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Surface modifications of aromatic polyimides by RF-oxygen plasma and pulsed electrical discharges in water

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Aromatic polyimide films were subjected to RF-oxygen plasma and pulsed electrical discharges in distilled water treatment for 2, 4, and 6 minutes. The film surface was investigated by means of Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy, and contact angle measurements. It was observed that the polymer film surface became more hydrophilic after the RF-oxygen plasma exposure due to the formation of the oxygen-containing polar groups, while the sample surface became more hydrophobic after the water plasma treatment due to the surface segregation of the CF_3 groups.

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1. Introduction

Polyimides have drawn a lot of attention in the microelectronic industry due to their excellent electrical, thermal, and mechanical properties [1-4]. The aromatic polyimides are prepared from inexpensive monomers and have low moisture absorption and good thermal properties, being suitable for the microelectronic applications [5-7]. Due to the infusibility and poor solubility in common organic solvents caused by strong inter-chain forces or inherent macromolecular stiffness, the aromatic polyimides usually encounter processing difficulties [8,9]. One of the successful approaches used to overcome these drawbacks is the introduction of flexible linkages into the backbone of fully aromatic polymers [9]. The synthesis of polyimides containing hexafluoroisopropylidene (6F) groups is a promising way to process easily compounds having high thermal stability.

The surface wettability, roughness, and cross-linking density are important for the application in the microelectronic industry. Several surface treatment techniques are used to modify, such as plasma discharges, electron beams, x-rays etc. Electrical discharges in vacuum or at atmospheric pressure were used as an effective tool for yielding mostly polyimide with modified surface wettability [1,5,10]. The reactive species formed in the plasma interact with the polymer to attach functional groups to the surface. The RF-oxygen plasma treatment of the fluorinated polyimide induced oxidation and a significant decrease of the C-C/C-H bonding in the phenyl structure [1]. The polyimide films treated by unipolar nanosecond-pulse DBD in atmospheric air determined the rise of hydrophilicity, surface oxidation and the enhancement of surface roughness [5]. The air plasma attacked the C-C groups, introducing the oxygen-containing groups responsible for a higher adhesion or hydrophilicity of the PI surface. Some authors have also found that the $C\text{-}F_x$ bonding on the surface of the polyimide film were formed after the $N_2/He/SF_6$ plasma treatment, resulting in an increase in the contact angle of the sample surface [11].

Among other plasma processes, electrical discharge in liquids has become an interesting technique used for the functionalization of the surface polymers [12-14]. The hydrogen, oxygen, and hydroxyl radicals formed in liquids plasma may react with the polymer surface, inducing surface modifications and the attachment of functional groups to it [15-17]. The water molecules dissociation occurs before the plasma breakdown when a high electric field is applied to the electrodes which are immersed in the liquid. The mechanism is similar to that of the water electrolysis in which the H^+ and OH^- are formed [18]. A further increase of the applied voltage determines a local increase of the current density and gaseous bubbles are formed due to the Joule heating. Highly conductive channels called streamers develop between the electrodes and the plasma is spontaneously formed in the interelectrode gap [19]. A high amount of excited species are produced in these channels due to the electrons which efficiently excite and ionize water molecules. Some authors stated that the water molecules break up near the plasma/liquid interface forming hydrogen and hydroxyl radicals due to the highly energized $H_2O^+_{gas}$ that escape from the plasma which impinge onto the water surface with kinetic energies higher than 100 eV [20]. UV radiation generated in the discharge has an additional effect in the formation of reactive species in the liquid [21, 22]. The UV radiation is absorbed by the water layer surrounding the plasma, determining a strong hydroxyl radical emission around the plasma channels [21]. The hydroxyl radical is a very powerful oxidant that has the potential to oxidize organic compounds [23,24]. The water conductivity measured in the discharge chamber was also seen to increase after the plasma breakdown, indicating the presence of chemically active species in the liquid volume [18]. These species may interact with the polymer film immersed in the water, at a certain distance from the plasma core, determining the attachment of functional groups on its surface. Using the electrical discharges in water techniques some authors found that the content of the functional groups containing oxygen (such as hydroxyl, carbonyl, or carboxyl) was found to exceed by a factor of two that of the oxygen glow discharge plasmas [13]. Almost 30% of all oxygen functional groups attached on the polymer surface were OH-groups, compared to less than 10% OH produces in gaseous oxygen plasma [14]. Thus, the discharge in liquids technique seems to be suitable for an efficient and selective surface functionalization of a wide range of polymers.

The purpose of this study is to realize a comparative study between the RF-oxygen plasma and pulsed electrical discharges in water used to induce surface modifications of aromatic polyimides. Electrical and optical diagnostic techniques were employed for the investigation of the plasma characteristics. Therefore, current-voltage characteristics were acquired in order to establish the discharge type initiated between tungsten electrodes. Optical emission spectroscopy was used for the identification of reactive species formed in plasma and their evolution with the discharge time. The static contact angle (θ) of water (doubly distilled) was measured with a goniometer to investigate the surface wettability. The modifications produced at the polymer surface due to plasma treatment were also examined by the FTIR and AFM techniques.

2. Experimental configuration

2.1 RF-oxygen plasma configuration

The experiments were realized using a plasma chemistry reactor Emitech K1050 X Plasma Asher (capacitor plate plasma, CPP (Emitech Ltd, UK). The device consists of a solid state RF generator designed to provide up to 100 watts of continuous wave 13.56 MHz power to the reaction chamber. The reaction chamber system includes two pieces Pyrex chamber and two semicircular electrodes. The output impedance of the RF generator matching with the capacitive load of the reaction chamber is provided by two variable capacitors. The plasma was generated using a low pressure, RF induced oxygen discharge. The chamber pressure was set at 5×10^{-1} mbar. The oxygen gas was introduced into the chamber at a flow rate of 50 sccm. Aromatic polyimide films of 15x15 mm^2 size were placed into the chamber and treated by oxygen plasma. The input power was 60W, while the treatment time was 2, 4, and 6 minutes.

2.2 Water plasma reactor

The pulsed electrical discharges were generated in a cylindrical Pyrex vessel between tungsten electrodes immersed in 250 ml distilled water. Ceramic tubes were used as insulator material (Nilaco) and the protrusion of the electrodes from the insulation was 1 mm, with a flat end. The electrodes of 1.6 mm diameter (99% purity, Nilaco) were placed in the center of the vessel in a rod-to-rod configuration. The interelectrode gap was set to 0.1 mm. The experimental configuration is shown schematically in the Fig. 1. In all the performed experiments the applied pulsed voltage was provided by a unipolar power supply having a 30-μs rise time—5 kV maximum voltage pulse. The voltage pulse width was set to 50 μs and the repetition frequency was 7 kHz. The details of the pulsed power construction are described elsewhere [17]. The current and the voltage waveforms were measured using a current probe (Tektronix P-6021) and a voltage probe (Tektronix P-6015) respectively, connected to an oscilloscope (Tektronix TDS 310). The plasma could be generated in distilled water at a voltage of 5 kV (peak-to-peak voltage) and a current of 11 A. The repetition rate of the voltage pulses was set to 7 kHz. A stable discharge between the electrodes could be obtained at about 2 kV, and the discharge current was of the order of 70 mA. Assuming that the distribution of the electric field was quasiuniform between the electrodes, we have used the relation $E = U/d$ to calculate the electric field in the discharge regime, where U is the discharge voltage (peak value) and d is the interelectrode gap. The electric field required for the discharges in water was of about 200 kV/cm.

The polyimide (PI) film of 40 μm thickness and the size of 15 x 15 mm^2 was mounted on a metal support and immersed in distilled water (Fig. 1). The distance between the interelectrode gap and the polymer surface was set at 20 mm. The film was subjected to the plasma treatment for 2, 4, and 6 minutes.

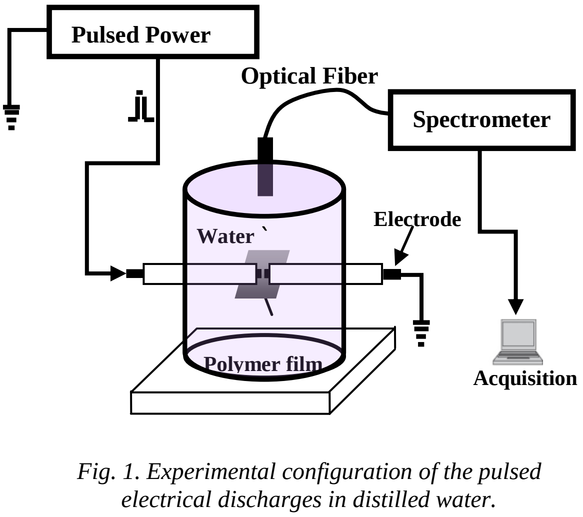


Fig. 1. Experimental configuration of the pulsed electrical discharges in distilled water.

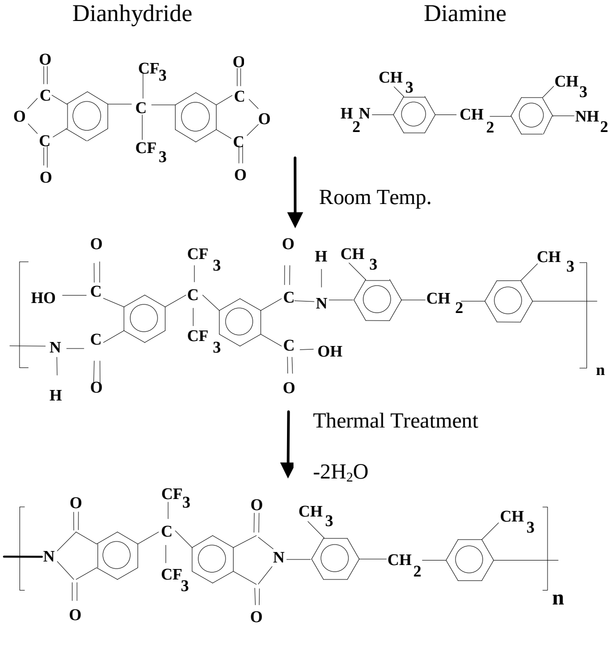
2.3 Optical emission spectroscopy

The light emitted by the reactive species formed in the water plasma was collected with an optical fiber immersed in water at 5 mm above the gap between the electrodes, using a PTFE tube ended with a fused silica window of 2 mm width and 15 mm diameter. The optical fiber was connected to a spectrograph (Spectral Products SM 242) which has an optical resolution of 0.4 nm from 200 to 1050 nm. The experimental conditions were kept constant during the detection of the spectra, except for the discharge time. The electrode erosion and the slightly change of the interelectrode gap determine the generation of the instabilities in water plasma which were not reproducible for the same experimental conditions. The intensity fluctuations in the acquired emission spectra averaged over 30 sweeps was of about 12%.

2.4 Materials

Aromatic polyimides have been synthesized by solution polycondensation of certain aromatic dianhydrides, namely hexafluoroisopropylidendiphthalic dianhydride (6FDA) with aromatic diamines: 4,4'-diamino-3,3'-dimethyl diphenylmethane (MMDA) by a method previously reported [9]. The polyimide (PI) films were obtained by casting onto glass plate the solution of the PI in DMAc followed by thermal treatment in a vacuum oven to remove the solvent (in the case of polyimide solution) (Scheme 1). The detailed procedure is described elsewhere [9].

The treated RF-oxygen plasma and water plasma samples were investigated by means of FTIR, AFM, and static contact angle measurements to observe the surface modifications induced after the plasma exposure.

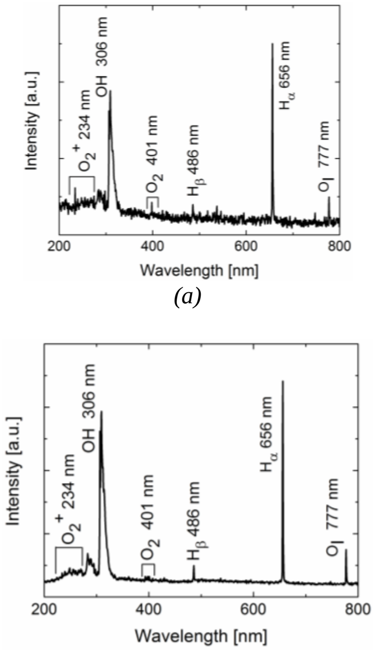


Scheme 1. Synthesis of the polyimide 6FDA-MMDA.

3. Results and discussion

3.1 Optical emission spectroscopy

In the electrical discharges in water the hydroxyl radicals, oxygen and hydrogen excited atoms and molecules were investigated by optical emission spectroscopy. The experimental conditions were kept constant during the spectra acquisition (discharge voltage U = 1700 V, frequency ν = 7 kHz, pulse width 50 μs). The same type of excited species were generated in the plasma before and after the immersion of the polymer film in the water, suggesting the fact that the polymer surface was not drastically affected during the discharge (Fig. 2 (a) and (b)). Therefore, the excited states of atomic hydrogen of the Balmer series H_α at $\lambda = 656.28$ nm, H_β at $\lambda = 486.13$ nm, and atomic oxygen O_I ($3p^5P \rightarrow 3s^5S^0$ at $\lambda = 777.5$ nm) were detected in the emission, as well as the molecular bands of the hydroxyl radicals OH (Emission System, $A_2\Sigma^+ \rightarrow X^2\Pi$ at 306.4 nm (Fig. 2 (a) and (b)). The weak emission band with the band head at $\lambda = 400.9$ nm might be attributed to the O_2 Chamberlains airglow system ($C^3\Delta_u \rightarrow a^1\Delta_g$) [25, 26]. The O_2^+ second negative system ($A^2\Pi_u \rightarrow X^2\Pi_g$ at $\lambda = 240$ nm) could be distinguished in the spectra. The O_3 Ultra-Violet System ($^1B_2 \rightarrow {}^1A_1$) at $\lambda = 310$ nm may overlap the molecular bands of the hydroxyl radicals. The color of the polymer was not changed and no significant gloss reduction was observed after 2, 4, or 6 minutes of plasma treatment.



(a)

(b)

Fig. 2. Optical emission spectra of pulsed electrical discharges in distilled water (a) before and (b) after the immersion of the polymer film.

Fig. 3 shows that the hydrogen emission intensity ratio $(I_{H_\alpha}/I_{H_\beta})$ increased with the water plasma treatment time. Under the assumption of a local thermal equilibrium (LTE) [18,27], the mean electron temperatures calculated during 6 min of discharge was in the range of 0.5 ± 0.1 and 2.5 ± 0.3 eV.

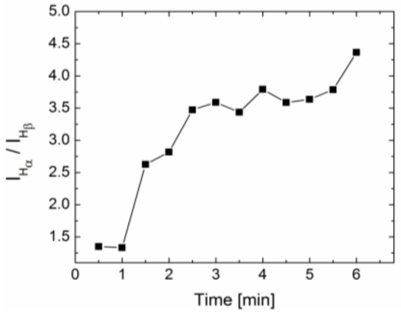


Fig. 3. The hydrogen emission intensity ratio's dependence on discharge time during 6 min of electrical discharge.

Therefore, the generation of the reactive species in the plasma increased with the increase of the electron temperature. The electron temperature dependency on time played a major role in the polymer surface modifications after plasma exposure, as will be discussed later on in this paper.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

A detailed study of ATR-FTIR spectra of pristine polymer film along with different oxygen plasma and water plasma treated polymer samples were performed within 6 min of PI surface treatment (Fig. 4). The spectra were assigned as I for the untreated plasma samples, II, III, and IV for 2 min, 4 min, and 6 min RF-oxygen plasma treated samples, respectively. The water plasma treated films were assigned as V, VI, and VII for 2 min, 4 min, and 6 min exposure, respectively. For the untreated plasma sample, several characteristic peaks were attributed to the imide structure, such as: the carbonyl group of the imide ring at 1770–1780 and 1710–1720 cm^{-1}, and the characteristic band for the C–N vibration at 1360–1375 and 720–730 cm^{-1} [9, 28]. The absorption peaks at 2940 and 2870 cm^{-1} are attributed to the methyl and methylene groups. The characteristic absorption bands of hexafluoroisopropylidene are present at 1260 and 1210 cm^{-1}. For the RF-oxygen plasma treated samples (Fig. 4, II - IV) the same absorption peaks were identified in the spectra as in the case of the untreated PI sample. This may imply the fact that oxygen plasma did not affect the chemical structure of the PI film surface.

For the water plasma treated samples (Fig. 4, V - VII), shift and broadening of the infrared absorption lines could be observed in the spectra. The C=O band of the imide group shifted gradually to the lesser wavenumbers (from 1730 cm^{-1} for the 2 min plasma treated sample to 1670 cm^{-1} for the 6 min plasma treated sample). The shift and broadening of the infrared absorption bands are caused by the collision and scattering between phonons [29]. This implies a scission of the imide group. It was previously shown that the generation of the reactive species formed in the plasma was enhanced with the discharge time (Fig. 3). It may be assumed that highly energetic excited species may reach the polymer surface by means of bubbles and streamers, producing the scission of the polyimide structure into its component groups, i.e. aromatic dianhydride (hexafluoroisopropylidendiphthalic dianhydride-6FDA) and aromatic diamine (4,4'-diamino-3,3'-dimethyl diphenylmethane-MMDA). The increase in the temperature may determine the broadening of spectral line and a decrease in the relative intensity. The added thermal energy may gradually overcome the intermolecular and intramolecular forces, and less energy is required to excite the vibrational dipoles. Thus, the spectral peaks will appear at lesser wavelengths corresponding to an increasing structural material disorder [30]. For the 6 min plasma treated sample (VII) could be observed a splitting in the C=O of the imide ring in two well-defined peaks (1745 and 1788 cm^{-1}). The same behavior was observed by authors in the case of the $(CO)_2NC$ imide group which were separated into two different peaks due to the increase in the cure temperature. The electron temperature increased (up to 2.5 eV) with the increase of the water plasma treatment time. Thus, an increase in the local surface temperature may induce the formation of more carbonyl groups (C=O) on the polymer film surface.

The absorption band at 1860 cm^{-1} (CO-O-CO) was also identified in the spectra only for the plasma treated samples (V - VII) and indicates the presence of the anhydride. The band at 1540 cm^{-1} (υ amide C-N) is also present in all the FTIR spectra (I - VII). The fact that only the 1860 cm^{-1} band exists in the spectra of the plasma treated samples may suggest a scission of the polyimide structure in its own components, namely the aromatic dianhydride and aromatic diamine. The imide cycle may be broken after the interaction with the reactive species formed in plasma and the components used initially for the polyimide synthesis are now present on the film surface.

The characteristic absorption band of the amide group are evidenced at about 3870 cm^{-1} (COOH and NH_2 vibrations) only in the case of the plasma treated samples (V - VII) [31]. The band was also formed in the spectra as a consequence of the PI separation into aromatic dianhydride and diamine which contain the functional groups responsible for this absorption region.

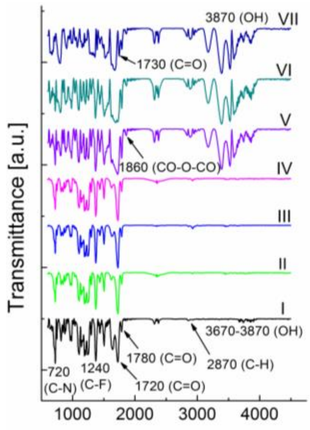
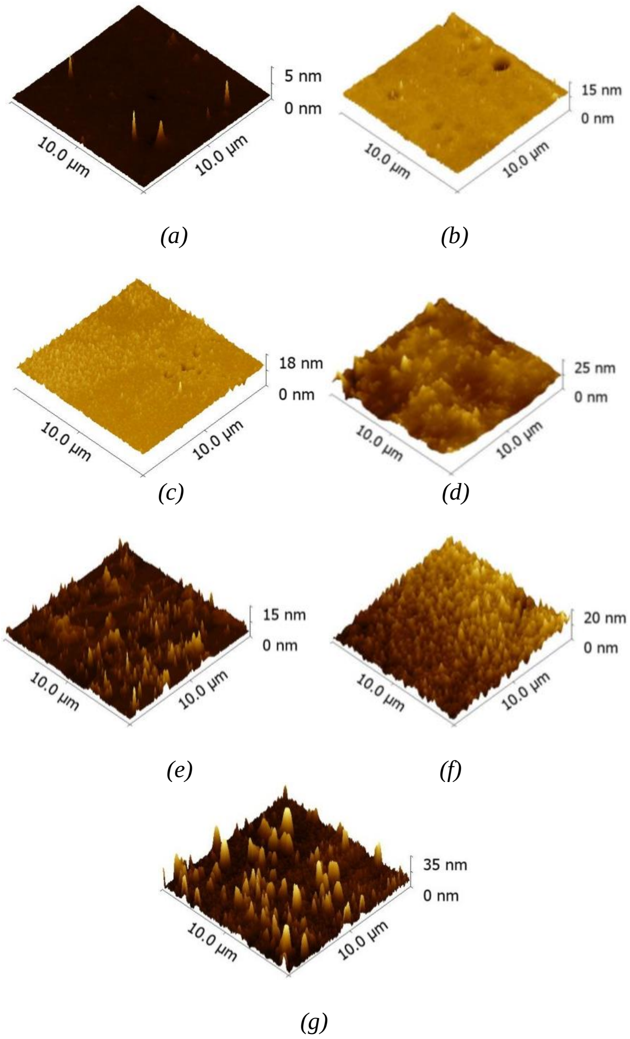


Fig. 4. ATR-FTIR spectra of (I) the untreated plasma sample, RF-O_2 plasma treated samples for (II) 2 min, (III) 4 min, and (IV) 6 min and the water plasma treated PI films for (V) 2 min, (VI) 4 min, and (VII) 6 min of plasma discharge.

3.3 Atomic Force Microscopy (AFM)

The surface morphology of the plasma treated PI was investigated by Atomic Force Microscopy (Ntegra Spectra, NT-MDT). An area of 10 x 10 µm was scanned for each sample (Fig. 5). The surface roughness of the PI film was evaluated in terms of root mean square (rms) of the roughness. The untreated PI films are very smooth with a rms of only 2 nm, while after 2 min of RF-oxygen plasma the surface roughness increased to 15 nm (Fig. 5 (a), (b)). The rms values increased with the discharge time. A rms of 18 nm was measured for the samples treated for 4 min, while for the 6 min plasma treatment the rms was 25 nm (Fig. 5 (c), (d)). The increase of surface roughness in the plasma treated samples may be the result of the etching and ion bombardment during the plasma discharge.



(a) *(b)*

(c) *(d)*

(e) *(f)*

(g)

Fig. 5. 3D AFM images of (a) the untreated PI film, of the RF-O_2 plasma treated PI films for (b) 2 min, (c) 4 min, and (d) 6 min, and of the water plasma treated samples for (e) 2 min, (f) 4 min, and (g) 6 min.

The surface roughness also increased after water plasma treatment of the polymer film. The surfaces showed a rms of 14 nm after 2 min of plasma exposure (Fig. 5 (e)). For the 4 min treatment time, the rms was 18 nm, while for the 6 min treatment time, the roughness increased to 32 nm (Fig. 5 (f), (g)). It may be assumed that the excited species generated in the plasma induced changes in the surface morphology due to the interaction with the PI functional groups.

3.4 Contact angle measurements

The water static contact angle between the liquid meniscus and the polymer surface was measured by means of the sessile drop technique to determine the polymer surface tension. The measurements were performed before and after the RF-oxygen plasma and water plasma treatment of the polymer films using a goniometer KSV CAM 101. Uniform distilled water drop of 1 μL volume was placed on the polymer surface and the contact angle was measured for 20 sec with a video-based optical contact angle measuring device. The fluorine-containing species on a polymer surface determine low surface tension, due to the physical forces which held together the molecules. The contact angle of the untreated sample was 74^0. In the case of the RF-oxygen plasma, the contact angle gradually decreased to 40^0, 35^0, and 25^0 after 2 min, 4 min, and 6 min of plasma exposure, respectively (Table 1). Thus, it may be assumed that the C-C bondings were damaged and the C-O bondings increased. The AFM measurements (Fig. 5, (b) – (d)) have also shown an increase in the surface roughness with the treatment time, suggesting that new oxygen based functional groups were formed at the surface as a consequence of the etching and ion bombardment. An increased hydrophilicity, caused by a movement of the oxygen-containing polar groups into the bulk of the PI films due to the oxygen plasma treatment, was also suggested by some authors [1].

The contact angle measured for the water plasma treated sample has increased to 82^0, 87^0, and 91^0 for the 2, 4, and 6 min plasma treated samples (Table 1). Thus, the energetic particles of the water plasma induced modifications of the surface properties. The surface segregation of the CF_3 groups might have determined an increase in the surface hydrophobicity of the polymer [32]. The increase in the water contact angle may be also attributed to the increase in the degree of imidization of the PI [32]. During the imidization, more polar carboxylic (COOH) and amide (CONH) groups become less polar imide groups, leading to a significant decrease in the strength of the polar part free energy. As a result, the surface free energy of the resultant PI film is diminished.[7]

Table 1. Contact angle values in (^{0}) of the O_2 plasma and water plasma treated PI samples.

Untreated sample [^{0}]	Plasma treatment time [min]	O_2 plasma treated film [^{0}]	Water plasma treated film [^{0}]
74	2	40	82
	4	35	87
	6	25	91

4. Conclusions

Aromatic polyimide films were treated by RF-oxygen plasma and pulsed electrical discharges in water techniques for 2, 4, and 6 minutes. It was observed that the polymer film surface suffered modifications, depending on the type of the plasma discharge. The RF-oxygen plasma induced an increase in the surface roughness as a consequence of the ion bombardment and etching. The hydrophilicity of the sample surfaces increased with the increase of the discharge time, due to the formation of the oxygen-containing polar groups on the PI surface.

The water plasma treatment of the PI films induced modifications of the chemical composition of the polyimides surface by breaking the polyimide structure into its initial components used for the film preparation, followed by an imidization process of the polyimide. These modifications have led to an increase in the surface hydrophobicity of the polyimide samples, confirmed by the static contact angle measurements, which have shown an increase in the contact angle values with the increase of the discharge time.

Therefore, the results suggest that the RF-oxygen plasma and the plasma formed in water may be used for controlled and efficient surface modification methods of the polymer films, suitable for a wide range of industrial applications.

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