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Effect of Electron Density and Temperature in Oxygen Plasma Treatment of Polystyrene Surface

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Abstract. A plasma treatment of polymeric materials has become one of the most important methods to enhance the surface wettability without affecting the bulk material features. Oxygen plasma treatment of polystyrene surfaces deposited on a QCM sensor was evaluated by relating the plasma parameters, surface roughness, and the wettability. The internal plasma parameters investigated in this work were the electron temperature (T_e) and the electron density (n_e). The oxygen plasma was generated using an RF power generator. The power was varied by applying a voltage from 60 volts to 100 volts. An Optical Emission Spectroscopy (OES) was used to determine the plasma species, the T_e and the n_e during the plasma oxygen process. The dominant species in the plasma was excited atomic oxygen or activated oxygen (OI) which was detected from the 774 nm and 842 nm emissions. The higher applied RF voltage resulted in the higher T_e and n_e. The effect of the T_e and n_e on the polystyrene surface was observed on the change of the surface roughness. The surface roughness significantly related to the surface wettability observed with a contact angle measurement. Furthermore, the plasma treatment greatly changed the surface from hydrophobic to hydrophilic via reactive processes by the excited atomic oxygen species. This was confirmed by the increase in C=C and C=O functional groups observed using a Fourier transform infrared (FTIR) spectroscopy. The T_e and n_e may also affected the character of the plasma in terms of its reactivity.

Keywords: Oxygen plasma, OES, electron temperature, electron density, surface wettability, polystyrene

1. Introduction

Oxygen plasma is widely used in many plasma processing such as etching processing, surface modification, biomaterials processing, and so on [1–3]. In the plasma system, the oxygen plasma is created by utilizing an oxygen source. Surface modification by oxygen plasma is one of the crucial factors to change the surface properties of the materials for the application in a sensor. Surface properties commonly are related to the wetting behaviour of the polymer′s surfaces. The polymer of such a polystyrene recently was used as a matrix layer for the interaction between bio molecule and surfaces in the application of biosensor based on quartz crystal microbalance (QCM) [4–7]. In the previous work, the polystyrene surface was successfully modified to change the wettability of the polystyrene′s surfaces by UV irradiation [6] and nitrogen plasma treatment [4]. It was reported that the polystyrene has changed the surface roughness, contact angle and also related to the new functionality of nitrile group which caused the polystyrene′s surfaces change to hydrophilic. However, the study on the oxygen plasma parameter related to surfaces properties of polystyrene has not been reported yet.

In the plasma processing, various external plasma parameters are essential for controlling the characteristics of the material′s surfaces. The condition of external plasma parameters includes the power generator (applied field, frequency), type of gas (atomic or molecular), gas flow rate, and gas pressure [8]. The state of the plasma can be represented by internal plasma parameters that characterize the plasma. The internal plasma parameters are governed by the electron temperature and electron density. The electron temperature and electron density can lead to control the external parameters in the plasma, for example, the power density, gas flow rate and pressure, and hence resulted in the film properties.

Plasma emission spectroscopy such as optical emission spectroscopy and Langmuir probe is a common method to measure the species, T_e and n_e in the plasma processing. The OES method is non-intrusive measurement method and low cost-effective compared with direct measurements using Langmuir probe to characterize this oxygen plasma. So, in this study, the OES measurement was used for examining various plasma parameters. The effects of radio frequency (RF) generator related to the surface topography, functional group, oxygen species, and character in the plasma (T_e and n_e) are discussed.

2. Methods

In this work, the polystyrene as a coating material was purchased from Sigma-Aldrich. The polystyrene with a molecular weight (wt) of 192.000 gr/mol was dissolved in toluene solvent with 6% mass of polystyrene, and then it was coated on the QCM surface by using spin coating method. The spin speed for the coating of polystyrene was 5 RPM and time deposition of 5 min. The oxygen plasma was treated on the polystyrene surface layer using radio frequency (RF) plasma generator of 2 MHz. The condition of plasma treatment is as follows: the total pressure in the chamber was 40 Pa and the flow rate was 40 ml/min. The RF voltage was varied at 60, 70, 80, 90, and 100 volts. Each treatment was performed for 2 minutes.

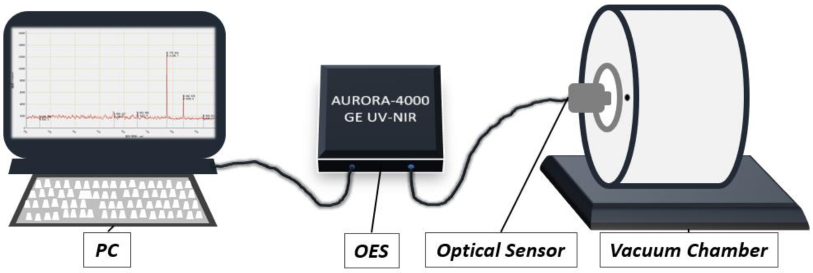

Figure 1. Schematic diagram of the optical emission spectroscopy for emission diagnostics.

An optical emission spectroscopy (AURORA-4000) was employed to measure the emission intensity peaks vs wavelength (λ) (Figure 1). Automatic monochromator in the spectrometer can be used to measure the range of wavelength from 200 to 900 nm. The atomic lines determination was performed with NIST atomic spectral database. The atomic lines was used to determine the species plasma including atomic/radical, molecule and ion, T_e and n_e. In this work, the electron temperature and the electron density were calculated by utilizing the intensity ratio of two oxygen atomic (OI) spectral lines appeared at the wavelength of 774 nm and 842 nm. The electron temperature (T_e) is determined by using Equation 1 [9,10].

$$T_e = \frac{1}{k} \frac{E_1 - E_2}{\ln\left(\frac{I_2}{I_1}\right) - \ln\left(\frac{\left(gfv^3\right)_2}{\left(gfv^3\right)_1}\right)} \tag{1}$$

where E_1 and E_2 are related to the center of the spectral lines which were 774 nm and 842 nm, respectively. k = Boltzmann constant, I_1, I_2 = intensity of emission line, and g = statistical weight. The density of the electron in the plasma can be predicted from the spectral bandwidth of a particular line in the optical spectrum of the plasma. The line is not sharp but is usually broadened. The broadening can be related to the *Stark* and *Doppler* broadening. The Stark broadening is the result of emitter's spectral lines shifting and splitting due to the existence of an external electric field. Meanwhile, the Doppler broadening is caused by the distribution of the thermal motion of the photon emitter. Since the plasma was in a quasi-equilibrium state, only the Stark broadening $\Delta\lambda_{1/2}$ or full width half maximum (FWHM) that was considered in this work. The density of the emitter and hence the electron (*ne*) was deduced from the equation (2) and (3):

$$\Delta\lambda_{1/2} = 2\omega\left(\frac{n_e}{10^{16}}\right) \tag{2}$$

$$\left(\frac{\Delta\lambda_{1/2}10^{16}}{2\omega}\right) \tag{3}$$

where,

$\Delta\lambda_{1/2}$= Stark broadening (FWHM) in nm

ω = electron impact width parameter

n_e = electron density in m^{-3}

However, the deduction is valid when the density of the electron is equal or more than the minimum limit which is determined by equation (4) [9,11].

$$n_e \geq 1.6\times10^{16} T_{1/2}\left(\Delta E\right)^2 \tag{4}$$

where,

ΔE = energy difference $\left(E_1 - E_2\right)$

The contact angle of the samples was observed and characterized by the contact angle measurement [12]. The topographical surface roughness measurements were performed by an interferometric surface micro-profiler (*TMS 1200 Polytech TopMap-μLab*). The identified polar functional groups were observed by using FTIR before and after treated by nitrogen plasma.

3. Results and Discussion

The oxygen plasma was generated by an RF generator in a fixed pressure vacuum system. The RF power was varied by applying different RF voltage across the electrodes in the plasma chamber. The power delivered to the plasma was maximized by an automatic impedance matching circuit working at the frequency around 2 MHz. The RF voltage affects the state of the plasma in the chamber. The optical emission spectroscopy system was utilized to determine the state of the plasma. The oxygen plasma produced a spectrum exhibiting two dominant spectral lines at the wavelength of 774 nm and 842 as shown in Figure 2. The peaks are related to the emission from excited atomic oxygen (OI).

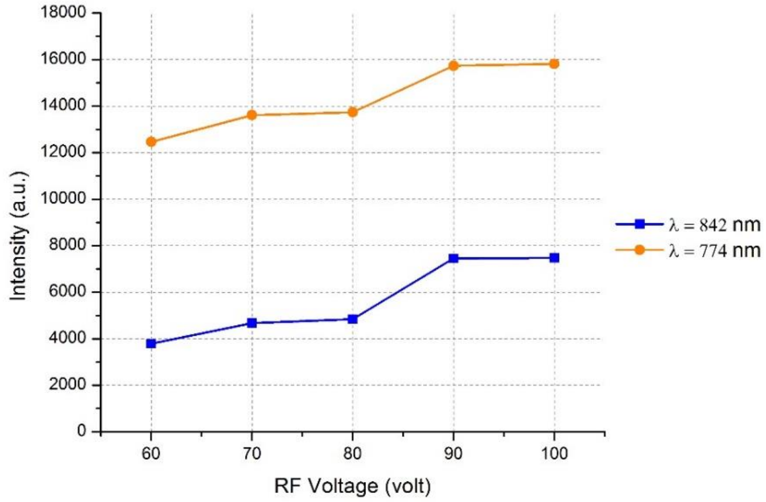

Figure 2. OES spectrum of oxygen plasma at RF voltage of 90 V

The spectra of the oxygen plasma at various RF voltages showed a similar pattern. The effect of the RF voltage on the intensity of the peaks is shown in Figure 3.

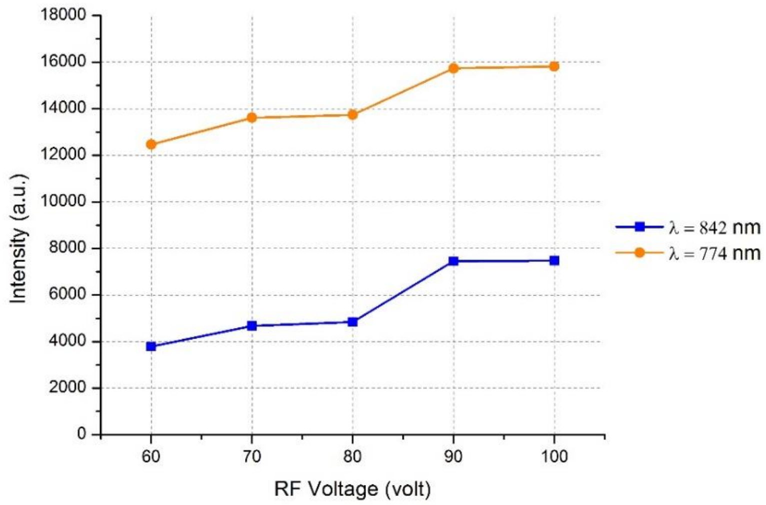

Figure 3. The intensity of emission spectrum OI in the polystyrene surfaces during the plasma process

The two peaks for the excited oxygen atom OI or O* were also reported by Wang *et al.* According to Wang, the line spectrum of the atomic oxygen is produced by two kinds of processes i.e., direct emission of excited oxygen atoms and emission of oxygen molecules [13]. The excitation of the atomic oxygen is caused by the interaction of atomic oxygen and energetic electrons as shown in the Equation 5.

$$O + e^- \rightarrow O^* + e^- \quad (5)$$

On the other hand, the production of an excited oxygen atom from molecular oxygen is led by a dissociation reaction of the oxygen molecule as shown in the equation (6):

$$O_2 + e^- \rightarrow O^* + O + e^- \quad (6)$$

The intensity of the emission spectrum greatly affects the temperature of the electron and the density of the electron. Equation 1 was used to determine the electron temperature. The two distinct peaks at around 774 nm and 842 nm were the only peaks which can be utilized to calculate the energy difference and intensity ratio. The data of the two peaks were obtained from the NIST atomic database and is shown in Table 1 below.

Table 1. Identified emission spectra of oxygen peaks and its corresponding spectroscopic data

Species	Wavelength (nm)	Transition	Statistical Weight g_k	Transition Probability (A/S^{-1})	Level Energy (E/cm^{-1})
OI	774.194	$2s^22p^3(^4s^0)3s\ ^5s^0 \rightarrow 2s^22p^3(^4s^0)3p\ ^5p$	5	3.69 x 10^7	73768.200
OI	842.625	$2s^22p^3(^4s^0)3s\ ^3s^0 \rightarrow 2s^22p^3(^4s^0)3p\ ^3p$	3	3.22 x 10^7	76794.978

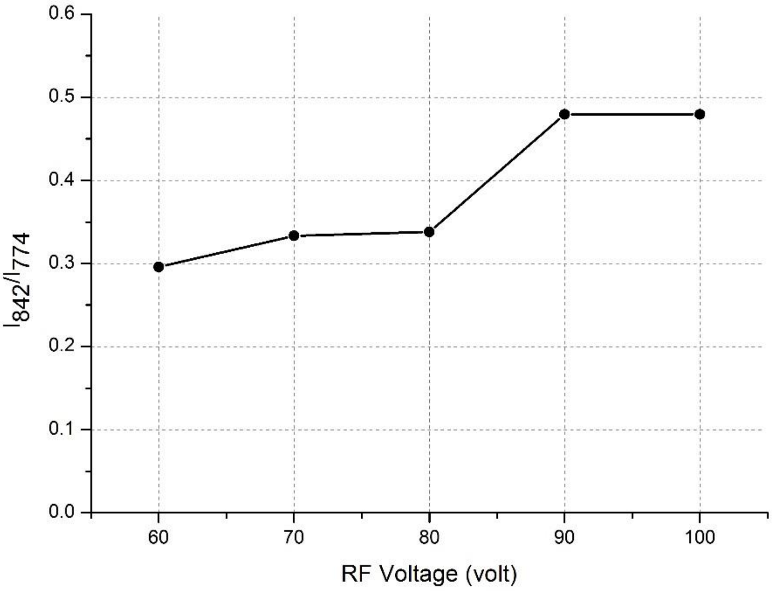

Figure 4. The variation of (a) I(842 nm)/I(774 nm) depends on the RF voltage

Figure 4 shows the relationship between the applied RF voltage and the ratio of emission intensity at 842 nm and 774 nm of the optical spectra. In one step reaction, the ratio reflected the electron temperature [14]. The electron temperature increased with the increase of the RF voltage. The increase of the electron temperature, in turn, leads to more excitation and ionization processes in the plasma. This will expectedly increase the electron density resulted from the processes. The density of the electron was determined by considering the *Stark* broadening of the peaks. The calculation was carried out using equation 3 in the method section. The validity of the calculation was ensured by determining the minimum density $n_{e(\min)}$ of the electron which can be calculated from equation 4. Table 2 presents the results of calculation of the $n_{e(\min)}$ using the peak at around 774 nm and ΔE = 1.595 eV.

Table 2. The calculation of the $n_{e(\min)}$ using the peak at around 774 nm and ΔE = 1.595 eV

λ (nm)	V_{RF} (Volt)	T_e (eV)	$n_{e(\min)}$ (cm^{-3})
774.705	60	0.814	5.28384E+16
774.592	70	1.105	7.17322E+16
774.570	80	1.202	7.80266E+16
774.671	90	21.776	1.41389E+18
774.731	100	39.898	2.59051E+18

The 774 nm peak was chosen with the assumption that the local thermodynamic equilibrium (LTE) state is dominant in the highest intensity. The FWHM of the peaks for the various RF voltage spectral data were measured using a peak fitting routine. The results of the electron density together with the electron temperature calculation are plotted in Figure 5.

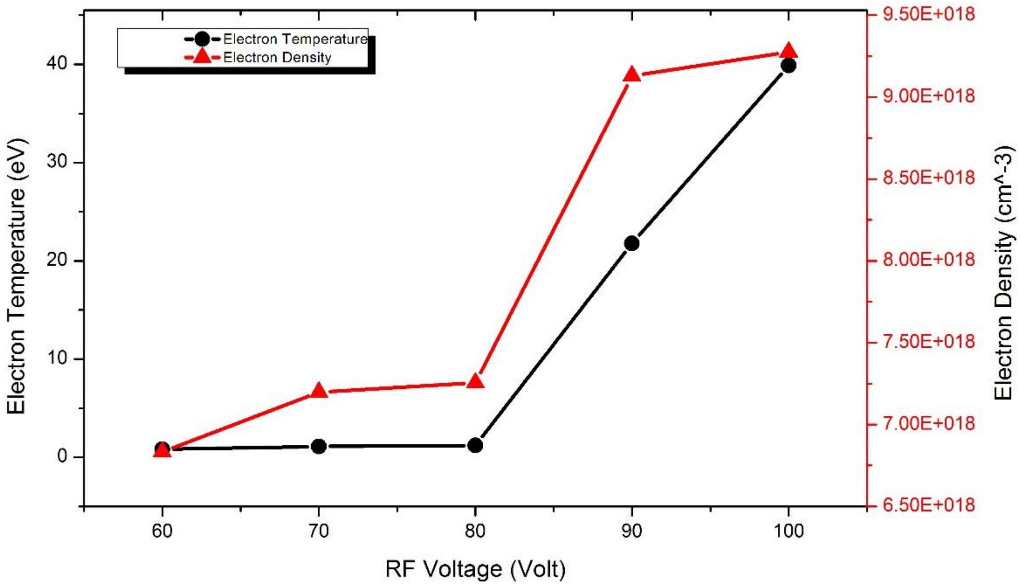

Figure 5 The dependence of the electron temperature and electron density upon the RF voltage

As can be seen from Figure 5, the electron density for the variation of RF voltage from 60 volts to 100 volts was in the range of 6.8×10^{18} and 9.3×10^{18} cm^{-3}. The result was valid since the $n_{e(\min)}$ values were below the actual density, n_e. The variation of the electron density and temperature due to the RF voltage affected the treated surface. The T_e and n_e represent the character of the plasma leading to a particular behavior related to the generation of plasma species. They also affected the reactions in the plasma and the interaction between the plasma and the surface of the material. In this work, the oxygen plasma is expected to modify the surface of a polystyrene thin film deposited on a QCM sensor. The change of morphology and microstructure of the surface was observed through its hydrophobicity. By a contact angle measurement, it can be seen that the hydrophobicity of the surfaces could be examined. Figure 6 describes the relationship between the applied RF voltage and the change of the contact angle.

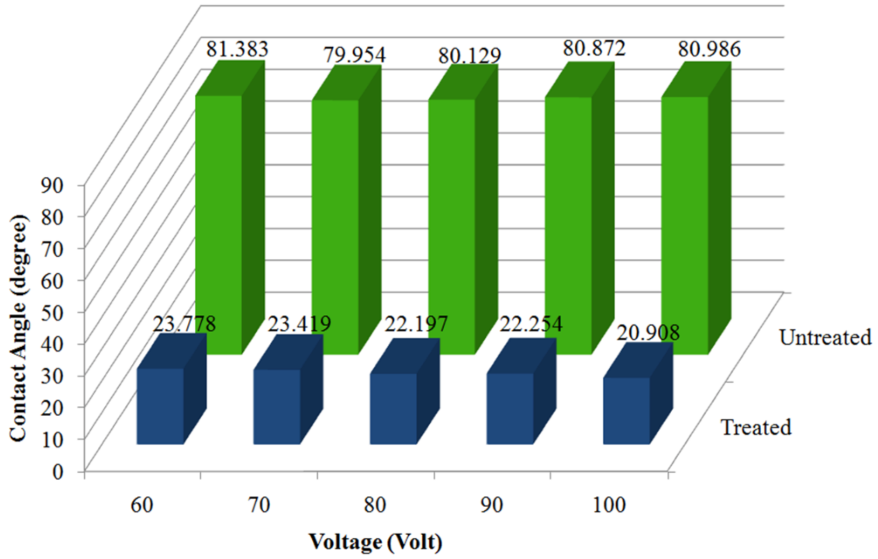

Figure 6. The Contact angle of the polystyrene for untreated and treated by oxygen plasma at various RF voltage

The plasma treatment drastically reduced the contact angle from 80 degrees (hydrophobic) to around 20 degrees (hydrophilic) depending on the applied RF voltage. The effect of the RF voltage to the measured contact angle was significant. The observation showed that the higher RF voltage application produced the smaller contact angle. The hydrophobicity of surface is usually related to the surface roughness (Ra). This work also observed the change of the surface roughness due to the variation of RF voltage as depicted in Figure 7.

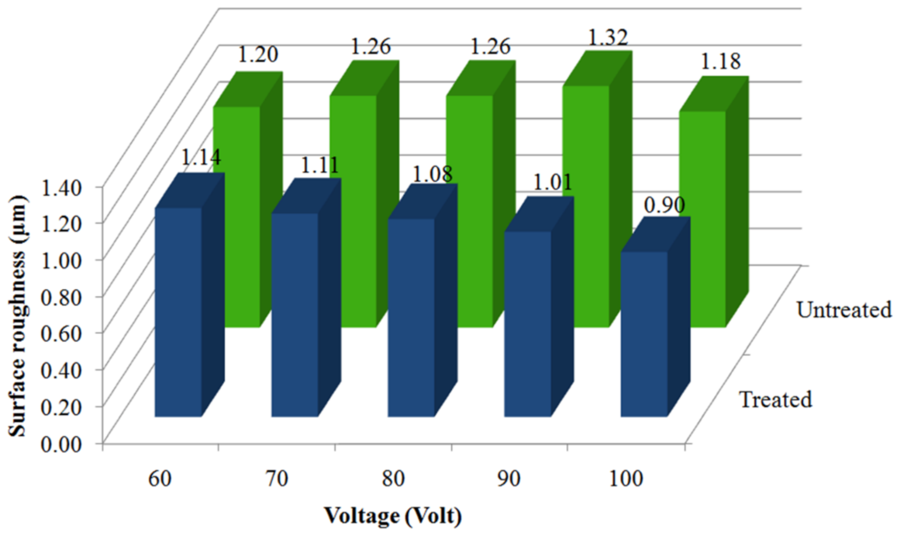

Figure 7. The surface roughness of the polystyrene for untreated and treated by oxygen plasma at various RF voltage

As can be seen from Figure 7, the higher applied RF voltage reduced the surface roughness since the temperature of the electron directly related to kinetic energy of the electron. The higher T_e and n_e resulted in more collisions in the plasma as well as bombardments on the surface of the treated material. The more energetic particles gave rise to stronger surface interactions and hence modifications. The polystyrene chains could be sliced and recombined into a new surface morphology which directly observed as the change of surface roughness. The knowledge which relates the electron temperature and density and the resulted surface properties can be used to optimize the plasma treatment process in the future. Comparing the dramatic decrease of the contact angle before and after treatment to the small decrease of the surface roughness brings about the idea that the change of the surface property was not only due to the change of the roughness. To find out the cause of the dramatic change, infrared spectroscopy was employed to characterize the surface before and after the plasma treatment. Figure 8 describes the FTIR spectra of the untreated and the plasma treated sample.

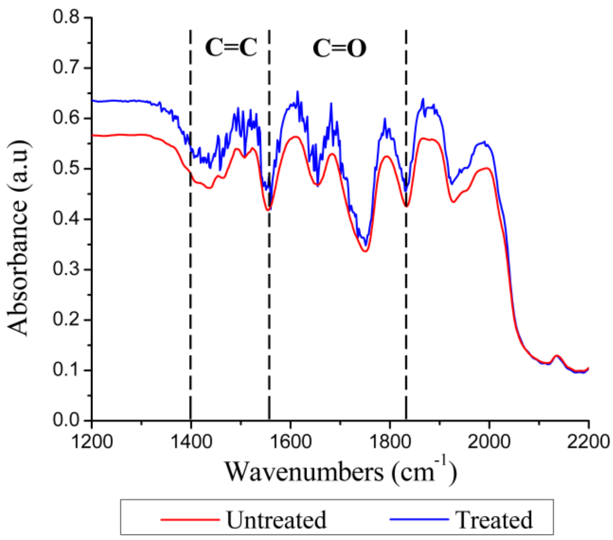

Figure 8. FTIR spectra of the C=C group and C=O group of the polystyrene for untreated and treated by oxygen plasma

The infrared spectra revealed that the plasma treatment increased the coverage of some functional groups on the polystyrene thin film surface i.e., C=C group at 1400-1600 cm^{-1} and C=O group at 1600-1800 cm^{-1}. Both of the groups were polarly producing the hydrophilic surface. The production of the functional group was controlled by a chemical reaction primarily caused by the existence of the excited atomic oxygen. Some of the reactions terminate the broken chain creating the C=C group. On the other hand, the oxygen is also attached in the structure giving rise to the C=O group.

4. Conclusion

The effect of electron density and electron temperature in oxygen plasma during the plasma treatment of polystyrene surface was studied. Optical emission spectroscopy revealed the active species in this work was OI assigned to the excited atomic oxygen. The electron temperature, T_e was deduced successfully from the ratio of the spectral intensity at 882 nm to 774 nm. On the other hand the electron density, n_e was inferred from the measurement of the Stark broadening of the peak at 774 nm. The T_e and n_e were affected by the applied RF power, especially at the voltage higher than 80 volts. The T_e and n_e significantly affected the surface roughness through bombardment processes. However, the dramatic change of the polystyrene property was caused by the reactive process by the excited atomic oxygen which could be observed by the increase of the polar functional group after the plasma treatment. Further studies are needed to investigate the relationship between the electron temperature and the active plasma species controlling the functionalization process.

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