

# Acetylene plasma-polymer films treated by argon plasma immersion ion implantation

## Filmes de acetileno polimerizados a plasma e tratados por Implantação Iônica por Imersão em plasma

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### ABSTRACT

Structural and surface properties of acetylene plasma polymer films were studied as a function of treatment time via Plasma Immersion Ion Implantation (PIII). The polymer films were obtained from acetylene and argon mixture using radiofrequency glow discharge and then treated by argon PIII. XPS (X-ray photoelectron spectroscopy) was used to analyze the composition of the films before and after PIII treatment. With rising exposure time, XPS revealed an increase of oxygen-to-carbon (O/C) atomic ratio from 0.23 to 2.43. It can be explained by recombination processes between dangling bonds or radicals created in the polymer structure and atmospheric water and/or oxygen. It was observed that the film structure is predominantly formed C-H and C-C bonds, and there was an increment of the C=O proportion bonds upon argon PIII treatment. The wettability of the polymer films was investigated using contact angle measurements for water and diiodomethane droplets on the film surface. After the argon ion implantation, the contact angle was reduced from 55 to 24 degrees, attributed to incorporation of polar groups in the polymer structure. Upon aging in atmosphere, all samples lost the high wettability, but the hydrophilic character of the films was maintained. It was used atomic force microscopy (AFM) to investigate the roughness of the samples. After argon PIII treatment, the roughness of the polymer films decreased from 8.1 to 5.5 nm, mainly due to ablation processes like sputtering one. The hardness and elastic modulus of the polymer films were investigated by nanoindentation technique. The hardness was enhanced from 0.68 to 5.35 GPa and the elastic modulus increased from 28 to 97 GPa. In general, the results show that argon PIII turned acetylene plasma polymer films smoother and mechanically more resistant, but its effect depends on treatment time.

**Keywords:** Acetylene; Ion implantation; XPS; Wettability; Hardness.

### RESUMO

As propriedades estruturais e superficiais de filmes de acetileno polimerizados a plasma foram estudados como função do tempo de tratamento por Implantação Iônica por Imersão em Plasma (IIIP). Os filmes poliméricos foram obtidos a partir de uma mistura dos gases argônio e acetileno em descargas excitadas por radiofrequência, e então tratados por IIIP em atmosfera de argônio. A espectroscopia fotoeletrônica de raios-X (XPS) foi usada para analisar a composição dos filmes antes e após os tratamentos. Esta análise revelou que o aumento do tempo do tratamento, induziu o aumento da proporção atômica oxigênio-carbono (O/C) de 0,23 para 2,43. Isto é explicado pelos processos de recombinação entre as ligações pendentes, ou radicais criados na estrutura polimérica, e a água ou oxigênio do ar atmosférico. Observou-se também que a estrutura dos filmes é predominantemente formada por ligações C-C e C-H, e que ligações C=O aumentam após o tratamento por IIIP. A molhabilidade dos filmes foi avaliada usando medidas de ângulo de contato entre gotas de água, e diiodometano, e a superfície dos filmes. Após a implantação dos íons de argônio, o ângulo de contato diminuiu de 55 para 24°, justificado pela incorporação de grupos polares na estrutura polimérica. Entretanto, durante o envelhecimento em ar atmosférico, todas as amostras perderam a alta molhabilidade, adquirida após o tratamento, mas mantiveram o caráter hidrofílico. A microscopia de força atômica (MFA) foi usada para investigar a rugosidade das amostras. Após o tratamento por íons de argônio, a rugosidade dos filmes diminuiu de 8,1 para 5,5 nm, principalmente devido aos processos de ablação por sputtering. A dureza e módulo de elasticidade dos filmes poliméricos foram medidos pela técnica de nanoindentação. A dureza aumentou de 0,68 para 5,35 GPa, e o módulo de elasticidade aumentou de 28 para 97 GPa. Em geral, os resultados mostram que o tratamento por IIIP em atmosfera de argônio podem tornar os filmes poliméricos a plasma mais lisos e mecanicamente resistentes, mas seu efeito depende do tempo do tratamento.

**Palavras-chave:** Acetileno; Implantação iônica; XPS; Molhabilidade; Dureza.

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## INTRODUCTION

Despite the advent of the atmospheric pressure plasma, the low pressure discharges are in constant ascension as a clean, easy and economically viable way to change the surface properties of materials. Amongst others, this approach allows the deposition of organic coatings from a series of compounds that do not polymerize via the conventional polymerization process, including benzene, methane and acetylene<sup>(1)</sup>. In general, any kind of organic compound that could be evaporated to the reaction chamber can be used to prepare a coating. Interestingly, the properties of the films are strongly related to the deposition parameters, allowing their control. However, it has been demonstrated that post-deposition ion bombardment is a rather effective way of controlling the properties of this materials. Previous works have demonstrated the effectiveness of the beam line implantation on the modification on the properties of plasma polymerized films<sup>(2-4)</sup>. Whereas alterations are controllably imposed on the molecular structure, electrical resistivity, optical gap and mechanical properties of the coatings, large scale applications are hampered by the high costs and complexity involved with the beam implantation. Trying to overcome this drawback, some studies have already been developed in order to better understand the effect of the plasma immersion ion implantation, PIII, an alternative ion bombardment procedure, on the properties of plasma polymer films<sup>(5-7)</sup>. According to that, a target material is placed in plasma containing the species to be implanted, and a series of high-voltage negative pulses are simultaneously applied to it. The plasma ions, which are attracted by the target potential, bombard the target surface, promoting electronic excitation, ionization, scission, crosslinking, molecular emission and the creation of radicals, unsaturated bonds, compounds and phases<sup>(8,9)</sup>. As in the conventional beam implantation, such interactions induce compositional and structural changes and, consequently, modifications of surface properties. The parameters of the plasma (power, pressure, exposition time and ion species, among others) and parameters of the pulse (shape, length, magnitude, frequency), as well as the target material, determine the degree of modification induced by the PIII process<sup>(10-12)</sup>.

Aside to the vantages and disadvantages of each ion bombardment approach is the economical appeal of the PIII. Therefore, a series of new practical applications would be created for the plasma polymerized films, if the results obtained with the beam line treatment could be reproduced using PIII. Based on that, the proposal of the present work was to investigate the effect of the PIII, specifically, the argon bombardment time, on the properties of plasma-polymerized a-C:H films, once this parameter affects the overall energy delivered to the coating and is of relevance for practical reasons. For this study, plasma-polymers were synthesized from an acetylene-argon mixture and then treated by argon ions via PIII. Their chemical structure, thickness, roughness, wettability and mechanical properties were evaluated as a function of treatment time.

## MATERIALS AND METHODS

Microscope slides and silicon wafers (Semiconductor Wafer Inc.) cut into rectangular shapes (15 mm × 20 mm) were used as substrates for the growth of a:C-H films. These substrates were ultrasonically cleaned to ensure the good adhesion of the films on the surface. The cleaning procedure is described elsewhere<sup>(6)</sup>.

The films were synthesized by plasma enhanced chemical vapor deposition (PECVD) performed in a plasma system belonging to the Plasma Laboratory of Unesp – Guaratinguetá. The system is composed of a stainless-steel cylindrical reactor with internal electrodes capacitively adjusted. A radio-frequency (RF) power supply with an operating frequency of 13.56 MHz was used to establish the plasmas. A detailed description of the plasma system is provided by Rangel et al.<sup>(5)</sup>. The parameters adopted for PECVD were 12.7 Pa of work pressure (8% of acetylene + 92% of argon), 80 W of RF power and 20 min of deposition time. After the deposition process, the samples were removed from the reactor. In order to do that, argon was used to vent the reactor prior to its opening. Those samples were stored in a dry environment, but in an atmosphere air, until the ion implantation treatment. PIII was performed in the same system, adjusting the conditions to 1.8 Pa of argon pressure, 70 W of RF power and an exposure time ranging from 15 to 120 min. The substrate holder was polarized with negative sawtooth-like pulses with a magnitude, frequency and duration of 25 kV, 30 Hz and 0.15  $\mu$ s, respectively. The procedure used to adjust the pressure in both deposition and implantation processes is detailed elsewhere<sup>(6)</sup>.

A Veeco Dektak 3 profilometer (IFGW – Unicamp) was used to determine the thickness of the as-deposited and treated films, and the presented results correspond to the average of the data acquired at three different positions of the films.

A Ramé-Hart 100-00 goniometer (Unesp – Sorocaba) was employed to evaluate the wettability of the films, measuring the static contact angles of polar (distilled water) and apolar (diodimethane) liquid droplets on the film surfaces. The results are the average of thirty values measured at three different locations of the film surfaces.

The surface chemical structure of the films was investigated by X-ray photoelectron spectroscopy (XPS) using a VG ESCA 300 instrument (UFPR – Curitiba). Mg Ka radiation (1253.6 eV) and a base pressure of  $2.0 \times 10^{-8}$  Pa were used to analyze the samples. The instrument was calibrated to the peak of carbon (C) 1s at 284.6 eV, with a FWHM of 3.0 eV. Line-shape analyses were performed using a least-square deconvolution routine employing line shapes with Gaussian character and a linear base. In these analyses, the sample substrates used were silicon (Si) wafers to distinguish the elements from the films.

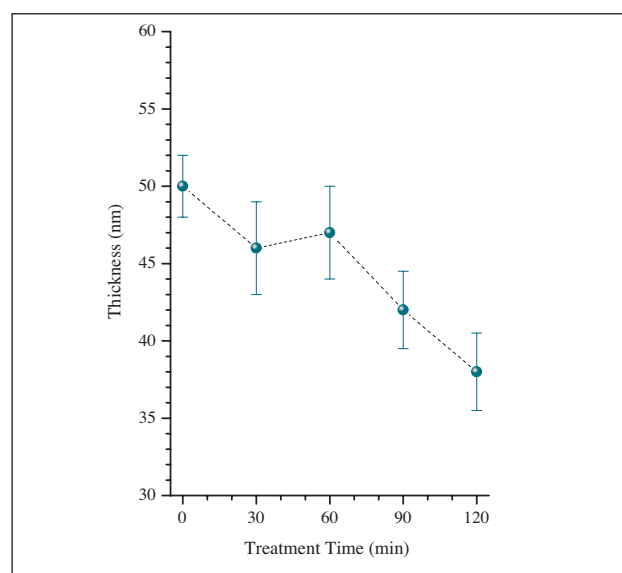
Nanoindentation was employed to estimate the hardness and elastic modulus of the films. A commercially available Hysitron Triboindenter (Unesp – Sorocaba), with a controlled load ranging from 1  $\mu$ N to 10 mN and Berkovich indenter tip, was used to carry out the measurements. The measurements were performed

at eight different positions of each sample using eight different maximum loads (20 – 1000  $\mu\text{N}$ ), resulting in 64 indentation per sample.

An atomic force microscope (AFM) attached to the nanoindenter system was used to measure the surface roughness of the samples. The average roughness was calculated from five measures taken at different surface positions over an area of  $20\ \mu\text{m} \times 20\ \mu\text{m}$ .

## RESULTS AND DISCUSSION

Figure 1 shows the thickness of the samples as a function of treatment time ( $t$ ). As shown, the average thickness of the as-deposited film ( $t = 0$ ) was 50 nm, and the thickness decreased as the implantation time increased.



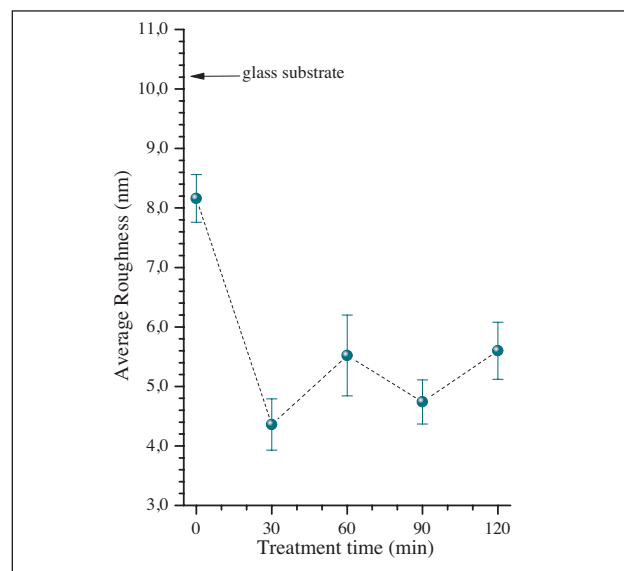
**Figure 1:** Thickness of the plasma-polymerized acetylene films as a function of treatment time. As-deposited sample is shown at  $t = 0$ .

One of the reasons for the observed decrease in film thickness is the ablation of low-molecular-weight species from the surface by physical sputtering. When an ion impinges on the target, its energy is transferred to the structure via atom collision, and this energy transfer continues to neighboring atoms until one of them is emitted from the surface to the plasma. The sputtering process is more pronounced for heavy ions than for smaller ones; thus, this sputtering process is expected to reduce the target thickness during argon ion implantation<sup>(1)</sup>. Another reason for the reduction in sample thickness after ion implantation can be associated to the densification of the film structure<sup>(1,9)</sup> through crosslinking and unsaturation processes. After energy transfer, various physical and chemical processes take place in the polymeric structure, such as electronic excitation, ionization and hydrogen emission, among others<sup>(9,13)</sup>. Such events result in the generation of free radicals or dangling bonds, which lead to the formation of unsaturated double and triple bonds, as well as the crosslinking of neighboring

chains<sup>(9,14)</sup>. It is known that plasma polymers absorb ultraviolet (UV) radiation, which provides enough energy to break their bonds<sup>(1)</sup>, and hence, UV radiation probably also contributes to formation of free radicals. Both sputtering and crosslinking processes occur simultaneously, but one of them may dominate depending on the treatment time. At short times ( $t < 30$  min), the pendant bonds are sparsely distributed on the surface, and consequently, recombination chemical reactions are difficult or impossible to be carried out<sup>(15)</sup>. As result, sputtering may be dominant in reducing the target thickness regardless of the ion species used in the process. On the other hand, with increasing implantation time, the dangling bonds become sufficiently close to one another to allow unsaturation and crosslinking reactions; therefore, these processes may dominate over sputtering, and probably the films can be denser. Considering that the regime for sputtering and crosslinking depends on electronic and nuclear collisions, the balance between the processes depends on the ion species used. Argon atoms are non-reactive and exhibit shallow penetration depths; therefore, their effect on the thickness of plasma-polymers may be less intense than that of smaller and/or reactive atom. This observation is in agreement with results obtained in other studies in which plasma-polymerized acetylene films were treated by nitrogen PIII<sup>(6)</sup> under the same conditions adopted here. However, the general trend is that the thickness of PIII-treated samples diminishes with process time.

The average roughness of the plasma-polymerized acetylene films ( $t = 0$ ) and PIII-treated films as a function of the process time is shown in Fig. 2. As shown, the average roughness of the as-deposited film is 8.2 nm, decreasing by almost 50% after 15 min of implantation.

Even with the constant trend inversions, roughness keeps nearly constant with increasing the bombardment time. Roughness is characterized by peaks and valleys on the film

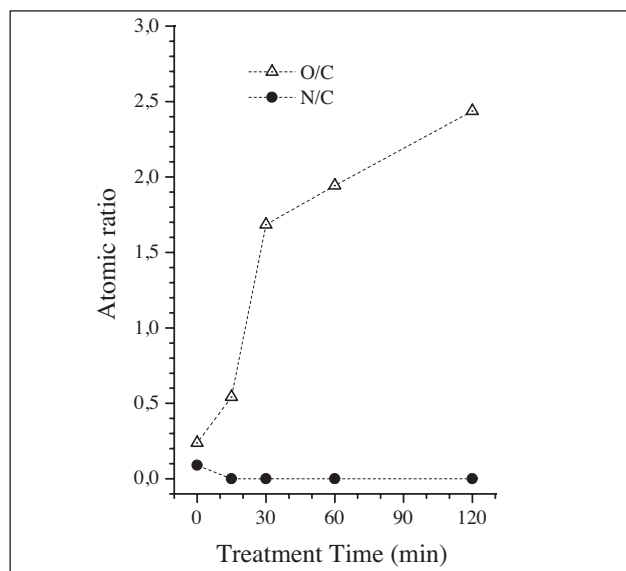


**Figure 2:** Average roughness of the as-deposited ( $t = 0$ ) and treated plasma-polymerized acetylene films as a function of process time.

surface, and it is believed that peak removal occurs during the early stages of the PIII process via sputtering, reducing the height of the peaks. But structural compaction, induced by electronic events, also contributes to the disappearance of the larger scale waviness from the film surface. Thus, both electronic and nuclear events should contribute to the reduction in the roughness upon ion bombardment, and the films become less rough and thinner due to material removal from both the valley and peak areas, but no evidence of micron size craters resulting from localized etching was observed. Another process that may contribute, especially at longer implantation times, is the diffusion of ions<sup>(16)</sup>. The diffusional movement depends on the kinetic energy of particles and therefore increases with temperature. During implantation, argon ions penetrate the target material, reaching depths of approximately 50 nm according to the SRIM simulation program<sup>(17)</sup>. This depth is exactly the thickness of the films prepared here; therefore, these ions may have been located at the film-substrate interface. As a result, if the substrate temperature rises during the PIII process, ion diffusion toward the surface may occur, thereby enhancing the roughness. Similar results have been obtained in plasma-polymerized acetylene films using nitrogen PIII<sup>(6)</sup>.

In XPS survey spectra of the as-deposited acetylene plasma polymeric films, the peaks relative to carbon (C), oxygen (O) and nitrogen (N) were identified. And based on the integrated area under the high-resolution scans of the C 1s, O 1s and N 1s peaks, O/C and N/C atomic ratios were calculated as shown in Fig. 3.

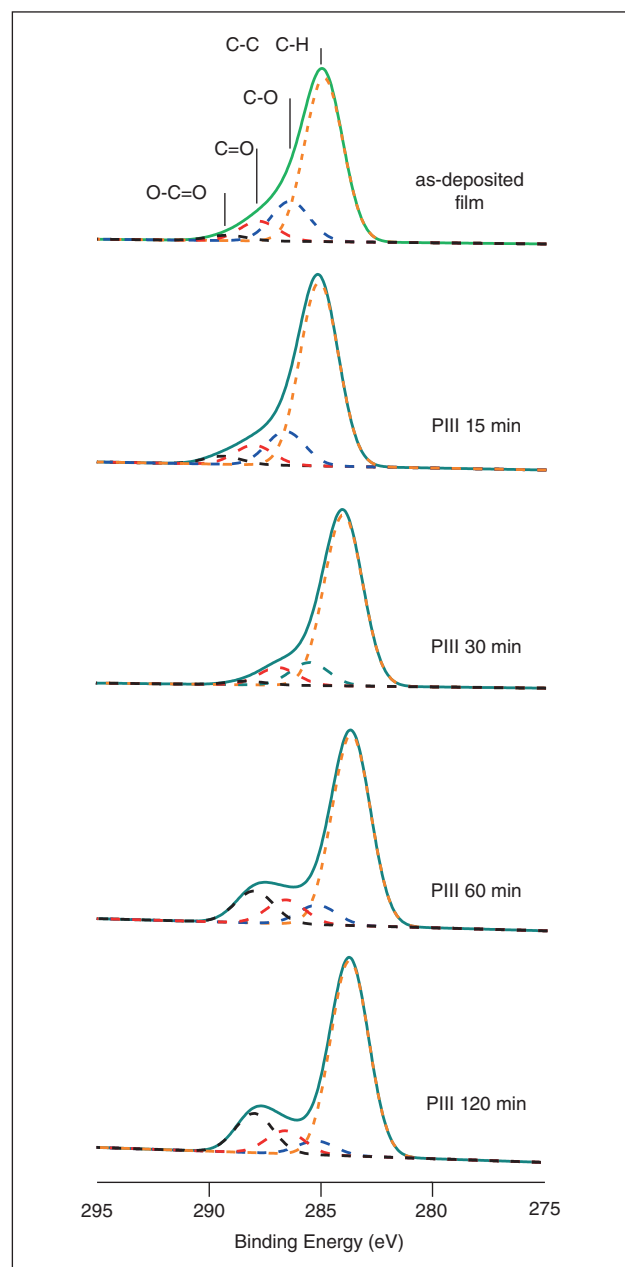
Oxygen and nitrogen gases were not purposely introduced into the deposition process; therefore, their presence is attributed to the post reaction of long-lived radicals trapped in the polymeric structure, particularly when the samples were removed from the plasma reactor<sup>(18,19)</sup>. As can be observed, after argon PIII treatment O/C atomic ratio increases from 0.23 to 2.43, while



**Figure 3:** O/C and N/C atomic ratios as a function of treatment time.

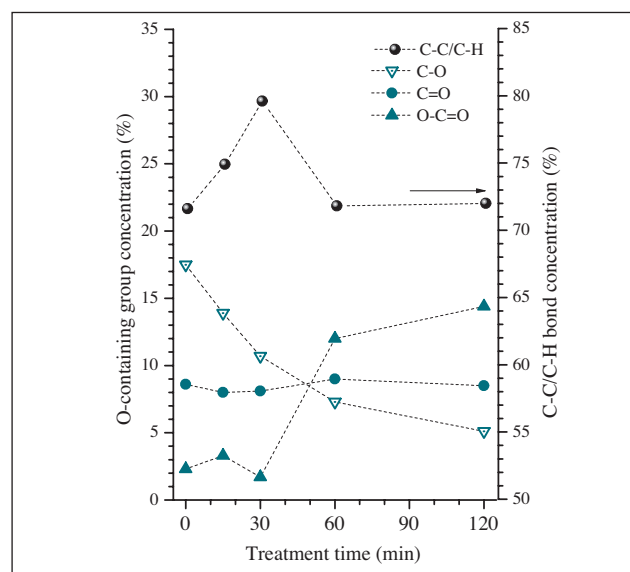
N/C one vanishes probably due to the creation of volatile nitrogen compounds that were etched from the film surfaces. As early discussed, interactions between ions and polymeric structure promotes free radicals or pendant bonds and when those radicals are not passivated by unsaturation or crosslinking processes, they capture oxygen from environment and, evidently, the oxygen proportion is enlarged in the film structure. In this sense, O/C variation is an indicator of the presence of residual radicals in the samples<sup>(15)</sup>.

The C 1s spectra of the plasma-polymerized acetylene films treated for different times with argon ions are depicted in Fig. 4. The analysis of those spectra reveal four distinct carbon bond species: C – C at 284.6 eV, C – O at 286.1 eV, C = O at 287.5 eV



**Figure 4:** C 1s XPS spectra of acetylene plasma polymeric films treated by argon PIII for different times.

and  $O-C=O$  at 288.9 eV.  $C-H$  bonds are not estimated by XPS, but its binding energy probably is overlapped with  $C-C$  bonds at 284.6 eV<sup>(20)</sup> and, as well as  $C-O-H$  bonds can be overlapped with  $C-O$  bonds at 286.1 eV<sup>(21)</sup>. Watching the spectra, the shape of the  $C 1s$  peak is modified as the treatment time increases; it is noticeable the drop in the intensity of the  $C-O$  peak (286.1 eV) and the rise in the intensity of the  $O-C=O$  (288.9 eV). Thus, the bond concentrations were calculated from the integrated area under each component of the  $C 1s$  spectra, and the results a function of treatment time is shown in Fig. 5. As can be observed, at short exposure times ( $t < 30$  min), the  $C-O$  and  $C=O$  bond contents decrease, whereas the  $O-C=O$  bond content shows a slight increment. However, the decrease in the  $C-O$  bond content is seven times greater than that of the  $C=O$  content, demonstrating that double bonds are stronger than  $C-O$  bonds and also suggesting that  $C-O$  bonds may be related to  $C-O-H$  species because hydrogen is more weakly bound. Simultaneously, the  $C-C$  bond content increased within the same time range.

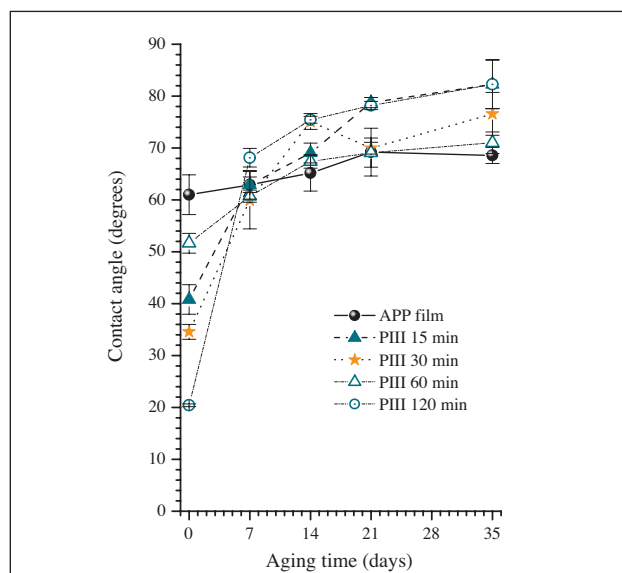


**Figure 5:** Oxygen-containing group and carbon bond proportions as a function of exposure time.

If ion bombardment preferentially induces the breaking of  $C-H$  bonds, because hydrogen is weakly bonded at the chain termination<sup>(1,14)</sup> dangling bonds or free radicals created by hydrogen emission can be consumed by  $C-C$  and  $O-C=O$  bonds, increasing the proportion of these species. Comparatively, the  $C-C$  concentration increased to a greater extent than the  $O-C=O$  concentration, which suggests that the quenching of radicals via crosslinking among the polymer chains dominates over oxidation<sup>(19)</sup>. Since in this structure hydrogen is the weakest bonded species, its emission upon ion bombardment is very prone to occur, as verified and accepted by many researches<sup>(1,9,19,20)</sup>. With increasing treatment time and then the total energy transferred to the structure, the amount of emitted hydrogen is postulated

to growth, establishing a balance between the generation and extinction of oxygen-containing groups. As consequence, the saturation behavior of the  $C-C$  and/or  $C-H$  curve can be ascribed to a mixed effect of the reduction in the  $C-H$  content and the  $C-C$  enrichment.

Figure 6 shows the contact angles of the PIII-treated films as a function of aging time in air. As shown in this figure, the contact angles measured immediately after the deposition varied from 20° to 61°, which indicates the hydrophilic character of the plasma-polymerized acetylene films.

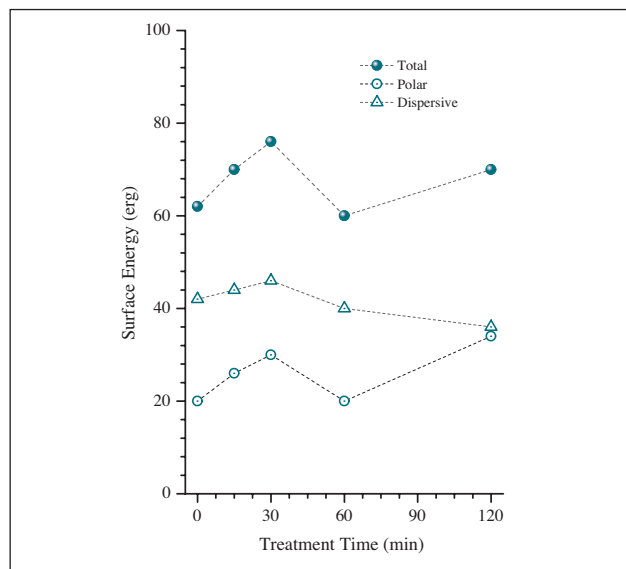


**Figure 6:** Temporal evolution of contact angle of plasma-polymerized acetylene films treated by argon PIII.

The untreated film presented a contact angle of approximately 61°, whereas the other films presented lower contact angles, which seem to be dependent on process time. It is known that during implantation,  $C-H$  bond scission results in hydrogen desorption from the film surface, and dangling bonds trend to establish new reactions, catching oxygen or water vapor from the surrounding environment. This is a common effect of plasma treatment and results in the introduction of polar groups from the surrounding environment onto the surface, increasing its wettability<sup>(21,22)</sup>. Nevertheless, the appearance of polar groups on the surface increases the surface energy, leading to an energy gradient between the film and its environment. In response, immediately after the process, treated surfaces tend to exhibit reconstruction to dilute the higher concentration of polar groups on the surface toward the bulk. Consequently, the wettability of the polymer films decreased with time, as shown in Fig. 6. This reconstruction or hydrophobic recovery is often observed in polymeric materials after a few hours of plasma treatment, but the emission of species from the surface also contributes to it<sup>(19,21,22)</sup>. Surface restructuring is a process driven by the interfacial enthalpy and translational entropy of a system<sup>(23)</sup>. The former is correlated with a higher concentration of polar groups on a polymer film surface, and the



latter is associated with the restriction of the motion of polymer chains at the surface relative to the bulk polymer. Thus, at longer times (days or months) the structure is stabilized, and the surface density of polar groups in the treated films is lower than that of the as-deposited ones, making the films less hydrophilic. In this work, the wettability of the as-deposited film changed slightly after 35 days of aging, from 61° to 68°. On the other hand, all of the argon PIII-treated samples practically lost their highest hydrophilicity after 7 days. Those samples treated for 15 and 120 min showed significant modification immediately after the treatment, but they suffered higher hydrophobic recovery rates. The films treated by argon PIII for 60 min presented a weaker immediate effect and lower recovery rate, while an intermediate extent of evolution was observed for the sample treated for 30 min. After 35 days, all of the treated films presented less hydrophilicity than the as-deposited one, especially those samples treated for 15 and 120 min (82°). A similar result was observed for nitrogen-ion treatment<sup>(6)</sup>. It is known that reconstruction is inhibited by the crosslinking of polymeric chains<sup>(19,22)</sup>, and our as-deposited plasma-polymer acetylene film appeared to have been highly crosslinked. The slight decrease in the wettability of that sample probably occurred due to the emission of polar groups from the film surface. The surface enthalpy is determined by the surface energy of the samples. Fig. 7 shows the surface energy measured immediate after argon ion implantation, as well as its two components, polar and dispersive. The observed increase in total energy is almost the same as that observed for the polar component, which confirms the introduction of polar groups onto the surface.

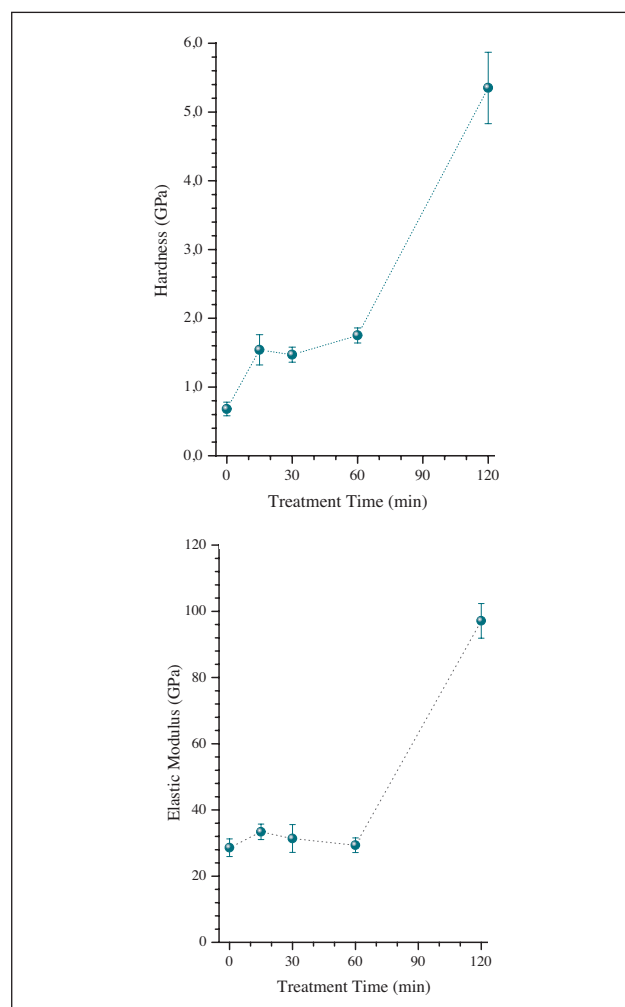


**Figure 7:** Surface energy of the films treated by argon PIII as a function of treatment time. As-deposited film is presented at  $t = 0$ .

As discussed in the XPS analysis, it appears that longer treatment time leads to chemical reaction saturation; therefore, in this case the dominant mechanism of argon ion implantation is probably sputtering, which causes the emission of functional

groups from the surface and, consequently, the decay in surface energy. Moreover, at further treatment times, new radicals or pendent bonds are created on the surface and the introduction of new polar groups restarts, increasing the surface energy. The dispersive energy slightly increases over short treatment times and decreases at longer times. Some studies consider that this component is an indication of the crosslinking degree of plasma-polymers<sup>(24,25)</sup>. In this sense, treatments shorter than 30 min enhance crosslinking, whereas longer treatments induce bond scission, which is probably the reason why the polar component is diminished due to functional groups emission. Notwithstanding, this crosslinking degree may be related to the shallow layer of the samples, and this degree of crosslinking should not match the extent of crosslinking in sublayers, where argon ions may promote a higher degree of ionization according to SRIM simulation. In conclusion, argon ion implantation can be applied to modify the functionality of plasma-polymerized acetylene films, even over short treatment times.

The elastic modulus and hardness of the films as a function of treatment time are shown in Fig. 8 (a, b), respectively. These



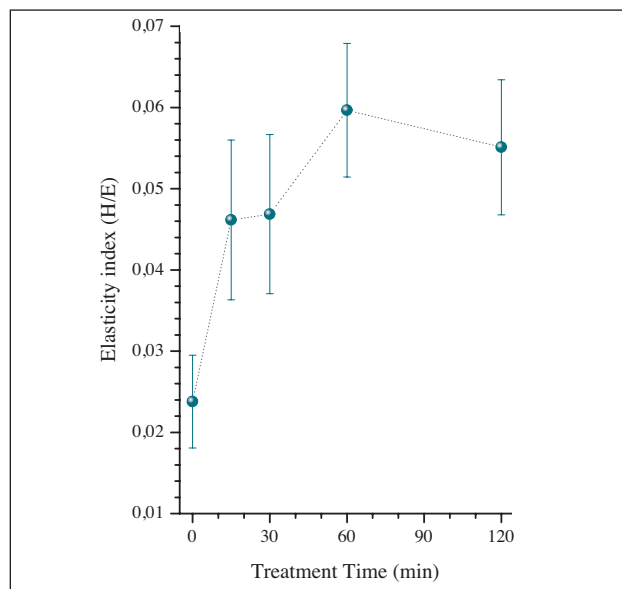
**Figure 8:** Hardness (a) and elastic modulus (b) of the as-deposited ( $t = 0$ ) and treated plasma-polymerized acetylene films as a function of process time.

measurements were obtained at most at 20% of the film thickness unless for the sample exposed to the longest bombardment time (120 min) in which the mechanical properties were derived at 6 nm (12% of the film thickness) a region still free from the substrate interferences. As shown in Fig. 8a, the elastic modulus of the as-deposited film was 28 GPa, which increased to 33 GPa for samples treated for 15 min, indicating a slight improvement in film rigidity. These values are significantly higher than the modulus of conventional polymers (<10 GPa) and lower than that of the glass substrate (74 GPa). But at the longest process time, the elastic modulus reached 97 GPa.

In Fig. 8b, the hardness is observed to increase mainly after 60 min of process. The as-deposited sample presented a hardness of 0.68 GPa, which increased to 1.8 GPa after 60 min of implantation. In the longest treatment, the hardness suddenly increased, reaching 5.35 GPa. Therefore, upon the most intense bombardment condition employed here, the films become harder than stainless steels (2 – 3 GPa)<sup>(14)</sup>. The enhancement in the elastic modulus and hardness is related to that in the extent of crosslinking, although the unsaturation process may also contribute. Higher hardness values (10.6 GPa) were already reported for Ar<sup>+</sup> bombarded plasma polymers derived from acetylene using conventional beam implantation<sup>(2)</sup>. In that case, however, the achieved crosslinking degree was substantially higher due to the energies and fluences involved in the process (150 keV, 1021 m<sup>-2</sup>). According to the XPS analysis, the saturation of the C – C, C – H and C = O bond concentrations at long treatment times is an indication of both processes. The stabilization of such bonds suggests that the radicals created in the structure recombine via unsaturation or chain crosslinking, probably promoting the densification of the sample. Because the elastic modulus and hardness of the plasma-polymers are enhanced by PIII treatment, it is expected that the tribological resistance of the samples is changes as well. The ratio between the hardness and elastic modulus (H/E), referred to as the plasticity index, is significant in determining the limit of elastic behavior of a contact surface, which is used to predict the wear rate of materials<sup>(26,27)</sup>. The plasticity index of the films is shown in Fig. 9. As can be observed, the index tends to increase with increasing process time. The sample treated for 60 min shows a higher index and would be tribologically more resistant than the other samples. Shorter process times ( $t < 30$  min) lead to an index as good as that achieved after the longest process time. Therefore, considering the nanoindentation results, even short-duration argon PIII could produce acetylene plasma polymeric films mechanically more resistant.

## CONCLUSIONS

Acetylene plasma-polymerized films can be modified by argon plasma immersion ion implantation, whose effect is more pronounced after long treatment times. Following bombardment,



**Figure 9:** Plasticity index of the as-deposited ( $t = 0$ ) and argon PIII acetylene films as a function of process time.

the films became thinner and smoother, probably due to the combined effect of sputtering and crosslinking. The hydrophilic character of the films was greatly enhanced immediately after the process, but upon aging under atmospheric conditions, all of the samples lost their high hydrophilicity at different recovery rates. The wettability of the samples treated for 15 and 120 min were more affected by the aging. The hardness and elastic modulus of the films increased after argon PIII, but the sample treatment featuring the longest exposure time (120 min) led to the highest mechanical properties. The wear resistance of the samples is expected to improve following bombardment owing to better plasticity index. The results obtained in this work demonstrate that argon PIII can be an efficient treatment in enhancing the mechanical properties of acetylene plasma-polymer films.

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