Surface modification of white PVC polymer by different plasma immersion techniques

Modificação superficial do polímero PVC branco por diferentes técnicas de imersão em plasma

Péricles Lopes Sant'Ana[1,*], José Roberto Ribeiro Bortoleto[1], Nilson Cristino da Cruz[1], Elidiane Cipriano Rangel[1], Steven F. Durrant[1]

ABSTRACT

Polymer substrates have several distinct advantages, such as, robustness, low density, impact resistance, and conformity over glass substrates for optical applications. Some applications are impeded, however, owing to its low adhesion to thin films, surface roughness, and low gas permeability. In this work, the wettability and the surface morphology of Poly(Vinyl) Chloride, PVC, samples were modified by plasma immersion. PVC was chosen because of its already wide use and low cost: PVC is used in floor coverings, plumbing, electrical insulation, hoses, containers, and other accessories. In this work, plasma immersion was used to modify the chemical structure of white PVC, producing high values of contact angles ($\theta > 100°$) in fluorine plasmas, measured immediately after treatments, and until 30 days after. Also, it was detected low values of contact angles ($\theta < 50°$) in nitrogen plasmas. Atomic Force Microscopy revealed smooth surfaces, whose roughness, R_z, was less than ~13 nm, except for plasma immersion cathode, which yielded a R_z of ~213 nm.

Keywords: PVC, Plasma Immersion, PIII, Contact Angle, AFM.

RESUMO

Os substratos poliméricos possuem várias vantagens distintas, como robustez, baixa densidade, resistência ao impacto e conformidade sobre substratos de vidro para aplicações ópticas. Algumas aplicações são impedidas, no entanto, devido à sua baixa adesão a filmes finos e resistência, rugosidade da superfície e baixa permeabilidade ao gás. Neste trabalho, a molhabilidade e a morfologia da superfície de amostras de policloreto de vinila (PVC) foram modificadas por imersão em plasma. O PVC foi escolhido devido ao seu uso já amplo e baixo custo: o PVC é usado em revestimentos para pisos, encanamentos, isolamento elétrico, mangueiras, contêineres e outros acessórios. Neste trabalho, a imersão em plasma foi utilizada para modificar a estrutura química do PVC branco, produzindo altos valores de ângulo de contato ($\theta > 100°$) em plasmas de flúor, medidos imediatamente após o tratamento e até 30 dias após. Além disso, foram detectados baixos valores de ângulo de contato ($\theta < 50°$) em plasmas de nitrogênio. A microscopia de força atômica revelou superfícies lisas, cuja rugosidade, R_z, era inferior a ~13 nm, exceto pela imersão no plasma com rf polarizada no catodo, que produziu um valor de R_z de ~213 nm.

Palavras-chave: PVC, Imersão em Plasma, IIIP, Ângulo de contato, AFM.

INTRODUCTION

The non-equilibrium plasma is used in many technological applications of interest to readers of this journal. The reason is that the gas molecules and ions, the "heavy" particles, can be kept "cold" (near ambient temperature, 300 K), while the electron gas can be made very "hot", well above 10^4 K. These highly energetic electrons are responsible for initiating chemical reactions by breaking covalent chemical bonds of ground-state gas molecules in the course of collision-induced energy transfer. Through the judicious selection of gas or gas mixture, method of energy input, and reactor geometry, one can optimize the conditions for a very wide range of technological applications, including for polymers.

Polymers are characterized by an inherently low surface energy (or surface tension), which accounts for why liquids form bead-like drops instead of wetting the surface, and why coatings tend to adhere only poorly, if at all. However, when the surface is functionalized by exposure to suitable plasma,[1] its energy can be raised and the above-mentioned drawbacks can be resolved. These principles find application in all industries that make extensive use of plastics, be it in packaging, health care, textiles, etc.

This article discusses the effects of the plasma composition, plasma treatment techniques, and radiofrequency power on the optical and morphological properties of the PVC surface by plasma immersion and plasma immersion ion implantation. Surface morphology influences wettability, and is therefore also investigated in this work. A suitable technology for ion implantation of polymers is plasma immersion ion implantation (PIII), which is also applied to many other materials[2,3]. This technology offers the possibility to independently change the current density during the pulsed ion implantation process as well as the average dose of the incident ions. Moreover, PIII offers the possibility of large-area ion implantation at reasonable cost.

Radiofrequency plasma technologies using fluorinated gases are currently employed in materials science presenting advantages such low-temperature reactions (in many cases the treatment can be achieved at ambient temperature, which avoids the thermal degradation of the material). Direct fluorination is an effective method for improving the surface properties of pristine polymer materials, including barrier properties, adhesion, printability, gas separation properties, chemical resistance, antibacterial properties (biocompatibility), etc.[4] In this work, surface wettability of white PVC was measured via contact angle measurements and surface morphology studied using atomic force microscopy for three different electrical configurations of the plasma immersion systems, aiming to obtain, hydrophobic or hydrophilic surfaces and low roughness.

EXPERIMENTAL PROCEDURE

The experimental setup used consists of a stainless-steel vacuum chamber (30 cm in height and 15 cm of diameter) with two horizontal parallel circular internal electrodes of equal dimensions (11 cm of diameter), separated by 11 cm. Substrates were placed on the stainless-steel electrode and the system was evacuated by a rotary pump, model EM-18 from Edwards (18 m^3/h), down to a pressure of ~2,66645 Pa. Needle valves of nylon were employed to control the gas feed (both with high purity: ~99.95%), and a capacitive pressure sensor, model Pirani, to monitor the chamber pressure. Twenty-seven samples of white PVC (2.5 cm × 1.5 cm, and 1 cm of thickness) were directly exposed to the plasma environment established by the application of radiofrequency power (13.56 MHz) coupled to match in box circuit from Company Tokyo Hi Power. For these treatments, sulfur hexafluoride (SF6) and nitrogen gases were used as sources of fluorinated and nitrogen plasma, respectively, under different RF plasma immersion modes (at low and high energy ion implantation) and three different discharge conditions. A treatment time of 300s was used at a temperature of 60.0 ± 1ºC (~358 K inside reactor), as measured using a digital thermometer.

The substrates were treated in three different RF plasma immersion modes, as indicated in previous literature[5, 6-9], and summarized as follows:

(i) *The sample holder and the chamber walls were grounded while rf power was connected to the opposite electrode: PI anode.*
(ii) *The rf power was connected to the sample holder while the other electrode and chamber walls were grounded: PI cathode.*
(iii) *The rf power was connected to the other electrode while negative pulses of high voltage were applied to the substrate holder: PIII.*

The system accessories employed for these experiments are: (1) cylindrical stainless-steel chamber with two circular internal electrodes; (2) vacuum pump; (3) needle valves; (4) pressure gauge; and (5) radiofrequency source coupled to an impedance-matching circuit (matching box). High voltage source model RUP-6 and oscilloscope TDS from Tektronics company were employed for PIII experiments. The high negative voltage was -2400 V, frequency of 300 Hz and cycle time, calculated as being: $t_{on}/t_{on} + t_{off}$ and were fixed to 30μs for all PIII experiments. Fifteen samples (2.5 cm × 1.5 cm, and 1 cm of thickness) were treated with fluorine plasmas and twelve samples were treated with nitrogen plasmas. Figure 2 shows a photograph of the plasma treatment or deposition system employed, while Table 1 shows the conditions applied in these experiments.
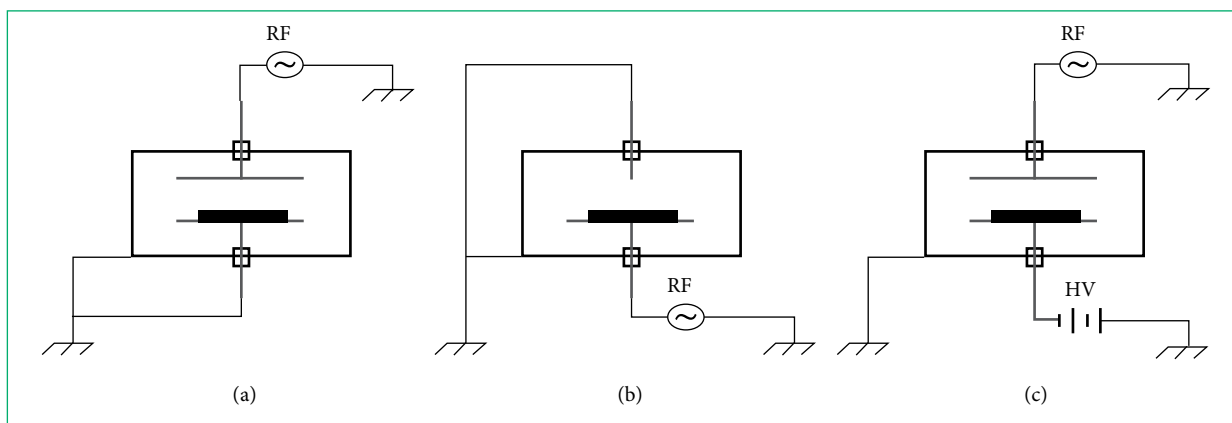
Figure 1: Electrical configuration of plasma immersion techniques applied in our experiments: (a) Plasma Immersion anode; (b) Plasma Immersion cathode; (c) Plasma Immersion Ion Implantation.[5,6,7,8]
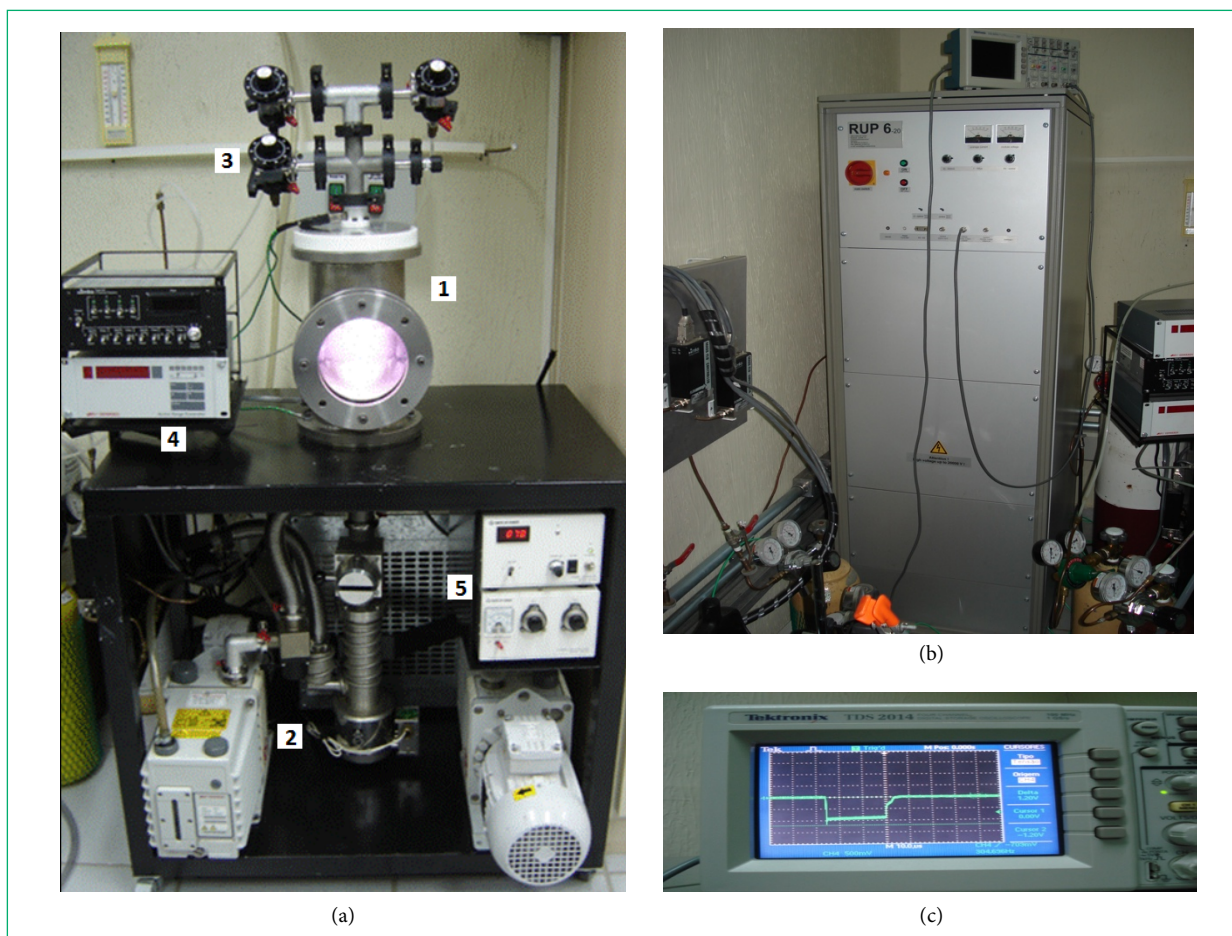

Figure 2: Photograph of the treatment or deposition system used for these experiments: in (a): (1) cylindrical stainless-steel chamber with two circular internal electrodes, (2) vacuum pump, (3) needle valves, (4) pressure gauge, and (5) radiofrequency source coupled to an impedance-matching circuit; (b) High voltage source; (c) Digital Oscilloscope recording in situ, pulses squares of waves on PIII.

Samples were characterized immediately after treatment. Contact angle measurements were made using a Goniometer (100-00, Ramé Hart) by sessile drop. There was made, three drops for each sample and the software calculates 30 measurements, being 10 for each drop, A standard deviation was acquired for each sample. Surface morphology was examined using atomic force microscopy (XE-100, Park Instruments) operating in air. Both 10µm x 10µm and 1µm x 1µm images were acquired and the surface roughness. For that, PVC samples were characterized by AFM, and software of equipment calculates root mean square roughness for all images.

Table 1: Plasma immersion procedure conditions for the PVC samples.

Substrate	PVC (ρ = 1.3 g/cm3)
PI parameters	
Gas system	SF6 and N2
Base pressure (Pa)	2,6665
Work pressure (Pa)	300
Treatment time (s)	25 to 150
RF power (W)	358
Temperature (K)	
PIII parameters	
High voltage (V)	-2400
Cycle time (µs)	30
Frequency (Hz)	300

RESULTS AND DISCUSSION

Wettability

Figure 3 shows wettability as a function of rf power obtained applying PI and PIII. In (a) using SF_6 plasmas (b) using N_2 plasmas.
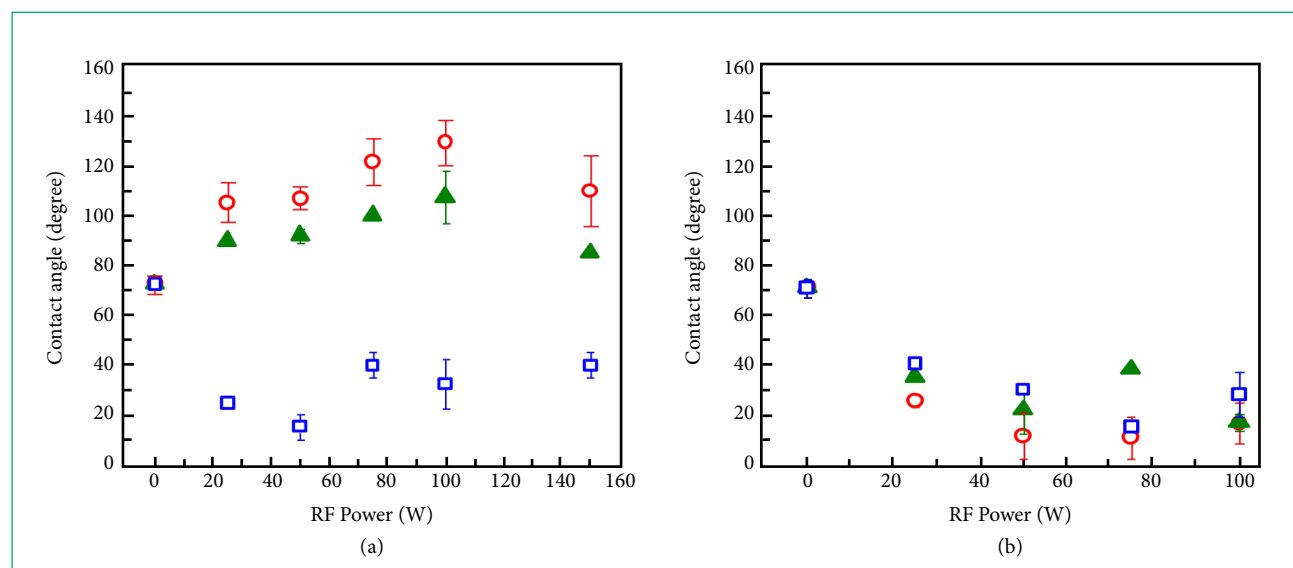

Figure 3: White PVC treated by: (a) SF_6 plasma and (b) N_2 plasma. The symbols on the graphs (Figure 1) are associated with the following plasma techniques: ○ (PI cathode), △ (PI anode), and ▭ (PIII), with respective standard deviation.

Contact angle measurements show that the wettability depends on the plasma technique applied. Plasma immersions at low energy decreases contact angles, while plasma immersion ion implantation decreases them, even in the fluorine-containing plasma. In this case, there are no chemical bonds between fluorine and the PVC substrate, since oxygen and water vapor from the ambient atmosphere are known to attach to the surface after treatment, therefore, increasing the hydrophilic behavior of PVC surface.

Initially, comparative analyses between the three techniques were done. Thus PVC was treated for 5min at 50 mTorr of SF_6 at rf powers of 25 W to 50 W. The parameters of PIII were 2400 V, 300 Hz and 30 µs. It is known that PI increases contact angles of samples for rf powers of up to 100 W. On the other hand, PIII decreases contact angles of samples at low RF power. The highest value of 140º occurred at 100 W. Treatment by plasma immersion changes the surface chemical structures. Thus PVC treated by PI became structurally similar to PTFE, whose contact angle, according to Braskem, is 126º. Figure 4 shows the chemical mechanism of activation on PVC using SF_6 and N_2 plasma, creating new radicals.
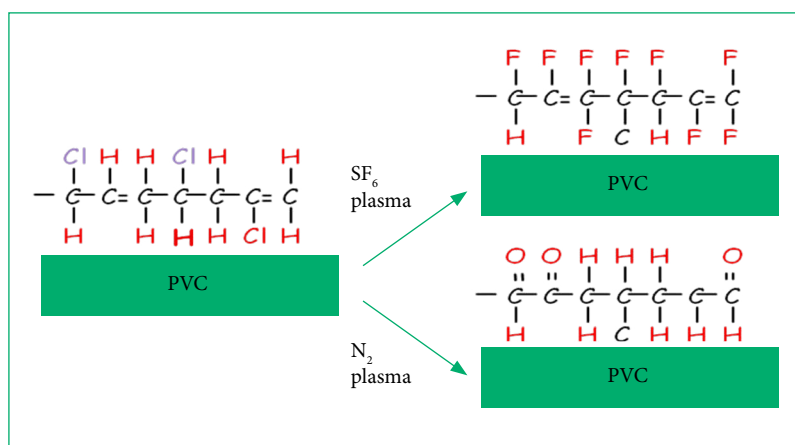
Figure 4: Chemical mechanism of activation on White PVC when treated by plasma immersion using: SF_6 plasma and N_2 plasma. H atoms are displaced by fluorine or oxygen atoms, producing CF or CO bonds.

Although C-F bonds are polar, this species on the surface of a material induces hydrophobicity. After fluorine insertion into the polymer backbone, the surface becomes hydrophobic. The repulsion between the oxygen in the water and the fluoride surface is greater than the attraction of the fluorine for hydrogen, which implies a non-chemical attraction between the fluorinated surface and the test fluid. The process of fluorination results in a substantial change of the chemical composition of white PVC. Owing to a relatively high C–F bond energy inside fluorinated layer, most of Cl or H-atoms are easily replaced for F-atoms, and double bonds are saturated with fluorine with formation of C–F bonds.

For comparison, a new series of treatments were made, maintaining the parameters fixed, except for rf power, which was applied only at 25 and 100 W. If we analyze Fig. 5, regarding the aging time to thirty days for white PVC treated in SF_6 plasma, it is possible to observe a chemical evolution, independent of applied rf power. These experiments were replicated to check repeatability.
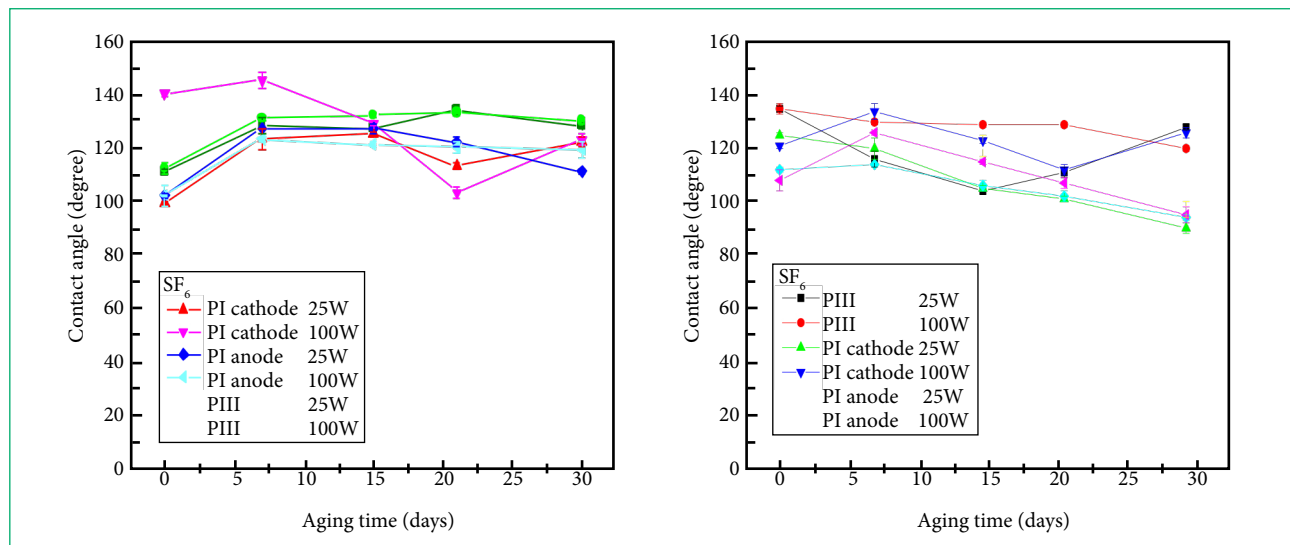

Figure 5: White PVC treated in two repeated series using SF6 plasma, for thirty days, summarizing: 6 experiments for each series in three different plasma immersion techniques. In all twelve treatments, the rf power was 25 and 100 W. Pressure of SF6 was 6.66 Pa, treatment time of 300s and temperature of 60 ºC (298 K). PIII parameters were kept constant: V = -2400 V, the frequency was 300 Hz and the cycle time was 30μs.

In all cases, PVC exhibited the same behavior, for all Plasma Immersion techniques. Polar groups can shift on the PVS surface upon aging. The observed small variation in the initial contact angle can be attributed to small initial differences in surface roughness.

Considering the chemical evolution of the material, some CF bonds are lost, and some retained, leading to a small reduction in θ. Rotation of chemical groups into the surface is also a recognized mechanism of changes in surface contact angle upon aging. At higher power it is also expected that ion bombardment is more effective, producing more dangling bonds, allowing the approximation of the neighboring chains.

The incorporation of fluorine resulted in the formation of different functional groups on the surface, which can be attributed to CF, CHF, CF_2, and CF_3 [10]. However, when changing the polarization of the rf power, that is, PI anode technique, there is no acceleration of ions towards samples set on the lower electrode, so this accounts for the reduction in contact angle, although samples are exposed to an SF_6 plasma. It is suggested that fluorination by plasma immersion resulted in disruption of C–H bonds followed by fluorine atom addition and a tendency to saturation of double (conjugated) C=C bonds with fluorine. C–N bonds are broken and fluorine atoms are attached to those of carbon.

Under the same conditions, PIII treatment produces hydrophilic surfaces [10]. The smallest value, ~15°, occurred at 50 W, caused by oxygen incorporation. Residual oxygen forms chemical bonds with free radicals during the plasma process. Post-treatment reactions with oxygen or water vapor or both are also known to occur. The concentration of CO-containing groups inside the fluorinated layer does not depend on its thickness and is increased at greater oxygen concentrations in the fluorinating mixture, even if O is provided by the ambient atmosphere after vacuum breaking.

It is suggested that the high energy acceleration of positive ions toward the lower electrode promotes higher rates of sputtering or etching or both. Also, the high temperature resulting from the greater bombardment can inhibit the incorporation of fluorine into the surface of polymeric substrates because it reduces the adsorption of precursor species. Thus, changes in θ were caused by the dynamics of adsorption and desorption on the surface, which induce compositional and structural changes. On exposure to ambient conditions, the treated surface readily incorporates oxygen or water vapor or both on active surface sites, and the high temperature acts as a catalyst for oxidation processes, which explain the reduction in θ after PIII treatment in a heated environment.

To analyze the effect of plasma composition, treatments using nitrogen were undertaken. Initially, 50 mTorr of N_2 was used for 5min for rf powers from 25 W to 100 W. Parameters for PIII were 2400 V, 300 Hz and 30µs. The change in the surface hydrophilicity is caused by the replacement of C–C or C–H group on the surface of PVC by C–O or C=O groups [11-15]. These radicals may take part in reactions resulting in scission of polymer chains and formation of polar groups.

Surface roughness

To investigate the morphology of PVC, as shown in Fig. 6, AFM images (10µm × 10µm) were taken. The roughness of the non-treated PVC (a) is 4.38 nm, typical of conventional polymers [16]. According to Fig. 4(a), virgin PVC possesses a high density of *pinholes* [17], which is caused by the absence of polymeric chains in those regions. These *pinholes* have depths of a few nanometers, being deeper than the R_{rms} of PVC (4.38 nm). According Fig. 6(a), the *pinholes* have depths of some tens of nanometers, that is many times the RMS roughness of PVC (4.38 nm). Concerning PVC treated by plasma immersion, Fig. 6(b), there was a considerable increase of roughness, about ~50 times, owing to ion bombardment. This reinforces the explanation of the increase in hydrophobicity since the area available to accept C-F bonds increased. Increased cross-linking reduced the presence of pinholes, as seen in Fig. 6 except for PI at 100 W, in which the sample did not yield pinholes (dark points). The white spots on the images are surface peaks.
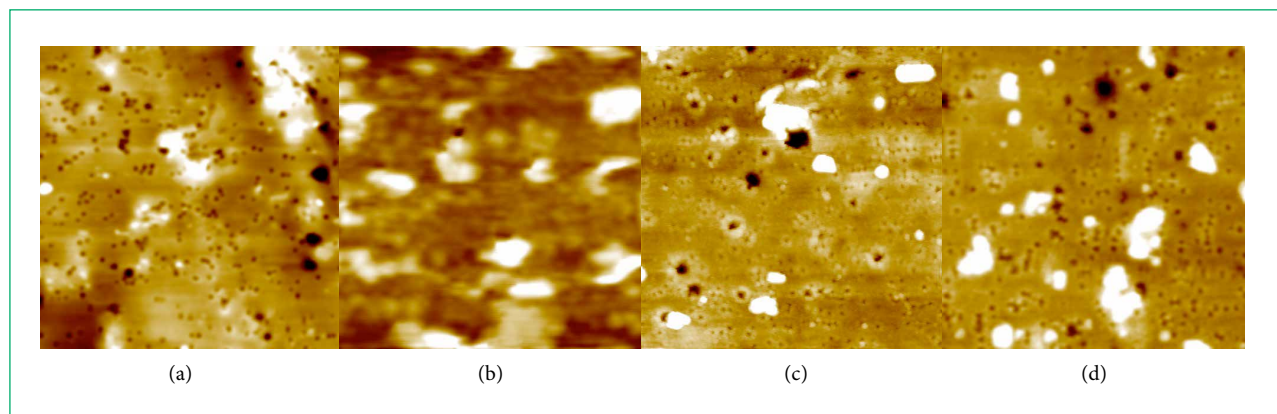

| (a) | (b) | (c) | (d) |

Figure 6: AFM images. SF_6 plasma treatment (a) PVC virgin, R_z = 4.38 nm (b) Plasma immersion cathode, 100W, R_z = 213.00 nm (c) PIII 25W, R_z = 6.14 nm; and (d) PIII 100W, R_z = 12.59 nm.

In relation to virgin PVC, PIII increased surface roughness, from 4.38 to 6.14 nm and 12.59 nm, respectively, for samples treated in rf powers of 25 W and 100 W. For treatment by PI cathode, we believe that high ion bombardment can break Hydrogen and Chlorine atoms, which can be liberated from the polymer, causing cross-linking, resulted in recombination in form of covalent bonds between carbon atoms from neighbor chains. For engineering applications, the degree of cross-linking and scission as well the depth of the modified layer can be tailored by the electronic-to-nuclear interactions by a judicious choice of ion species and ion energy [17]. For two

situations, Fig. 6(c) and 6(d), it is suggested that there was no significant reduction in the density of pinholes, representing a relatively low number of lateral links, that is, a lower degree of intertwining. Two factors were instrumental in the increase of hydrophobicity: (i) the degree of fluorination; (ii) the surface roughness.

The degree of wetting of the samples immediately after treatment has its effect amplified by the increased surface roughness, which increases the area available for ions or even for neutral species from the plasma to bind chemically with the surface atoms. On the other hand, the main mechanism responsible for the hydrophilic behavior of the samples treated with N_2, is the incorporation of polar groups[8,10]. The reactor also influences the degree of ionic bombardment.

In PIII, ions are projected into the polymer matrix in a discrete quantity, lodging in its vacancies (regions not occupied by atoms or molecules). If we consider that the concentration of ions in plasma is 5 orders of magnitude lower than the neutral particles, plasma is rarefied. Considering also that the PIII under this condition did not change its shape and roughness values significantly, it seems that the pulse applied has less (or no) effect compared to the effect of power.

CONCLUSION

Modifications produced by plasma treatment of white PVC improved wettability and retained low roughness, except for PI at 100 W, once this condition yield on PVC, relatively a moderate roughness, (213.0 nm) in relation to PVC surfaces treated by PIII on the same 100 W (12.5 nm). Moreover, the hydrophobicity of PVC surfaces was increased by SF_6 plasma treatment; while the hydrophilicity of PVC surfaces was increased using N_2. Two factors were instrumental in the increase of hydrophobicity: (i) the degree of fluorination; (ii) the surface roughness. The degree of wetting of the samples immediately after treatment has its effect amplified by the increased surface roughness, which increases the area available for ions or even for neutral species from the plasma to bind chemically with the surface atoms. On the other hand, the main mechanism responsible for the hydrophilic behavior of the samples treated with N2 is the incorporation of polar groups10. Treatment using nitrogen did not significantly introduce nitrogen, but considerable amounts of oxygen were present. The AFM images show pinholes typically present in PVC surfaces are only suppressed when this mode is employed. Hydrogen and chlorine atoms may also be liberated from the polymer, causing cross-linking between neighbor chains. As a result of the small instability of the species generated during and after plasma modification, however, the hydrophilic properties achieved by plasma surface modification are lost under some conditions. This process is well known as *hydrophobic recovery*[10]. Changes in contact angle with aging can be much smaller for polymers that contain many cross-links since these limit the mobility of polymeric chains and therefore impede the reorganization of polar groups. For engineering applications, the degree of cross-linking and scission as well as the depth of the modified layer can be tailored by the electronic-to-nuclear interactions by a judicious choice of ion species and ion energy, and we strongly recommend these discussions for the next experiments.

ACKNOWLEDGEMENTS

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