Research Article

Degree of Wettability and Aging of PVC and PET Polymers Treated by Plasma Immersion or Deposition

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Abstract: The wettability, aging characteristics, and optical transmittance in the visible region following Plasma Immersion (PI) or Plasma Immersion Ion Implantation (PIII) treatment of polymers were studied. In addition, structural and chemical modifications of the polymers were examined. The polymers investigated were white Polyvinyl chloride (PVC) and Polyethylene terephthalate (PET). Initially, plasmas of nitrogen (N_2) were employed, aiming to produce hydrophilic surfaces. In contrast, sulfur hexafluoride (SF_6) plasma treatments produce high surface fluorination, which tends to increase hydrophobicity. Isopropyl alcohol (IPA) was mixed with SF_6 or N_2 to deposit a series of organic films. Aging effects over 30 days on the contact angle, θ, were measured for the polymer surfaces. Conventional plasma immersion (PI) tended to decrease of θ for N_2 plasma treatments, with or without IPA, and to increase θ values for samples immersed in IPA/SF_6 plasma. The highest value of θ was 140º for IPA/SF_6 plasma treatments, while the smallest θ was 20º for N_2 or IPA/N_2 treatments. There was an ideal condition under which θ was stable upon aging. The results obtained suggest the developed treatment enables the preparation of polymers with distinct wettability properties depending of the nature of the plasma with overall reasonable aging stability. Moreover, the opaque character of these materials makes them interesting for the production of bags, boxes, bottles, food packaging, among others.

Keywords: PVC; PET; wettability; infrared spectroscopy; optical transmittance

1. Introduction

When, in a suitable vacuum reactor, an electric field of sufficient magnitude is applied to a gas/vapor mixture at low pressure (typically below 10 Torr) a non-equilibrium cold plasma can be ignited. The electric field accelerates naturally-occurring ions and electrons in the feed, triggering an avalanche of ionization, excitation and bond breaking reactions. Active species such as atoms, radicals and molecules in ground and excited states, Vis-UV photons, as well as new ions and free electrons are produced [1], which are able to react and to change the

chemical groups and the structures on the surface of a treated polymer. In addition, cold plasmas fed organic gases or vapors, deposit thin film plasma polymers [2].

The wide-ranging applications of industrial polymers are often limited owing to their poor surface properties. Hence, new technologies, such as physico-chemical surface treatments, may be applied to allow new applications. In this sense, Plasma immersion (PI), PECVD or Plasma immersion ion implantation, excited by RF power, are excellent choices, able to change and define the wettability (highly hydrophilic or highly hydrophobic) of polymer surfaces with control of the aging time. Moreover, the same treatments were able to considerably improve gas barrier properties [3–11]. In principle, the plasmas generated from N_2, SF_6 and isopropyl alcohol (IPA) are able to change and define the wettability of the treated surfaces. One challenge, however, is to produce transparent polymers, with good optical transmittance in the visible range, via surface treatments of polymers.

PECVD films generally have a thickness in the range 10 nm^{-1} µm, and are usually smooth and conformal to the substrate (even on three dimensional (3D) samples). The building blocks of such coatings are radicals, in a neutral or ionic state, generated by the plasma fragmentation in the gas feed. Since the species that originate from the fragmentation of the gas/vapor precursor are various and with a broad chemical distribution, the coating stoichiometry may be varied with the experimental parameters. For this reason, and because of the energy input of the ions impinging on the growing film, the chemistry of PECVD coatings is very different from that of conventional polymers, which are suitable to functionalize organic coatings (carboxylic or amino-groups rich films) [12].

2. Methods

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. Glass *(microscope slide),* commercial White PVC, white PVC from Brasken company, transparent PET and PET from coke bottle (2 L), were cut (2.5 cm × 1.5 cm, and 1 cm of thickness and cleaned as follows: The substrates were first washed in an ultrasonic bath (CRISTÓFOLI USC 3881, 2.5 L capacity, operating at 0.17 KW and 0.8 A) with distilled water. They were then washed with detergent powder (DET LIMP S32 from FARQUIL) diluted in water (1g: 100 ml) for the removal of organic waste. Finally, the samples were immersed in an ultrasonic bath containing isopropyl alcohol - ACS (C_3H_8O) density 786 kg/m³ and molar mass 60.1 g/mol, from IMPEX Company with a minimum purity of 99.5%. In each of the steps the samples remained in the ultrasonic bath for 20 min. After the washing process under running water, the samples were individually dried using a thermal blower (HG 2000 - B2 from BLACK & DECKER).

After cleaning, the samples were placed on the stainless-steel electrode and the system was evacuated by a rotary pump, model EM-18 from Edwards (18 m³/h), down to 10⁻¹ Pa. Needle valves of nylon were employed to control the gas feed (both of high purity: ~ 99.95 %), and a capacitive pressure sensor, model Pirani, to monitor the chamber pressure. For these treatments, the total pressure was 50 mTorr of nitrogen (N_2) or sulfur hexafluoride (SF_6), pure or mixed with isopropyl alcohol (C_3H_8O), density 786 kg/m³ and molar mass 60.1 g/mol.

The polymers were exposed directly to the different plasma environments at several RF powers (13.56 MHz coupled to a matching box circuit from Tokyo Hi Power), for different treatment times. The substrates were treated in three different RF plasma immersion modes, as seen in Fig. 1, 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* density 786 kg/m³ and molar mass 60.1 g/mol, from IMPEX Company with a minimum purity of 99.5%. In each of the steps the samples remained in the ultrasonic bath for 20 min. After the washing process under running water, the samples were individually dried using a thermal blower (HG 2000 - B2 from BLACK & DECKER).

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.
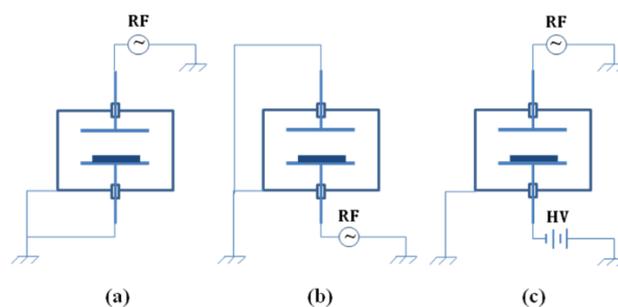
Figure 1. Electrical configuration of plasma immersion techniques applied in our experiments. (a) Plasma Immersion anode; (b) Plasma Immersion cathode; (c) Plasma Immersion Ion Implantation

Figure 2(a) shows the plasma treatment or deposition system. Fig. 2(b) shows details of accessories and connections of the system. Table 1 indicates the conditions of plasma treatments for the polymers investigated.

(a)   (b)
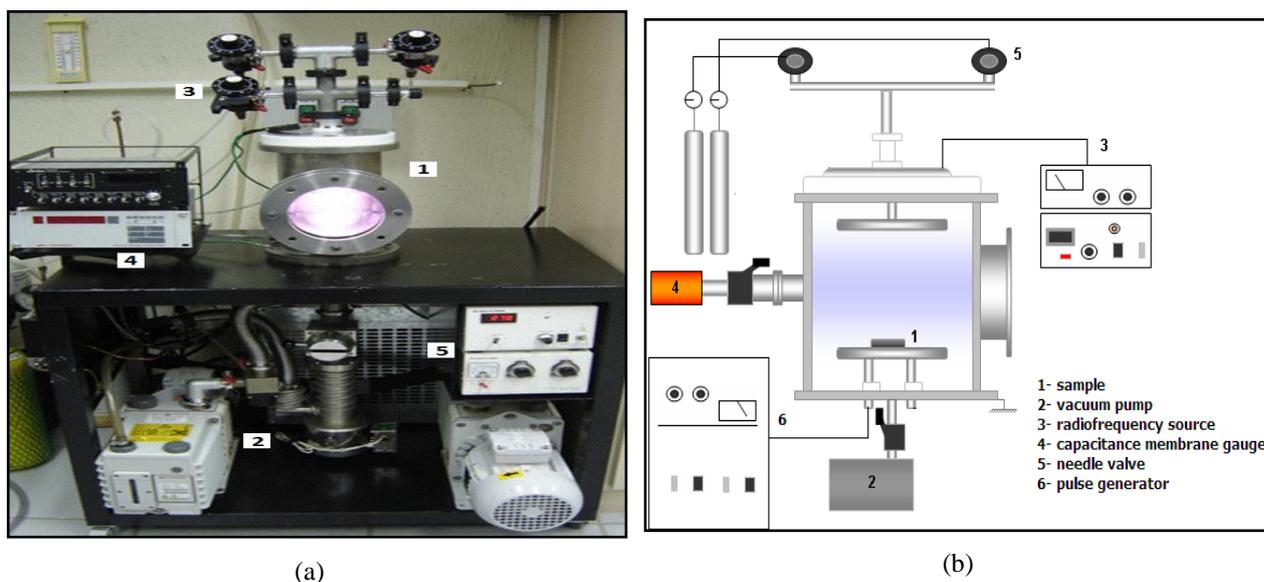
Figure 2. (a) The plasma treatment or deposition system: (1) stainless steel cylindrical chamber (2) vacuum pump (3) needle valves (4) pressure gauge (5) radio frequency source. Fig. 2(b) Details of the system [1–9]. *Reproduced with permission of the Brazilian Journal of Vacuum Applications*

Table 1. Plasma treatment conditions. *Plasma Temperature: (~60 º C for 25 W and ~80 ºC for 150 W)*

Substrates	Commercial white or transparent PVC: $\rho = = 1.30$ g/cm^3
	Transparency PET or PET from Coke bottle 2 L. $\rho = = 1.39$ g/cm^3

PI Treatment parameters	
Gas system	SF_6, N_2 and alcohol isopropyl (C_3H_8O)
Base pressure (Pa)	2.66
Total gas pressure (Pa)	6.65
Treatment time (min)	5 to 60
RF power (W)	25 to 150

Temperature	(ºC)	Plasma Temperature or 25
PIII parameters		
High voltage	(V)	−2400
Cycle time	(µs)	30
Frequency	(Hz)	300

Water contact angle measurements, Θ, were obtained using the sessile drop method, immediately after treatment as a mean of three drops deposited at random points on the polymeric samples, using a Goniometer (100-00, Ramé Hart). The effects on θ of aging up to 30 days were also studied. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy, FTIR, was implemented with a Jasco 410 Spectrometer (256 scan at 4 cm^{-1} of resolution of spectrum). Atomic Force Microscopy was employed as a supplementary technique for surface morphology analysis and Roughness RMS calculations made using a Parker Instruments, model 100-00 containing a SiN tip, oscillating at 256 Hz, over an area of 5 µm × 5 µm or 10 µm × 10 µm. Transmittance spectra were obtained in the 190 nm to 3300 nm wavelength range, using a Perkin Elmer spectrometer (Lambda 750 UV-vis-NIR) to evaluate the degree of transparency or optical transmittance of the polymers investigated.

3. Results

3.1 *Contact Angle and Aging*

Results for the analysis of plasma immersion using the three techniques, PI cathode, PI anode and PIII treatments, on θ, as function of RF Power is shown in Fig 3, for PVC samples (a), and for PET samples (b). For these studies, 50 mTorr of N_2 gas was established in the reactor, for 5 min per treatment. A negative voltage of -2400 V, cycle time 30 µs, and frequency 300 Hz were employed.

(a)   (b)
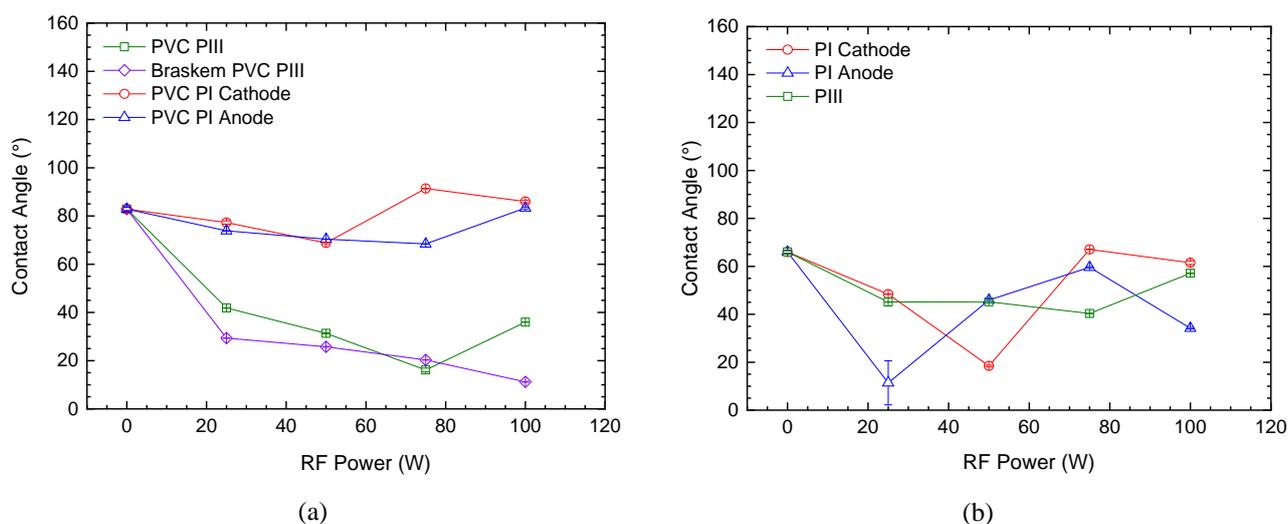
Figure 3. θ as function of aging time for 3 different plasma configurations: PI cathode, PI anode and PIII. In (a) the white PVC and white PVC from Braskem company were treated with 50 mTorr of N_2 for 300 s. In (b), the PET was treated with 50 mTorr of N_2 for 300 s. In all series, the RF power was changed from 25 to 100 W. The temperature of sample-holder was about 25º C, measured immediately after vacuum breaking

The results indicate the tendency for N_2 plasmas to produce hydrophilic surfaces. Possibly, chemical evolution occurs for all the polymers investigated. Oxygen incorporation may also occur, since O bonds with water, which explains the reduced values of θ. Oxygen molecules are captured from the ambient atmosphere upon removal of the samples from the reactor. Also, some polymers contain oxygen introduced during their process of fabrication, and which may be released into the plasma phase when the surfaces are bombarded by ions, electrons and neutral species.

When the surface is treated with nitrogen the degree of fragmentation of chemical bonds increases, as does the emission of species from the solid. As hydrogen and chlorine atoms are side groups in the PVC structure, they

are very likely lost after bombardment. Analogously, C-O and C-H bonds can be lost from PET. The free radicals generated can react with atmospheric H_2O and O_2, incorporating O and O-containing groups within the treated layer. Oxygen in the reactor, derived either from residual gas or from the surface of the glass chamber near the electrode region, may also contribute to this process. Therefore, the wetting of the bombardment surface is attributed to the electrostatic attraction between dipoles formed by O and O-containing groups on the surface of the polymer.

Fig. 4 shows the wettability results via analysis of θ as a function of deposition time for the commercial white PVC, white PVC from Braskem Company and PET (from 2L Coke bottles). Initially, a pretreatment was performed with 50 mTorr of N_2 for 5 min. at 100 W of power. Then, 40 mTorr of N_2 + 10 mTorr of Isopropyl alcohol (IPA) were deposited at an RF power of 100 W. Deposition times of 1.0, 2.5, 5.0 and 10.0 min were used.
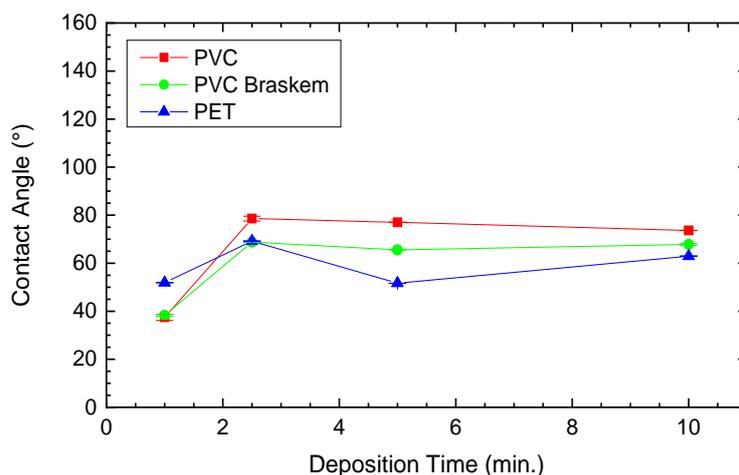
Figure 4. θ as a function of deposition time for the commercial white PVC, white PVC from Braskem Company and PET from 2L Coke bottles. Initially, a pretreatment was performed with 50 mTorr of N_2 for 5 min. at 100 W of power. Then, 40 mTorr of N_2 + 10 mTorr of Isopropyl alcohol (IPA) were deposited at 100 W of RF with deposition times of 1.0, 2.5, 5.0 and 10.0 min

The graphs reveal a tendency to remain hydrophilic after the organic films were deposited onto the polymer samples. Contact angles were not as low as those found after a typical treatment using N_2 plasma, which generates a high density of surface oxygen groups. It is suggested that C and H predominate and that there was little oxygen connections.

Moreover, Fig. 5 shows the results of Θ as function of treatment time for PET and PVC treated in fluorine plasmas. RF power was fixed at 100 W, and the temperature of the sample holder, measured immediately after breaking the vacuum, was about to 60 ℃ for treatments of 5 min. and about 80 ℃ for treatments of 60 min.

The contact angle measurements reveal that the wettability behavior following treatment depends on the chemical composition of the plasma. Immersion in plasmas containing a fluorine source makes the samples considerably hydrophobic, while immersion in nitrogen plasmas makes the samples considerably hydrophilic, regardless of the electrical configuration applied to the system.
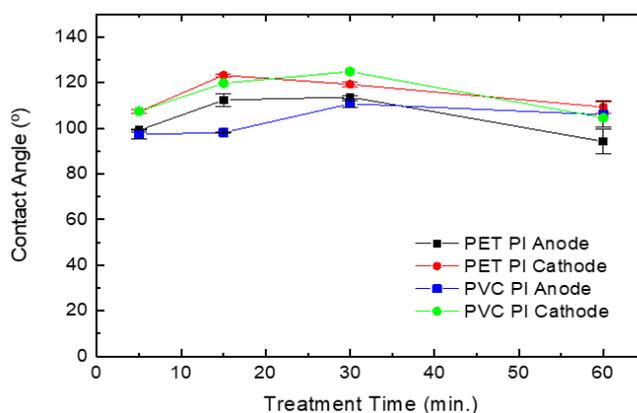
Figure 5. θ as a function of treatment time for PET and blue PVC immersed under total pressure of 50 mTorr of pure SF_6 plasma using anode or cathode electrical configuration and 50 mTorr of isopropyl alcohol + pure SF_6 plasmas. RF power was fixed at 100 W. The lowest temperature of the sample holder measured immediately after breaking vacuum was around to 60 ℃ for 5 min. while the highest temperature was around to 80 ℃ for 60 min. of treatment

When treating polymers with SF_6, fluorine incorporation occurs on the surface, and under the right conditions can reach saturation. The insertion of fluorine into a surface leads to the formation of groups containing C and F, resulting in repulsion in the water drop test, resulting greater contact angles.

By observing the results of the wettability of the PVC and PET samples, it was noted progressively greater Ɵ values for treatment times between 15 and 30 min. It is suggested that, in this interval, there was the greatest fluorine insertion on the polymer surfaces. Again, owing to the reactions occurring inside the reactor, the breaking of covalent chemical bonds C-Cl, C-H or C-O, or even C_xH_y and their subsequent recombination, may lead to the formation of C-F or CF_x bonds during or even immediately after the treatment with a fluorine source in the PI configuration [9].

Moreover, Fig. 6 shows θ values as a function of RF power from 25 to 150 W.
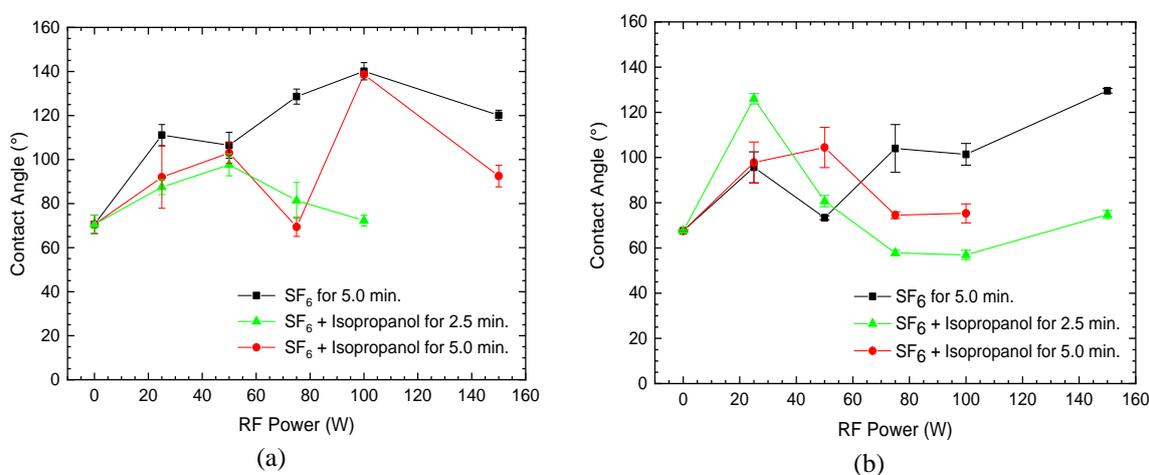
Figure 6. θ as a function of RF power from 25 to 150 W for (a): blue PVC; (b) for PET. A pre-treatment applying 50 mTorr of pure SF_6 for 5 min. was used. Subsequently, films of the IPA/SF_6 mixture in equal proportion (50% each) were deposited for 2.5 min. and, in the other treatment, for 5 min

Fig. 6 shows the conditions for (a): blue PVC was initially submitted to a pre-treatment applying 50 mTorr of pure SF_6 for 5 min. Subsequently, films of the IPA/SF_6 mixture in equal proportion (50% each substance) were deposited for 2.5 min. and, in other treatment, for 5 min. The graphs reveal a tendency to greater hydrophobicity caused by fluorine incorporation when the polymers were treated in pure SF_6 plasmas. In mixtures with IPA no obvious tendencies in the behavior of θ are apparent. There may be competition between surface incorporation of O and F, which leads to different results as the RF power is increased.

Reinforcing our discussion, after fluorine insertion into the polymer backbone, the surface becomes hydrophobic, owing to the process of fluorination, which results in a substantial change of the chemical composition of PVC and PET. Owing to a relatively high C–F bond energy inside the fluorinated layer, most of O, Cl or H atoms are easily replaced by F-atoms and double bonds are saturated with fluorine to form C–F bonds. Although C-F bonds are polar, when these species are present on the surface of a material, they become responsible for increasing the hydrophobic character. As electronegative as fluorine is, its repulsion with the oxygen in the water is stronger than its attraction for the hydrogen in the water, which implies that there is no chemical attraction between the treated surface and the test liquid [4, 6].

Upon aging, the tendency is for contact angles to return to values close to the value before treatment. In certain cases, the treated surface is reported to change from hydrophobic to hydrophilic. Such instability may not be suitable for certain applications. Thus, the behavior of the contact angle with aging time, θ (t), was evaluated for hydrophobic and hydrophilic samples.

To analyze the aging stability of the contact angle, Fig. 7 shows θ measured over 30 days. Fig 7(a) and (b) show the results for treatment of PVC, and of PET and transparency paper, respectively. The samples were

submitted to a pre-treatment performed with 50 mTorr of SF_6 for 5 min. at 100 W. Subsequently, films of the IPA/SF_6 mixture were deposited for 5 min. at 100 W, at 25 mTorr of SF_6 and 25 mTorr of IPA.

(a)

(b)
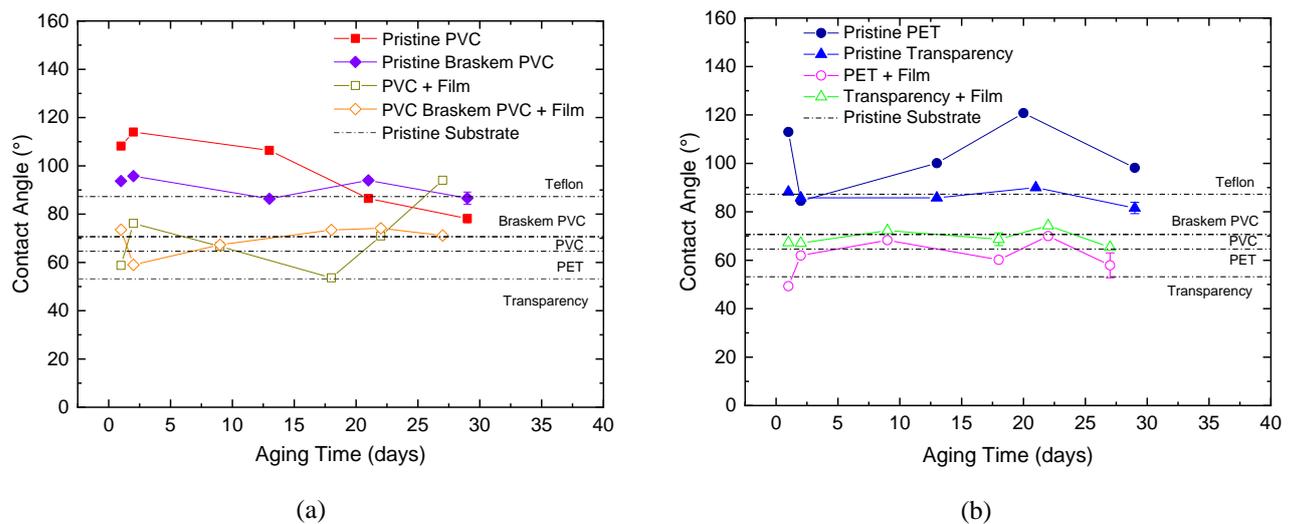
Figure 7. θ as a function of aging time over 30 days. Samples were initially, submitted to a pre-treatment performed with 50 mTorr of SF_6 for 5 min. and 100 W. Subsequently, films of the IPA/SF_6 mixture were deposited for 5 min. at 100 W, with 25 mTorr of SF_6 and 25 mTorr of IPA. In (a): for PVC samples. In (b): for PET and transparency paper treatments

Fig. 8 (a) and (b) show θ as a function of aging time for PVC, and PET and transparency paper, respectively. Initially, a pre-treatment was performed with 50 mTorr of SF_6 for 5 min. at 100 W. Subsequently, films of the SF_6/IPA mixture were deposited for 2.5 min. and 50 W of RF power, being 25 mTorr of SF_6 and 25 mTorr of IPA.
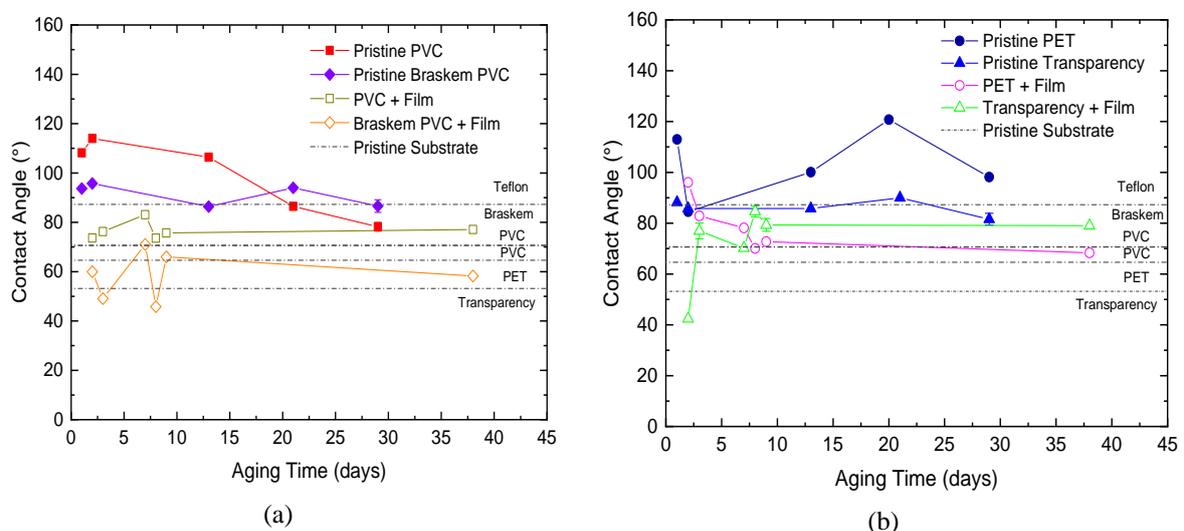
(a)

(b)

Figure 8. shows θ as a function of aging time over 30 days. Initially, a pre-treatment was performed with 50 mTorr of SF_6 for 5 min. at 100 W of RF Power. Subsequently, films of the SF_6/IPA mixture were deposited for 2.5 min. and 50 W, being 25 mTorr of SF_6 and 25 mTorr of IPA. Parts (a) and (b) show, respectively, results for PVC, and for PET and transparency paper

Figures 9 (a) and (b) depict θ as a function of aging time over 30 days for PVC samples, and PET and transparency sheets, respectively. Initially, a pre-treatment was performed with 50 mTorr of SF_6 for 5 min. at 100 W. Subsequently, films of the SF_6/IPA mixture were deposited for 10 min. and 50 W of RF power, with 25 mTorr of SF_6 and 25 mTorr of IPA.
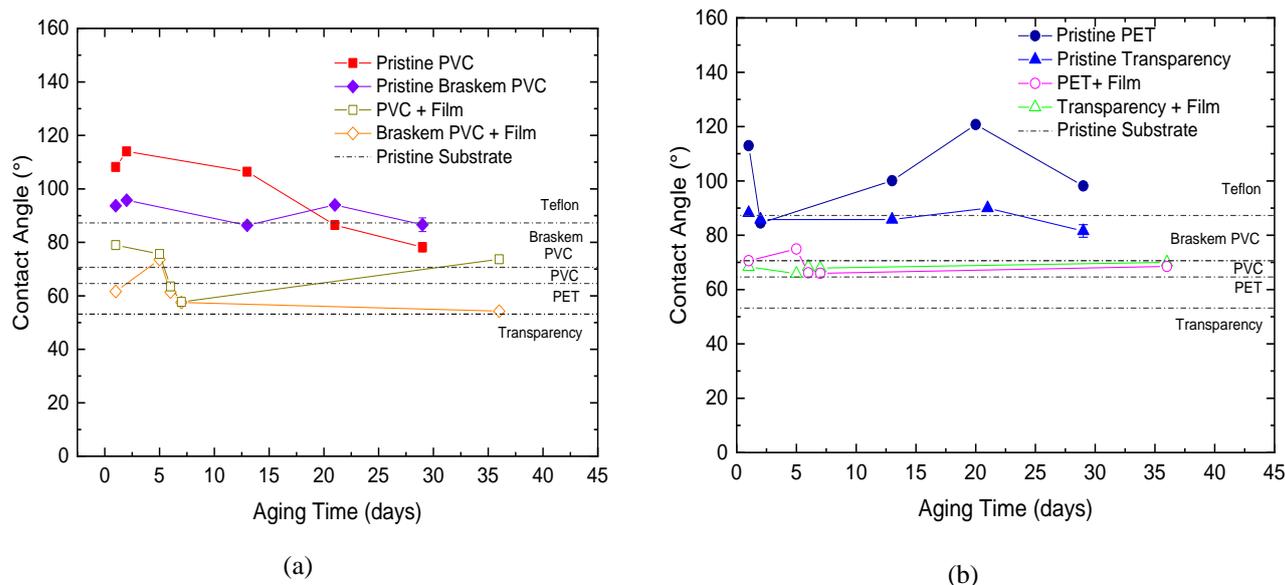
Figure 9. θ as a function of aging time over 30 days. Initially, a pre-treatment was performed with 50 mTorr of SF₆ for 5 min. at 100 W. Subsequently, films of the SF₆/IPA mixture were deposited for 10 min. at 50 W, with 25 mTorr of SF₆ and 25 mTorr of IPA. Parts (a) and (b) show, respectively, the results for PVC, and PET and transparency

In all the graphs related to aging time, for hydrophobic surfaces θ tends to decrease slightly with time. In general, however, the contact angles are relatively stable. The treatment using fluorine makes the degree of wettability considerably stable in the aging time, that is, with low fluctuations, while the treatment using nitrogen shows a clear tendency to induce water repellence even with the aging time. To become chemically stable, polymer chains on the surface tend to minimize their free energy. In this case, the diffusion of short chains or oxidized groups to more superficial layers of the substrate may have occurred [9]. Oxidized groups, such as C-O, C=O and –OH are typically found in polymers treated in low pressure plasma, and a large number of free radicals can react with oxygen and water vapor.

As mentioned earlier, nitrogen-treated PVC samples are highly hydrophilic immediately after removal from the reactor and their high wettability is associated with their chemical composition as revealed by XPS [6]. During the treatment, the relatively weak chemical bonds between carbon and hydrogen atoms are broken, and thus produce binding sites or pendant bonds. This explains the tendency to the incorporation of polar groups containing oxygen, which have a high chemical affinity for deionized water.

Owing to the action of the plasma, the breaking of covalent chemical bonds C-H, CH$_x$, C-O or even CxHy and their subsequent recombination can lead to the formation of C-F bonds after treatment with a fluorine source using PI or PIII. The fluorination promotes the hydrophobic character of PVC. Treatment by fluorine PI at increasing RF power stimulates ion bombardment on the sample surface, leading to greater values of Θ.

The hydrophobic character of the fluorinated surface is gradually lost with aging time, owing to the instability of the chemical bonds formed after the treatment. It is believed that fluctuations in θ values may be much smaller for polymers that contain many cross-links or entanglements because this increases the stiffness of the polymeric chains and decreases their movement dynamics [10], which can lead to a decrease in the chemical reorganization or restructuring or even the replacement of atoms in the pendant sites.

3.2 Infrared Analysis

With respect to the chemical structure of PVC and PET, Fig. 10 and 11 shows the infrared spectra obtained using the ATR accessory for samples with N₂/IPA films, for different deposition times.
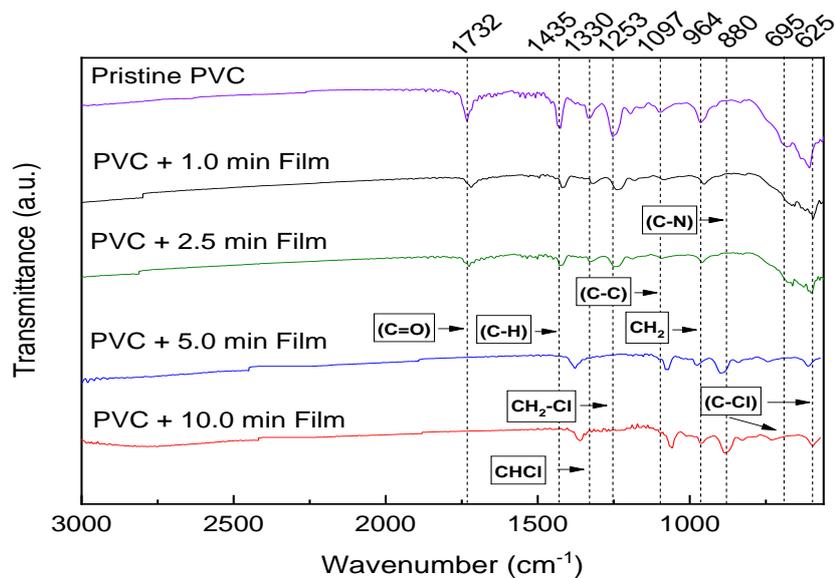
Figure 10. Infrared spectra of PVC treated with films from N_2/IPA mixtures. Initially, a pre-treatment was done with 50 mTorr of N_2 for 5 min. at 100 W. Then, films of N_2/IPA mixtures were deposited, under 25 mTorr of N_2 and 25 mTorr of IPA, at 100 W, for different deposition times
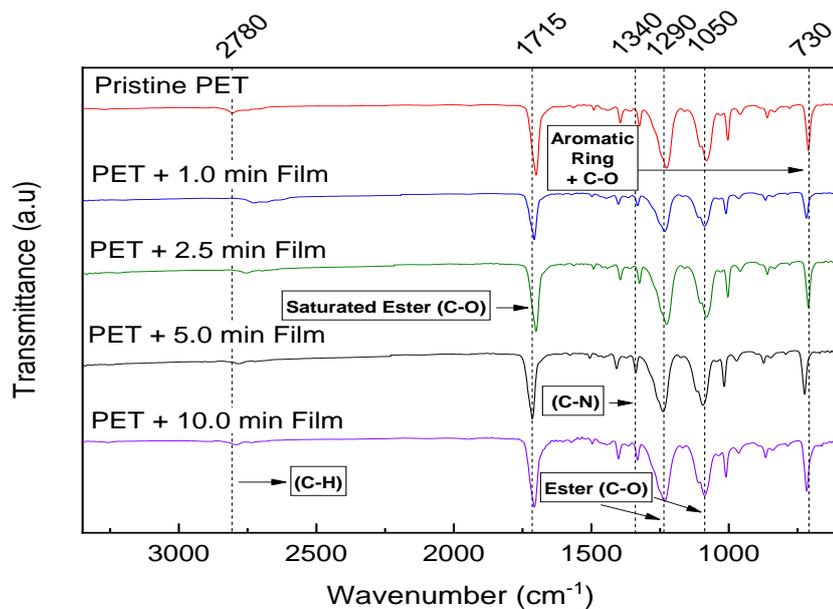
Figure 11. Infrared spectra of PET treated with films from N_2/IPA mixtures. Initially, a pre-treatment was done, with 50 mTorr of N_2 for 5 min. at 100 W. Then, films from N_2/IPA mixtures were deposited with 25 mTorr of N_2 and 25 mTorr of IPA, at 100 W, for different deposition times

Fig. 12 and 13 shows the infrared spectrum obtained using the ATR accessory for samples with SF_6/IPA films, for different deposition times. In all cases, the comparison between the main bands present on the spectrum of the untreated plastics with the main bands present for the treated plastics, allows the investigation of possible structural modifications after treatment.
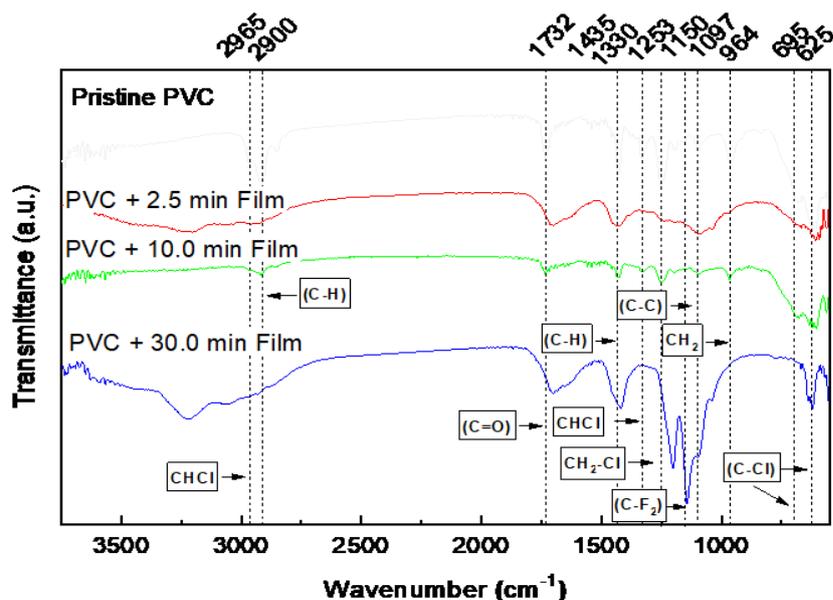
Figure 12. Infrared spectra of PVC treated with SF$_6$/IPA mixtures. Initially, a pre-treatment was done with 50 mTorr de SF$_6$ for 5 min. at 100 W. Then, films from SF$_6$/IPA mixtures were deposited with 25 mTorr of SF$_6$ and 25 mTorr of IPA, at 100 W, for different times
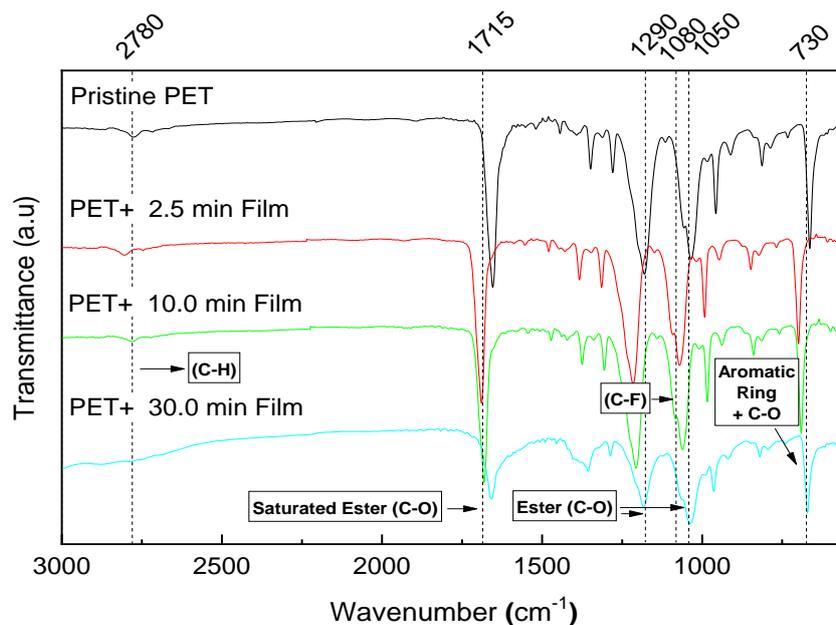
Figure 13. Infrared spectra of PET treated with SF$_6$/IPA mixtures. Initially, a pre-treatment was done with 50 mTorr de SF$_6$ for 5 min. at 100 W. Then, films from SF$_6$/IPA mixtures were deposited with 25 mTorr of SF$_6$ and 25 mTorr of IPA, at 100 W, for different times

Table 2 shows the full assignments of molecular groups and covalent bonds of white PVC, with attributions of the C-Cl groups between 625 cm^{-1} and 695 cm^{-1}, owing to the stretching of the carbon-chlorine bond, whose types of vibrations can be conformational at 690 cm^{-1} and tactic at 635 cm^{-1}, and between 960 cm^{-1} and 2965 cm^{-1}, which show chemical bonds, mainly formed by carbon and hydrogen or oxygen in low concentrations, characteristic of the alkanes. The presence of oxygen in PVC is also shown, which probably originated during the processing of this material. This hypothesis was confirmed later by XPS, which detected the percentage of O for the untreated material of around 11%.

Table 2. Infrared absorption bands of PVC

Absorption (cm^{-1})	Bond	Assignment
2965	(C-H) from CHCl	Stretch
2900	(C-H)	Axial deformation
2851	(C-H) aliphatic from CH$_2$ and CH$_3$	Axial deformation
1732	(C=O)	Stretch
1435	(C-H)	Deformation
1330	(C-H) from CHCl	Deformation
1253	CH$_2$-Cl	Angular symmetric deformation
1194	(C-O) of phenols	Angular deformation
1097	(C-C)	Stretch
964	CH$_2$	Rotation
681	(C-Cl)	Angular deformation
Between 625 and 695	(C-Cl)	Axial deformation
N$_2$/IPA films		
1340	C-N	Stretch
SF$_6$/IPA films		
1150	CF$_2$	Deformation

The infrared spectra of Table 3 revealed the identification of the main chemical groups present in the untreated PET [4] (from a (2L) Coke bottles, with density 786 kg/m³ and molar mass 60.1 g/mol, from IMPEX Company with a minimum purity of 99.5%. In each of the steps the samples remained in the ultrasonic bath for 20 min. After the washing process under running water, the samples were individually dried using a portable thermal blower (HG 2000 - B2 from BLACK & DECKER). The ATR accessory was used to obtain the spectra.

Table 3. Infrared absorption bands of PET

Absorption (cm^{-1})	Bond	Assignment
3430	(O-H) assigned	Axial deformation
2965	(C-H) aliphatic from CH$_3$ and CH$_2$	Axial deformation
1715	Carbonate of saturated esters	Axial deformation
1580	NH$_2$	Axial deformation symmetric in plane
1504	N-H	Axial deformation
1460	-(CH$_2$)-$_n$	Axial deformation
1407	CH$_2$ adjacent	Axial deformation
1338	SO$_2$ (sulfone)	Axial deformation unsymmetric
1240	(C-O) from aromatic ether	Axial deformation
1094	(C-O) of secondary alcohol	Axial deformation
1017	S=O (sulfoxide)	Axial deformation due to conjugation
970	-CH=CH-	Angular deformation
872	R$_2$C=CH$_2$	Angular deformation
792	R$_2$C=CHR	Angular deformation of C-H out of plane
724	-(CH$_2$)-n (to n>3)	Angular deformation of chain

N₂/IPA films		
1350	NO₂	Deformation
Between ~1200 and 1340	C-N	Stretch
SF₆/IPA films		
Between 1000 and 1400	C-F bonds	Deformation

For PET, the spectrum revealed the presence of bands at 1715 cm^{-1} associated with the stretching of the C=O bond of the carbonyl group, at 1246 cm^{-1} referring to the C-O bond stretching of the ester group carboxyl, 1100 cm^{-1} of the O- bond -C group of the O-CH₂ group and a 724 cm^{-1} band characteristic of out-of-plane vibration of the adjacent hydrogens of the aromatic ring. The C=O stretching bands are, for the most part, more intense, having a medium width, that is, they are not as acute as those related to C=C bond stretches, nor as wide as -OH stretching bands. An absorption band at 2970 cm^{-1} can be observed by the C-H stretch and at around 3050 cm^{-1} of the C-H bond to the aromatic ring. In addition, there is also an absorption band at 3430 cm^{-1} related to the stretch of the OH group, which may indicate the presence of additives.

Another possibility is the hydrophilization of the most superficial region of the material by the diffusion of water vapor present in the atmosphere. This diffusion mechanism occurs more intensely in the amorphous regions of the material, or even on the surface where the atoms have greater mobility.

In all cases, in the N₂/IPA films, low concentrations of N were found, and at higher concentrations, C bonds, and low concentrations of O bonds. On the other hand, for SF₆/IPA films, the presence of strong bands caused by C-F covalent bonds was noted, which substitute in part, bonds containing C-H, C-O or C-Cl. In all cases, N and O bonds were present in N₂/IPA films, and F and O bonds for SF₆/IPA films, which explains the results of high hydrophilization ($10 °< θ < 80 °$) in first case, and moderate to high θ for the second case ($60 < θ < 140 °$) depending on the degree of fluorine or oxygen incorporation. In pure SF₆ plasmas, the treated surfaces became more hydrophobic than in SF₆/IPA. Finally, it is difficult to be sure how many O, N and F bonds were produced as a function the thickness of the treated layers, since PI and PIII generated similar θ values for PET and PVC.

4. Optical Transmittance

Fig. 14 shows the optical transmittance spectra of PET. Initially, a pre-treatment was done with 50 mTorr of SF₆ for 5 min. at 100 W. Subsequently, PIII was applied using SF₆ plasmas for 5 min., 50 mTorr changing RF power.
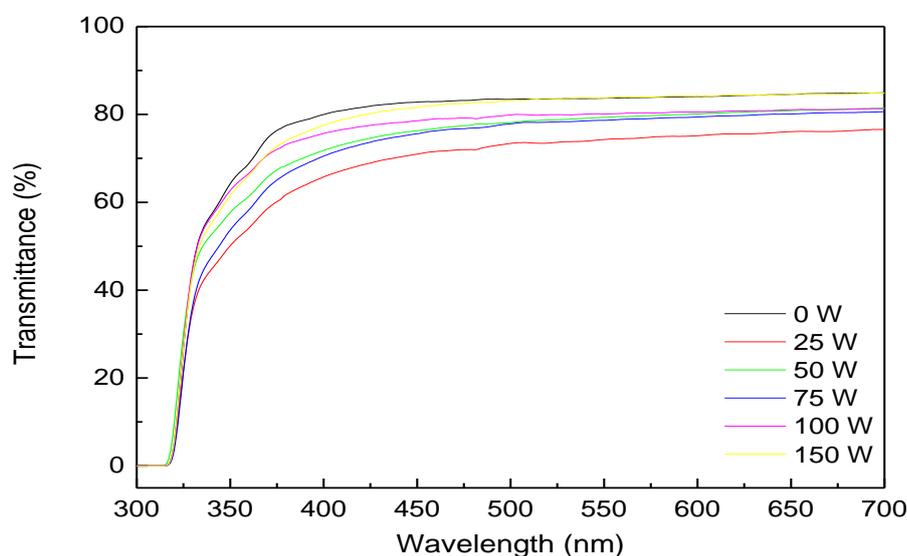
Figure 14. Optical transmittance spectra of pristine and treated PET from a (2L) Coke™ bottle. Initially, a pre-treatment was done with 50 mTorr of SF₆ for 5 min. at 100 W. Subsequently, Plasma Immersion Ion Implantation was applied using SF₆ plasmas for 5 min. at a pressure of 50 mTorr while the RF power was changed between 25 and 150 W. The PIII parameters were -2400 V, 300 Hz and 30 μs

In this case, there is a high transmittance in the visible region, with a strong decrease in the curves below about 400 nm. The highest optical transmittance of PET in the visible region is approximately 80%. For those treatments at high RF powers, such as 100 and 150 W, there was high transmittance in the visible compared to

that observed at lower RF power. However, in all cases, the effect of ion implantation reduces $T(\lambda)$ in the visible range. It is assumed that, owing to the presence of implanted fluorine atoms in the top-layers, and sub-top layers; a closed and dense polymer matrix with anchor points, unsaturation and tangled chains are formed. These effects may be responsible for the observed reduction in transmittance.

Another possibility to explain the loss in transmittance is the heating effect expected with high energy treatments, which may cause the temperature to rise above the glass transition point. Hence, a slightly opaque PET is produced as result of PIII treatments. The effect of bombardment heating may influence the depth of penetration, since the interatomic distances increase, and the covalent bond strength is reduced, such that the structure becomes less resistant to ion penetration.

Typically, in PIII, ion concentrations follow a normal distribution (Gaussian) with depth, which is similar for all polymers. Therefore, most of the implanted ions are lodged in the intermediate regions, with a relatively low concentration in the topmost layers. It is suggested that the thin barrier of implanted ions contributes significantly to the absorption of incoming radiation, thus explaining the reduction in transmittance.

In all cases, an opaque or semi-crystalline PET is useful for the production of bags, boxes, bottles, packaging for chemical compounds, stoppers, jars, lids, food packaging, etc. In addition, considering that UV radiation is present in the plasma environment, to which the samples are exposed, the polymer has high absorption in the ultraviolet range. It is known that plasma treatment will render the treated packages sterile. The radiation incident on these plastics, in the range 230 nm $\leq \lambda \leq$ 280 nm, is efficient for the reduction of *B. Atrophaeus* spores on the surface. For other spores (e.g., Aspergillus Niger), radiation below 200 nm is more efficient. These points are of obvious importance in the food and pharmaceutical industries.

5. Discussions

In all cases, if the surface roughness is increased by an order of magnitude owing to the ion bombardment, there is an increase in surface area, which results in a greater probability of chemical bond formation on the polymer surfaces, which accounts, at least in part, for the increased hydrophilicity following N_2 treatments and in hydrophobicity following SF_6 treatments.

For the nitrogen treatment, the combination of polar functional groups on the surface usually leads to the greater hydrophobicity of the material. When polar groups such as C-O, C=O, C-OH and (C=O)-O, are present on the surface and the liquid used is also polar, such as deionized water, electrostatic attraction prevails. In this case, the attraction between the surface oxygen and the hydrogen from water is greater than the repulsion between the oxygen atoms (surface/ liquid). So the higher the proportion of oxygen on the surface, the more hydrophilic it will be.

The type of functionalization can be varied by a selection of the plasma gas (Ar, SF_6, N_2, O_2, CO_2, and NH_3) and processing parameters (power, time, pressure, temperature and gas flow rate). An effect of hysteresis in θ may occur after plasma treatments. In this regime, a suitable surface texturing may promote self-cleaning surfaces [13]; and, on a textured surface, a saturated and stable value of θ may be reached. The variations may be associated with the chemical and morphological evolution, concomitant to the rotation of polymeric backbones.

To conclude, while SF_6 plasma provides C-F bonds, and hydrophobic surfaces, oxygen plasma provides different functional groups on the polymer surface, such C–O, C=O, or in some cases, O–C=O groups, as was confirmed in other investigations [14]. Numerous authors have also reported excellent results in changing the wettability of several types of polymers, including PET [15–17] and PVC [18–19], etc.

In addition, the limitations of cold plasma treatment were presented. The modification of polymer surfaces with cold plasma processing may not be maintained over time, but is more stable for treatments at lower RF power. Because of the minimization of the free surface enthalpy, dynamic processes are observed on all functionalized surfaces which reduce the initial modification effect [20]. It is believed that fluctuations in θ values can be much smaller for polymers that contain many crosslinks or entanglements because these increase the stiffness of the polymeric chains and thus decrease their movement dynamics [6, 9], which can lead to a decrease in the chemical reorganization or restructuring or even of the replacement of atoms on the active sites. In the literature, it is possible to observe a wide spectrum of surface functionalizations to introduce specific species onto the treated surface, aiming, for example, to transform the surface characteristics from hydrophilic to hydrophobic using fluorine plasma, or the reverse using nitrogen plasmas [21, 22].

Moreover, in relation to the decrease in optical transmittance in the visible region, an opaque surface may be associated with the mechanism of radiation absorption until the point of saturation, which commonly occurs in polymers containing organic molecules with conjugated π bonds [6]. This phenomenon observed in the non-linear optical properties of the polymers can be explained by the structural alteration of the chemical bonds of the surface, owing to the treatment with plasmas excited by RF power. For implanted samples, a dense matrix of ions fills the

amorphous and empty regions on the surface. An important observation was that the surface roughness does not influence the optical transmittance of the samples (R= 4.4 nm for PVC and R=1.8 nm for PET) because samples of different roughness (from R=1.8 nm, for the smoothest; R=12.3 nm, for the roughest) present almost identical spectral curves. It is believed that an increment of about 10 nm or more in R, does not cause a considerable increase in reflected or diffuse radiation.

6. Conclusions

The main mechanism responsible for the hydrophilic behavior of samples treated with nitrogen plasmas is the incorporation of polar groups with chemical affinity with the liquid drop. Although the treatment results in the incorporation of polar groups, the wettability of polymers does not only involve oxidative reactions. Loss and insertion of new species in addition to oxygen-containing groups can occur with aging [6]. In parallel studies, XPS analyses showed an increase from 11 at% to about 33% of oxygen in PVC after ion implantation in nitrogen plasmas. The presence of oxygen in the reactor can come from residual gases or from the reactor walls in regions close to the electrodes, which can also contribute to the hydrophilization process. A chemical evolution can occur with aging, that reorganizes chemical groups in the polymer chains, and which reduces the surface free energy until the saturation period or chemical stabilization.

The incorporation of fluorine, however, results in the formation of different functional groups on the surface, such as CF, CF_2, CF_3 and other groups containing C-F. The replacement of hydrogen atoms by fluorine atoms decreases their surface energy because C-F covalent bonds have stronger binding strength and less polarizability than C-H bonds [7–12].

In all cases, it is suggested that the chemical stability of the treated surface may be determined by the extent of reorientation of the polymeric chains, whose restrictions are associated with the number of cross-links between the polymeric chains, as a result of ionic implantation. The increase in the number of covalent bonds between neighboring chains, known as anchor points, limits rotational and vibrational movements within the chains. As a consequence, polymer chains become tightly connected or rigid. The change from intermediate to hydrophilic wettability is caused by the substitution of C-O and C=O bonds in place of C-C and C-H. As reported in the literature [23], oxygen-based plasmas can increase the concentration of hydrophilic groups, such as carboxyl, hydroxyl, and carbonyl, generating high wettability.

In relation to the chemical analysis by Infrared Spectroscopy, it was useful to identify F or N and O insertion, and in all cases, there is a chemical evolution, and some amount of oxygen may be provided by the atmosphere when the samples are removed from the reactor.

In relation to the optical transmittance analysis, a decrease in T (λ) in the visible was observed, which could be attributed to an increase in diffuse radiation for rougher samples after the treatment concomitant with the production of dense and tangled chains, which impede the passage of the radiation. Virgin PET absorbs radiation at $\lambda < \sim320$ nm.

It is suggested also that, excited states in molecules or atoms, which were generated owing to the high absorption of photons or even ultraviolet radiation, may occur and still show saturation characteristics. The high absorption is dependent on the intensity, wavelength and the lifetime of the excited states. In this case, high absorption was noted for λ values below 300 nm of the spectrum in all cases. In materials containing organic molecules with π-type conjugated bonds, the saturation of the absorbed radiation can be the main phenomenon responsible for the increase in T (λ) in the visible region. This occurs close to 300 nm due to the π–$\pi*$ transitions.

Finally, we draw attention to reviews of plasma techniques for achieving desired surface modifications published recently [24, 25], including one dealing with parallel-plate reactors with a capacitively coupled plasma system [25].

Conflict of interest

There is no conflict of interest for this study.

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