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Study of wettability and optical transparency of pet polymer modified by plasma immersion techniques

Estudo da molhabilidade e transparência óptica do polímero PET modificado por técnicas de imersão em plasmas

Péricles L. Sant'Ana[1], José Roberto Ribeiro Bortoleto[1], Nilson C. da Cruz[1], Elidiane C. Rangel[1], Steven F. Durrant[1]

ABSTRACT

Polymers substrates have several distinct advantages, such as ruggedness, robustness, ultra-lightness, conformability, and impact resistance over glass substrates for optical applications. However, it is required high transparency, proper surface roughness, low gas permeability and high transparent electrode conductivity of the plastic substrate for commercial applications. In this work was analyzed the surface morphology of polymer samples modified by plasma immersion techniques. Polyethylene Terephthalate (PET) polymers were treated by different RF plasma immersion modes (at low and high energy ion implantation) and discharge conditions. Sulfur hexafluoride (SF_6) and nitrogen (N_2) gases were employed as a source of fluorine and inert plasma, respectively. Wettability surface shows that, it is possible to reach either high or low contact angle values, ($10^o < \Theta < 130^o$), depending on the plasma technique and gas employed. The surface morphology was measured with atomic operating on air. Both 10 × 10 μm and 1 × 1 μm images were acquired and the surface roughness was characterized in terms of the root mean square roughness, Rz, for both imaged areas. In general, the smoothness of PET was maintained for some plasma treatments. Optical Transmittance, T (λ), was performed using a UV-Vis-NIR spectrometer ranging from 190 nm to 3300 nm. The results show that the low energy ion implantation is more efficient to promote the loss of T (λ) at visible light, making the PET surface hydrophilic, even in fluorine plasmas. The treatments were satisfactory, daring to maintain, or even, to increase the PET transparency at visible light in restrict conditions.

Keywords: Wettability; AFM; Optical transmittance: PET; Plasma

RESUMO

Os substratos poliméricos possuem várias vantagens distintas, como robustez, ultra-leveza, conformabilidade e resistência ao impacto em substratos de vidro para aplicações ópticas. No entanto, é necessária alta transparência, rugosidade adequada da superfície, baixa permeabilidade ao gás e alta condutividade de eletrodos transparentes do substrato plástico para aplicações comerciais. Neste trabalho foi analisada a morfologia superficial de amostras de polímeros modificadas por técnicas de imersão de plasma. Os polímeros de tereftalato de polietileno (PET) foram tratados por diferentes modos de imersão de plasma de RF (em implantação de íons de baixa e alta energia) e condições de descarga. Os gases de hexafluoreto de enxofre (SF_6) e nitrogênio (N_2) foram utilizados como fonte de flúor e plasma inerte, respectivamente. A molhabilidade mostra que, é possível atingir valores de ângulo de contato altos ou baixos ($10^o < \Theta < 130^o$), dependendo da técnica aplicada ao tratamento a plasma e do gás empregado. A morfologia da superfície foi medida com a operação atômica no ar. As imagens de 10 μm × 10 μm e 1 μm × 1 μm foram adquiridas e a rugosidade da superfície foi caracterizada em termos da rugosidade quadrática média da raiz, Rz, para ambas as áreas das imagens. A Transmitância Óptica, T (λ), foi realizada usando um espectrômetro UV-Vis-NIR variando de 190 nm a 3300 nm. Os resultados mostram que a implantação de íons de baixa energia é mais eficiente para promover a perda de T (λ) na luz visível, tornando a superfície do PET hidrofílica, mesmo em plasmas de flúor. Os tratamentos foram satisfatórios, ousando manter, ou mesmo, aumentar a transparência de PET na luz visível em condições restritas.

Palavras-chave: Molhabilidade; AFM; Transmitância óptica; PET; Plasma.

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INTRODUCTION

Polymers fluorinated by plasma have been applied in many processes due to certain properties such as flexibility, lightness, low electrical and thermal conductivity(1). However, several applications are still restrict due to softness, low adhesion and corrosion resistance(2). Therefore, a treatment able to change the surface properties of the polymers without changing bulk properties can be attractive, once the materials results will meet a lot of commercial applications.

In particular, the PECVD technique (*Plasma Enhanced Chemical Vapor Deposition*)(3,4) allows to obtain thin films with a wide range of properties through the control of process parameters. The examples are the layered insulating / conductive (with controlled thickness) which are used in the manufacture of electronic devices(5), transparent films suitable for application such as optical windows, anti-reflective layers, coatings of lenses and/or sports glasses(6), biocompatible films(7) and hydrophobic materials suitable for applications in food packaging and / or solar cells(8).

More intense changes are obtained when the sample exposed to plasma is polarized pulses with high negative voltage, thus attracting the positive ions. The interaction of these energetic ions with the atoms of the solid can cause excitation, ionization, fragmentation of chemical bonds, issuance of species and atomic displacements, inducing compositional changes and structural rearrangements. This process is known as immersion ion implantation in Plasma (PIII) and was created by Conrad(11) and Tendys(12) to overcome certain limitations of the conventional implantation with ion beams. Works in the literature demonstrated the efficiency of the PIII tracked changes in the properties of polymeric materials(13-15).

However, the organic light emitting diodes (called OLEDs), require a transparent and conductive (TCO) electrode not only for the injection of charge carriers but also not to block the output of light emitted. In this context, to fully exploit the flexibility of large area electronic devices based on this technology (e.g., TV monitors, neon signs and even flexible solar cells), it is essential that the deposition of TCO be made of plastic substrates, which automatically prohibits the use of processing techniques at high temperatures. In this case, deposition techniques of treatment with low temperatures, which emphasize the various techniques of the plasma, become essential for technological progress in this area of opto-electronics(16).

EXPERIMENTAL

The experimental setup used herein consists of a stainless steel vacuum chamber with two internal electrodes. The substrates were placed on the stainless steel electrode and the system was evacuated by a rotary pump (18 m^3/h) down to 10^{-1} Pa. Needle valves were employed to control the gas feeding and a Barocel pressure sensor to monitor the chamber pressure. The samples were exposed directly to the plasma environment established by the application of radiofrequency power (13.56 MHz.) to an atmosphere composed by N_2 and SF_6 and their mixture with isopropyl alcohol. Three different arrangements of electrical discharge were applied keeping the total pressure constant at 6.66 Pa: (i) The substrate holder and the chamber walls were grounded while the RF power was connected to the opposite electrode – PI anode configuration, (ii) RF power to the substrate holder while the opposite electrode and the chamber walls were grounded – PI cathode, (iii) the radiofrequency power to the opposite electrode while negative pulses of high voltage were applied to the substrate holder (299 Hz, 30 µs and 2400 V). The deposition time was ranged from 150 s and 1800 s and RF excitation power was ranged up to 100 W – PIII. Contact angles measurements were made by goniometer Rame-Hart 100-00 and the optical transmittance of plasma treated PET samples was investigated in the range from 190 nm to 3300 nm by a lambda 750 spectrometer (Perkin Elmer). The surface roughness of PET samples was investigated taking 5 um × 5um AFM scans using an XE-100 (Park Systems).

RESULTS

Contact angle (wettabilitty)

The wettabiliy behavior has been assorted in the three different techniques applied, although similar for all rf power conditions.

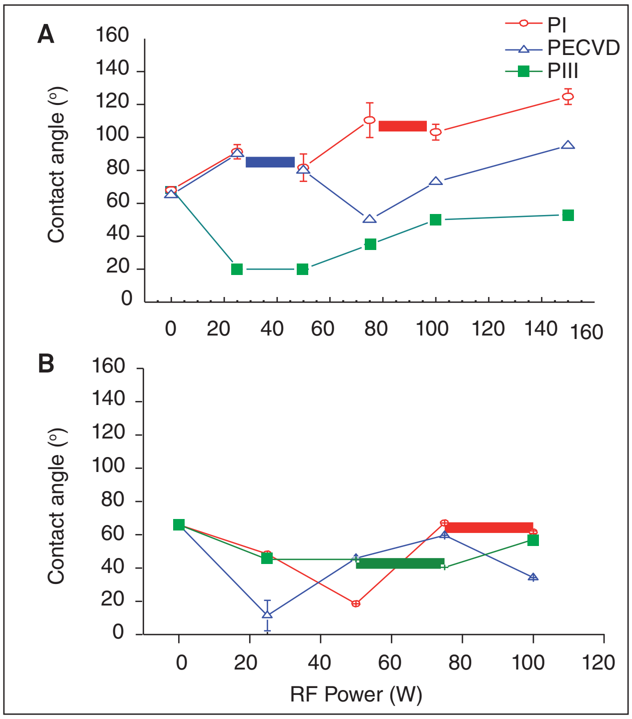

Figure 1: (A) contact angle of water with PET as a function of power supplied to the electrical discharge. The treatment time was 300 s and the pressure of SF_6 in the reactor was 50 mtorr. (B) The contact angle of the water with PET as a function of the power supplied to the electrical discharge. The treatment time was 300s and the pressure of N_2 in the reactor was 50 mtorr.

Fig.1a shows that all plasma treatment using fluorine has increased the values of contact angle for samples treated by PI technique, however presented low values of contact angle of PET samples for those which were implanted. Plasma treatment decreased optical transmittance at visible range; therefore, this effect was more pronounced for PIII than PI techniques. The measurements of the contact angle and transmittance showed their dependence on the parameters investigated. The AFM results show that the low energy ion implantation is more efficient to promote cross-link on the polymer surface.

Initially, a comparative analysis of techniques PI and PIII was made, and the partial results of this study indicated that the first technique greatly increases the values of contact angles of PET samples for RF discharge powers up to 100 W. Moreover, the PIII technique causes a decrease in the values of the contact angle concurrently with the low power radio frequency. This comparative analysis between the different techniques of plasma deposition was undergoing PET samples treated for 300 s, at a pressure of 50 mtorr SF_6. In this series, it was ranged the power of radio frequency electrical discharge, from 25 W until 150 W. The parameters of ion implantation were 2400 V, 30 µs and 300 Hz.

The graph in Fig. 1a shows the result of the plasma treatment of SF_6 to PET. It is noteworthy that the value of the contact angle for the raw material corresponds to 0 W power radio frequencies (RF). The graph in Figure 1b, in turn, shows the values of the contact angle of PET treated with 50 mtorr of N_2 for 300 s. In this series, the ranging power to radio frequency discharges from 25 W to 100 W while the parameters of the ion implantation were 2400 V, 30 ms and 300 Hz.

Although C–F bonds are highly polar, when these species are present on the surface of a material, they will increase its hydrophobicity. The more electronegative the fluorine is, the repulsion between the oxygen in the water and the fluoride surface is greater than attraction of the fluorine by hydrogen. However, reversing the polarization of the radio frequency, there is no acceleration of positive ions toward the substrate, so there is a trend of stabilization in the values of the contact angle, even with the increase of the average kinetic energy of molecules in the plasma. Yet, as the substrate is present in the reactive atmosphere in a small addition of fluorine on the surface, it causes a slight increase in the values of the contact angle.

Under the same conditions, the ion implantation with deposition (PIII) has many hydrophilic samples of PET. The lowest contact angle was detected for the deposition of 25 W for PET (18°). In fact, two mechanisms may have contributed to the reduction in the values of the contact angle for PIII: increasing the surface roughness of the polymer, which in turn leads to an increase in the contact area, that is, increasing the number of species chemically bind with water molecules. This roughness effect may have occurred in PET because of the fall of chains caused by the shock of the species found in plasma, or ultraviolet radiation provided by the plasma which can lead to the degradation of PET, since this polymer is sensitive to this radiation(17).

Another mechanism would be the increase occurred in the amount of hydrogen and oxygen species that would bind chemically with the water in the syringe, thus causing a decrease in the values of ϴ. The presence of oxygen can be explained by the formation of free radicals in the film during deposition and treatment.

The residual oxygen present in the reactor can bind chemically to these radicals during the process, and these dangling bonds can capture oxygen and/or water vapor from the environment when the sample is removed from the reactor(18). Hydrogen atoms present in lateral connections are easily lost due to weak links(19). It is interesting to note that, although the mechanism of implantation causes hydrophilization, this process is attenuated to the radio frequency power above 50 W. With increased power, the previously discussed mechanism of fluoridation becomes dominant in relation to the bombing generated by PIII.

Superficial Morphology

A complement to wettability of PET is confirmed by AFM images (10µm × 10µm area) of the surface of plasma treated PET. Figures 2a and 2b shows respectively, the AFM images (10µm × 10µm area) of the surface of untreated and treated PET in plasmas of SF_6 pressure of 50 mtorr for 300 s by the conventional

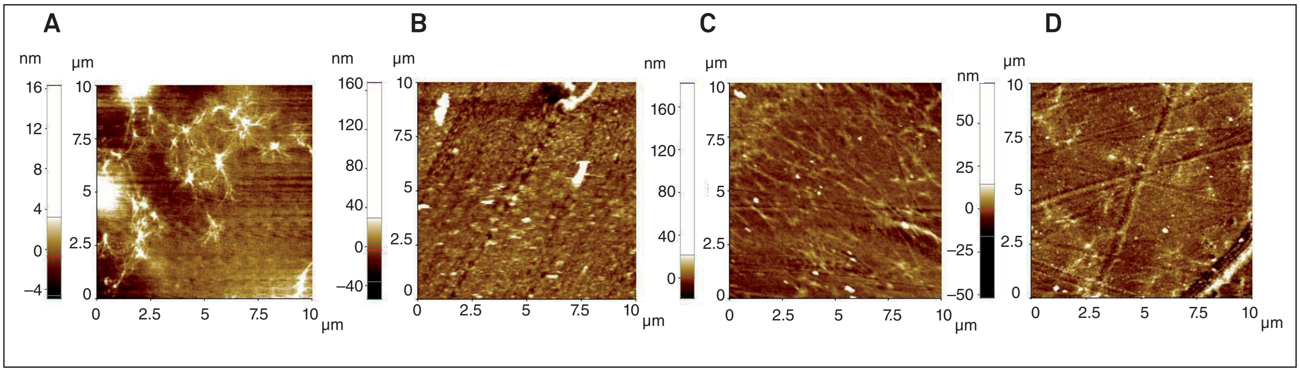

Figure 2: AFM images (10 µm × 10 µm area) of the PET surface (A) untreated (B) treated with plasmas of SF_6 by PI cathode at 100 W (C) treated by PIII 25 W of RF (D) PIII treated by 150 W RF source.

PECVD technique to the different powers applied. Figs. 3c and 3d show respectively, the AFM images of the PET surface treated by PIII 25 W and 150 W of RF, respectively.

Note that the surface of untreated PET 2 (Fig. 2a) is smooth showing no holes (pinholes), evidenced by the average surface roughness value of 1.7 nm RMS. For PET treated, Fig. 2b, there is a considerable increase in the surface roughness, which in turn, was 11.9 nm. Also, in relation to virgin PET, there was a slight increase in surface roughness of the samples that were implanted, which were 4.9 nm and 4.4 nm for the powers of 25 W and 150 W of radio frequency, respectively. In this occasion, the roughness increases, contributing to the greater number of polar bonds which were introduced on the surface, and thus increasing the hydrophilization. In both situations, Figs. 2c and 2d, there are risks inherent to the process of the PET samples cleaning.

Optical transmittance

The graphs in Figs. 3a, 4a and 5a show the optical transmittance spectra of the PET treated with plasmas of SF_6 by PECVD, PI and PIII respectively, while the graphs in Figs. 3b, 4b and 5b show the transmittance spectra of the PET treated with N_2 plasmas. First, the pre-treatment with: 50 mtorr of SF_6 for 300 s and 100 W of RF power. Later, the immersion ion implantation in SF_6 plasmas for 300 s at a pressure of 50 mtorr while the rf power was varied between 50 W and 150 W. The PIII parameters were: –2400 V, 300 Hz and 30 μs. The same conditions were applied to the samples treated with N_2.

As a general trend, the transmittance remains practically constant in the range of λ 400-700 nm (visible) and progressively decreases for λ below 400 nm, considering little loss of T (λ) in visible light.

As a general trend, the transmittance remains practically constant in the range of λ 400-700 nm (visible) and progressively decreases for λ below 400 nm; however, a great loss of visible light transmission was noted independently of the gas employed. Thus, the plasma treatment techniques influenced distinctively in the transmittance of PET. At high powers there is a greater fragmentation of species by bond breaking, and subsequently the recombination between different species of the plasma, causing greater distortions in the chains entanglement and rearranged. Thus, can reducing the free path of the incident radiation(20).

More intense changes can be observed by the spectra of the samples subjected to the process of PIII. As an energetic ion penetrates the material, it transfers energy to the polymer structure through the mechanisms of electronic braking and nuclear braking. By electronic braking, the ions transfer enough energy to the polymer structure to trigger processes of excitation, ionization, vibration and break connections. Break connections usually occur in side groups, releasing chemical species in the structure, such as H, N, O, CO, CHx(21). Free radicals and dangling bonds left in the structure tend to rearrange to minimize their concentration. This reorganization might

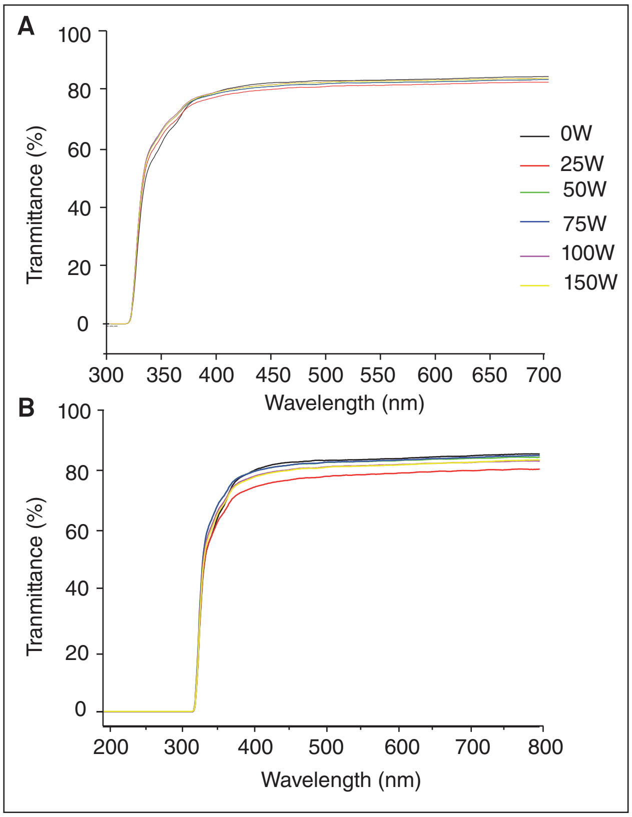

Figure 3: Optical transmittance spectra in the visible range (300-700 nm) for samples of PET treated by PI anode: (A) SF_6 and (B) N_2.

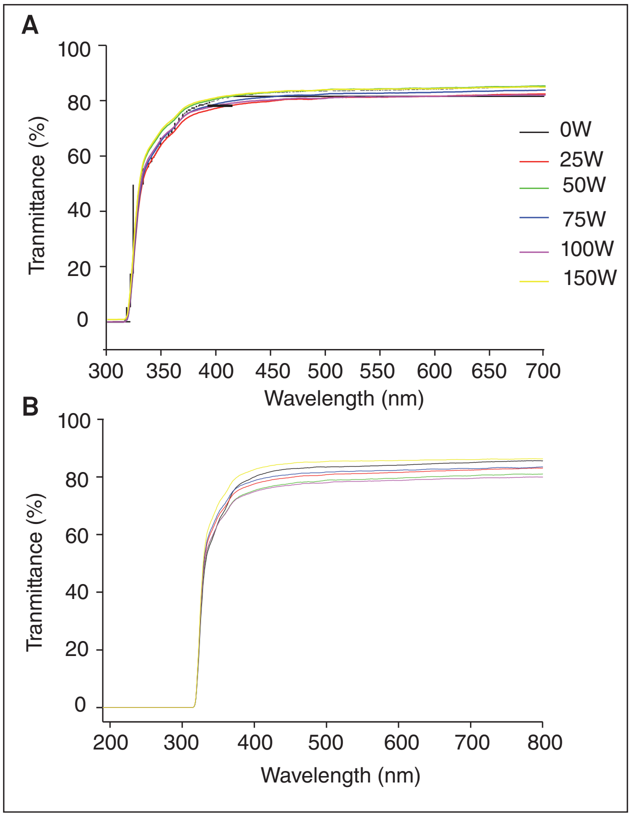

Figure 4: Optical transmittance spectra in the visible range for samples of PET treated by PI cathode: (A) SF_6 and (B) N_2.

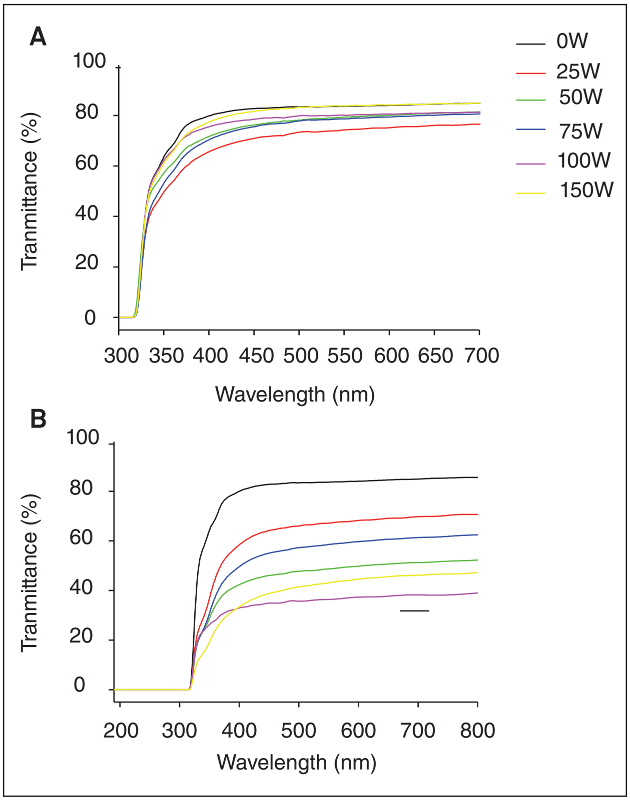

Figure 5: Optical transmittance spectra in the visible range for samples of PET treated by PIII: (A) SF$_6$ and (B) N$_2$.

result in carbon unsaturated double (C = C) and triple bonds (C ≡ C), or processes of entanglement or cross link via covalent bonds when the radicals are created in adjacent chains, thus decreasing the free passage of the incident radiation samples.

DISCUSSIONS

Due to the action of plasma, the breaking of covalent chemical bonds C-H or C-O or even C-xy and their subsequent recombination may lead to the formation of C-F bonds after the fluoride treatment by PI, which in fact proves the increased hydrophobic character of the polymers undergoing this treatment. In the case of treatment by PI, the increasing power supplied to the SF$_6$, plasma enhances ion bombardment. Thus, a greater number of fragmented species on the surface offers a greater number of active sites for binding C-F, which justify the higher values θ immersion. Inthe reactor also there are influences of ionic bombardment. In the present case, where the ballast is equipped by parallel circular which is excited by RF electrodes, the more intense bombardment occurs at the bottom electrode (specimen holder), and can be explained by D'Agostino(22).

It was noted that the same mechanism does not occur in comparison to the PIII technique, which in turn becomes hydrophilic samples of PET, even in an atmosphere containing fluorine. Thus, the lower θ values were: 18º for the PET. It is believed that the high energy acceleration of the positive ions toward the lower electrode, promotes higher rates of sputtering and, or etching. Also, the high temperature resulting from the bombardment in a larger amount can inhibit the fluorine insertion on the surface of polymeric substrates because it reduces the adsorption of precursor species. Thus, it occurred a change in θ because the dynamics of adsorption and desorption on the surface induces composition and structural changes on the surface. After breaking, the vacuum containing species easily incorporates the active sites on the surface, and high temperature acts as a catalyst for oxidation processes, which explain the lower θ values in PIII in a heated environment.

It is considered to this point of the discussion that two factors were instrumental in the increase of hydrophobicity: (i) the degree of fluorination; (ii) surface roughness. The degree of wetting of the samples straightaway after treatment has its effect amplified by increasing the surface roughness because it increases the area available so that ions from the plasma can bind chemically with the surface atoms. The higher the degree of the fluorine incorporated on the surface, the more hydrophobic the character, confirmed by the high values of θ, which implies non-chemical attraction between the fluorinated surface and the test fluid.

Moreover, in the ion implantation, the degree of bombardment and the resulting temperature increase become predominant at increasing distance of chemical bonds, weakening the strength of connections and thus promoting greater tendency to break chemical bonds on the surface. These results in the increased surface energy, then free radicals and dangling bonds tend to capture atmospheric oxygen, especially after breaking the vacuum, in which oxygen-containing groups and other polar radicals can recombine by hydrogen bonds.

The availability of fluoride ions in the plasma immersion can be a determining factor in the reorganization of molecular and free radical groups, which influences the Θ values. In the case of fluoride intake inside the reactor, they are hardly available, because the ionization energy F+ ions are relatively high (17.4 eV). They may be available in the plasma phase clusters with charge 1, for example, CF$_2$+, but not in plasmas containing pure sulfur hexafluoride.

Since the F- ion is not attracted to the electrode with negative pulses (exclusively for the PIII treatments), it might explain the absence of a hydrophobicity agent (which would be the fluoride uptake in the implanted samples in this condition). In fact there was an increase in the hydrophilic character of the surface of the polymeric substrates after ion implantation, measured after breaking the vacuum, even in an atmosphere containing reactive fluorine. Subsequently, housed ions diffuse to the surface.

This idea is relevant, because through aging measures, a significant increase was observed in θ values after a certain period, which explains the low initial values of θ, measured immediately after the vacuum break(23). We did not find a clear trend of the

RMS roughness with plasma conditions that might depend on the spot of the AFM tip probe on the fiber surface.

This result is in agreement with Jiang et al, in which the rms roughness is not a clear function of plasma parameters and the intensity of C-F bond groups(24). It is not obvious that the new surface morphology induced by plasma treatment is not sufficient to contribute to the improvement of the hydrophobicity by the known "Lottus effect". Essentially, droplets can achieve a smaller contact area being supported at the top of the sharp features of the surface minimizing the interaction energy. It was reviewed that, the structured surface of many water-repellent leafs consists of the height of the elevations ranging from 5 to 100 mícrons and the distance between the elevations ranging from 5 to 200 mícrons. Due to the different order in the height and the distance compared with the size of water drops, it is clearly seen that the Lottus effect is not the main reason for the improved hydrophobicity for PET samples(25).

For the nitrogen treatment, the combination of polar functional groups on the surface and surface morphology led to the hydrophilicity of the material most of the times. The necessary conditions for hydrophilic of PET do not allow a detailed hypothesis on the interaction between reactive particles of low potential energy, and it is neglected any kinetic effects of gas being maintained at low temperatures. Since the potential energy of O-containing groups was the highest among the particles available in the plasma-phase, the functionalization was often attributed to theses radicals. The atoms and O-groups, together, cause easier etching of PET materials, mainly on the amorphous spots.

The penetration depth of such ions is only a tenth of a few nm, so they cannot cause substantial modification on the subsurface layer. Small differences in the polymer structure are reflected in different etching rates resulting in the evolution of the surface morphology for the PET samples. A synergic effect of Ultra Violet radiation causes modification of several 10 nm tick subsurface layer. The presence of O groups in the plasma phase caused etching of less resistive component of the polymer(26).

For high powers, it is no greater fragmentation species for bond breaking and consequently the recombination between different species of the plasma, causing greater entanglement and distortions in the rearranged chains thereby diminishing, the free path of radiation incident on the material(27). It explains why the transmittance loss visible is more pronounced in PIII in relation to PI, since the PIII, the energy incident on the plasma is much higher than in the PI due to the high acceleration of ions toward the substrate, and the resulting structural derangement is more intense, leading to the polymers subjected to ion implantation.

In PIII, ions are projected into the polymer matrix in 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 effect (or no) compared to the power of the effect. Thus there is no evidence of PIII technical effect with considerable loss of changes of T (λ).

It is assumed then that the temperature effect is predominant in the loss of transmittance due to the structural disorder resulting in high plasma treatment without cooling system. In the proposed applications, the results were not satisfactory for both techniques, despite the PI, some of the RF power conditions maintained high transmittance of the material in its visible region. It is expected therefore, that the change in plasma chemistry composition does not change the conclusions obtained in this discussion, since the temperature inside the reactor will also increase significantly into the nitrogen plasma.

CONCLUSIONS

This work included the analysis of wettability of plasma treated PET, as well as its optical transparency to visible light, since these two properties are determinant factors in the adhesion of layers, and consequently, in the preparation of polymeric plastic such as flexible deposition of oxide films.Thus, the resulting material becomes a potential one for the development of flexible flat panel displays for mobile phones, computers, optoelectronics, photovoltaic panels, touchscreen panels, among other products that are consolidated as new technological trends. Therefore, plasma techniques become attractive because theyare relatively cheap, clean to use as a tool evacuated system avoiding the emission of greenhouse gases in the atmosphere. Furthermore, the treatment time is short samples and finally, the properties of the sample surface can be controlled by the parameters of treatment.

Given this, in the modifications of the plasma treatment, the samples were positive on the basis of selectivity in the character of wettability and optical transparency, thereby increasing the hydrophobicity and optical transparency to visible light of samples of PET through the techniques of plasma. It is worth mentioning that the samples of plasma treated PET selected was two-liter bottles of coke, contributing to the reuse of recycled material, a factor which has become imperative in today's society through environmental issues.

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