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Tribological properties of amorphous carbon films obtained by electrodeposition from DMF using 2HEAL protic ionic liquid as dopant

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ABSTRACT

Amorphous carbon films are widely used for improving the surface mechanical properties of metallic materials, substantially increasing the wear resistance [1,2]. Traditionally this type of film is obtained by vapor phase methods, which, in spite of being in a high technical and scientific development level have been associated with a number of limitations, in particular with regards to the implementation cost and large film production. In this context, electrodeposition shows itself as an alternative to traditional methods: it has low cost and limits the use of complex techniques, which generally require high temperatures and vacuum and cannot be applied for coating on substrate with complex shapes and large dimensions. It is true that the electrodeposition of carbon films also has experimental limitations, such as the limited deposition rate and, therefore, the aim of this work is to investigate the influence of the ionic liquid 2-Hydroxyethylamine Lactate (2HEAL) in obtaining amorphous carbon films. An improvement in deposition rate by increasing electrolyte conductivity with the addition of ionic liquid is expected. This work is meant to investigate the changes occurring in the films with the addition of ionic liquid, especially from the standpoint of surface mechanical properties such as tribological behavior and interfacial properties. The results show that the addition of the ionic liquid led to change in the structure of the film, resulting in an improvement in the mechanical properties, as observed by reduced friction coefficient. An increase of abraded area of counterface and an increase of elastic work also indicates that behavior.

Novelty statement: The aim of this study was to obtain carbon films by electrodeposition using 2-Hydroxyethylamine Lactate doped *N,N*-Dimethylformamide as electrolyte, in order to increase deposition rate. It will be the first report about the use of ionic liquids as dopants in the electrodeposition of carbon films. In addition, mechanical properties of the obtained films were evaluated and their relationship with the amounts of dopant was explored.

1. Introduction

Carbon films present excellent tribological properties and they can be used as coatings of metallic materials in various applications, especially in order to increase wear resistance [1–5]. For this purpose, carbon coatings show up as an interesting alternative coating of titanium alloys for biomedical [6–9] and aerospace applications [10,11]. Traditionally this type of coating is obtained by physical or chemical vapor deposition [12–15]. However, these techniques are expensive and require complex experimental apparatus. In this way, to obtain carbon films directly on

the surface of titanium alloys, in an efficiently and economically viable manner becomes a challenge.

In this context, the electrodeposition shows enormous potential, especially for not requiring vacuum systems and high temperature [16,17]. In addition, this technique allows coating components of complex geometry and it has several operating parameters that allow controlling the properties of the films. Typically, the electrodeposition of carbon films uses organic solvents as electrolyte, and *N,N*-Dimethylformamide (DMF) and Acetonitrile (ACN) are among the most widely explored in the literature [17,18]. However, the deposition with these solvents leads to experimental limitations, in particular with respect to deposition time and to voltage required for polarization, activation and reaction of organic molecules [17].

Some work has been reported on the use of dopants in deposition solutions, in order to increase the conductivity of the electrolyte. These dopants are mostly aqueous solutions containing possibly some kind of salt [19,20]. The problem of this dopant type is inevitable

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occurrence of parallel reactions during the deposition and the compatibility with the original organic solution.

Aiming to improve the characteristics of the electrolyte leading to an increase in the deposition rate of the films, this research proposes the use of ionic liquids as dopants, operating as supporting electrolyte and consequently increasing the conductivity of the deposition solution [21,22], favoring polarization of organic molecules. After the deposition, the different films obtained were compared regarding their morphological, structural, tribological and mechanical properties, checking the effect of doping on their characteristics.

2. Materials and methods

The substrate used in this work was a titanium alloy, Ti6Al4V disks that were mechanical polished using #600 #4000 SiC sandpaper and subsequently polished with 1 μm size diamond paste. The samples were cleaned with distilled water and ethanol.

Electrodeposition technique was used for the deposition of carbon films. The cell was a traditional two electrodes: a working and a counter electrode. The working electrode was the substrate sample itself, in a Teflon holder, with a constant exposed area of 0.31 cm^2 , and the counter electrode was a graphite plate, 10 mm distant from the working electrode. Temperature was kept constant at 20 $^\circ\text{C}$ using a thermostatic bath. For the deposition, an electric voltage of 1200 V was applied between the electrodes using a high voltage source, many authors reported this magnitude of voltage in order to obtain carbon films with amorphous characteristics [18,23–25]. In all systems, the deposition time was 24 h.

One of the most important parameters in the electrodeposition process is the electrolyte composition. In this work NN; DiMethylFormamide (DMF) (FMAia 99%) was tested as electrolytes, as well as mixtures of DMF and 2-HydroxyEthylAmine Lactate (2HEAL), used as dopant, in order to increase the electrolyte conductivity, it is common to use ionic liquids as support electrolyte in electrodeposition process [26–29]. Normally, aprotic ionic liquids are used in this way, however this kind of ionic liquid have high cost and low stability, for this reason in this work a protic ionic liquid is used. The main difference of protic ionic liquids compared to the traditional aprotic is the presence of at least a proton, which is/are able to promote extensive hydrogen bonding [30]. In addition this family of ionic liquids are interesting alternative due their low cost and simple synthesis route [31]. Three concentrations of this ionic liquid in the electrolyte were tested: 0.03 vol% (DMF30LI), 0.05 vol% (DMF50LI) and 0.1 vol% (DMF100LI).

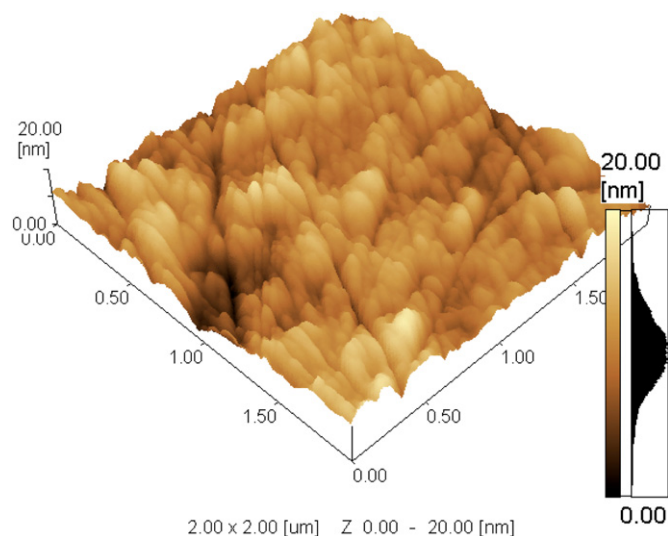


Fig. 1. AFM image of the polished substrate before deposition.

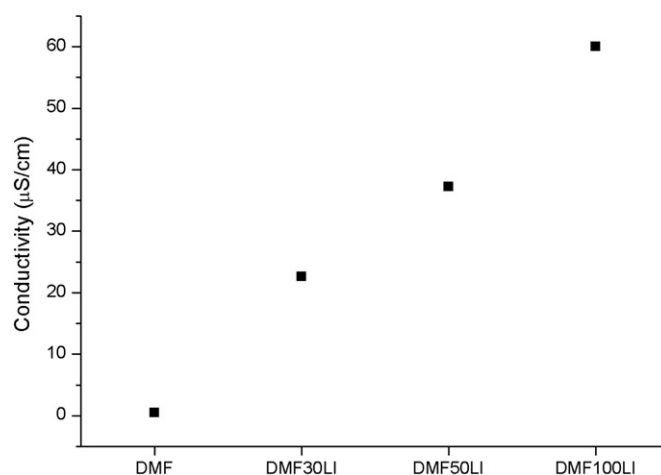


Fig. 2. Conductivity of the tested electrolytes.

Morphology of the samples before and after the deposition of the films was observed by atomic force microscopy (Shimadzu contact mode, size 2 $\mu\text{m} \times 2 \mu\text{m}$), scanning electron microscopy (Jeol, 6060, 20 kV, Secondary Electron and Backscattered Electron Imaging mode) and optical microscopy (Keyence 3D optical microscope). The local roughness was measured using the profiles of AFM. Raman spectroscopy (Renishaw; laser 514 nm, 5 accumulations, exposure time 20 s 120 s) was used in order to analyze the type and amount of carbon bonds in the structure of the film, this procedure allows evaluating the type of amorphous carbon film obtained. The reference used for peak position was based on the studies of Beeman et al. [32], Dillon et al. [33] and Ferrari and Robertson [34].

Adhesion of the films was investigated by Scratch tests, with a Nano Scratch Tester (CSM Instruments) with spherical diamond indenter (diameter of 5 μm) applying a progressive loading from 3 to 500 mN. The facies and the optical critical loads of tracks were analyzed by optical microscopy, and the elastic recovery of the groove was evaluated by measuring the penetration depth during the scratch test and after the test. The mechanical properties (Young's modulus, surface hardness) were evaluated using nanoindentation test (UltraNanoIndenter, CSM Instruments) with a normal force of 10 mN, with a modified Berkovich indenter. The Oliver & Pharr analysis method [35] was used for calculation.

Friction tests were performed on a linear ball on plate tribometer (CSM Instruments). To evaluate the tribological behavior of the films, sliding was conducted with a reciprocal linear motion of an alumina ball (diameter of 6 mm). Constant normal force of 1 N, corresponding to an average Hertzian pressure of 400 MPa; sliding speed of 0.63 cm/s and track length of 2 mm were used. The dimensions and facies of the tracks were evaluated by optical and electronic microscopy.

3. Results and discussion

The analysis of the substrate indicates that the mechanically polished surface is characterized by a uniform texturing which could favor the deposition, providing well distributed sites to anchor the

Table 1
Layer thickness of the films obtained from organic liquids with and without dopant.

System	Layer thickness (μm)
DMF	4.5 \pm 0.2
DMF30LI	8.1 \pm 0.4
DMF50LI	12.9 \pm 1.8
DMF100LI	18.1 \pm 0.5

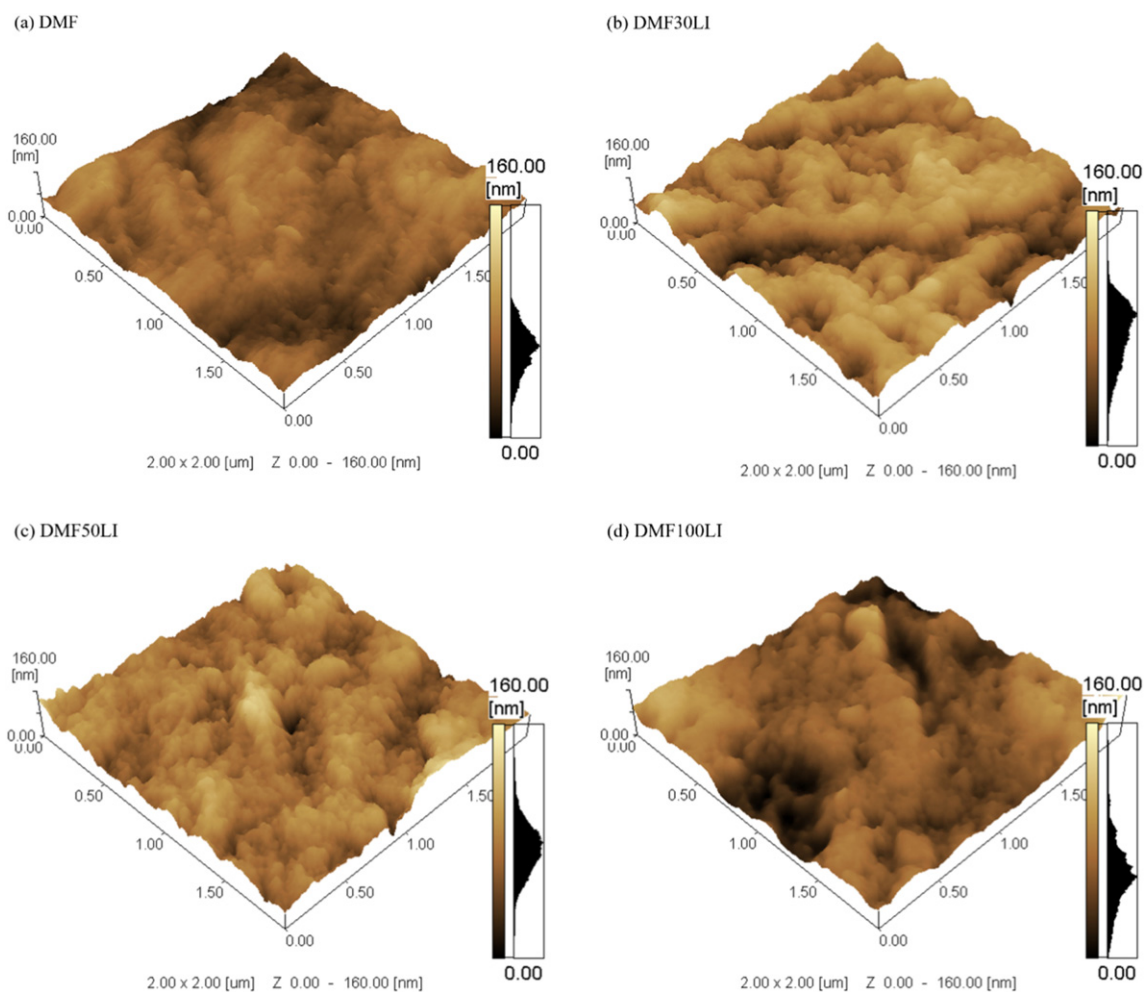


Fig. 3. AFM image of the film surface obtained from: (a) DMF; (b) DMF30LI; (c) DMF50LI; (d) DMF100LI.

film, as shown in the AFM image (Fig. 1). The substrate presents very low local roughness as showed in Fig. 4. However, after deposition there was a clear change in the appearance of the surface: globular formations of the film onto the substrate lead to an increase in surface roughness (Fig. 3a). This fact is associated with a phenomenon of preferential polarization, wherein the material is favorably deposited on the substrate inhomogeneities or defects, such as peaks or valleys on

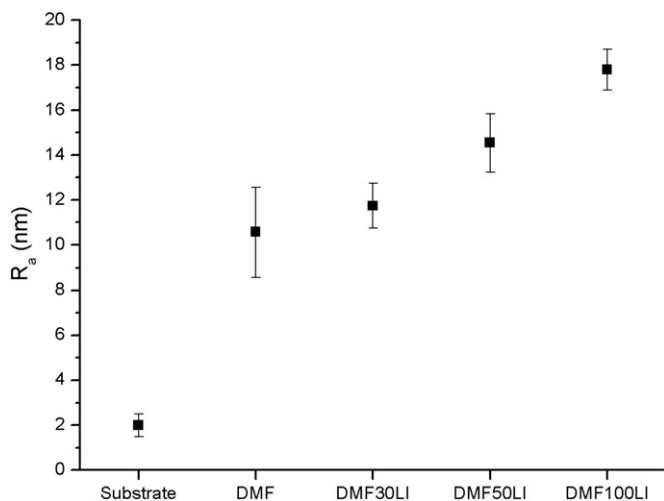


Fig. 4. Average local roughness of the studied systems obtained by AFM measurements.

the surface. As observed by Zhang [36] and Gupta [37,38], after the nucleation phase, the carbon nuclei come into a growth phase, and began to thicken the film. As the deposition rate is low, the carbon globules formed were coarse.

The insertion of protic ionic liquid in DMF increases the conductivity of the solution as can be seen in Fig. 2, thereby increasing the

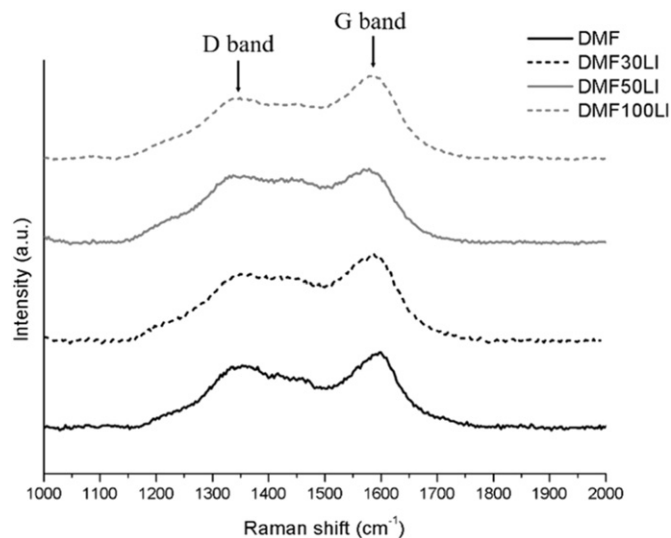


Fig. 5. Raman spectra of the films obtained from different electrolytes.

Table 2Positions of the D and G bands and intensity I_D/I_G ratio for the films.

System	D center (cm ⁻¹)	G center (cm ⁻¹)	I_D/I_G
DMF	1341 ± 0.58	1591 ± 0.6	0.73 ± 0.006
DMF30LI	1341 ± 0.60	1585 ± 2.5	0.67 ± 0.010
DMF50LI	1340 ± 1.53	1586 ± 0.6	0.69 ± 0.015
DMF100LI	1336 ± 1.15	1579 ± 1.5	0.72 ± 0.021

electrodeposition current density and consequently increasing the deposition rate (Table 1). AFM images of the films obtained from solutions containing 0.03 vol%, 0.05 vol% and 0.10 vol% of ionic liquid Figs. 3b; c; and d, respectively show a globular structure with agglomerates constituting the film. The same mechanism of nucleation and growth in thickness was observed. However, since the deposition rate is higher for systems with dopant, a larger quantity of nuclei was formed, followed by growth in thickness. This effect, locally observed by AFM, showed a structure with finer agglomerates with increasing amounts of dopant, leading to increased local roughness (Fig. 4), as observed by Zhang [36].

In addition, the presence of dopant caused a progressive increase in the thickness of the films measured from cross sections by scanning electron microscopy, as can be seen in Table 1. This increase is related to the higher conductivity of the electrolyte and the consequent increase in current deposition, leading to a higher deposition rate. In fact, the films obtained without the dopant showed a deposition rate of 190 nm/h while the addition of 0.1 vol% of 2HEAL led to an increase to rates around 750 nm/h.

Regardless of presence or absence of ionic liquid in the deposition solution the films have typical characteristics of amorphous carbon films, as can be observed in the Raman spectra (Fig. 5). These spectra show the presence of G band associated with the presence of sp^2 type hybridizations and D band associated with the disorder of sp^2 bonds, this disorder may be associated with the presence of carbon atoms bonds with sp^3 type hybridizations.

The positions of D and G and the I_D/I_G ratio can be correlated with the percentage of four fold coordinate bonds, characterizing the sp^3 type hybridizations [32] and the number and/or size of graphite crystallites [33]. The I_D/I_G intensity ratio was calculated and the values were around 0.73 for DMF and between 0.67 and 0.72 for the systems that uses ionic liquids as dopants in the deposition solution. The crystallite size could be calculated through the linear model proposed by Dillon et al. [33], leading to typical crystallite size of 25 nm. These values are consistent with those proposed in the literature, both for films obtained by electrodeposition, as those obtained by vapor phase techniques. As reported by Dines [39], a C carbon films obtained by PVD can present I_D/I_G ranging between 0.82 and 1.62. Carbon films obtained by electrodeposition

Table 3

Interfacial properties of the films obtained from different solutions.

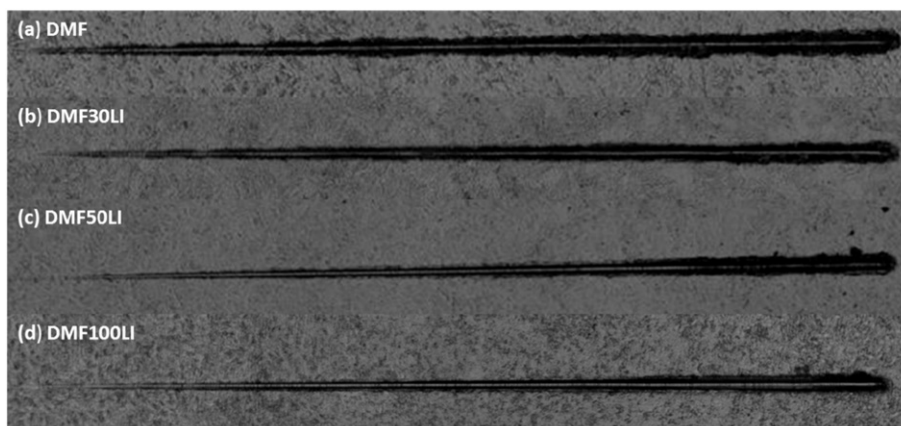
System	W_{elast}/W_{total}	Critical load to lateral pile-up formation [mN]
DMF	68%	11
DMF30LI	76%	35
DMF50LI	77%	35
DMF100LI	83%	40

using organic liquid and organic liquids in aqueous solutions showed I_D/I_G between 0.4 and 1.4 [38,40–42].

The analysis of D and G bands enables interpreting the influence of the ionic liquid in amount of sp^3 hybridizations and graphite crystallites [34,43]. All the films presented a graphitic character with presence of graphitic clusters. Fig. 5 and Table 2 show the dependence of ionic liquids content in the position and intensity of D and G bands. The position of D band shifted slightly down with increased amount of dopant, while the I_D/I_G ratio shifted slightly upwards, which could indicate a greater amount of sp^3 hybridizations and a reduction in number and/or size of graphite crystallites when the amount of ionic liquid increases. However, the most noticeable effect is the downward displacement of the G band with the amount of dopant, possibly indicating a reduction in the amount of sp^2 hybridizations.

Changes in the structure of the carbon films influenced their physicochemical characteristics and therefore their properties. From the viewpoint of surface mechanics, scratch tests showed that the films obtained from DMF showed no delamination of the coating, only lateral material displacement was observed, with lateral pile up formation, which indicates good adhesion between the film and the substrate, as can be seen in the images of scratch tracks in Fig. 6 but plastic character. Plastic deformation indeed occurs at the beginning of the test, indicating that the minimum load is sufficient to permanently deform the films. The addition of ionic liquid to deposition solution did not affect significantly the interfacial properties of carbon films, in the same way as for systems without dopant are observed scratch tracks with plastic deformation since the beginning of load application, but induce a shift in the critical load value for lateral pile up formation

Lateral pile up formation begins for slightly higher loads for the systems with addition of ionic liquids (Table 3). In the case of pure DMF, the critical load to lateral displacement was 11 mN and after addition of dopant, critical loads ranged from 35 mN to 40 mN. There appears to be no significant influence of the amount of ionic liquid to the critical load of material displacement because even low dopant concentrations have increased their value, and the addition of a greater amount does only result in a slight increase in resistance to displacement. This increased resistance to lateral pile

**Fig. 6.** Scratch tracks of the films obtained from: (a) DMF; (b) DMF30LI; (c) DMF50LI; (d) DMF100LI.

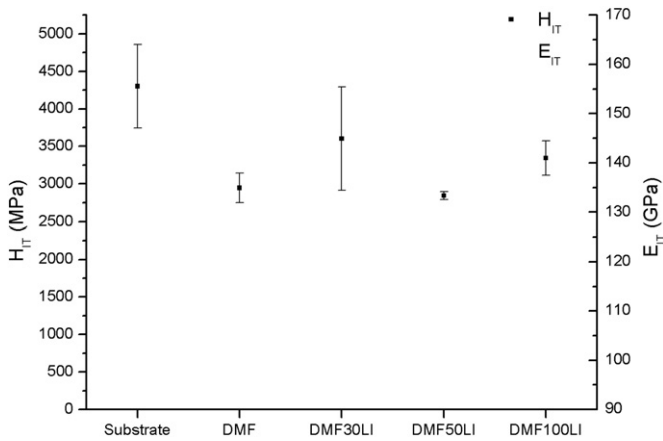


Fig. 7. Influence of the dopant in the hardness and the Young modulus of the film compared to the uncoated substrate.

up plastic formation can be related to the increase of the elastic nature of the films obtained with the addition of dopant, as evidenced by an increase in elastic work ratio during scratch test shown in Table 3.

Nanoindentation tests performed on the top surface of the studied films result in dispersed values of surface hardness. Probably this is related to the lack of surface homogeneity of the films in relation to the low load applied during the tests. Nevertheless, the substrate presents hardness reliable with titanium alloys, around 4400 MPa [44,45]. Among the films all had the same hardness range of between 3000 MPa and 3500 MPa (Fig. 7). These values are relatively smaller than those traditionally found by carbon films with high amount of sp^3 hybridizations, between 10 GPa and 30 GPa [43,46–49], however, were consistent with those observed by Thejaswini et al. in the case of sp^2 rich films [50].

Young modulus of uncoated substrate (125 GPa) and films obtained with and without addition of ionic liquid are shown in Fig. 7. Substrate presents values befitting to the literature [44,45,51]. In the case of carbon films, a reduction in elastic modulus with increasing the amount of ionic liquid was observed; this is in good agreement with the increase of the elastic nature of the films as evidenced by scratch tests (Fig. 7). Chung et al. [52] studied the deposition of amorphous carbon films onto Si by Plasma Assisted CVD (PACVD) and proposed a direct relationship between the reduction of elastic modulus to the shift in G band to

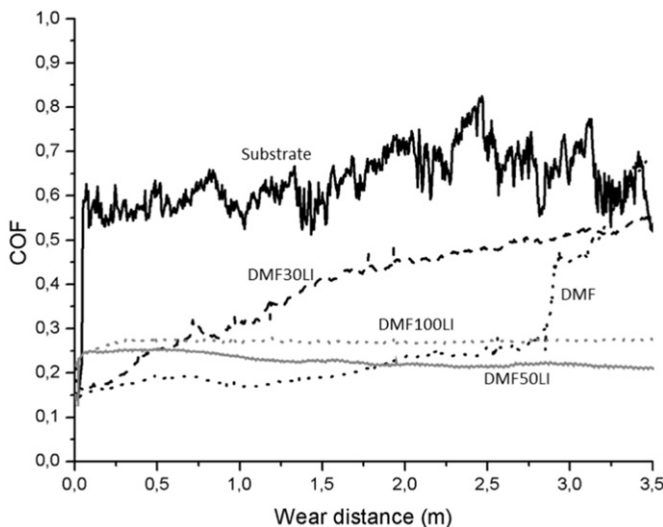


Fig. 8. Influence of the dopant in the Coefficient Of Friction (COF) for the film compared to the uncoated substrate.

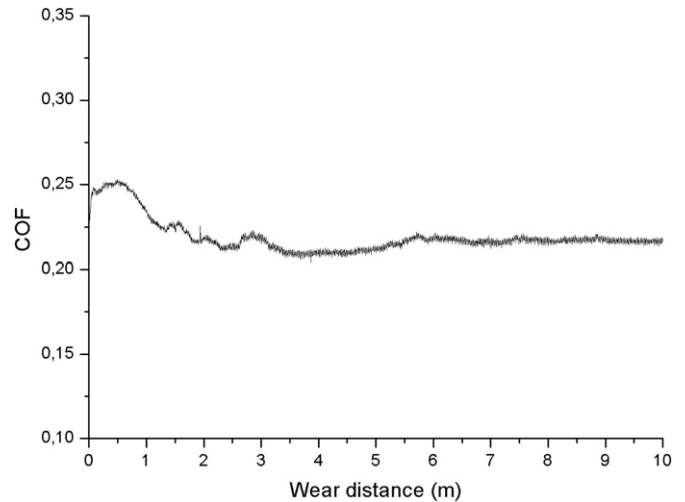


Fig. 9. Long duration friction test for DMF50LI system.

lower wavelengths, the same behavior was observed with the addition of ionic liquid. Furthermore Jardret et al. have shown that the proportion of plastic deformation during scratch test increases with the E/H ratio [53]. This could explain the increase of the elastic deformation ratio with the dopant addition.

Observing comparatively the coefficient of friction (COF) curves for all systems studied (Fig. 8) is quite clear the influence of the type of electrolyte in the mechanical characteristics of the surface of the coated systems.

The coefficient of friction of the uncoated substrate showed an initial period in which polished substrate sliding against the alumina ball, followed by a period where COF oscillates around a mean value. This is due to the presence of a large number of particles (third body) arising from the worn substrate in the contact with the counterface [54]. When these particles were removed from the interface during the test, there was a reduction in the coefficient of friction which increased again when new particles are formed and injected into the contact interface.

For the friction tests on the sample coated with a film obtained from DMF, the initial profile present very low COF values, between 0.2 and 0.3; this value were in agreement with typical carbon films for similar sliding conditions [15,20,55] and remains in this range until three meters slip. Thereafter, the film began to delaminate and consequently the COF began to increase and goes to values around 0.7, these values coincide with those of the uncoated substrate.

Films obtained from DMF with addition of ionic liquid exhibited low coefficient of friction in relation to sliding distances tested. The system that used 0.03 vol% dopant showed a progressive increase in the coefficient of friction did not exceed 0.5. Even though slightly above typical COF of amorphous carbon films, it was still relatively lower than the uncoated substrate. For the films with higher ionic liquid concentration, in the case of adding 0.05 vol% or 0.10 vol% the coefficient of friction was lower than 0.25 throughout the sliding distance tested. This behavior

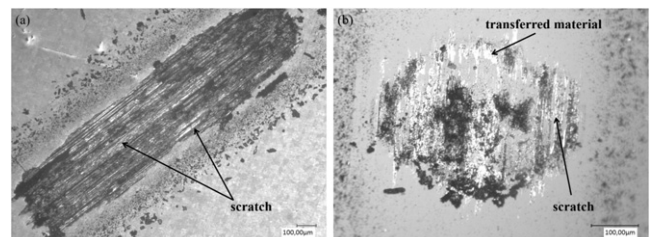


Fig. 10. Appearance of uncoated substrate wear: (a) track; (b) counterface.

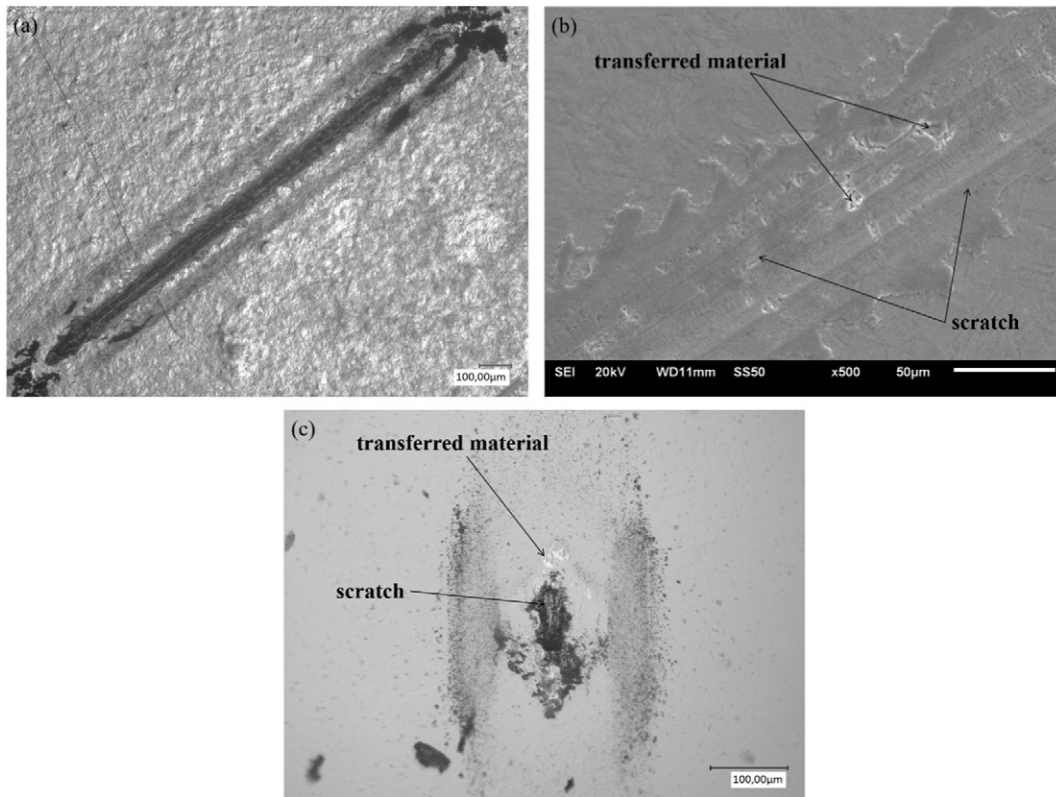


Fig. 11. Appearance of film obtained from DMF wear: (a) optical image of track; (b) SEM image of track; (c) counterface.

is associated to the structure of the film, with increased amount of sp^3 hybridization giving better surface properties while the presence of certain amount of hybridization sp^2 imparts a self lubricating nature to the films.

The friction coefficient observed for the films obtained from DMF with addition of ionic liquid, remained low in long term tests, without showing catastrophic wear of the film even after significant worn distances (Fig. 9).

The analysis of uncoated substrate wear tracks showed typical scratch marks of abrasive wear both on the track (Fig. 10a) and on the counterface side (Fig. 10b). Material transferred to the counterface surface (Fig. 10b), typical of adhesive wear, was also observed. Considering these two phenomena the wear mechanism of the substrate was a mixture of abrasive and adhesive wear, as expected for wear of metallic materials [56].

The appearance of the wear tracks and the alumina counterface for the coated system indicated the same mechanism observed for uncoated substrate, scratch marks of abrasive wear can be viewed in SEM

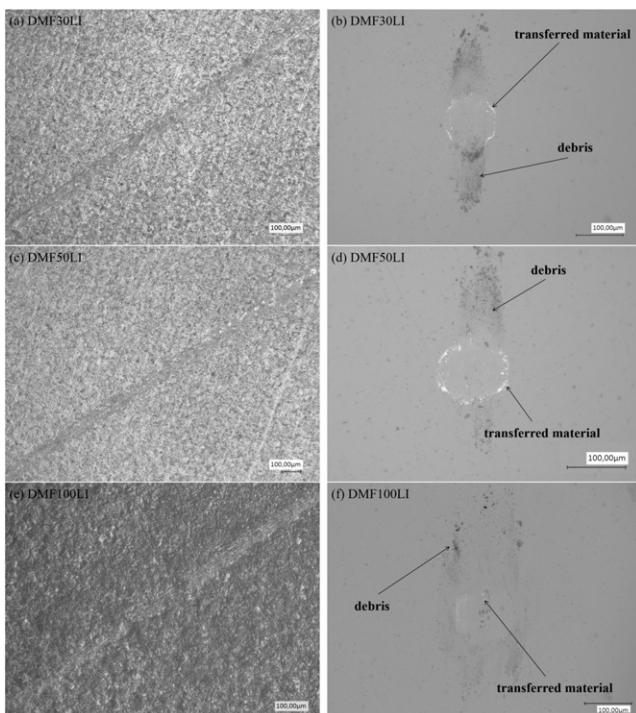


Fig. 12. Appearance of wear tracks: (a) DMF30LI; (c) DMF50LI; (e) DMF100LI; and counterfaces: (b) DMF30LI; (d) DMF50LI; (f) DMF100LI.

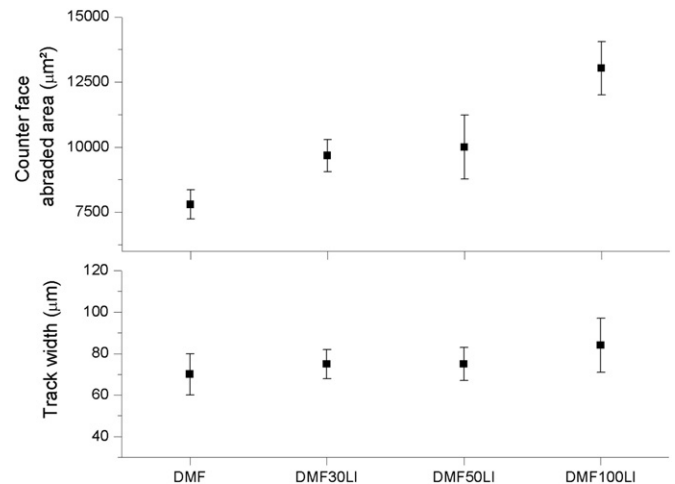


Fig. 13. Influence of dopant in the track width and counterface abraded area.

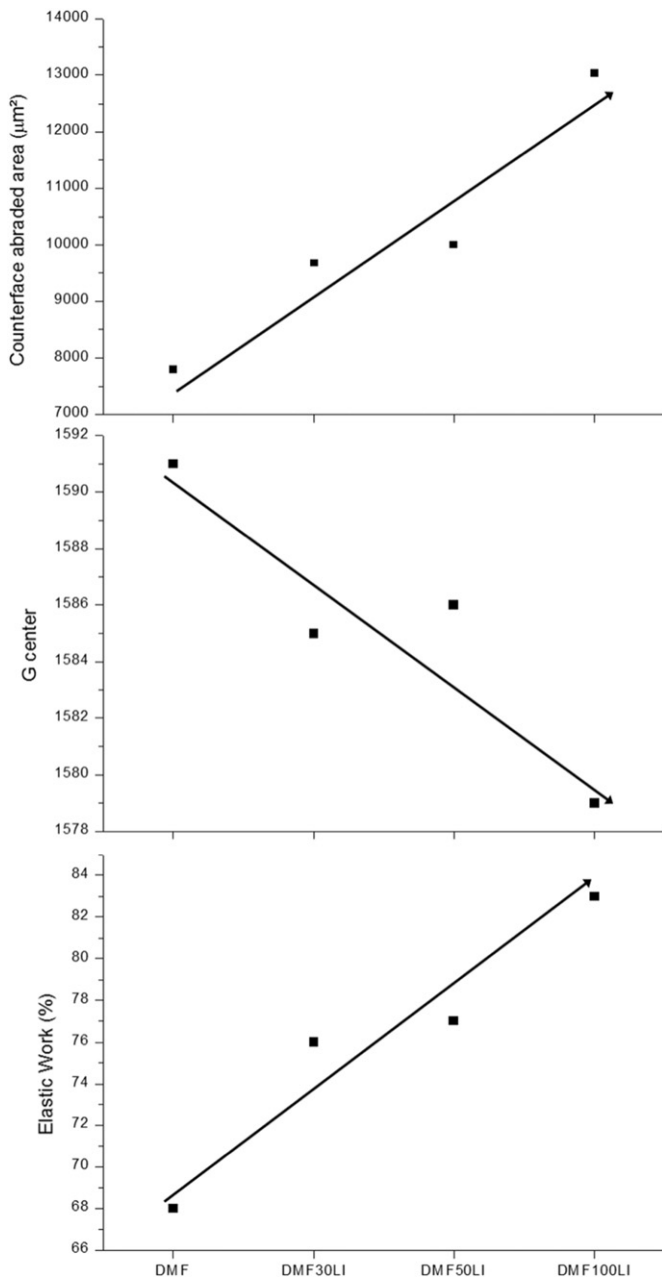


Fig. 14. Relationship between wear, Raman and interfacial parameters of the films.

image (Fig. 11b). However, there was a reduced wear evidenced by the large reduction in track width (Fig. 11a) and the abraded area in the alumina ball (Fig. 11c). There appears to be less amount of material transferred to the counterface, as shown in Fig. 11c.

The addition of ionic liquid to the electrolyte resulted to a change in the wear mechanism: without scratch marks of abrasive wear (Fig. 12a, c and e), both in the film and in the counterface. While the analysis of the counterface (Fig. 12b,d and f) shows adhered material, indicating adhesive wear mechanism, with presence of debris shifted to the extremities of the abraded area. This change of wear mechanism may be associated with more elastic character of these coatings as shown by the interfacial behavior analysis (Table 3).

Comparative analysis of wear tracks and counterfaces (Fig. 13) showed that, regardless the presence and amount of ionic liquid, there was no significant change in the width of the wear tracks. On the other hand, an increase in the abraded area of the sphere was observed with addition of small amounts of dopant, and an even greater increased

with the addition of larger amounts of dopant. This phenomena is in good agreement with the increase of the contact area due to the reduction of Young modulus predicted by the Hertz contact model. The expected contact diameters for the test configurations are between 0.63 µm and 0.65 µm, in concordance with de values reached for the track width of the coated systems.

This increase of abraded area could be related with the amount of sp^2 hybridizations in the film, the displacement of G band to lower wavelengths evoked the reduction of amount and size of graphite clusters in the film, this reduction limited the lubricating characteristics, increasing counterface wear. Fig. 14 shows that additions of small amounts of dopant led a significant influence in graphite clusters, which means there was an important increase in counterface wear.

4. Conclusions

The films obtained had typical characteristics of amorphous carbon structure, formed by sp^3 and sp^2 bonds and presence of graphite clusters. Ionic liquid influenced the structure of the film, probably increasing the amount of sp^3 bonds and reducing the amount sp^2 hybridizations, even if a more detailed and in depth Raman analysis, beyond the scope of this paper, would be necessary to better understand the coating structure. This amorphous carbon nature gave the film interesting properties with regard to wear resistance, reducing the COF for much lower (0.25) than the uncoated substrate values (0.7). An optimum combination between the amount of sp^2 and sp^3 hybridization was observed for the films obtained from DMF with 0.05% of 2HEAL, resulting the lowest COF value, which was accompanied by intermediate wear against the face of alumina.

It was observed good adhesion between the film and the substrate, which showed only lateral pile up pad formation without delamination, regardless the presence or absence of dopant in the deposition solution. The ionic liquid addition led to an increased resistance to lateral pile up pad formation, which was observed to four times higher loads for systems containing dopant. Furthermore, addition of dopant modified elastoplastic character of the films, being observed an increase in the percentage of elastic work with the amount of ionic liquid, this influenced the wear mechanism, reducing the abrasive nature and leading to a more adhesive nature for the wear, possibly allowing easier tribofilm formation. No clear evidence of hardness evolution could be shown but there was a tendency of reduction of Young modulus with increasing amount of dopant, in good agreement with the increase of the elastic recovery obtained by scratch tests.

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