Synthesis and Surface Characterization of PMMA Polymer Films in Pure Oxygen, Argon, and Nitrogen Glow Discharge Plasma

Zainab J Jaffer¹, Sabah N Mazhir¹, Mohammed K Khalaf² and Marwa S Hanon³

¹Department of Physics, College of Science for women, University of Baghdad, Iraq
²Directorate of Materials Research, Ministry of Higher Education and Scientific Research, Iraq
³College of Medicine, Al-Iraqia University

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

Abstract. The anticorrosion effect and biocompatibility property of Poly (methyl methacrylate) (PMMA) materials have been used in a variety of commercially available products and medical devices for many years. In this work, the treatment of surfaces prepared PMMA films by oxygen, argon and nitrogen plasma, requires understanding the effect of low energy ions on the surface modification of the film of PMMA. Due to this, the samples of prepared PMMA were exposed to three different gases at the same discharge conditions. Changes within the morphology and surface hydrophilicity of the treated samples were characterized by optical microscope images and the measurements of contact angle. Treatment of PMMA with O₂, N₂, Ar gases displayed a decreasing in the contact angle that results in increasing surface free energy. Oxygen –plasma treatment of PMMA films leads to high aspect ratio topography, with increased roughness for (5-30) minute process durations.

Keywords: Polymers, PMMA, Contact angle, Plasma treatment.

1. Introduction

Polymers have been utilized successfully in numerous applications due to the light weight, the mechanical properties and chemical stability in addition several design possibilities. Polymers are very well enforced in the engineering of tissue, in particular, in many aspects of mechanical, chemical and physical properties, microstructure, biodegradability and cytocompatibility [1, 2]. The composition of chemical, morphology and structure for polymers impact the surface-free energy and thus have a big impact on wettability [3, 4]. Wettability may be a crucial property of solid-state surfaces that plays vital parts within the many fields [5]. Assessment of the wettability, can too be utilized to ultimate the surface stabilization of the polymer of modified [6, 7].

Poly (methylnethacrylate) PMMA is one of the foremost broadly utilized polymer nowadays, has been widely utilized in biomedical, optical and different industrial applications for its of chemically inert, transparent and excellent mechanical properties such as ease of manufacture [8]. PMMA could be a polymer that's broadly utilized in implantable the devices of medical due to its low inflammatory response, simple process ability and the characteristics of biocompatible [9]. PMMA have a few drawbacks for example low chemical resistance and brittleness which can be removed by physical or chemical adjustment. PMMA includes hydrophilic (carbonyl) and hydrophobic (methylene)
assemblies in each unit [10]. Several strategies are utilized to alter the polymer surfaces, for example chemical, mechanical t, thermal and electrical treatments (glow discharge treating by plasma or corona) [11,12]. All the a for mentioned strategies, has been broadly utilized to alter the properties of polymer surface with no changing the bulk properties in low temperature glow discharge plasma. Additionally, it could be this a dry treatment strategy, which is superior suited for several purpose [13]. The utilizing of plasma treatment has particular focal points such because it alters of the material surface properties any near-surface layer ordinarily with profundity 0.005 to 0.05 µm [14]. Fundamentally, a glow discharge treating by plasma gives numerous possibilities to refine the surface of polymer, empowered by the alteration of parameters for example treatment time, pressure, gas flows and power. based on the types of gas and the conditions of plasma [15-17].

The plasma is competent to apply four main impacts, (i) the cleaning of surface, (ii) etching, (iii) adjustment of the surface chemical structure, (iv) surface cross-linking, happening that in situ [18,19]. These impacts based on a being of the effective species in plasma (radicals, ions, photons, electrons) that interact with polymer surfaces [20]. Counteractions between polymer surface and plasma species make it conceivable to forms polar bunches on the polymer surface. The chemical bunches of polar such as COOH, CHO, C-OH, C=O can shape the bonds of chemical reaction and thus can cause an increment of the wetting quality and the energy of surface [21,22]. The goals of plasma surface adjustment in the applications of biomedical are adhesion promotion, improved surface wettability, spreading, and diminished surface friction.

2. Experimental work

2.1. Preparation of glass substrates

The cutter of diamond was used to cut the glass before deposition process into dimensions (2x 2) cm. Following, the substrates of glass was cleaned utilizing acetone and distilled water) in ultrasonic bath for ten minutes. Finally, they were rinsed with distilled water and dried.

2.2. Preparation of PMMA films

Preparation PMMA- solution. PMMA (has medium molecular weight, Chemical formula (C5O2H8) and purity 99.9 %). First, it is added 1 gm of powder PMMA was broken up in 30 ml of Toluene solution (C 7H8) in a beaker and stirred for 5 min at room temperature by magnetic stirrer. Thereafter, prepared solution is converted into a sealed glass container and left for a full day in room temperature to complete the dissolution process. PMMA films was preparation utilizing the deposition system that contains of glass container of size 100 ml with 1 mm inner diameter nozzle sprayer and an air blower or compressor. The deposition method involves decomposition (PMMA) spraying the solution onto substrates installed 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 of 2 min, the number of sprinkles is five times, as well as the time period between one spraying and another was also 2 min.

2.3. Plasma treatment process and conditions

Surface modification (PMMA films) is achieved by treating incandescent direct current DC Glow discharge plasma using gases such as O₂, N₂, and argon. The PMMA samples were cut into little slides with dimensions of 2cm x 1cm for the treatment of plasma. The samples were placed within a vacuum chamber with vacuum of 10⁻² mbar was maintained inside the chamber using a vacuum rotary pump. The samples were backed on a glass stage and put in sit on spacing 2.5cm from cathode. The time of treatment by plasma was changed (5 - 30) min. and the working parameters are represented in Table 1.
2.4. Characterization instruments
Optical Tensiometers, theta Lite (TL 100 and TL 101), USA, contact angle meter for records drop pictures and consequently automatically analyzes the drop shape. Contact angle describes the shape of a liquid drop resting on a solid surface. The contact angle and the drop shape moreover based on the solid properties (e.g. topography, surface free energy SFE). Morphology was studied by utilizing Optical Microscopy (type LTD, Made in Japan). The surface of samples was inspected with a magnification of x 500 and x 100 for each sample.

3. Results and Discussion
3.1. Contact Angle measurement
Hydrophilicity and hydrophobicity of materials are evaluated on the premise of the contact angle measurement. The bigger the angle between the surface of biomaterial and fluid drops, the more the hydrophobic properties exhibited in the biomaterial. The angle of contact is a quantitative extent of the wetting of the solid by the liquid. Polymer surface tension could be obtained by the measurements of contact angle. Utilizing the sessile drop technique [23]. Water contact angle (WCA) could be a famous process for deciding if a surface has been activated. Little microliter water (distilled water) droplets are put on the surface and the angle at the edge of the droplet is recorded employing a goniometer. This is method is similar to the WCA information have been calculated for polymer and composite [24-26].

The measured contact angle decreased with the increase in treatment time for the treated PMMA films (Figure 1). The values don't alter altogether after taking more exposure time as saturation by plasma impact on the films of PMMA. Where the contact angle decreased from 76.06° to 26.96° for their PMMA film at 20 min of treatment time and for O₂ plasma. The effect oxygen plasma on PMMA films where that creating big amount of active species that reactive promptly on the surface of polymer. This leads to consolidation of oxygen-containing polar bunches for example OH, C=O, and O=C=O on the film surface of the treated plasma lead to a diminish in the contact angle [27,28]. As shown in Table 2.

### Table 1. Working parameters for plasma treatment

| Parameters          | Values applied |
|---------------------|---------------|
| Working pressure    | 6.5 x 10⁻¹ 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    |

### Table 2. The contact angle measurement for various exposure times

| Plasma treated | Exposure time (min) | Contact angle |
|----------------|---------------------|---------------|
| (PMMA)         | 0                   | 76.08°        |
| PO₂ (PMMA)     | 5 min               | 52.52°        |
| PO₂ (PMMA)     | 10 min              | 40.29°        |
| PO₂ (PMMA)     | 20 min              | 26.96°        |
| PO₂ (PMMA)     | 30 min              | 37.27°        |
Figure 1. Reliability of the WCA of PMMA films on exposure times of O\textsubscript{2} plasma.

Figure 2. Contact angle measurement of oxygen plasma at different exposure times.
Note the contact angle of different PMMA samples for different gases plasma under the same conditions in Figure 3. It has been watched that the utilization of O$_2$ plasma produces that a relative decrease in the contact angle for PMMA followed by treatment with Ar and then N$_2$. As shown in a Table 3. At the time of treating by plasma, interaction of the surface of polymeric with charged species direct to the generation of surface free radicals in the compound of chemical that could interaction with oxygen its essentially introduce the oxygen functional on the surface of polymer. All plasma shaping gases influences the hydrophilic character of the PMMA surface after treating by plasma. The difference of the energy of surface and contact angle may be clarifying by the incorporation of reactive polar bunches and alter of surface chemical states on the surface of polymer. The results imply that the drop spreads inside the solid texture resulting in contact angle decrease, and after that coexist with the solid filled with fluid. As follows, it is reasonable to conclude that the increased nanotextured area of O$_2$ plasma treated samples could be effectively used as the adsorbent by the adsorbate.

Table 3. contact angle for oxygen, argon and nitrogen plasmas.

| Plasma different gases | Samples | Exposure time | Contact angle |
|------------------------|---------|---------------|---------------|
| Oxygen gas Plasma      | PMMA    | 20 (min)      | 26.96°        |
| Argon gas Plasma       | PMMA    | 20 (min)      | 40.98°        |
| Nitrogen gas Plasma    | PMMA    | 20 (min)      | 53.23°        |

Figure 3. contact angle measurements for oxygen, argon and nitrogen plasma treated PMMA films.

3.2. Optical Microscopy measurement

2D topographical images of untreated and oxygen, argon and nitrogen plasma treated PMMA thin films are shown in Figure 4. The optical microscopic images at different magnification powers, for untreated (PMMA) thin film and treated (PMMA) deposited on glass, it was found that treatment by oxygen plasma and treatment times from 5 to 30 min that produce obvious changes on morphology.
and roughness of the PMMA surface. We note presence of engraving or etching on surface. Figure 4 shows the various morphologies formed on the surface conjointly at changing the working gas and compared to the control (PMMA-Pure) sample. This process illustrates the high level of oxidation induced by the discharge of plasma as the molecular oxygen that is basic entrained in the inter-electrode gap from the contacting air and activated, ionized and dissociated in the discharge to deliver intensely reactive oxygen species that reaction effortlessly with the substrate surface. Dramatically, suggesting that new oxygen-containing polar moieties were formed on the surfaces after plasma treatment. However, the suitable topography results obtained for the Ar and N$_2$ discharge suggest that the nitrogen and argon species are the most efficiently activated due to heat transference from environment species [29].
Figure 4. Optical micrographs image of as deposited and oxygen, argon and nitrogen plasma treated PMMA films.

4. Conclusion
The treatment of plasma was found to improve the hydrophobic properties for the films of PMMA. The increment in hydrophobic together with the fluency can be attributed to cross-linking impact that happened by which two free dangling bonds on the chains unite of adjacent. such plasma-PMM films are expected to find wide applications for a new generation of surface-based biomedical and optical sensing applications.

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