Studying the Structural and Morphological Properties of (PMMA) Film under D.C Discharge Plasma

Mohammed K. Khalaf¹, Sabah N. Mazhir²*, Zainab J Jaffer²

¹Directorate of Materials Research, Ministry of Higher Education and Scientific Research, Iraq
²Dept. of Physics, College of Science for women, University of Baghdad, Iraq.

E-mail: sabahnm_phys@csw.uobaghdad.edu.iq

Abstract. In this paper, a lab-scale direct current (DC) glow discharges plasma system was used to adjust the surfaces of polymeric films. Characteristics of the plasma system have displayed under the discharge of three gasses (O₂, N₂ and Ar). DC-Plasma system has been used for the adjustment of polymethyl methacrylate surface as a function of treatment time and the types of gases. The modified surface was characterized in terms of crystal structure and surface morphology by the analysis of X-ray diffraction, scanning electron microscopy (SEM) and atomic force microscopy (AFM). A comparison between treated and untreated films was also made. The roughness and the root mean square (RMS) for pure PMMA films were continuously increased with increasing the exposure time for different gasses. SEM images observed degradation of the surface with granular spots due to the chain missioning and cross-linking effects. An efficient method of treatment for enhancing the surface roughness of pure-PMMA polymer is the using of argon plasma compared to O₂, N₂ plasma

Keywords: Polymers, PMMA, Plasma Treatment, Discharge Plasma.

1. Introduction
Polymers have been widely used in several scientific, industrial and biological fields like biomaterials, thin-film technology, adhesion, wear composites and friction, protective coatings, and microelectronic devices. In common, they were from successful applications that are widely requested because of private surface characteristics with respect to roughness, chemical composition, hydrophilicity, crystallinity, and cross-linking density [1,2]. Polymers are commonly used for a given purpose in many medical fields because of their bio inert characteristics and their ease of customizing their chemical and physical properties. Poly-methyl-methacrylate (PMMA) is a polymer with several attractive properties. It has environmental stability, low cost, and good optical properties [3]. In addition to its superior physical and chemical properties, PMMA is also being extensively used in numerous fields of life in recent years [4,5]. It is superior light transmittance, mechanical properties (impact strength, durability) and low density that superior to glass [6]. Simple manufacturing and low cost of production also lead to its widespread use. Its biocompatibility makes Poly-methyl methacrylate particularly desirable in medicine as a drug delivery agent, eye and contact lenses, orthopedic surgery, or dentistry [7,8]. A hydrophilic surface was observed to be formed by surface alteration and the creation of new functional groups on the surface by (DC) direct current plasma treatment [9,10]. It is significant that the surface modification of PMMA improves its biocompatibility and reduces implantation complications while maintaining its
excellent bulk properties [11]. In this paper, plasma processing has become one of the most promising strategies due to the combination of its advantages, including quick, environmentally friendly, solvent-free processing, low operational and maintenance costs [12].

2. Experimental Part

2.1. Substrate Preparation

By means of the spray pyrolysis method, Pure PMMA thin films were prepared. The glass sheets were sequentially washed in an ultrasonic bath with ethanol and acetone. Lastly, they were eventually rinsed with purified water and dried up. The deposition method involves decomposition (PMMA) spraying the solution onto substrates placed at a distance of 25 cm from the spray nozzle at 30-40 °C depositing temperature. Then, the process of spraying the liquid inside the spray device is controlled in terms of the spray time to 2 min, the number of sprinkles is five times, as well as the time period between one spraying and another was also 2 min.

2.2. Plasma treatment process and conditions

Surface modification of the PMMA films is achieved by treating incandescent Direct Current glow discharge plasma for different gases such as (O₂, N₂, Ar). The samples were cut into little slides with dimensions of (2x1) cm before the treatment of plasma. The samples were placed inside a vacuum chamber under a pressure of 10⁻₂ mbar. The samples were backed on a glass rode and put in sit on spacing of 2.5 cm from cathode. The time of treatment by plasma was changed from (5 - 30) min. The working parameters are listed in Table 1.

| Parameters               | Values applied |
|--------------------------|----------------|
| Working Pressure         | 6.5 x 10⁻⁴ mbar|
| Electrode separation     | 5.5 cm         |
| Power Supply             | 690 Volt       |
| Flow rate of gas         | 750 cm³/min    |
| Exposure time            | 5 - 30 min     |
| Working gas              | O₂, N₂, Ar     |

2.3. Characterization instruments:

X-ray diffraction (XRD) a non-devastating method for substances is commonly used to identify structural characteristics. The qualitative analysis may be conducted on the premise of peak height or peak zone. The peak angles may be utilized to decide particle diameters and the degree of crystallization. The X-ray spectra were gotten through utilizing copper filtered Cuku radiation λ=1.54060 (Å) worked at 40 (kV) and 20 (mA) kind (SHIMADZU-6000) made in Japan. Field emission scanning electron microscope (FESEM), Hitachi (S-4160) with a continuous magnification capacity from 6x to 100,000x and Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, an x-ray technique used to identify the elementary structure of materials. Atomic Force Microscopy (AFM) is the device used for type inspection (AA3000 Scanning Probe Microscope SPM, NSC35/AIBS tip) that used to analyse the morphology and the roughness of the surfaces.

3. Results and Discussion.

3.1. Analyzing X-ray Diffraction

The x-ray diffraction spectra were used to analyse the crystalline structure of pure-PMMA films. It is clear that pure-PMMA film possesses no crystalline structure therefore, the XRD pattern reveals amorphous scattering around 2θ = 12.50 and 25° from ratio of diffraction peak areas for crystal structure analysis before and after oxygen plasma treatment where the peak is even more intense for the treated film due to increased crystallinity. After oxygen plasma treatment and for different exposure times (5-30 min), there were variations in the form or location of diffraction peaks in Figure (1). The XRD patterns
for pure-PMMa films before and after plasma-treatments for various gases (O2, N2, Ar) as indicated in figure (2). It is noticed an increase in the density disparity to regions for the pure-PMMa films treated by (O2, N2, Ar) plasmas over the same exposure period for untreated samples [13]. All these peaks' intensities also increased and contributed to the dominant disordering and thus affected the crystalline structure. In addition, due to the formation of the disordered structure in the plasma-treated PMMA polymer, the full width at half maximum (FWHM) of the peaks are broadened.

**Figure 1.** X-ray diffraction patterns of (a) PMMA-Pure (b) PMMA-PO2 (5min) (c) PMMA-PO2 (10min) (d) PMMA-PO2 (20min) (e) PMMA-PO2 (30min).

**Figure 2.** X-ray diffraction patterns of (a) PMMA-Pure (d) PMMA PO2(20min) (f)PMMA-PAr(20min) (h) PMMA-PN2 (20min).

### 3.2. Surface morphology analysis.

The AFM images for untreated and treated pure-PMMa films were shown in figure (3). Figure 3 (a) shows that the surface of untreated pure-PMMa film is smooth with the presence of conical protuberances and slight roughness. With increasing the exposure times of O2 plasma treatment, the
surface roughness and the scale of the conical protuberances increased as seen in figure 3 (b - e). The roughness and the root mean square of untreated and treated pure-PMMA films are listed in Table 1. It is seen that the values of the RMS gradually increased with increasing the exposure time. The surface roughness is increased due to the removal of few top monolayers of the polymer films caused by the impact of plasma species on the surface [14]. The surface roughness increases the wettability and the bonding strength. The surface roughness Ra (evaluated from the AFM images) was 0.904 nm for untreated pure-PMMA, and it increased to be (3.98, 4.67, 5.33, and 4.16) nm after the treatment of 5, 10, 20, and 30 min respectively. As shows in table 2, it is noted that after the treatment with O₂ plasma, the roughness of the PMMA surface significantly increased during the treatment time, ranging from 5–30 min. The small decrease in Ra at a high treatment time value is possibly due to the cross-linking of newly formed surface radicals that may partially change its orientation and fill up the surrounding valleys, thus decreasing the roughness of the surface. This behavior agrees with references [15,16].

Table 2: Average diameter, Roughness average and the root mean square for pure-PMMA untreated and treated by O₂ plasma

| Sample          | Average diameter (nm) | Roughness average (nm) | The root mean square (nm) |
|-----------------|-----------------------|------------------------|---------------------------|
| PMMA-Pure       | 73.11 nm              | 0.904 nm               | 1.48 nm                   |
| PMMA-PO₂(5min)  | 78.96 nm              | 3.98 nm                | 4.99 nm                   |
| PMMA-PO₂(10min) | 87.57 nm              | 4.67 nm                | 8.02 nm                   |
| PMMA-PO₂(20min) | 93.25 nm              | 5.33 nm                | 9.01 nm                   |
| PMMA-PO₂(30min) | 70.48 nm              | 4.16 nm                | 5.24 nm                   |
Figure 3. AFM measurements of (a) PMMA-Pure (b) PMMA-PO$_2$ (5min) (c)PMMA-PO$_2$ (10min) (d) PMMA-PO$_2$ (20min) and (e) PMMA-PO$_2$ (30min).

The influence of the cross-linking is observed by noticing the dependence of PMMA surface roughness on the ion energy. The surface roughness of PMMA films shows an opposite dependence on the ion energy following Ar, N$_2$, O$_2$ plasma exposure. The improvement by increasing the ion energy results in observing the variations in the surface roughness dependency on the ion-bombing energy. The results also showed that after long treatment with Ar and N$_2$ plasmas, the surface roughness of the pure PMMA films is much larger dispersed than plasma O$_2$, since the processes of plasma etching can be lower in inert Ar and N$_2$ gases than from reactive gases. This result confirms that there was a greater etching process in plasma generated in reactive (or electronegative) gases than from inert gas as shown in fig4. This behavior agrees with references [17,18]

Table 3: Average diameter, Roughness average and the root mean square for pure-PMMA untreated and treated by different gases plasma

| Sample        | Average diameter (nm) | Roughness average (nm) | The root mean square (nm) |
|---------------|-----------------------|------------------------|---------------------------|
| PMMA-Pure     | 73.11 nm              | 0.904 nm               | 1.48 nm                   |
| PMMA-PO$_2$(20min) | 93.25 nm              | 5.33 nm               | 9.01 nm                   |
| PMMA-PAr(20min)   | 106.10 nm             | 13.4 nm               | 18.2 nm                   |
| PMMA-PN$_2$(20min)   | 107.27 nm             | 11.1 nm               | 12.8 nm                   |
(a) 3D and 2D of PMMA-Pure

(b) 3D, 2D of PMMA-PO2(20min)

(c) Granularity Cumulative Distribution Chart

(PMMA-Pure)
Avg. Diameter: 73.11 nm

(d) Granularity Cumulative Distribution Chart

(PMMA-PO2-20min)
Avg. Diameter: 93.25 nm
3.3. (FESEM) Field Emission Scanning Electron Microscopy.

SEM is used for analysing the changes in the surface morphology of pure-PMMA films before and after plasma treatment. Figure 5(a) shows that the surface morphologies of untreated pure-PMMA films have relatively smooth surfaces. On the other hand, Fig. 5(f, g, h, and i) shows the surface morphology of treated pure-PMMA films under the best conditions for the surface adjustment. It can be noticed that there are clusters of particles connected to the surface. Oxygen plasma was used to modulate the surfaces of pure PMMA film. The plasma has changed the surface from the chemical composition and
the morphology. It notes that increasing the plasma treatment time for pure PMMA films from (5-30) min causes a damage in the polymer chains, and the polymer becomes loosely packed, which in turn raises the etch-rate. Alteration of the etch-rate is high at the beginning and decreases at a higher period of treatment [19].

Table 4: Alteration of the etch-rate is high at the beginning and decreases at a higher period of treatment

| Samples                  | Maximum Grain size(nm) | Mean Grain size(nm) |
|--------------------------|------------------------|---------------------|
| PMMA-Pure                | 40.19 nm               | 58.06 nm            |
| PMMA-PO2(5min)          | 110.9 nm               | 123.18 nm           |
| PMMA-PO2(10min)         | 98.58 nm               | 69.07 nm            |
| PMMA-PO2(20min)         | 58.06 nm               | 44.66 nm            |
| PMMA-PO2(30min)         | 35.73 nm               | 29.03 nm            |
Figure 5. SEM and Edx measurements of (a) PMMA-Pure (f) PMMA-PO$_2$(5min)
(g) PMMA-PO2(10min) (h) PMMA-PO2(20min) (v) PMMA-PO2(30min).

Samples are analyzed by SEM microscopy of the pure-PMMA films treated by plasma for different gases (O2, N2, Ar) at the same time of exposure. It is noticed changes in the etch-rate of pure PMMA samples after exposure to the plasma as shown in figure 6 (a, h, k, m). Untreated pure-PMMA sample has a uniform texture which undergoes major changes when exposed to plasma. While, treated pure-PMMA samples describe rougher morphologies with etching appearances and irregular-shaped textures. The surface texture produced is related to the differences in the etch-rate of amorphous regions coexisting in PMMA. Continuous bombing of reactive plasma species contributes to alterations the surface morphology. It is also known that the morphology for pure PMMA films dramatically altered during O2 plasma treatment compared to the N2 and Ar plasma etching. This behavior is correlated with a higher etch-rate of O2 plasma in as seen figure 6h. It is noticed that the plasma of O2 causes a major deterioration of the surface of the sample as a result of plasma etching mechanisms. Thus, N2 plasma can be considered as an ideal alternative to boost surface properties with very low levels of degradation. This result is consistent with [20,21].

As a consequence of plasma processing, in addition to the oxidation effect of oxygen plasma, effective radicals (long-lived or met stable) present on the surface contribute to the restructuring of the surface. As described above, plasma etching, degradation and cross-linking happen concurrently on the surface of the polymer. Cross-linking and degradation will control the polymer etching and thus the surface topography.

Table 5: Cross-linking and degradation will control the polymer etching and thus the surface topography.

| Samples            | Minimum Grain size(nm) | Mean Grain size(nm) |
|--------------------|------------------------|---------------------|
| PMMA-Pure          | 40.19 nm               | 58.06 nm            |
| PMMA-PO2(20min)    | 98.58 nm               | 69.07 nm            |
| PMMA-PAr(20min)    | 523.3 nm               | 471.35 nm           |
| PMMA-PN2(20min)    | 35.73 nm               | 35.73 nm            |
Figure 6. SEM and Edx measurements of (a) PMMA-Pure (d)PMMA-PO2(20min)

(h) Sem and Edx of PMMA-PO2(20min)

(k)Sem and Edx of PMMA-PAr (20min)

(m)Sem and Edx of PMMA-PN2(20min)
4. Conclusion.

In summary, DC glow discharge plasma was used at various exposure times from (5-30min) for the modification of the pure-PMMA film surfaces by oxygen plasma where the results indicate increased surface roughness and increased crystallinity with increasing the exposure times. However, with the treatment for a long time, the value of the surface roughness significantly declined. While, the plasma treatment with various gases (O₂, N₂, Ar) for 20min at the same exposure time alters the surfaces in both of the chemical composition and the morphology. AFM and XRD studies showed an improvement in the surface roughness and increased the crystallinity. SEM images observed a degradation of the surface with granular spots due to chain missioning and cross-linking effects. An efficient method of treatment for enhancing surface roughness of pure-PMMA polymer is the using of argon plasma compared to O₂ and N₂ plasma.

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