir-Torres, J.I.; García, I.; Carvajal, H.; de Damborenea, J. Tribological behaviour of laser textured Ti6Al4V alloy coated with MoS 2 and graphene. *Tribol. Int.* **2018**, *128*, 240–247. [CrossRef]
22. Yu, B.; Liu, Z.; Zhou, F.; Liu, W.; Liang, Y. A novel lubricant additive based on carbon nanotubes for ionic liquids. *Mater. Lett.* **2008**, *62*, 2967–2969. [CrossRef]
23. Zhao, W.; Zeng, Z.; Peng, S.; Wu, X.; Xue, Q.; Chen, J. Fabrication and investigation the microtribological behaviors of ionic liquid-graphene composite films. *Tribol. Trans.* **2013**, *56*, 480–487. [CrossRef]
24. Fan, X.; Wang, L. High-performance lubricant additives based on modified graphene oxide by ionic liquids. *J. Colloid Interface Sci.* **2015**, *452*, 98–108. [CrossRef]
25. Pamies, R.; Avilés, M.D.; Arias-Pardilla, J.; Espinosa, T.; Carrión, F.J.; Sanes, J.; Bermúdez, M.D. Antiwear performance of ionic liquid+graphene dispersions with anomalous viscosity-temperature behavior. *Tribol. Int.* **2018**, *122*, 200–209. [CrossRef]
26. Avilés, M.D.; Carrión-Vilches, F.J.; Sanes, J.; Bermúdez, M.D. Diprotic Ammonium Succinate Ionic Liquid in Thin Film Aqueous Lubrication and in Graphene Nanolubricant. *Tribol. Lett.* **2019**, *67*, 26. [CrossRef]
27. Yadav, A.; Pandey, S. Densities and viscosities of (choline chloride + urea) deep eutectic solvent and its aqueous mixtures in the temperature range 293.15 K to 363.15 K. *J. Chem. Eng. Data* **2014**, *59*, 2221–2229. [CrossRef]
28. Troter, D.Z.; Todorović, Z.B.; Đokić-Stojanović, D.R.; Đorđević, B.S.; Todorović, V.M.; Konststinović, S.S.; Veljković, V.B. The physico-chemical and thermodynamic properties of the choline chloride-based deep eutectic solvents. *J. Serb. Chem. Soc.* **2017**, *82*. [CrossRef]
29. Mulia, K.; Putri, S.; Krisanti, E.; Nasruddin. Natural deep eutectic solvents (NADES) as green solvents for carbon dioxide capture. *AIP Conf. Proc.* **2017**, *1823*, 020022.
30. Kinoshita, H.; Kondo, M.; Nishina, Y.; Fujii, M. Anti-wear effect of graphene oxide in lubrication by fluorine-containing ionic liquid for steel. *Tribol. Online* **2015**, *10*, 91–95. [CrossRef]
31. Kinoshita, H.; Nishina, Y.; Alias, A.A.; Fujii, M. Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives. *Carbon* **2014**, *66*, 720–723. [CrossRef]
32. Guo, Y.B.; Zhang, S.W. The tribological properties of multi-layered graphene as additives of PAO2 oil in steel-steel contacts. *Lubricants* **2016**, *4*, 30. [CrossRef]
33. Berman, D.; Erdemir, A.; Sumant, A.V. Few layer graphene to reduce wear and friction on sliding steel surfaces. *Carbon* **2013**, *54*, 454–459. [CrossRef]