

COBEM2021-1930

EVALUATION OF TRIBOLOGICAL PERFORMANCE OF LIQUID IONIC AS ADDITIVE FOR VEGETABLE-BASED LUBRICANT

Márcio Segundo Medeiros

Hugo Vinicius Silva dos Santos

Universidade Federal do Rio Grande do Norte -Av. Sen. Salgado Filho, 3000 - S/N - Lagoa Nova, Natal - RN, 59064-720

marcio.segundo.091@ufrn.edu.br

vinicius.santos.017@ufrn.edu.br

Salete Martins Alves

Universidade Federal do Rio Grande do Norte -Av. Sen. Salgado Filho, 3000 - S/N - Lagoa Nova, Natal - RN, 59064-720

salete.alves@ufrn.br

Abstract. *Given the growing current demand for more efficient and sustainable lubricants, the study of ionic liquids (ILs) appears as an alternative with a great potential for success. ILs stand out concerning conventional lubricants, for forming tribofilm better, being less aggressive to the environment, and having great applicability. These are constituted of organic cations and anions, so they do not generate environmental impacts like current lubricants. ILs can be used both as a neat lubricant and as an additive, to increase lubrication efficiency in metal sliding pairs, decreasing friction and wear. In order to understand how ILs behave as lubricant and additives for vegetable-based lubricant, tribological characterizations were carried out in the high-frequency reciprocating rig (HFRR) tests of ionic liquid as a neat lubricant and as an additive in vegetable-based oil in different concentrations. These tests were carried out by a lubricated contact of a sliding pair ball-on-disk made of AISI 52100 steel, during the test the coefficient of friction (COF), the wear scar diameter (WSD), and the film percentage were measured, according to ASTM D6079-11. Based on the results it was possible to observe improvements in lubrication, with reduced coefficient of friction, reduced wear, and better formation of tribofilm, when used as an additive compared to the pure base oil. IL as a neat lubricant showed characteristics superior to pure oil and oil with additives.*

Keywords: *Ionic liquid, Lubricants, HFRR, Tribology, Vegetable oil, Boundary lubrication*

1. INTRODUCTION

Lubricants are widely used around the world in various applications, and their environmental impacts are a major concern, then it arises the need to develop more sustainable and less environmentally aggressive lubricants. A lot of studies have shown good results using vegetable-based lubricants, which are biodegradable, non-toxic and made from renewable raw materials, because of this properties, it has been shown to be a potential substitute for conventional mineral oils (Lathi & Mattiasson, 2007). However, their thermal, oxidation and hydrolytic stability is limited, an improvement of those characteristics of vegetable oils can be primarily achieved by a chemical modification, as epoxidation for example (Wagner et al., 2001).

Another way to improve the performance of lubricants is with the use of additives. There are many kinds of additives as anti-wear, antioxidants, dispersants (Alves et al., 2013). For tribological performance the main feature of an additive is the anti-wear and anti-friction abilities. Therefore, Ionic Liquids (ILs) have been used as lubricant additives in many studies and the results are promising. Sadanandan et al. (2020) used ILs as additives to a vegetable-based oil and had great results in friction coefficient reduction and anti-wear behavior at 0,5 to 3% concentrations of IL.

Ionic liquids are organic salts composed by the combination of cations and anions, they have been studied for a long time and in various applications since 1914 (Xiao, 2017). ILs have characteristics that make them very promising for use as lubricants and additives, these have low volatility, low melting point, good thermal stability, low vapour pressure, high combustible temperature and are very miscible with organic compounds (Amiril et al., 2017). Another important feature is that they are less aggressive to human health, due to its low volatility the ILs do not emit volatile organic compounds which can cause respiratory problems and skin diseases (Somers et al., 2013).

Based on similar research, it is possible to achieve good results with the addition of ILs in small concentrations. Qu et al., 2021 obtained good results using ILs as lubricant additives at concentrations of 0.3 to 1.5 wt%. Thus, in this paper was used two different ILs, 1-butyl-3-methylimidazolium octyl sulfate [BMIM OSU] chemical structure is in the "Figure 1" and 1-Ethyl-3-methylimidazolium chloride [EMIC] chemical structure is in the "Figure 2", as additives to a Soy bean epoxidized lubricant as base oil in concentrations of 0,5 wt%, 1 wt% and 1,5 wt%.

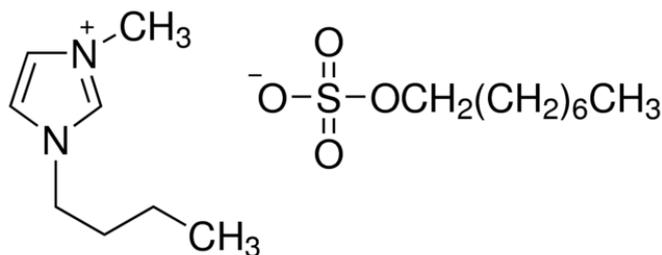


Figure 1. Chemical structure of [BMIM OSU]

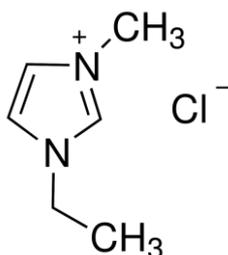


Figure 2. Chemical structure of [EMIC]

This paper aims to evaluate the effect of adding those ILs to the base oil on the tribological behavior of the lubricant. The anti-wear capacity and the tribofilm formation were studied using a High Frequency Reciprocating Ring (HFRR) equipment and optical microscopy.

2. EXPERIMENTAL METHODS

2.1 Blend preparation of ILs and oil

Soybean epoxidized lubricant was chosen as base oil, and blends of the ionic liquids were prepared by mixing a specified amount (weight) of ionic liquid to a known weight of base oil obtain the blends of 0.5%, 1%, and 1.5% (w/w%) concentrations. The mixture was stirred continuously at room temperature using a magnetic stirrer to get a homogeneous blend. Then the mixture was taken to an ultrasonically agitated bath for 15 minutes to ensure it was completely homogeneous. Thus, it was possible to conclude that [BMIM OSU] and [EMIC] are miscible in this base oil. Finally, tribo performance of the blends was carried out to evaluate their wear and friction properties.

2.2 Tribological performance test

The tests were made using high-frequency reciprocating rig (HFRR) equipment made by PCS Instruments. The HFRR system is shown in “Figure 3”, it is friction and wear tester, which consists of a ball-on-disk highly stressed contact under boundary lubrication.

A steel ball (570 – 720 HV) of 6.0 mm diameter reciprocates on a steel disk (190 – 210 HV) of 10 mm diameter and 3 mm thick; both were made of AISI 52100 steel, under fully submerged oil condition (Alves et al., 2013). All the tests were carried out using the same parameters, a normal load of 10N and 1 mm stroke length at a frequency of 20 Hz during 60 minutes, the lubricant temperature was kept constant at 50 °C.

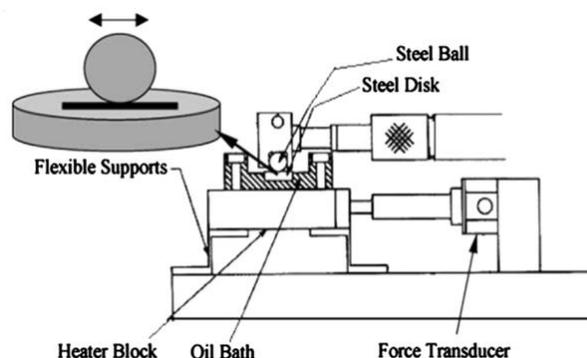


Figure 3. Schematic diagram of HFRR system.

The friction coefficient was measured by HFRR using a piezo-electric force transducer, and the tribofilm was measured by the ECR (Electrical Contact Resistance) technique. Based on those measurements, it was possible to analyze the effects of ILs addition into the base oil.

The mean friction coefficient was calculated from the arithmetic mean of all values measured during the test, the Table 3 shows this values.

Before all tests, both ball and disk and all the accessories involved in the trials were cleaned by an ultrasonically agitated bath of Isopropyl Alcohol to remove any contamination that could alter the results.

After each test, the wear scar on the ball was analyzed was optical microscopy, allowing to determine wear scar diameter and analyze wear aspects.

3. RESULTS AND DISCUSSION

The pure base oil and the IL blends were evaluated using HFRR. The results were compared to analyze the effect of adding ionic liquids to the lubricant and see if it improves the tribological performance reducing friction and wear.

3.1 Wear and friction behavior

The “Figure 4-a” shows the friction coefficient off [BMIM OSU] blends, and the “Figure 4-b” shows the friction Coefficient off [EMIC] blends in comparison to the pure base oil, thus is possible to observe the effect of the additives on the anti-friction behavior of the lubricant. “Table 1” exhibits the mean coefficient and standard deviation of that values in the tests.

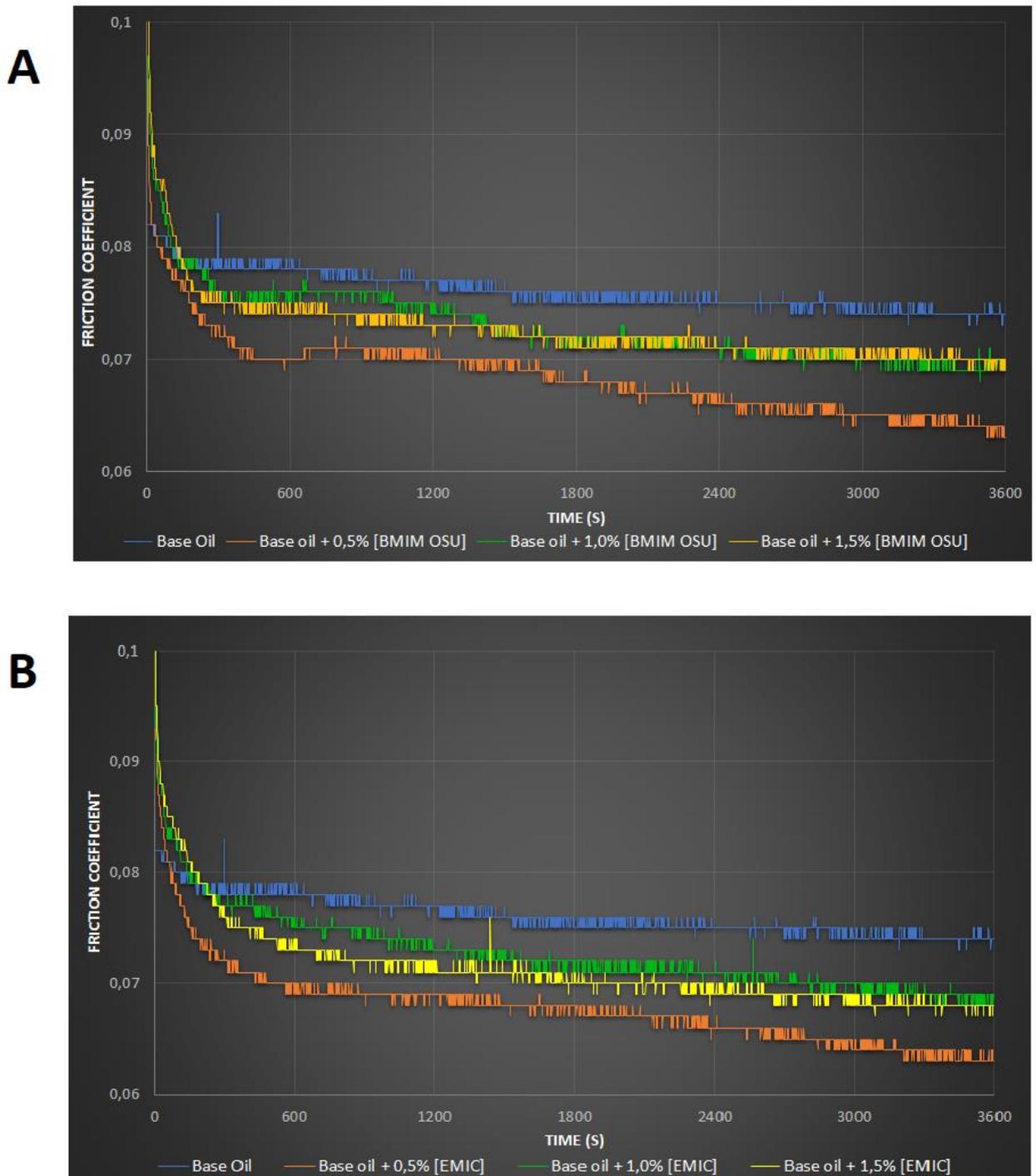


Figure 4. Friction coefficients as functions of time lubricated with pure oil base and with IL as additive in different concentrations: (a) 1-butyl-3-methylimidazolium octyl sulfate [BMIM OSU], (b) 1-Ethyl-3-methylimidazolium chloride [EMIC].

Table 1. Mean friction coefficient and standard deviation of each lubricant.

Lubricants	Friction Coefficient	Standard Deviation
Base Oil	0,076	0,001749958
Base Oil + 0,5% [BMIM OSU]	0,068	0,003606399
Base Oil + 1,0% [BMIM OSU]	0,073	0,003396891

Base Oil + 1,5% [BMIM OSU]	0,073	0,003293592
Base Oil + 0,5% [EMIC]	0,068	0,003777511
Base Oil + 1,0% [EMIC]	0,073	0,003643805
Base Oil + 1,5% [EMIC]	0,071	0,0038932

The pure base oil had the higher coefficient of all tests, as shown in “Figure 4” and “Table 1”; this indicates the capacity of ILs to reduce friction and increase the tribo-performance. Looking for concentrations and analyzing the friction behavior, it is possible to observe that in both liquids, the best was the 0,5 wt% because they showed the most significant friction reduction. That’s a very interesting result given the lower concentration had the best performance; thus, a considerable quantity of IL doesn't need to increase the lubricant's anti-friction capacity.

The results show an optimal IL concentration as an additive for the best tribological performance. However, after this limit, the additive causes adverse effects on lubrication. Li et al. (2021) saw the same relation of IL concentration and friction behavior on their paper, and they concluded that this occurs because the IL is not entirely dissolved in the base oil, generating an increase in the friction coefficient. Based on the results of HFRR tests and the research, it is possible to say that the concentration of 0,5 wt% probably the optimal one for the blends studied in this paper.

Thinking about practical application, this is a great result, since the lower concentration of additive greatly reduces lubricant production costs. Thus, the concentration of 0.5% is the best option considering the cost-benefit.

The “Figure 5” shows the film percentage off [BMIM OSU] blends and the “Figure 6” reveals the film percentage of [EMIC] blends in comparison to the pure base oil, thus is possible to observe the effect of the additives on the tribo-film formation behavior of the lubricant. Finally, “Table 2” exhibits the mean film percentage.

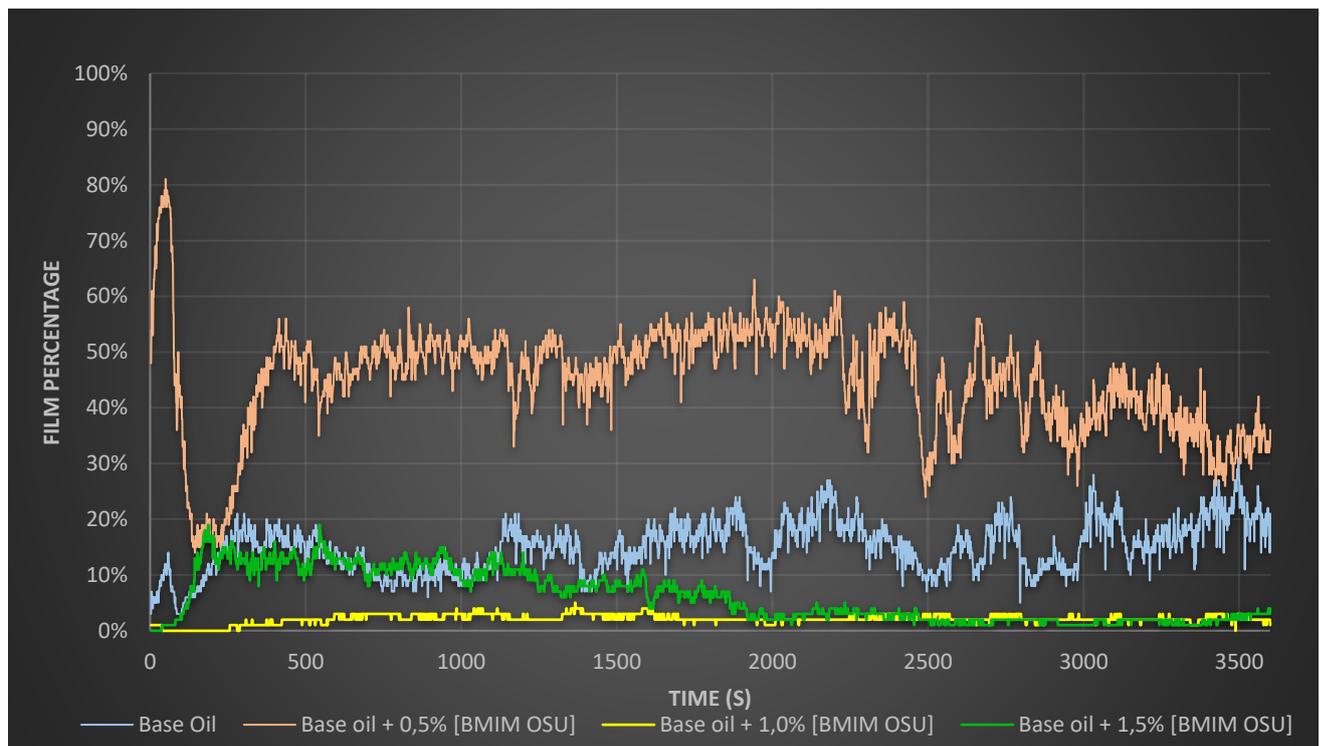


Figure 5. Film percentage as functions of time lubricated with pure oil base and with 1-butyl-3-methylimidazolium octyl sulfate [BMIM OSU] as additive in different concentrations. (b) 1-Ethyl-3-methylimidazolium chloride [EMIC].

Table 2. Mean film percentage off [BMIM OSU] blends

Lubricants	Film Percentage
Base Oil	15%
Base Oil + 0,5% [BMIM OSU]	45%
Base Oil + 1,0% [BMIM OSU]	2%
Base Oil + 1,5% [BMIM OSU]	6%

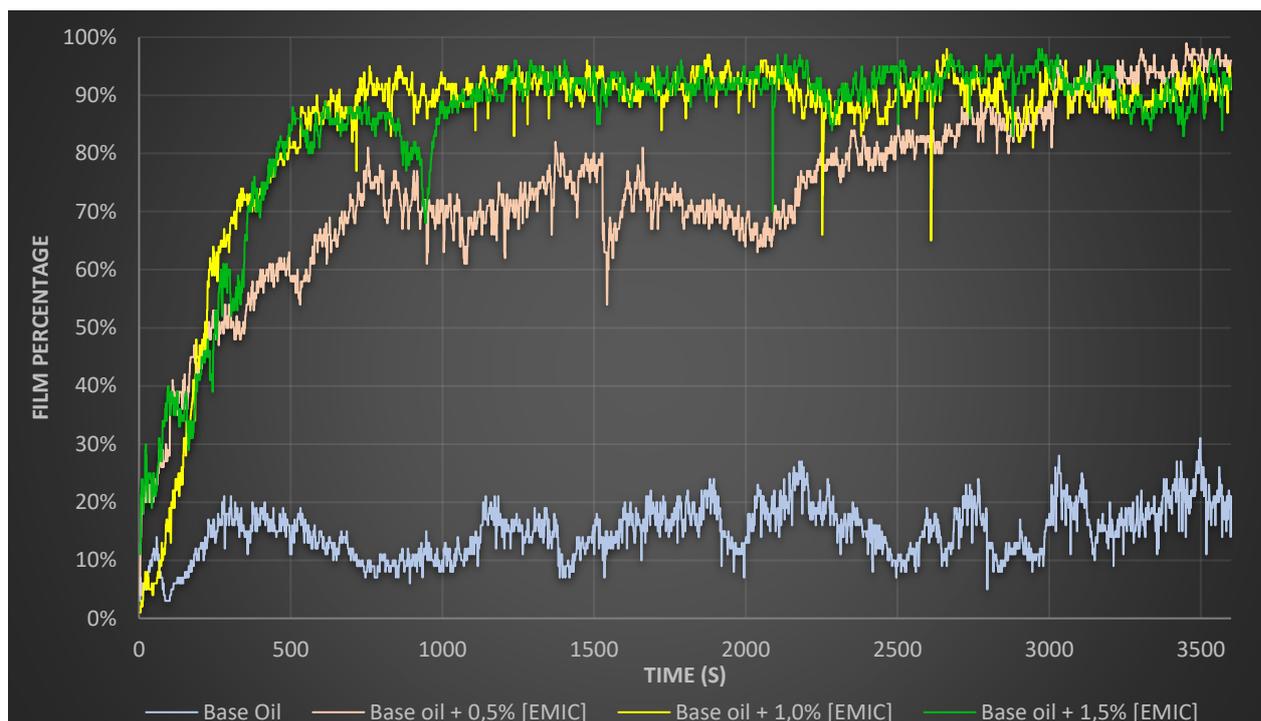


Figure 6. Film percentage as functions of time lubricated with pure oil base and with 1-Ethyl-3-methylimidazolium chloride [EMIC] as additive in different concentrations.

Table 3. Mean film percentage off [EMIC] blends

Lubricants	Film Percentage
Base Oil	15%
Base Oil + 0,5% [EMIC]	73%
Base Oil + 1,0% [EMIC]	85%
Base Oil + 1,5% [EMIC]	85%

Analyzing the film percentage formation off each IL blend becomes evident that the [EMIC] has superior performance than the [BMIM OSU] ones. Still, it had no direct relation to the friction performance. Looking for [BMIM OSU] behavior, the concentrations off 1,0 wt% and 1,5 wt% practically did not form the film. At the same time, the lowest concentration had the highest formation, which happened to the friction coefficient too. On the other hand, [EMIC] had better film formation than the other ionic liquid in all concentrations. The highest concentrations showed better formation; however, the friction behavior was not similar.

“Figure 7” shows the scar on the contact surface off the ball after the tests for [BMIM OSU] blends and the “Figure 8” for [EMIC] bends, the “Table 4” displays the average size of the scars. The wear width was measured horizontally and vertically and then the average between the two values was taken. Based on these data, the analysis of wear caused by friction during the tests is carried out. Comparing the “Figure 7” and “Figure 8,” it is possible to see that the [EMIC] had a better anti-wear performance as happened with friction than the [BMIM OSU].

Another aspect to observe is the depth of the scar; in this case, accurate measurement was not made, but it is possible to see that the scars of [BMIM OSU] tests are more profound than the other ones. Comparing “Table 1” “Table 4” is possible to understand that the friction coefficient and the wear directly correlate.

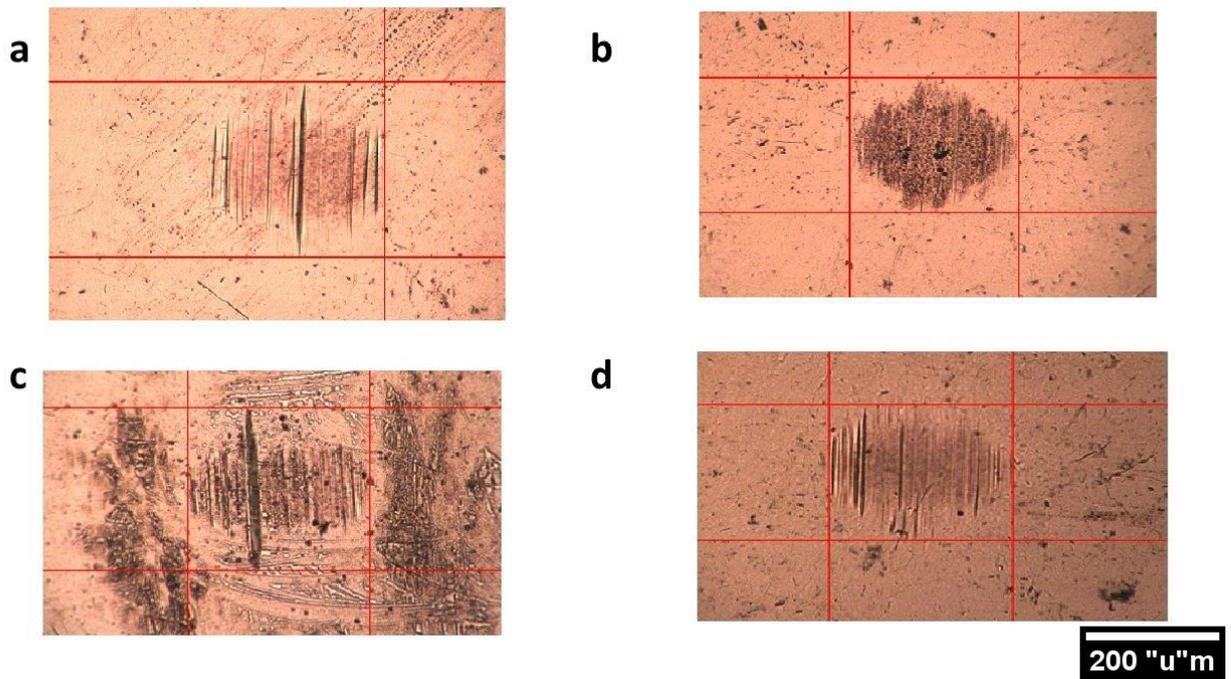


Figure 7. ball contact surface after testing: (a) base oil, (b) Base Oil + 0,5% [BMIM OSU], (c) Base Oil + 1,0% [BMIM OSU], (d) Base Oil + 1,5% [BMIM OSU].

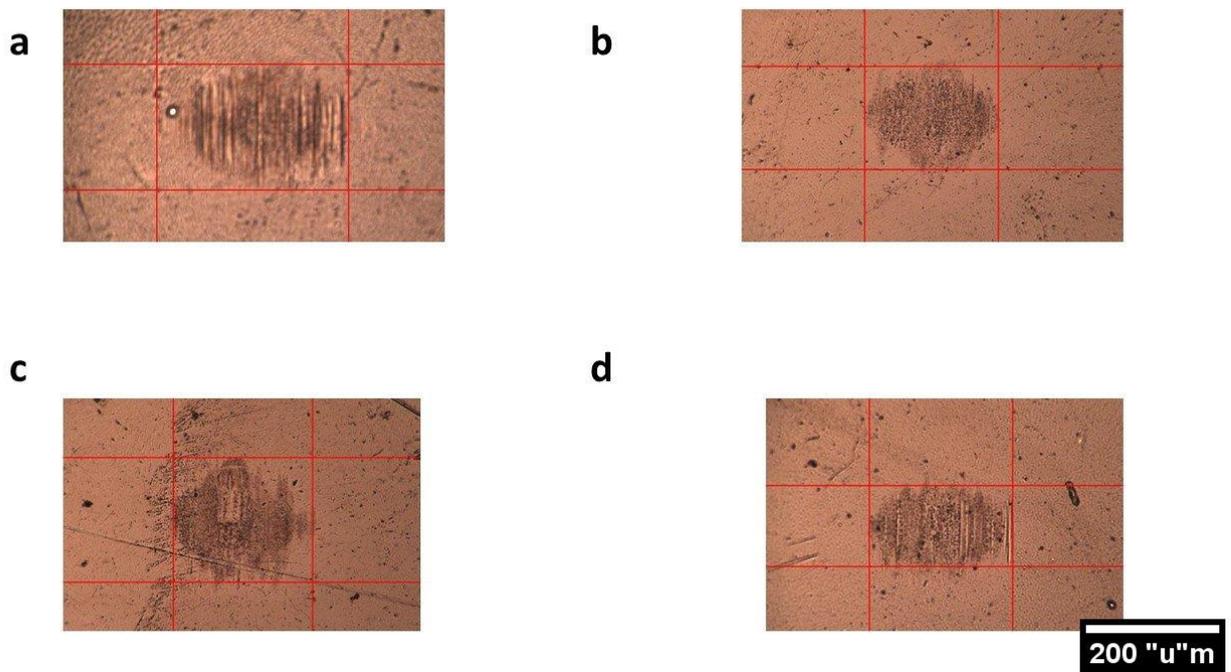


Figure 8. ball contact surface after testing: (a) base oil, (b) Base Oil + 0,5% [EMIC], (c) Base Oil + 1,0% [EMIC], (d) Base Oil + 1,5% [EMIC].

Table 4. Average scar size.

Lubricants	AVG Scar (μm)
Base Oil	234,0

Base Oil + 0,5% [BMIM OSU]	184,0
Base Oil + 1,0% [BMIM OSU]	225,5
Base Oil + 1,5% [BMIM OSU]	197,0
Base Oil + 0,5% [EMIC]	175,0
Base Oil + 1,0% [EMIC]	195,5
Base Oil + 1,5% [EMIC]	196,5

Based on all results, it was possible to confirm the expectations. The IL additives increase the tribological performance of the base lubricant in the anti-wear behavior. Furthermore, for the combinations of IL/oil used in this paper, the lower concentrations of 0,5 wt% performed better.

4. CONCLUSIONS

The effect of 1-butyl-3-methylimidazolium octyl sulfate [BMIM OSU] and 1-Ethyl-3-methylimidazolium chloride [EMIC] as additives tribological properties of the soybean epoxidized lubricant. Based on the results presented above, it can be concluded that:

The anti-wear behavior of the base oil was significantly improved with the additives in low concentrations due to the decrease of friction coefficient and the increase of tribo-film formation.

The [EMIC] generated better results compared to [BMIM OSU] under the same conditions.

Among the concentrations used in this paper, 0.5 wt% had the best results for both ILS, showing that it is possible to obtain optimal performance improvement using small amounts of additive, reducing production costs.

5. ACKNOWLEDGMENT

The authors wish to express thanks to the National council of scientific and technological development (CNPq) of Brazil for supporting this work within the framework of the Research of Project CNPq 311102/2020-4.

6. REFERENCES

- Alves, S. M., Barros, B. S., Trajano, M. F., Ribeiro, K. S. B., & Moura, E. (2013). Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions. *Tribology International*, 65, 28–36. <https://doi.org/10.1016/j.triboint.2013.03.027>
- Amiril, S. A. S., Rahim, E. A., & Syahrullail, S. (2017). A review on ionic liquids as sustainable lubricants in manufacturing and engineering: Recent research, performance, and applications. *Journal of Cleaner Production*, 168, 1571–1589. <https://doi.org/10.1016/j.jclepro.2017.03.197>
- Lathi, P. S., & Mattiasson, B. (2007). Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Applied Catalysis B: Environmental*, 69(3–4), 207–212. <https://doi.org/10.1016/j.apcatb.2006.06.016>
- Li, S., Chen, H., Luo, T., Wang, F., Xiao, G., Chen, Z., Yi, M., Sheng, C., & Xu, C. (2021). Tribological properties of 1-octyl-3-methylimidazolium lactate ionic liquid as a lubricant additive. *Journal of Molecular Liquids*, 332, 115828. <https://doi.org/10.1016/j.molliq.2021.115828>
- Qu, M., Yang, Z., Zhang, C., Yu, Q., Cai, M., & Zhou, F. (2021). Significantly enhancing lubricity and anti-wear performances of glycerol lubricant with urea-functionalized imidazolium-organophosphate ionic liquid as additive. *Tribology International*, 153(May 2020), 106602. <https://doi.org/10.1016/j.triboint.2020.106602>
- Sadanandan, A. M., Khatri, P. K., Saxena, R. C., & Jain, S. L. (2020). Guanidine based amino acid derived task specific ionic liquids as noncorrosive lubricant additives for tribological performance. *Journal of Molecular Liquids*, 313, 113527. <https://doi.org/10.1016/j.molliq.2020.113527>
- Somers, A. E., Howlett, P. C., MacFarlane, D. R., & Forsyth, M. (2013). A review of ionic liquid lubricants. *Lubricants*, 1(1), 3–21. <https://doi.org/10.3390/lubricants1010003>
- Wagner, H., Luther, R., & Mang, T. (2001). Lubricant base fluids based on renewable raw materials: Their catalytic manufacture and modification. *Applied Catalysis A: General*, 221(1–2), 429–442. [https://doi.org/10.1016/S0926-860X\(01\)00891-2](https://doi.org/10.1016/S0926-860X(01)00891-2)
- Xiao, H. (2017). Ionic Liquid Lubricants: Basics and Applications. *Tribology Transactions*, 60(1), 20–30. <https://doi.org/10.1080/10402004.2016.1142629>