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Plasma Processes as a Cleaner Alternative for Cleaning, Corrosion Resistance, and Functionalization of Metallic Surfaces

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Abstract

The development of clean and efficient high vacuum technologies to replace traditional methods for metallic or polymeric surfaces treatments to clean , deposit thin films , and functionalize surfaces , constitutes a very important area of research. The increasing concern regarding the development of environmentally friendly and sustainable technologies consists in an important objective in the modern world. In this context, cold plasma technology represents an efficient alternative, which has been object of increasing attention. In this work we evaluate the effect of plasma treatments on the removal of oil from aluminum surfaces. Furthermore, processes of deposition, and fine film activation, were studied on the surface previously cleaned. After a first plasma application to clean the oil contaminated aluminum surface, a thin film of HMDSO was deposited to achieve corrosion protection, and finally the deposited film was functionalized to obtain a surface with a higher energy , to favor adhesion to different polymers. The evaluation of the cleanness efficiency was conducted by means of the contact angle, and XPS. The nature of deposited and functionalized film was investigated using Fourier Transform Infra Red Spectroscopy (FTIR), angle of contact, and Scanning Electron Microscopy. A very significant reduction in the carbon content of the surfaces, was abserced . An increase in the surface energy of 95,48 mN/m was obtained . Cleaning, corrosion protection and functionalization utilizing high vacuum technology can completely substitute wet processes associated with undesirable high environmental impact**.** In the presentation other works developed by the research groups will be discussed

Keywords: Plasma, cleaning, surface modification, hexamethyldisiloxane.

1 Introduction

Currently, there is considerable interest in controlling the polymer-metal interface , motivated by wide demand of applications such as : formation of layers to improve paint adhesion in packaging ;o various uses in automotive and aerospace industries. Often polymeric materials, due to its chemical nature, do not have good properties of adhesion, unless some form of surface pre-treatment is involved [1]. The conventional treatments employed to change the chemical composition and morphology of the surfaces, to improve adhesion and corrosion resistance, in general involve considerable pollution. However , plasma treatments offer an ecologically friendly alternative for cleaning and functionalizing metal surfaces [2]. This paper presents a study of procedures for the use of plasma for

metal surface cleaning followed by plasma deposition of thin films of Hexamethyldisiloxane (HMDSO) on aluminum plates. An Argon plasma is used in the activation of the surface of the HMDSO, to increase of surface energy and, consequently, the improve adhesion. The anti-corrosive role of the HMDSO thin films was also analyzed. The nature of the process of activation was analyzed by means of measurements of contact angle, Fourier transform infrared spectroscopy (FTIR), and Scanning electronic microscopy (SEM). We will discuss in more detail, in this paper, the plasma technology applied to metal surfaces.

2.0 Materials and Methods

The surface of aluminum plates was first cleaned with a plasma induced treatment, and this process followed by the deposition of an HMDSO film with the objective to protect the surface against corrosion. Analyses of corrosion through a saline spray device were conducted to determine the level of protection obtained. The next step consisted of a process of activation of the surface of the HMDSO film using an Argon plasma, increasing the energy of surface of the HMDSO thin film by functionalization.

2.1 Cleaning Process

Aluminum plates with a layer of lubricating oil, with length of 60 mm and 30 mm wide were utilized to evaluate the effectiveness of the plasma cleaning process. The plasma treatment system was fabricated by y Diener Electronic - Plasma Surface Technology, Germany, Series Pico with a cylindrical chamber with capacity of 5 liters. The generator works with radio-frequency signal of 40 kHz and and maximum power of 200W. Was used a pump of empty Ilmvac mark, with 1.8 m^3/h and pressure of 3×10^{-2} mbar**.** Samples of aluminum plates contaminated with oil were first placed in the plasma chamber, and the vacuum pump was utilized to reduce the pressure to 0,075 Torr, and oxygen (99% of purity) immediately introduced. After the plasma treatment the aluminum plates were evaluated by contact angle measurements to determine the influence of the treatment in the energy of the surface and XPS electron spectroscopy was utilized to investigate the chemical nature of the surface. Values of measurements of the surface energy of the liquids used for the determination of the contact angles are listed in Table 1.

Table 1. Surface free energy; polar and disperse energy of water and ethylene glycol

	γ^d_L (mN/m)	γ^p_L (mN/m)	γ_L(mN/m)
De-ionized water	18.70	53.60	72.30
Ethylene glycol	29.30	18.20	47.50

Plasma treatments were applied in the ranges: Pressure (0.225 Torr- 0.60 Torr), Power (20 W-50W), Time (2-10 min). In the experiments was utilized Ar/H_2 and O_2

2.3 Deposition Process

Plasma Enhanced Chemical Vapor Deposition **(**PECVD) is a widely used technique to the deposition of thin films. In this study was used HMDSO as monomer and Argon

as co-reagent. Initial experiments of HDMSO deposition were conducted in the following conditions: HMDSO pressure: 0.03 mbar ; Ar pressure: 0.18 mbar ; Power: 30, 45,60W; time : 5-30min.
The thickness, refractive index, deposition rate, and contact angle of the deposited film were measured , as well as FTIR and SEM was utilized to evaluate the chemical nature and morphology of the deposited film.

2.4 Corrosion Assays

A corrosion test by exposure to salt fog was used to determine the degree of protection obtained with the DMSO thin film deposited. The test was performed on an equipment made using a saline salt spray mist, where the metal plates were kept upright The methods used were as follows: with respect to the characteristics of the apparatus of salt spray ; ASTM B 117; with respect to the evaluation samples submitted to accelerated corrosion test, ASTM D 1654, with respect to the test conditions, ABNT NBR 8094.

The test conditions used were: 5% ± 1% aqueous solution of sodium chloride (the pH of the solution was adjusted from 6.5 to 7.2). The air temperature was maintained at 35 ± 2 ° C. For comparison purposes, the test was conducted on metal plates unprotected and protected by the HMDSO thin films deposited. The evaluation of the plates was performed one, two, three and seven weeks after exposure to salt.

2.5 Activation Process

After the deposition of the layer of HMDSO the sample was submitted to the activation step with Argon. Was studied the following conditions: exposure time (30-60 sec), power (30-60 W). The sample with higher energy surface in each similar group of 30 samples was analyzed using FTIR and Scanning Electron Microscopy (SEM.

3.0 Results

3.1 Cleaning Process

The best cleaning results were obtained with 0.225 Torr, 50 W, and 10 minutes exposure time and they are listed in Table 2.

Table 2. Contact angle measurements.

	Contact Angle		Surface Free Energy (mN/m)		
	Pure water	Ethylene glycol	γ^d_L (mN/m)	γ^p_L(mN/m)	γ_L(mN/m)
Before plasma treatment	95.5	77.0	12.06	5.82	17.88
After Plasma treatment	7.6	16.8	2.46	79.30	81.76

Sample with the best result was analyzed by X-ray photoelectron spectroscopy. Figure 1 presents the atomic composition of the surface of aluminum before the

plasma treatment. The metal surface, covered with a layer of oil is also evaluated after the completion of the treatment by oxygen plasma.

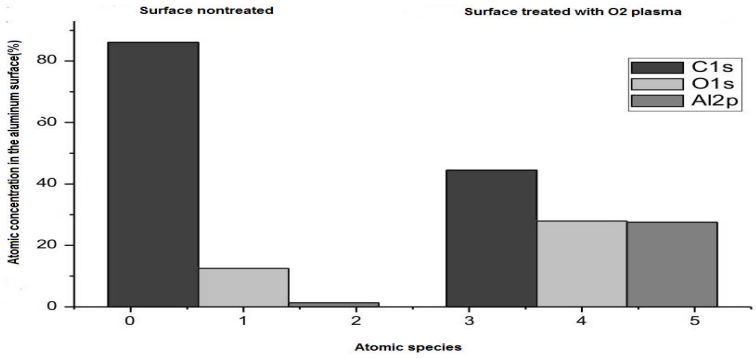


Figure 1. XPS measurements of aluminum samples

The curves obtained using XPS in the regions relative to C1s and Al2p allow the identification of the chemical groups before and after the plasma treatment present in the surface (Figure1 and Figure 2). The results to verify the reduction of the concentration of atomic C 1s from 86.14 to 44.47% due to the removal of the protective oil from the surface of aluminum, with an increase in the atomic concentration of O 1s from 12,55 to 27.97% , and an increase in the concentration of atomic Al 2p from 1.34 % to 27.55%. The increase in the concentration of oxygen (O1s) and aluminum (A12p) is due to the cleaning process and formation of the oxygen groups that provide adhesion to subsequent deposited layers [3].

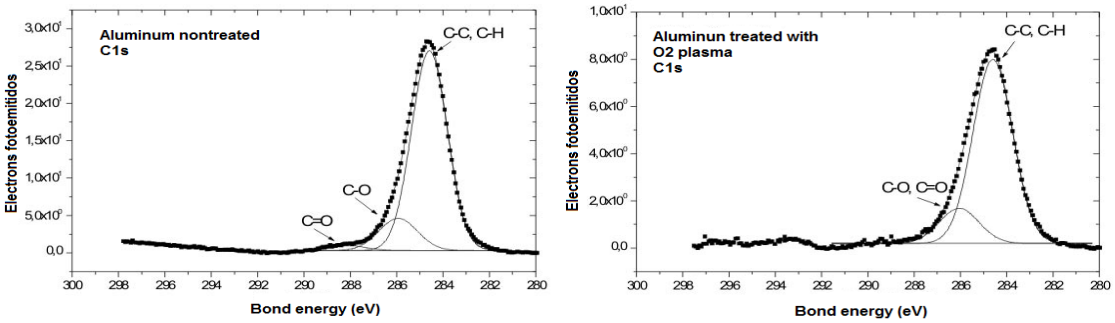
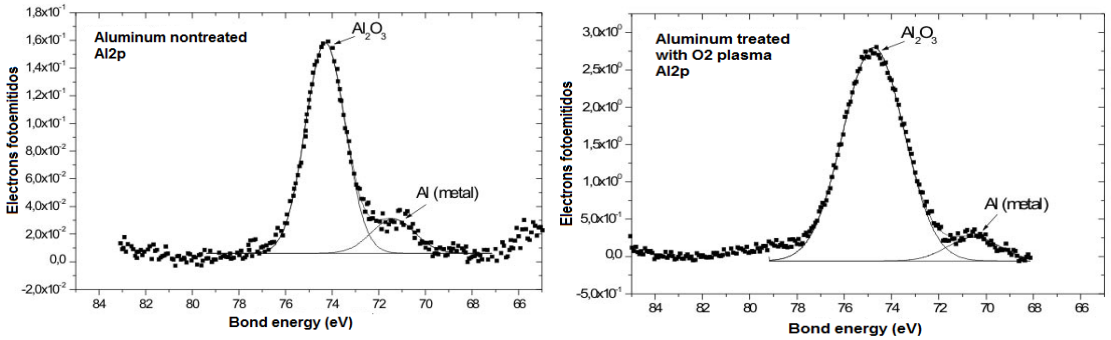


Figure 2. XPS measurements: region of C_{1s} a) Original Aluminum sample, b) Aluminum sample treated with plasma, respectively.



(a) **(b)**

Figure 3. XPS measurements: region of Al_{2p} a) No treated samples, b) Samples treated with oxygen plasma, respectively

It is observed that the samples that were not treated by plasma , the concentration of carbon is higher (86.14%) due to the presence of the protective lubricant oil, which explains the high value of the angle of contact with the de-ionized water (95.5 degrees). Samples treated with plasma showed a significant reduction in carbon concentration due to the removal of oil , with an increase in the concentration of oxygen, which is very important to promote interaction with functional groups with other layers, after receiving the corrosion protection. The results were very satisfactory in terms of the possible practical application of the method.

3.2 Results of the Process of Deposition and Activation

Based in the results obtained with the experiments, the best conditions for HDMSO film deposition were: HMDSO pressure: 0,03 Torr; Ar pressure: 0,15 Torr; Power: 30W; time: 15 minutes. In the characterization of the deposited thin films their thickness, index of refraction, deposition rate, and angle of contact were determined . The results obtained are: thickness of the layer: 943 *mm*; deposition rate: 62.9 *mm/min*; index of refraction of the after surface activation: 1.633. Was also made measurements using FTIR and SEM.

The most effective conditions to HMDSO film activation was obtained with a time of treatment of 30 seconds, and 60 W. With these parameters the energy surface increased by 95.48*mN/m* -the angle of contact with water obtained before the process of activation was 90 degrees, and after the activation process was 12.6 degrees. The free surface energy, after the activation process was 108.8mN/m. These samples were analyzed using FTIR and SEM. The results mentioned above are presented in Figure 4 and Figure 5

In Figure 4a) the peaks observed are the same, which suggests that the change is not of a chemical nature, but physical, as expected, due to the nature of the inert gas Argon. However, the intensities of the bands expressed as transmittance (T) were modified. The transmittance is the ratio between the radiant energy transmitted by a sample and the incident radiant energy. One hypothesis is that the treatment could be introduced changes in the degree of crosslink of the polymer. To further understand the nature of the change occurred, the same samples were analyzed, one week after treatment. The samples were stored at ambient conditions (*300 K and 1 atm*). The results are present in Figure 4b).

As we can show in Figure 4 when the film was measured immediately after treatment and was shows no major differences compared with the film deposited. However, after a week, it shows significant differences with respect to the original film. There is a peak of low intensity to 436 cm^{-1}, which can be attributed to the presence of SiO_x, [4]. A band of medium intensity in the range of 1500-1650 cm-1, also observed, can be attributed to the angular deformation of CH [5]. A broad band of medium intensity with maximum at 3367 cm^{-1}, is typical of the functional group -OH. It is believed that this group results from the reaction of Si-H group, represented by the band in the FTIR spectrum of absorption, with a maximum in 2145 cm^{1}, with oxygen from the air which insert the surface hydroxyl in the thin film . Another hypothesis is that the treatment given, in addition to inducing changes the crystallinity of the polymer, alters its hydrophilicity, which also explains the emergence -OH in the aged films, exposed to air. An additional difference between the material just after treatment and the aged material is the emergence of a weak absorption with a maximum of 436 cm^{-1}, corresponding to SiO_x groups, which are hydrophilic. It is also observed a change corresponding to the group Si-O-Si (1000 - 1150), indicating occurrence of this as the film ages exposed to air. This results leads us to conclude that treatment with plasma of Argon contributes to the reticulation of the film and results in the incorporation of-

OH groups, mainly due to the reactions that occurs in air, during the aging process. These results agree with those presented by D'Agostino (1993)

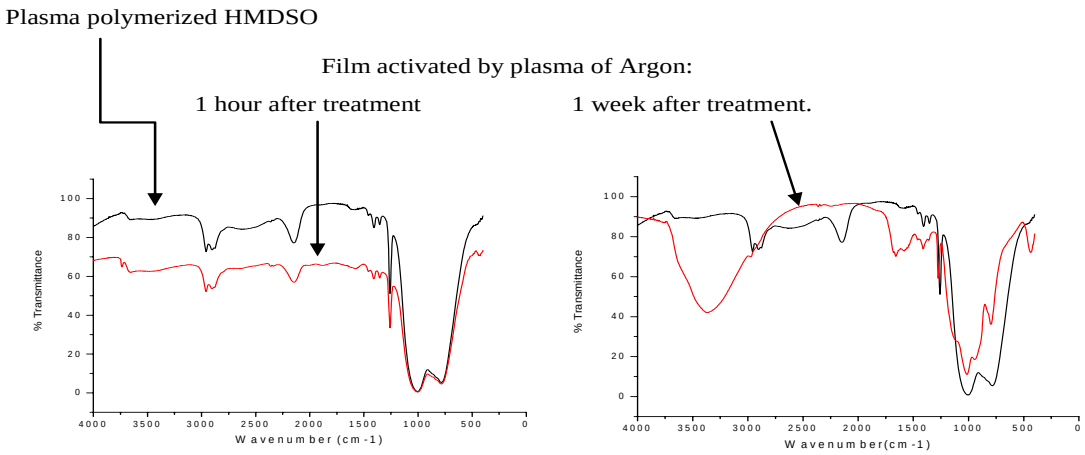
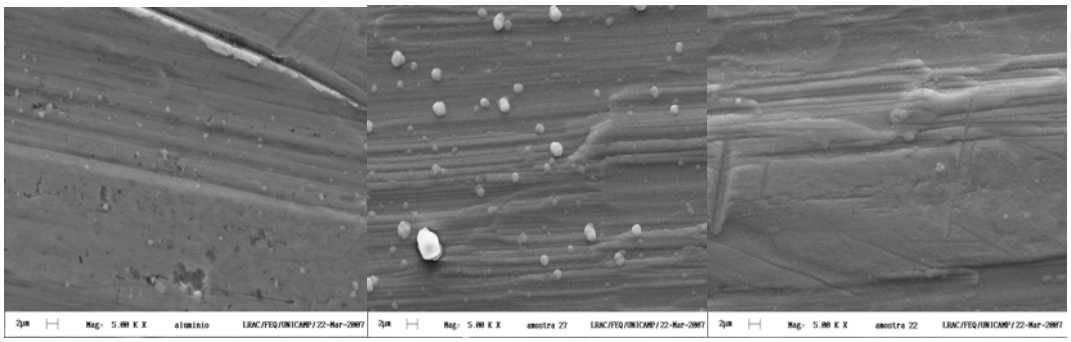


Figure 4. a) IR spectra of plasma polymerized HMDSO; 13.56 MHz, 30 W, Ar: 0.15 Torr, HMDSO: 0.03 Torr and IR spectra of the film activated by plasma of Argon 1 hour after treatment and b)1 week after treatment.

For analyzed morphological aspects was used SEM to examined the aluminum plate, the plates coated with a layer of HMDSO and modified HMDSO. The results are shown in Figure 5. It is observed that the layer deposited by plasma covers the plate, and appearance of beads is observed (3D beads) . These spheres presented a composition similar to that of the deposited layer, which suggests us to that this is beads are made of the polymer deposited. It is not uncommon the appearance of those clusters in processes of plasma deposition



(a) (b) (c)

Figura 5. SEM micrographs for: a) aluminum plate without treatment; b) Aluminum plate covered with HMDSO film; c) HMDSO film treated with low pressure Argon plasma.

3.2 Corrosion Tests

By comparison of photomicrographs of layers of HMDSO before and after treatment with plasma of Argon (Figures 5b and 5c), we can see that the beads on the 3D surface disappeared. This indicates that the Argon plasma has the effect of cleaning the surface. Also there is a considerable decrease in roughness. With the decrease in the amount of 3D spheres in the surface, roughness also decreases. This change

in the morphology of the surface can be tentatively attributed to molecular level reticulation in the layer deposited.
The samples were assessed one, three and seven weeks after the test started. The results obtained are described below :

With **one week exposure :** *Unprotected plates :* After seven days (168 hours) in the salt spray chamber started presenting the typical white oxidation in the edges . *Plates with protection* **:** The metal plates with protection also presented beginning of white oxidation , but a only after 14 days (336 hours) in the salt spray chamber. The behavior after 3 weeks was quite different. The plate without protection presented generalized white corrosion *Plates with protection:* The plate with protection presented some corrosion in places where the protection was not well deposited – places where holes were made and edges , with significant areas well protected and without corrosion .After seven weeks. *Samples without protection*: The plate is 80% opaque demonstrating widespread white corrosion. *Protected plates:* The sample is 60% protected, without corrosion. The other 40% present the typical white corrosion. The plate with protection was around 60% intact after seven week exposure, with 40% of the exposed area completely corroded. This fact suggest that the depositing of the protective layer has to be better studied. Where adequately protected, the HDMSO protection was significantly better with respect to corrosion when aluminum plates protected by other technological processes, as reported in the literature[7].

4.0 Conclusions

The experimental results show that:

- Using plasma technology is possible develop process to clean, deposit and activate surfaces.
- The modification of Aluminum plates with plasma of low pressure technology effective significat alter the layers of HDMSO deposited. Significant surface modification was obtained with plasma treatment times of 30 seconds.
- Using Argon plasma, after the activation step the contact angle obtained was 12.6°, resulting from an increase in surface energy of 95.48 *mN/m*;
- The Argon plasma doesn't introduces new chemical groups in the surfaces. But is effective in surface cleaning, and surface crosslinking. However we observe the introduction oh –OH groups, when the sample is exposed to air, after the Argon plasma treatment.
- The plasma process is clean, with very low production of residues, consisting in a ecologically friendly technique.

5.0 References

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