WETTABILITY IMPROVEMENT OF PMMA FILMS WITH HIGH FREQUENCY RF PLASMAS

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Highlights

- Nitrogen (N) and argon (Ar) plasmas can be used to obtain hydrophilic PMMA surface.

- To reach the lowest contact angle value of PMMA surface, high plasma power is needed.

- High frequency (40.68 MHz) CCP RF plasmas can be used effectively to enhance the wettability of polymer surfaces.

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ABSTRACT: Poly(methyl methacrylate) (PMMA) has a wide variety of applications due to its attractive physical and optical properties. Due to its hydrophobic (water-repellent) character, the surface of PMMA should be modified before being used in applications. In this study, the surface of PMMA films were modified by 40.68 MHz high frequency CCP (capacitive-coupled plasma) RF system with nitrogen (N) and argon (Ar) gases. The experiments carried out under various plasma powers while the pressure and treatment time were kept constant. The wettability of the plasma treated surfaces was analyzed with contact angle and surface free energy (SFE) measurements. Also, the change in the chemical structure of the surfaces was investigated with X-ray photoelectron spectroscopy (XPS). The results showed that all plasma treatments enhanced the hydrophilicity of the surfaces and the lowest contact angle values obtained at high plasma power. The total SFE of the treated surfaces increased with power and the main contribution to total SFE came from polar components. The polar groups formation on the surface after plasma treatment was proved with XPS results. Hence, it was found that high frequency CCP RF plasmas can be used effectively to obtain hydrophilic polymer surfaces.

Keywords: Surface Engineering, Plasma Surface Modification, PMMA, Wettability, Polymer

1. INTRODUCTION

PMMA is a low cost material and it has exceptional features such as thermal stability, chemical inertness and flexibility. It is widely used in applications in membranes [1], photonics [2], coatings and biomedicals [3]. In addition, it is an alternative to glass materials due to its high light transmittance [4,5]. The main problem of PMMA is its hydrophobic surface which leads to pore adhesiveness. Therefore, it is necessary to modify the surface of the polymer to obtain hydrophilic surfaces before being used in some applications especially in biomedical fields where the metal films, proteins and cells adhering to the polymer surface [6,7]. There are various surface modification techniques for polymers such as wet chemical modification [8] and plasma treatment [9]. The most advantageous method in tailoring the surface is plasma treatment, since the bulk properties of the material remain unchanged and only the surface of the material is modified. Moreover, plasma modification is time efficient and solventless method. In addition, this process is carried out without generating chemical waste. Plasma, partially ionized gas, consists of electrons, ions and reactive neutral particles with high energy levels. These energetic particles interact with the material surface and give their energy to the material through the collisions. As a result, some bonds on the surface are broken and radicals are formed leading to cross-linking [10,11] and formation of functional groups on the surface with the interaction of particles with plasma and enviroment [12-14]. Plasma parameters such as plasma power, gas, pressure etc. affects the treatment process.

Nitrogen containing plasmas are used to improve surface wettability [15], electrical conductivity [16] and biocompatibility [17]. Nitrogen gas plasma contains molecules located at many different electronic levels. Therefore, it is a rich source of excited molecules. Argon plasma, on the other hand, is used for many purposes such as removing surface contamination [18] and cross-linking [19]. Although argon is a noble gas, its plasma causes the formation of polar groups on polymer surfaces [20]. Oxygen (O) and nitrogen containing groups on the surface are responsible of hydrophilicity.

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PMMA surface treatments before used in applications has been investigated for a long time [21] and still the effect of different plasma systems on modification of PMMA films has been studied [22, 23]. In the literature, for capacitevely coupled RF plasmas, the system which has 13.56 MHz driven frequency were used generally for processing polymer surfaces [24-26]. In this study, PMMA surfaces were exposed to plasma generated at high frequency (40.68 MHz) CCP RF system at constant pressure with different plasma powers. Both the wettability of films and the effect of high-frequency plasmas on the processing of polymer material surfaces were investigated. It was found that high frequency CCP RF plasmas can be used effectively for surface modifications of PMMA.

2. MATERIAL AND METHOD

2.1. Preparation of PMMA Films

PMMA powder, the chemical structure of which is given in Figure 1, (Molecular weight 120.000 Da) was dissolved in chloroform (20%, w/w) at room temperature (25 °C) and a homogeneous mixture was obtained by mixing the solution with a magnetic stirrer for two hours. Then it was poured onto microscope glasses in order to obtain PMMA films. The films were kept at room temperature for 7 days and dried by allowing the solvent to evaporate.
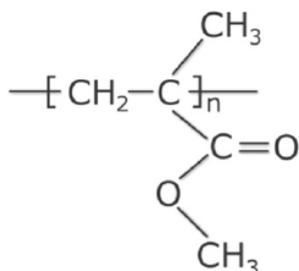

Figure 1. Chemical structure of the monomer unit of PMMA

2.2. Plasma Surface Treatment

The surface of PMMA films were treated with CCP RF plasma system. It consists of a cylindrical reactor with two aluminum electrodes placed parallel to each other, a 40.68 MHz RF power supply, a matching network and vacuum pumps (Figure 2.). The diameters of the electrodes used in the system are 200 mm. The distance between these two identical electrodes is 30 mm. Plasma processes were carried out under vacuum conditions in order to protect the surfaces from the effects of air molecules. The rotary pump reduces the internal pressure to 10^{-2} torr, while the turbo molecular pump reduces this value to 10^{-3} torr. The matching network is placed between the reactor chamber and the RF power supply in order to provide maximum power transfer to the reactor chamber by minimizing the power reflected from the reactor through the circuit elements. After the PMMA films were placed in the system, the system was put into vacuum and then gas was supplied to the system. Argon and nitrogen gases as plasma were used in the experiments. Since pressure increased due to plasma during the experiment, the system pressure was kept at constant value by means of valves. Longer exposure times did not cause any significant effect on the contact angle values in our high frequency RF system. So, only the plasma power effect on the wettability of polymer films was investigated. All of the experiments were performed at different plasma powers (25 W, 100 W and 150 W), at a constant pressure of 0.7 torr and treatment time of 5 minutes. After the surface treatment process, the system was filled with the working gas to stabilize the polymer surfaces and prevent it from direct contact with air. Then, the system was removed from the vacuum and the surfaces of the materials were analyzed.
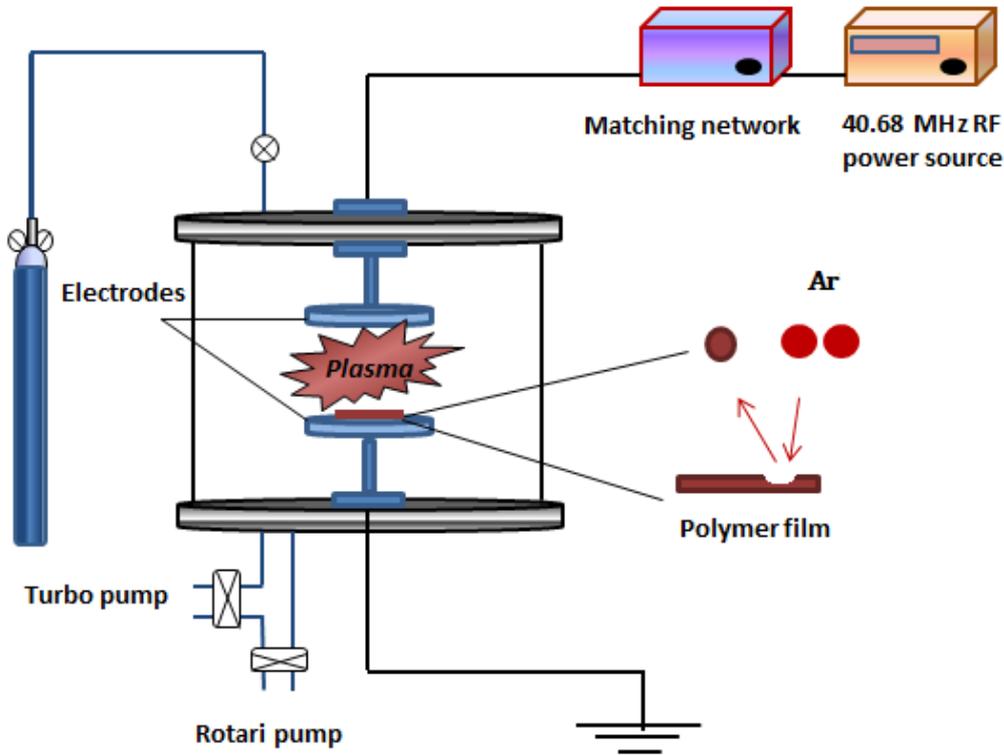
Figure 2. Experimental set up of plasma treatment

2.3. Contact Angle and SFE Measurements

Wettability is a measurement of liquids ability to spread over the surface of a particular solid. The contact angle of the surface is a measure of the wettability, and defined as the angle at which the liquid gas interface meets the solid surface. When water contact angle decreases, the wettability of the surface increases, or vice versa. Moreover, chemical groups on the surface of solid material affect wettability. One of the measurement methods that gives information about these groups is the SFE. SFE is the work that is necessary to increase the surface area of a solid and it has an influence on the wettability of solids by liquids. The relation between contact angle and SFE is given with Young's equation and defined as

$$\gamma_s = \gamma_{sl} + \gamma_l cos(\theta) \tag{1}$$

where γ_l is the SFE of the liquid, γ_s is the SFE of the solid material, γ_{sl} is the solid-liquid interface free energy, and θ is the contact angle. There are some methods in the literature to find γ_s using contact angles of different liquids [27]. Among them, geometric and harmonic mean approaches are widely used to calculate the SFE of polymers [27,28]. SFE has dispersive and polar components that can be calculated from the geometric mean and harmonic mean approaches. In order to find the SFE of the solid surface, at least two contact angle measurements are required. So, not less than two liquid selections is necessary.

One of the test liquids must be selected from the polar liquids, and the other liquid must have dispersive effect. Water, diodomethane and formamide can be used for SFE measurements [28]. In this study, the surface contact angles of the treated and untreated PMMA films were made with Attension Theta goniometer. The static contact angles of the film surfaces were measured by dropping 5 µl drop of distilled water, diiodomethane (DIM, Sigma-Aldrich) and formamide (FA, Sigma-Aldrich) onto the surface at 25 °C room temperature. All plasma treatment experiments were carried out three times and contact angle values were taken for all the surfaces with five different points in order to obtain more

accurate results. SFE values of PMMA films were obtained by using the contact angle values of liquids with both geometric and harmonic mean approaches.

2.4. XPS Measurement

XPS is a high precision surface analysis technique. When the material exposes to X-rays, the electrons are emitted from the surface and the kinetic energies of the electrons are analysed by a detector. These energies are related to the bonding energies of the atom and by measuring them the information of elemental composition and bonds on the surface can be obtained.

In this study, XPS measurements were carried out with the PHI 5000 VersaProbe 55 brand XPS device with aluminium monochromatic X-ray source, at a 45° take off angle both on the treated and untreated surfaces of PMMA films. For detailed peak analysis XPS peak program was used.

3. RESULT AND DISCUSSION

3.1. Contact Angle Results

In order to investigate the plasma effect on the surface, contact angle measurements of different liquids (water, diodomethane and formamide) were carried out. The contact angle values of the surfaces treated with argon and nitrogen plasmas under different plasma conditions are given in **Table 1** and the graphics of contact angle values of PMMA versus plasma power for nitrogen and argon plasmas are given in Figure 3.. The water contact angle for the untreated PMMA film surface is 71.3°. As can be seen from this table, a serious decrease in water contact angle was observed even at 25 W plasma power on the surface treated with both nitrogen and argon plasmas. The water contact angle values decreased as the plasma power increased and the most hydrophilic surfaces were obtained for the films treated with argon and nitrogen plasmas at 150 W plasma power. While the contact angle change of formamide showed similar behavior with water contact angle for nitrogen plasma, surface treatments did not cause great changes in contact angles of diodomethane. The similar behavior of formamide and water on the treated surfaces is due to polar structure of formamide and water. Diodomethane is a non-polar liquid. So, small changes in the contact angles of diodomethane may be due to the increase of polar groups on the surface and the decrease of dispersive groups such as C-C and C-H. Dorranian *et al.* [29] found that diodomethane contact angle slightly change with plasma treatment time while water contact angle decreasing due to increase of polar groups on the surface.

Table 1. Water (θ_w), diodomethane (θ_d), formamide (θ_f) contact angle values on PMMA film surfaces treated with nitrogen and argon gas plasma at different plasma powers

Sample	Power	Contact Angle		
		θ_w (°)	θ_d (°)	θ_f (°)
Untreated	0 W	71.3	32.4	54.8
Treated in nitrogen plasma	25 W	46.7	32.1	15.5
	100 W	40.6	32	12
	150 W	17.2	31.1	7.5
Treated in argon plasma	25 W	42	34	16.1
	100 W	32.9	31.7	12
	150 W	20.9	13.9	8

For argon plasma, water and formamide contact angle decreased with power increase similar to the results of nitrogen plasma treatments. However, as different from nitrogen plasma process, there is a

sharp decrease in diodomethane contact angle when the power reached 150 W. The decrease of contact angle value of all liquids may stem from the change in surface roughness for argon plasma at high plasma power. It is the aim of our further study to investigate the surface morphology in detail.
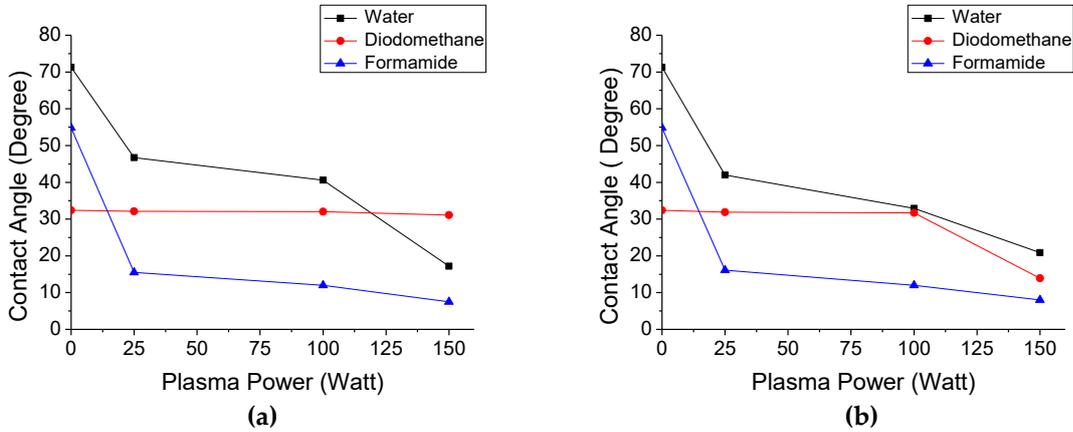

Figure 3. Contact angle values of PMMA films treated using (a) nitrogen, (b) argon plasma with respect to plasma power

3.2. SFE Results

SFE and its components give important information about which chemical effects dominate in making the surface hydrophilic. The measured contact angles of water and different liquids are used to calculate the total SFE and its components. The results obtained for different plasma conditions is given in Table 2, and the grafics of SFE of PMMA versus plasma power for nitrogen and argon plasma are given in Figure 4. Surface energy consists of two different components: polar and dispersive. Both of them contribute to total surface energy. While the polar component is responsible for the polar groups on the surface, dispersive one shows the hydrophobic character of the surface or crosslinked structure. γ_{geo}, γ_{geo}^{p}, γ_{geo}^{d} show the total SFE calculated by geometric mean approach, its polar and dispersive components respectively. In addition, γ_{har}, γ_{har}^{p}, γ_{har}^{d} show the total SFE calculated by the harmonic mean approach, its polar and dispersive components, respectively. Total SFE of untreated PMMA film obtained with geometric mean approach is 42.7 mJ/m^2 and harmonic mean approach is 45.8 mJ/m^2. These values increased to 68.8 and 73.1 mJ/m^2 for nitrogen plasma treatment at 150 W plasma power.

Table 2. Total SFE and its polar and dispersive components of nitrogen and argon plasma treated PMMA films calculated with harmonic and geometric mean approaches

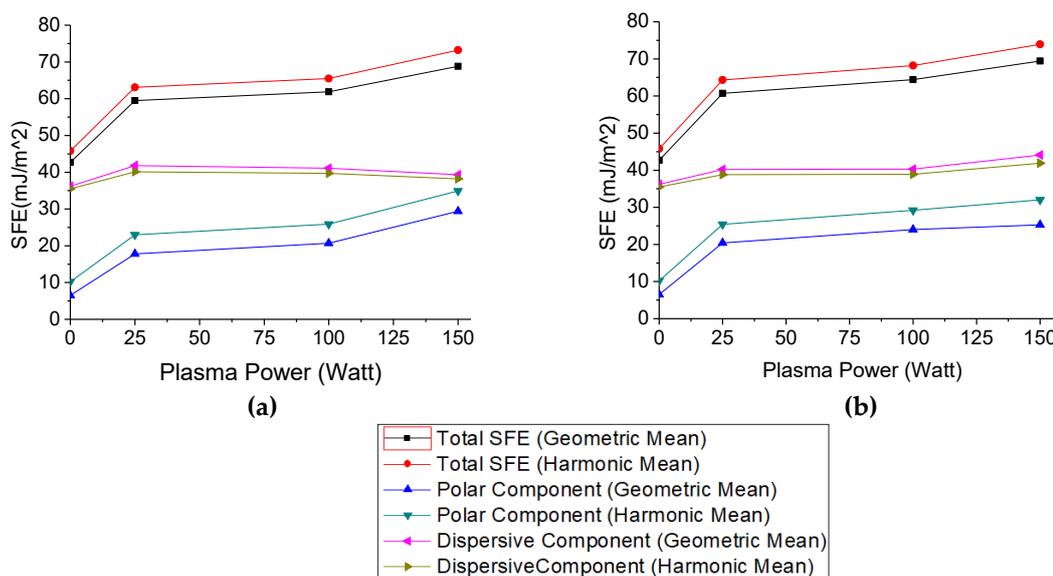| Sample	Power	Total SFE (mJ/m^2)		Polar Component (mJ/m^2)		Dispersive Component (mJ/m^2)	
		γ_{geo}	γ_{har}	γ_{geo}	γ_{har}	γ_{geo}	γ_{har}
Untreated	**0 W**	42.7	45.8	6.5	10.2	36.2	35.6
Nitrogen plasma	**25 W**	59.6	63.1	17.8	23	41.8	40.1
	100 W	61.8	65.6	20.7	25.9	41.1	39.7
	150 W	68.8	73.1	29.4	34.9	39.4	38.2
Argon plasma	**25 W**	60.6	64.2	20.4	25.4	40.2	38.8
	100 W	64.4	68.2	24	29.2	40.4	39
	150 W	69.4	73.9	25.3	32	44.1	41.9

Figure 4. SFE of PMMA films treated using (a) nitrogen, (b) argon plasma with respect to plasma power

The calculations made with the geometric mean approach show that while the increase of polar component is 22.9 mJ/m^2, that of dispersive component is 3.2 mJ/m^2. For harmonic mean these values are 24.7 mJ/m^2 and 2.6 mJ/m^2, respectively. It is clear that the contribution to the total SFE is mostly due to the polar component regardless of the approach. Since the polar component stems from the orientation of permanent electric dipoles, involving charge transfer interactions, dipole-dipole interactions, dipole-induced dipole interactions, hydrogen bonds, etc., it is expected to see a decrease of contact angle value accompanying an increase of SFE with its polar component due to hydrogen bonding ability of the surface. The dispersive component is related to the internal electron motions, and it is independent of the dipole moments. So, when the polar group is introduced to a polymer surface, it has no much effect on dispersive part. This is the reason of slight change in dispersive components of SFE. When it comes to argon plasma treatments, the total SFE of all modified surfaces is higher than the value of untreated samples for both geometric and harmonic mean approaches. Just as the plasma power increased, the polar groups increased on the surface and the polar component gave the most contribution to the total SFE for both approaches. As it compared with nitrogen plasma, the increase in dispersive component with plasma power for argon plasma is slightly higher than obtained for nitrogen due to the crosslinked network which was supported with XPS results.

3.3. XPS Results

To investigate the change of chemical bonds on PMMA surfaces, untreated films and the films treated at 150 W plasma power, which form the the most hydrophilic surfaces, were analyzed by XPS. C1s XPS spectra of untreated, nitrogen and argon plasma treated (at 150 W) PMMA films are given in Figure 5. Since the bonds related to C atom in the untreated PMMA structure are C-C, C-H, C-O and O-C=O, C1s envelope is curve fitted into three components at binding energies of 285 eV(C-C/C-H), 286.7 eV (C-O) and 289 eV (O-C=O) [30]. The fitted curves of untreated, nitrogen and argon plasma treated (at 150 W) PMMA films are ploted in Figure 6.
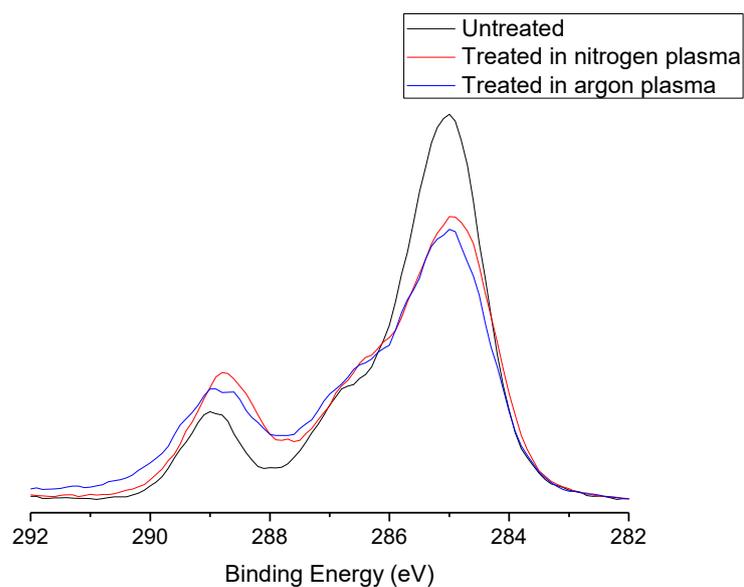
Figure 5. C1s XPS spectra of untreated, nitrogen and argon plasma treated PMMA films

Table 3. Concentration of chemical groups in the untreated and treated PMMA film surfaces with nitrogen and argon plasma at 150 W plasma power

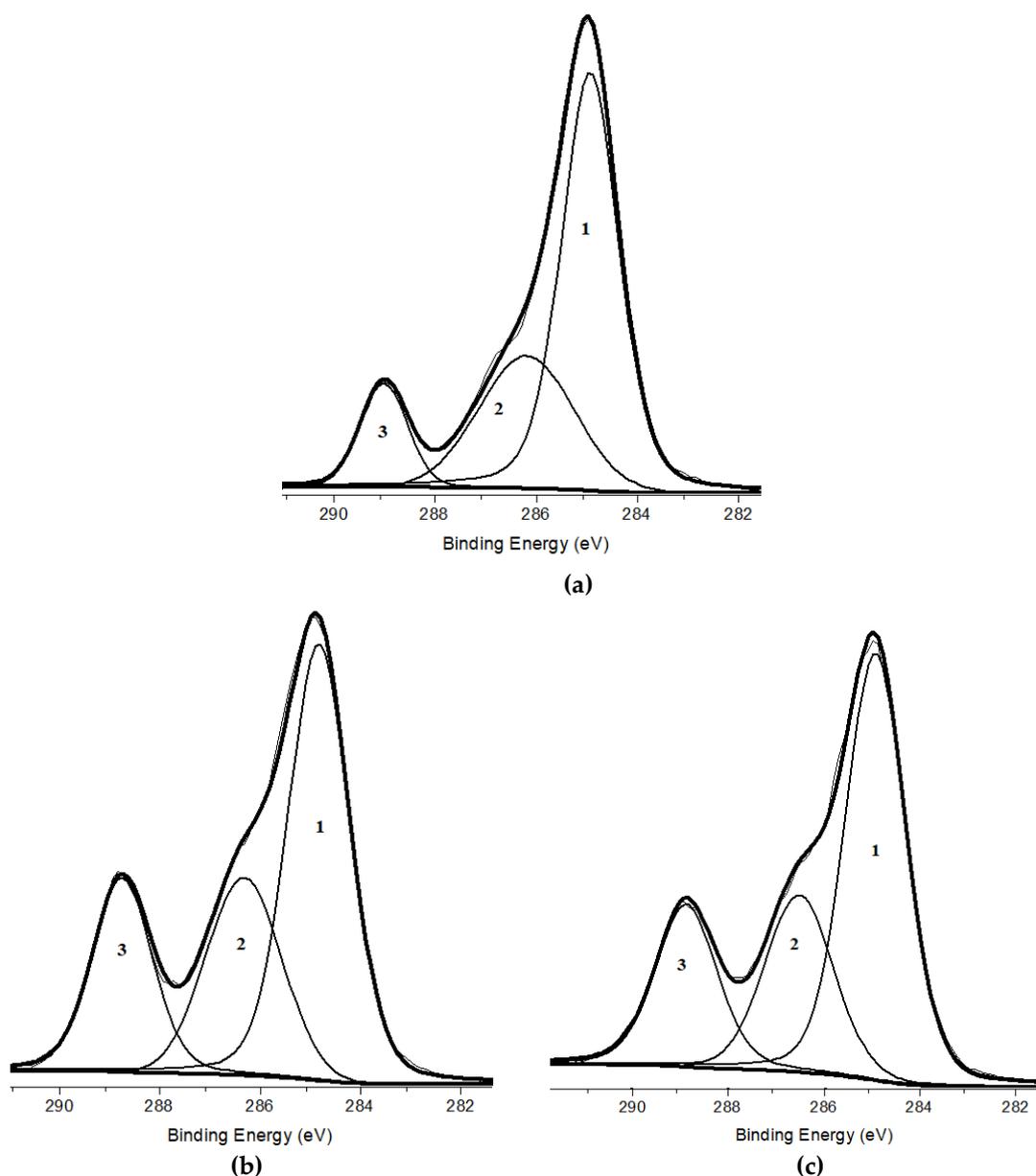| Sample	C-C/C-H relative peak area (%)	C-O relative peak area (%)	O-C=O relative peak area (%)
Untreated	60	27	13
Treated in nitrogen plasma	51	26	23
Treated in argon plasma	54	24	22

Figure 6. Deconvolved C1s XPS spectra of (a) untreated, (b) nitrogen and (c) argon plasma treated PMMA films (at 150 W). Peak 1(C-C/C-H), peak 2 (C-O), peak 3 (O-C=O).

For treated samples, as will be mentioned in N1s spectrum analysis, there are nitrogen containing functional groups such as C-N, C=N. But they overlapped with carbon-oxygen bond peaks and their concentration was very low (proved with the noise like structure of N1s) [31]. So it is difficult to distinguish them. In this study, it was focused on the change of main peaks in PMMA structure. In Figure 6 the C1s spectra of the untreated surfaces were compared with the C1s spectra of the plasma-treated surfaces. As can be seen in Figure 5. C-C/C-H peaks decreased and O-C=O peaks increased in C1s spectra for nitrogen and argon plasma treatments. With the aim of proving these results and for detailed analysis, the peaks were fitted and the areas of the peaks representing the bonds were calculated (Table 3).

The peak percentages of the bonds are 60% for C-C/C-H, 27% for C-O and 13% for O-C=O for untreated films. These data were in good agreement with the literature [32]. Gilliam *et al*. [32] found 57% for C-C/C-H, 29% for C-O and 14% for O-C=O for untreated PMMA surfaces. The C-C/C-H ratio for untreated PMMA decreased on treated surfaces whereas a significant increase in O-C=O bonds has been

observed. The particles with sufficient energy in the plasma broke C-C/C-H bonds in the polymer structure and caused the formation of polar groups which was demonstrated with SFE analysis. It is expected to see an increase for all oxygen containing bonds due to polar groups. However, C-O bond slightly decreased after treatments. This can be explained by disruption of the C-O bonds and formation of functional groups containing nitrogen, which has similar binding energies with O=C-O [33]. C-C/C-H bond percentage is slightly higher in argon plasma treatments than that of nitrogen plasma. This proves the formation of crosslinked network on the PMMA surface and increase in the dispersive component of SFE.

For nitrogen plasma, active nitrogen groups in plasma can break the bonds in the polymer chain, causing the formation of nitrogen containing polar groups (such as imine, amide and nitroso). In the literature, it was found that nitrogen containing groups generally have peaks around 400 eV for nitrogen plasma treated polymer surface [34]. To investigate the presence of nitrogen containing groups on the surface, N1s XPS spectra were examined for both untreated surfaces and plasma-treated surfaces (Figure 7). The C bond ratio in the PMMA structure is considerably higher than the nitrogen ratio on the treated surfaces. So, when the nitrogen peaks are magnified, noise-like peaks are observed, unlike the C1s spectrum. Since the PMMA polymer does not contain nitrogen in its structure, its ratio on the untreated surfaces in the N1s XPS spectrum is quite low.
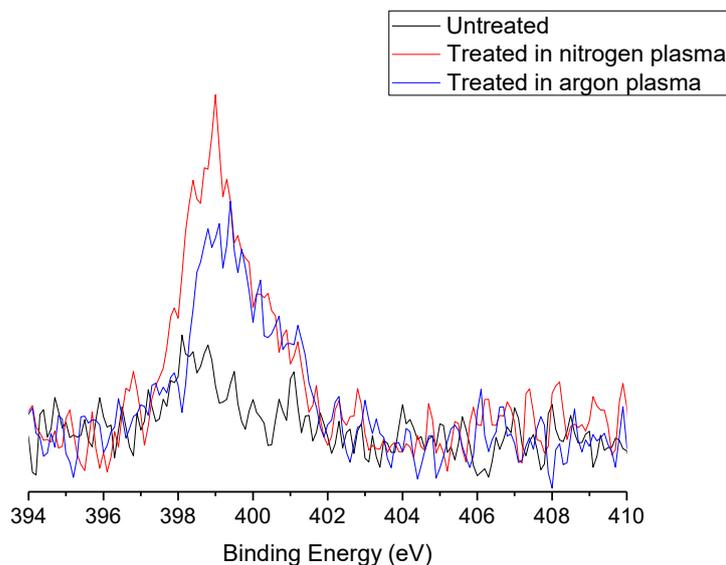

Figure 7. N1s XPS spectrum of PMMA films untreated, treated in nitrogen and argon plasma

On the plasma treated surfaces, peaks of nitrogen were observed between 398 eV and 402 eV. Therefore, nitrogen dependent groups were formed on the treated surfaces. An example reaction diagram of how these groups can be formed is given in Figure 8. Moreover, since the surfaces of the samples become active after treatment, the oxygen and nitrogen in the atmosphere after the treatment can be adsorbed on the surface and cause the formation of oxygen containing groups. The increase in O-C=O bonds for treated surfaces is caused by the atmospheric environment. Also, nitrogen peak was observed after argon plasma treatments (Figure 7). The nitrogen containing groups formation on polymer surface can be explained with the interaction of the surface with atmosphere after treatment. As a result, the formation of both O-C=O and nitrogen containing groups on the surface lead to an increase in the polar part of the SFE for all treatments.
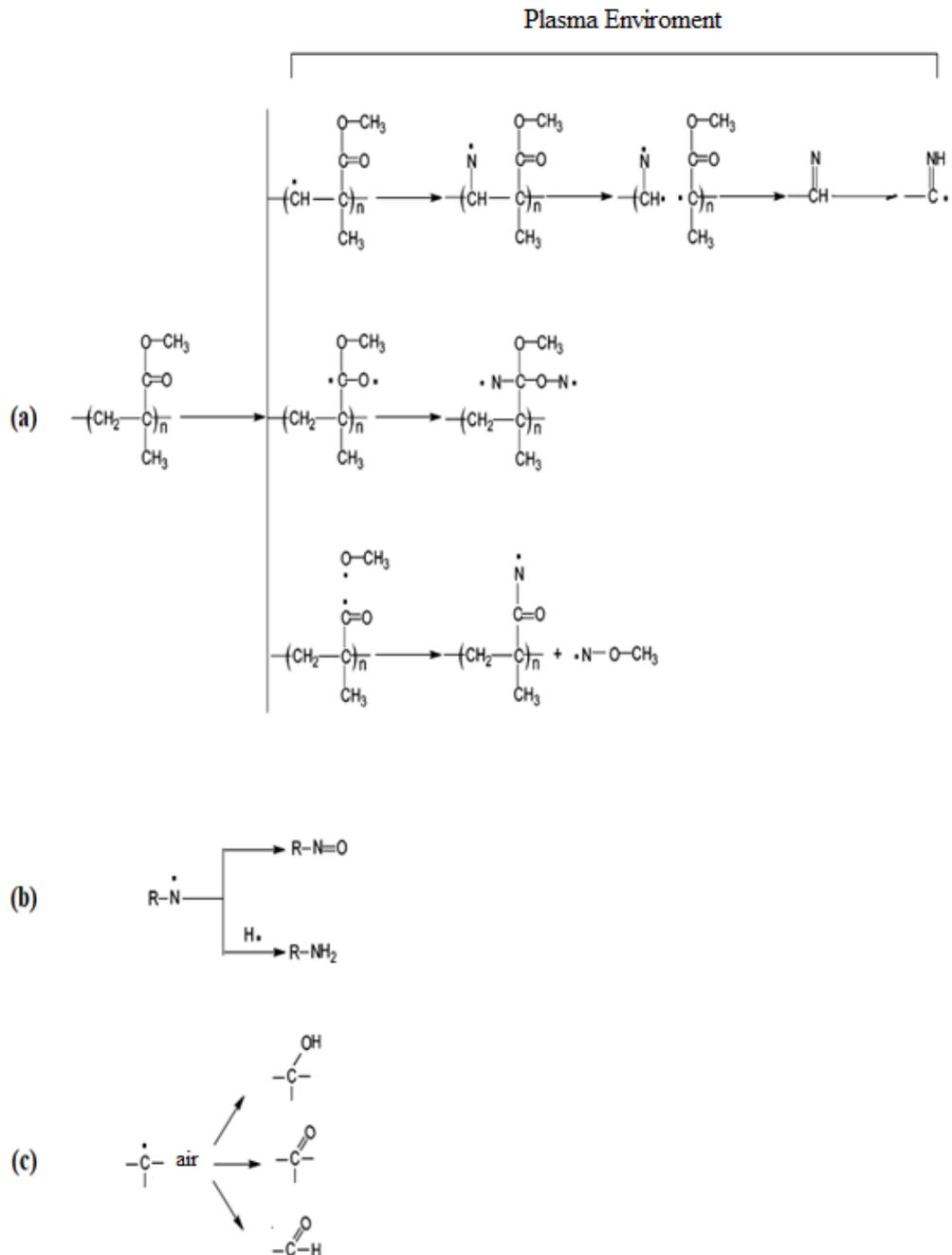
Figure 8. Some possible reactions that may occur on the surface as a result of the interaction of PMMA plasma with nitrogen gas plasma and air. (a) The process of activation of PMMA surfaces after plasma treatment, (b) the formation of stable nitrogen compounds with plasma [34], (c) The interaction of active surfaces with air.

4. CONCLUSION

This study clearly shows that high driving frequency CCP RF plasmas have important effect on PMMA surface modification. In all experiments the water contact angle of the surfaces decreased which proves the hydrophilic properties of the films. The lowest contact angle values obtained at high plasma power. When the SFE were examined, the highest total SFE values were found with both geometric and harmonic mean approaches at high plasma power and the most contribution comes from polar component due to the oxygen and nitrogen containing polar groups which was proved with XPS results.

These results show that high frequency (40.68 MHz) CCP RF plasmas can be also used to obtain hydrophilic PMMA films. The interactions of plasma particles (i.e radicals, ions and electrons) affect the surface wettability. Changing the plasma parameters such as plasma power changes the plasma environment and plasma-surface interactions. In order to analyse which processes in the plasma environment affect the surface chemistry, it is necessary to diagnose the plasma with the techniques such as optical emission spectroscopy and Langmuir probe [35, 36].

Declaration of Ethical Standards

Authors declare to comply all ethical guidelines including authorship, citation, data reporting, and publishing original research.

Credit Authorship Contribution Statement

Zahide TOSUN: Investigation, Analysis, Writing-Review & Editing
Ayhan ÖZMEN: Analysis, Writing-Review & Editing

Declaration of Competing Interest

The authors declare that they have no known financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

Research data has not been made available in a repository.

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