IRAQI JOURNAL OF MATERIALS
Volume (1) Issue (3) July-September 2022, pp. 95-106

Structural Characteristics of Polymer Surfaces Modified by DC Glow Discharge Plasma

Mohammed A.K. Ahmed

Material Engineering Department, Engineering Technical College, Middle Technical University (M.T.U.), Baghdad, IRAQ

Abstract
In this work, a low-pressure dc glow discharge plasma was generated and diagnosed using the electric probing method. Three different gases (Ar, N_2, and SF_6) were used to generate the discharge plasma. The generated plasma was used to treat the surfaces of thin films of polymeric materials (polycarbonate and polymethyl metha acrylic) prepared by solution cast method. The treatment process was performed at different treatment times. The morphological and topographical characteristics of the treated surfaces were introduced and compared to untreated surfaces. Results showed reasonable modifications in the surfaces as their roughness has increased. Also, the surfaces treated with SF_6 gas showed better characteristics than those treated with Ar and N_2.

Keywords: Surface modification; Plasma treatment; Polymer films; Polycarbonate; PMMA
Received: 16 January 2022; **Revised:** 20 April 2022; **Accepted:** 27 April 2022; **Published:** 1 July 2022

1. Introduction

The surface treatment is a kind of surface modification techniques to achieve required corrosion or oxidation resistance or to create new features on the surface without damaging the desired basic or mechanical properties of the substrate. Here, the surface texturing or restructuring is done by some surface modification techniques using external coating materials. However, in some special cases such as, for specific functional applications, the external substance or functional groups might be used to achieve the targeted performance. Surface treatments are one of the most effective ways to impart functionality to textiles and fibers. The surface is where a material first responds to and interacts with the environment. Ideally, a smart protective surface will sense the environmental hazard – thermal, radiation, or chemical in nature – and respond to it to block it from harming the human body, while not interfering with moisture and air interchange through it to provide comfort. Various surface treatment methods have been introduced to impart smart, adaptive properties for protective systems. They include the polymer brush system, which has gained considerable interest as it can achieve drastic surface modifications through chain conformation changes, and coatings that can be utilized to create smart surfaces for protective clothing. The coating methods of polymers also include descriptions of other coating methods and smart materials such as phase-change polymers, shape-memory polymers, nanoparticles, and conductive materials that can be introduced to textile systems through coating technology. Other novel techniques, such as nanolayer deposition and nanofiber coating, are also briefly discussed.

Modification in the physical and chemical properties of surface of a polymeric material without alteration of the bulk properties is of great interest. However, the average chemical composition and morphology of the surface of solid polymers are usually differing from those of the bulk [1-5]. The successful implementation of many of the above-mentioned applications is determined by the surface properties [6,7]. Up to now plasma treatment are the most widely used surface modification techniques, especially in industry, and the results have been extensively published [8-12]. Over the last four decades, polymers have been used successfully in many industrial applications, including adhesion, packaging, thin films, biomaterials, and coatings. Polymers have become a very important material in modern manufacturing processes and offer a wide variety of chemical, optical and mechanical properties applicable to numerous applications. We have used thermoplastic polymers in this study [13]. These are linear, one-dimensional polymers, which have strong intermolecular covalent bonds and weak intermolecular Van der Vaal bonds [14]. A growing interest in polymer applications in such fields as coatings, adhesion, composites, biomaterials, medicine, microelectronics, and thin-film technology requires special surface properties that could be tailored by flame treatment, radiation grafting, chemical treatment, photon irradiation, corona discharge and plasma treatments, as well as ion-beam modification [15-18]. In order to understand different polymers and their properties, which are usually classified into three groups: thermoplastics, elastomers and thermosets. Thermoplastics are linear or weakly branched polymers with negligible entanglement [19,20]. They can be crystalline or amorphous. Those, which crystallize, do not form perfect crystalline materials but instead are semi-crystalline with both amorphous and crystalline regions. Polymers in which chain motion is greatly restricted by a high degree of cross-linking [21,22]. Damage events such as ionization and recoil displacement result in the modification of the original polymer structure [23-25].

If the surface of a plastic can be non-destructive altered down to a depth of just a few molecules, it can make a profound difference in the practice's suitability for a broad range of applications [26-33]. Using a cold gas plasma reactor to design the surface by just a few angstroms is a very energy-efficient, clean and environmentally safe green method to change the basic polymer film properties in many applications [34]. Between the possible effects of plasma treatment on a polymer material may be included improved wettability, induced chemical reactivity, improved adhesion to coatings and matrices, hydrophobic properties, cleaning or disinfections [35].

In this study it is only considered plasma produced by the latter. In this situation, the field can be produced by direct current (DC) and radio frequency (RF) and the net effect of the electromagnetic field is to cause electrons to be removed from a reduced pressure gas near any electrodes. The same imposed field through the remaining gas and loose energy then accelerates these stripped electrons by collision with gas molecules. Thus, there are forming a variety of active species including additional electrons, free radicals, ions and neutral atoms. Any substance inserted into this plasma will be subjected to bombardment by these species and the kinetic or potential energy these products contain. The study only concerns with the type of plasma produced by strong electromagnetic field, in which the effective temperature of the larger ionized gas molecules is only a few tens of degrees. The free electrons in this plasma have relatively high energies (10-20 eV) and at these energies the electrons are of sufficient energy to ionize neutral gas molecules causing the visible glow commonly observed in these systems. Taking into account the position of the two electrodes, they are placed within the reactor. The installations in this category is utilized to induce or to modify some properties and to obtain new polymer materials by polymerization or grafting [36-38].

Plasma surface treatment allows the modification of the surface characteristic of polymers to obtain improved bonding, without affecting bulk properties [39]. Surface cross-linking is often used to enhance the performance of polymers. The activity of the plasma creates a higher cross-linking density within the material to depths of a few thousand angstroms [40]. The resulting increase in hardness and chemical resistance (grafting) and functionalization figure. The dissociation in the plasma of the monomer creates various active fragments that react to form a film on the surface of the subtract, whose properties are different from the properties of the bulk polymers [41,42].

In the plasma surface modification process, evacuating a reaction chamber and then refilling it with a low-pressure gas create low discharge plasma. The gas is then energized by direct current. The energetic species in gas plasma include ions, electrons, radicals, metastables, and photons in the short-wave ultraviolet (UV) range [43]. Surfaces in contact with the gas plasma are bombarded by these energetic species and their energy is transferred from the plasma to the solid. A wide variety of parameters can greatly affect the physical characteristics of plasma and subsequently affect the surface chemistry obtained by plasma modification [44]. Processing parameters, such as gas types, treatment power, treatment time and operating pressure, can be varied by the user; however system parameters, such as electrode location, reactor design, gas inlets and vacuum are set by the design of the plasma equipment. This broad range of parameters offers greater control over the plasma process than that offered by most high-energy radiation processes [45-47].

Bond Scissioning and cross linking are the main result of high energy ion interaction with the polymer surface. These reactions induce structural modification and change in physical properties [48]. Cross linking occurs when two radicals produce on the neighboring polymer units [49]. The relative molecular mass of the macromolecule increases which result in increase of melting point. Along with the cross linking, degradation also occurs by chain scission which leads to decrease in a molecular mass [50]. Grafted polymer can be produce when, for example, at the polymer backbone radical sites are formed which react with monomers present as a liquid or vapor. The cross linking or scissioning efficiency not only depends on polymer structure but also on the characteristics of radiation sources, ion energy and ion specie [51-53].

2. Experimental Part

The glow discharge chamber is used to produce plasma by gas ionization. Figure (1) shows the setup system used for glow discharge. The chamber consist of stainless-steel plasma cylinder reactor with 40 cm length and 30 cm diameter, electromagnetic energy (DC generator), an adjustment system, high voltage power supply along with milliammeter and high voltage voltmeter to record the dc-discharge current and the discharge high voltage respectively. The vacuum chamber connected to vacuum pumps consist of rotary and diffusion pumps, needle valve to control gas pressure, and process gas sources with gas regulators. The Langmuir single probe is located in side branch of the vacuum chamber, and it's connected to probe driving circuit. The probe tip is located inside plasma channel. The plasma generator chamber was evacuated by rotary and diffusion pumps. The initial vacuum pressure was 10^{-2} mbar, then higher vacuum was obtained by diffusion pump. The working pressure to produce plasma plume decreased down to 10^{-4} mbar. Different values of the discharge power can be varied by adjusting the input current. The experimental conditions used during the plasma generating were as follows: Initial gas pressure10^{-4} mbar, working pressure $3x10^{-2}$ mbar, discharge voltage is 4kV, discharge current is 4 mA, and the discharge power is 16 W. The initial free run of the system was done to check the system performance as the following sequence:

- Start-up the rotary pump for 60 minutes, the pressure inside plasma chamber decreased to 0.01 mbar
- Baking the DP for 20 minutes, and then changing the system to baking state. The pressure drop down to 10^{-5} mbar
- Run the system for 24 hours to eliminate degassing
- Apply 1 kV discharge voltage and 1 mA discharge current by connecting the metal grid to negative side of high voltage power supply, the positive side is connected to base. Using N_2 gas in 0.03 mbar. The system run for 10 minutes, the next step was reversing the polarity of the metal grid and the base and run the system for another 10 min to study plasma glow uniformity in both cases
- Replace N_2 by Ar gas and repeat the same work in previous step at same pressure, and observing the gas glow-discharge color for both gases, we noticed a clear violet color in N_2 gas and a blue-violet color in case of Ar gas

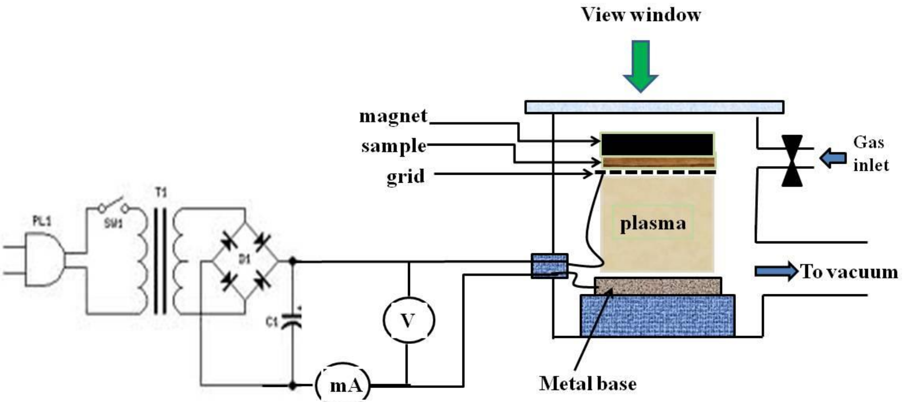

Fig. (1) Experimental setup for DC discharge plasma system

The use of low-pressure plasmas enables the modification of polymer materials. Various plasma components such as electrons, ions, radicals, meta-stables, as well as UV radiation are involved in this reaction processes. These components interact with the exposed surfaces. Since some parts of the surfaces are exposed to energies higher than the characteristic bonding energy of polymers, these parts undergo scission reactions and form new bonding configurations on the surface. Hence every plasma treatment, ablation and deposition, e.g. the generation of new functionalities on polymer surfaces, simultaneously takes place as elementary processes. Depending on the dominating process, which can be influenced by the parameter set, in the end either etching or coating will dominate. While the substrate and the reactor dependent parameters are often predefined, the treatment must be optimized by controlling the material flow into the reactor and by adjusting energy input into the plasma phase. Often an etch-step is performed prior to a deposition process, in order to remove weak boundary layers, and to produce radical sites on the surface [54]. Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites at the surfaces, which are subjected, to post-reaction [55].

The Glow discharge plasma technique is particularly useful for modifications of polymer membranes surfaces, because with these techniques it is possible to modify the outermost surface layer. The plasma is almost homogenous at a low-pressure glow discharge [56]. The treatment at polymer surface is oxidized yielding generation of several oxygen containing groups like hydroxyl, carbonyl and carboxylic acid groups on the surface [57-60]. Polymer films activated by Ar and N_2 through plasma treatment show good biocompatibility and useful for biomedical use [61]. The functionalization of polymer surfaces has been recognized as a valuable tool to improve their adhesion properties. Functional groups like hydroxyl, ketone and carboxylic acid groups have been introduced at surfaces to adjust the surface free energy. Furthermore these groups are used to increase hydrogen binding and facilitate chemical bonds between substrates and adhesion. Additionally, during the modification, weak boundary layers and surface contaminants are removed. All these factors improve the adhesion properties of polymer surfaces. Plasma treatments have been used for etching, crosslinking and functionalize surfaces. Actually all these processes occur simultaneously at a polymer surface exposed to plasma. The surface functional groups have been identifying with IR. Although there are powerful tool for surface analysis, it is not possible to unambiguously identify a specific functional group [55]. Surface activation takes place during the plasma processing mainly by hydrogen abstraction and radical formation, which results in modification of only the top-most nanometers of the polymer structure being altered. This means that the surface can be selectively modified for a specific application while the bulk properties of the polymer are unaffected [30]. Argon is the most common inert gas used in plasma technology. One of the major uses of Ar plasma in the sputtering processes used in the semiconductor industry, pretreatment of substrates for cleaning purpose and to improve the adhesive characteristics of polymers. As inert gas also serve as diluents or in the treatment known as CASING (cross linking by activated species of inert gases) [31,32]. Usually the preferred bombardment characteristics. Nitrogen, a gas commonly used in ion implantation, plasma diffusion treatment and reactive PAPVD (plasma assisted physical vapor deposition) system [18]. Direct energy transfer from energetic particles (i.e., ions and uncharged particles) to the polymer surface induces cross-linking [18-22]. Therefore, surface-specific methods resulting in polymer surface cross-linking while preserving the bulk properties are more effective than bulk treatments. The general consensus is that surface cross-linking involves three main process steps, namely, obstruction of hydrogen atoms from molecular chains by energetic species, such as ions, uncharged particles, and VUV/UV photons; formation of radicals at hydrogen obstruction sites; and reaction between produced radicals leading to the formation of a cross-linked surface layer [21-24].

Although oxygen-containing plasma species (arising from residual water) are also thought to be responsible for some functionalization [29]. A number of different plasma treatments have been used to incorporate oxygen into the surfaces of polymeric materials. The same is true with argon plasma treatment [26]. Nitrogen containing plasmas introduce carbon nitrogen functionalities required mostly for the improvement of wettability, printability, and bond ability.

In present study the PC films were exposed to N_2, Ar and SF_6 plasma. The plasma is almost as homogenous in a low-pressure glow discharge. In the plasma surface modification process, evacuating a reaction chamber and then refilling it with a low-pressure gas create low discharge plasma. The gas is then energized by direct current. The energetic species in gas plasma include ions, electrons, radicals and meta-stables photons in the short-wave ultraviolet (UV) range. The DC glow discharge is generated by applying a high voltage between two electrodes in the presence of magnetic field at low energy with time variation.

The details of the treatment technique are discussed in this chapter, which is employed for the preparation, irradiation and characterization of virgin and irradiated polymer film. In addition, the sample preparation techniques as solution casting and the treatment facility like DC glow discharge plasma treatment are also described.

The materials used in this study are following:

Polycarbonate (PC): Density (ρ)=1.2 gm/cm^3, Molecular weight =254.3 gm/mole,

Polycarbonate:

Polycarbonate has high-impact resistance and temperature resistance. Polycarbonates got their name having functional groups linked together by carbonate groups (-O-(C=O)-O-) in a long molecular back bone chain. The structural formula of PC is shown in Fig. (2). This polymer is highly transparent to visible light. Its glass transition temperature (T_g) is 145°C and melting temperature 225°C.

PC has been obtained in the pellet form. In the present study the films were prepared by solution-cast method [30]. It is usually important in dissolving Polymers to have the material as finely divided as possible and to have each particle thoroughly wetted by the solvent. Agitation of some kind is important, since the solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle, which retards further solvent diffusion into the polymer. Starting by calculation the polymer membrane mass by finding the volume of the membrane as follow:

$$V=\pi . r^2 . t \qquad (1)$$

Where r is the radius of Petri dish in (cm) and t is the thickness of membrane in cm, knowing the density of polymer, one can find the required mass as Mass = Density x Volume.

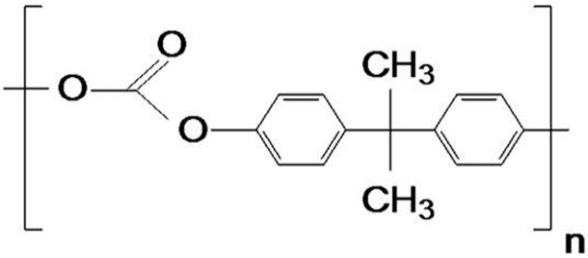

Fig. (2) Monomer structure of polycarbonate

The PC pellets were dissolved in dichloromethane (CH_2C1_2 -99%) separately and a 5% solution was prepared. The stirring is used for 10 hours, the solution was then put into flat-bottomed Petri dishes. The Petri dish containing solution was floated on mercury to ensure the uniformity in the thickness. The solvent was allowed to evaporate slowly over a period of 20-24 hours in the dry atmosphere. The films so obtained were peeled off and dried in vacuum at (50 °C) for 2 hours in order to ensure the removal of the solvent. The thickness of the films was 30-70 ±5 µm.

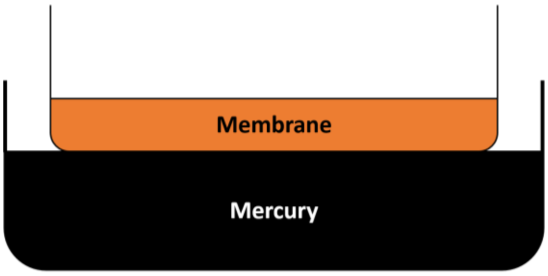

Fig. (3) Schematic setup of the Petri dish floating on mercury tray

The schematic diagram of set up for low-pressure, glow-discharge plasma treatment system on polymer films is shown in Fig. (3), an adjustment system, a device for electric field application, a reactor (combination of a vacuum chamber with vacuum pump and purge plumbing) in which the electric discharge will produce, process gas sources and regulators, different auxiliary devices (for measuring the power and other discharge parameters, cooling system, etc.). Also the set up for plasma treatment on polymer films is shown in Fig. (4).

Typical configuration of a complete plasma processing system is constituted by a stainless-steel plasma cylinder reactor with 40 cm length and 30 cm diameter, electromagnetic energy (DC generator), an adjustment system, high voltage power supply along with milliammeter and high voltage voltmeter to record the dc-discharge current and the discharge high voltage respectively. The vacuum chamber connected to vacuum pumps consist of rotary and diffusion pumps, needle valve to control gas pressure, and process gas sources with gas regulators. The SF_6 gas have been selected in plasma processing because it consider as anti-bacteria agents, this leads to use plasma treated PC membranes in different biological and medical applications. SF_6 plasma can change the PC membrane properties from hydrophilicity nature to be high hydrophobicity surface. Furthermore, SF_6 plasmas were more effective in improving the performance of medical grade PC films [31,32]. The negatively-charged metallic grid shown in Fig. (5) was used to repel the electrons and accelerates the positive ions to impact with PC membrane.

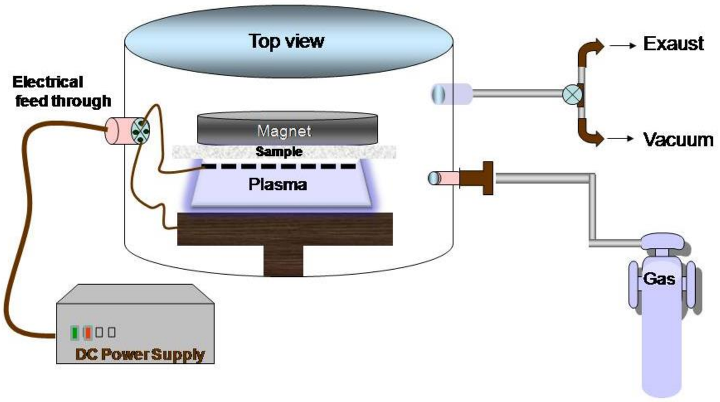

Fig. (4) Schematic diagram of DC discharge plasma setup

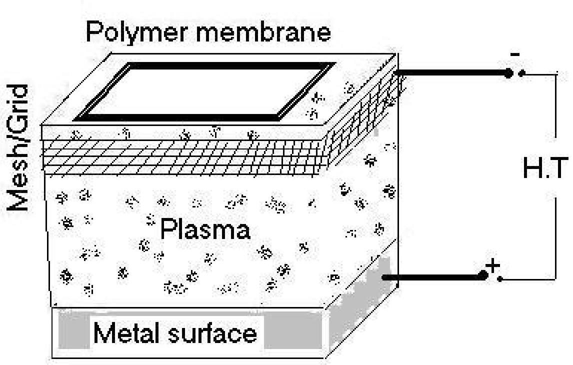

Fig. (5) Experimental setup of discharge DC-Plasma

The plasma plume can be confined by magnetic field applied by a magnet placed in the upper side of the grid. The confinement process of plasma field can improve interaction between plasma species and PC film due to uniform distribution of the activation species within discharge area which can produce good surface. The magnet is positioned to get a magnetic field inside the plasma chamber. The gas is used for containing plasma (either nitrogen, argon or SF_6) is admitted into the source chamber using a flow controller and applying the DC power between two electrodes in magnetic field. The confined plasma in the chamber is used for the surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge. The chamber is evacuated to initial pressure of 10^{-4} mbar and the working pressure is maintained at $3x10^{-2}$mbar by admitting the appropriate gas. The PC membrane was treated by N_2, Ar and SF_6 plasma at various exposure times and different output power.

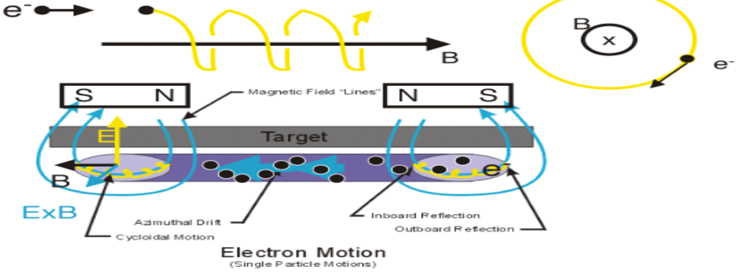

Fig. (6) Confined plasma with Magnetic field

Different values of the discharge power can be varied by adjusting the input current. The experimental conditions used during the plasma treatment were as follows: Initial gas pressure10^{-4}

mbar, working pressure $3x10^{-2}$ mbar, discharge voltage is 4kV, discharge current is 4 mA, and the discharge power is 16 W. The polymer samples were located at the midpoint of the chamber with the help of glass support. In this work, we have used PC films for plasma treatment.

An initial operation for the plasma treatment system was held to check the ability of every part in the system. This test includes the following steps:

1. Start roughing mode for the vacuum unit (supplied by: Indian Vacuum Instruments) by running the rotary pump (RT), then baking the plasma chamber by diffusion pump (DP), with checking cooling system for the DP.
2. The chamber inside pressure decrease into 10^{-4} mbar, the operational time was 12 hours to eliminating degassing.
3. Checking the high voltage power supply.
4. Purging nitrogen gas into the plasma vacuum chamber and starting applied the high voltage to estimate the range of sufficient gas pressure and high voltage to start plasma glowing.
5. Replace the nitrogen by Argon gas and repeat the previous steps to generate Ar gas plasma.

The Optical microscope remains the fundamental tool for surface structures. The optical microscope magnifies an image by sending a beam of light through the object. The optical assembly nearest the eye, the eyepiece, further magnifies the magnified image formed by the objective, so-called primary image. An eyepiece does little to the primary image other than make it visible to eye. The resolution of the microscope is strictly limited by the illuminator-condenser and specimen-objective relationship. However, high quality eyepieces provide better color correction and a wider, flatter field of view, especially with highly corrected objectives. In addition, a good eyepiece can improve viewing comfort. The condenser lens focus the light on the sample and the objective lens (4x, l0x, 40x and 100x) magnifies the beam, which contains the image, to the projector lens so the image can be viewed by the observer. The Optical micrographs have been taken with LABOMED Microscope. The micrographs are stored in computer through CCD camera, which is attached to computer with standard software (HoneyTech). The scale on micrographs can be determined on comparing with electron microscopic grid. It is a circular grid having 3 mm of diameter and there are thousand small squares in 7.06 mm^2 area.

Atomic force microscopy (AFM) is a routine non-optical microscopy technique that allows one to interrogate surfaces and nanometer- to micrometer-scale structures in different media and atmospheres. In AFM a sharp probe tip is scanned across the sample to collect highly localized information about the sample surface and its structure. The basic objective of the operation of the AFM is to measure the forces at the atomic level between a sharp probing tip (which attached to a cantilever spring) and a sample surface. Scanning the sample relative to the probing tip and measuring the deflection of the cantilever as a function of lateral position take images. Typical spring constants are 0.001 to 1.00 N/m and motions from microns up to deflection sensor measure 0.1Å. The force between tip and sample is in the range from 10^{-11} to 10^{-6} N. For comparison the interaction between two covalently bonded atoms is of the order of 10^{-9} N at separation of $\approx$ 1Å. Therefore, non-destructive imaging is possible with these small forces. Here the laser beam deflection method is depicted onto its changes (it's reflected at different angles) and this deviation is detected by the photodiode. The cantilever bends due to force between the tip and the sample.

In scanning electron microscopy (SEM) the sample surface is raster-scanned in high vacuum with a focused beam of electrons. Secondary or backscattered electrons are detected to provide an image of the sample surface with up to nano-meter-scale resolution. In addition to structural imaging, the elemental composition of the surface can be assessed from characteristic X-rays that are emitted.

In general, sample surfaces for SEM analysis require pretreatment to render them clean and conductive to prevent the accumulation of charges in the specimens, this pretreatment may consist of a thin coating of metals, such as gold or platinum, or of graphite. In modern environmental SEM, the sample chamber may be at higher pressure than the rest of the microscope, thereby allowing for imaging at lower voltages and in some case under more realistic conditions (e.g hydrated samples).The advantage of a very large depth of field is compromised in some routine applications by the mentioned need for sample preparation that effectively limits studies of biological processes. However, most materials can very well be analyzed. If e-beam damage becomes a problem, SEM can also be performed at cryogenic temperatures. Due to its surface sensitivity, the secondary electron imaging mode is widely used. In this mode, low-energy secondary electrons (<50 eV) are detected that were ejected from specimen atoms by inelastic scattering interactions with primary electrons. The low energy hence leads to a limited escape depth of only a few nanometers.

Backscattered electrons possess much higher energy compared to secondary electrons and allow one to image with atomic number contrast (relation to Z).High atomic number elements backscatter the primary electrons more effectively compared to lighter elements, hence the contrast is related to atomic mass/number.

Characteristic X-rays are being emitted from atoms at depths of up to a micro-meter upon interaction with the incident electrons. The ejection of photoelectrons is followed by subsequent rearrangements of the electronic shells of the energetically excited atoms. One pathway for deactivation of the excited state is the emission of a characteristic X-ray photon. To analyze the X-rays the SEM must be equipped with an energy dispersive X-ray detector (EDX). Since the escaping photon is not charged, like for instance the mentioned secondary electrons, the escape depth is considerable [34].

To study surface morphology for synthesized PC membranes, an Optical Microscope type LABOMED CXL PLUS (Korea) was used. The effects of Nitrogen, Argon and glow-discharge plasma on the surface properties of PC polymer are investigated by SEM, AFM. To study surface roughness and changes due to plasma treatment an Atomic Force Microscope (AFM) type (Veeco, diCp-II). Plasma treated samples were investigated by AFM on randomly selected positions of 100 x100 mm^2 areas, the measurements was done in semi-contact mode. Changes in morphology were quantified by RMS roughness values. The Scanning Electron Microscope (SEM) from ZEISS model (EVD 18) with auxiliary gold sputtering unit were used. The samples of PC polymer were coated by gold thin film by gold sputtering unit to prevent degradation damages due to high energy electronic beam inside SEM cavity.

Travelling Microscope was used for contact angle measurements. The surface hydrophilicity of the PC treated membranes was characterized using the surface contact angle of distilled water and Glycerin drops respectively in air at room temperature. 3-axis optical travelling microscope provided with a micrometer scale along with a scaled- eyepiece connected to high resolution CCD camera was used. A precise micro syringe supplied with a steel needle was used to driven out very small drops on membrane surface. The scaled-eye piece in travelling microscope is mounted on vertical and horizontal slide rulers, and facing the lateral side of the sample, this arrangement can provide side view image of the sample under study. The diameter of the located drops and the angle between the normal to film substrate and the tangent line of the liquid drop can be measured from the printed image of the CCD camera. By measuring the base diameter(d), for several droplets of different volumes (V), then extrapolating the values of d^3/V to V = 0, and calculating θ from the following equation [17]:

$$\frac{d^3}{V} = \frac{24\sin^3\theta}{\pi(2-3\cos\theta+\cos^3\theta)} \qquad (2)$$

Many measurements obtained from five different membranes, and the measured values of the contact

3. Results and Discussion

Figure (7a) shows the corresponding AFM topographical images of the untreated membrane with root mean square roughness is 6.56 nm. Figures (7b) and (7c) show treated membranes by argon plasma for 10 min. and 30 min. respectively. It is well known, that the plasma treatment is slightly change the morphology of the polymer surface and can depend on the gas composition and pressure. Argon plasma treatment leads to the ablation of the polymer surface layers, the ablation rate being different for different polymers. As expected, the thickness of the ablated layer is an increasing function of the plasma exposure time [4]. The AFM measurements show clearly, that the short time argon plasma treatment does not influence the surface morphology as in Fig. (7b), whereas the root mean square value of roughness (R_{rms}) for treated film within 10 min time is 6.72 nm and increased to be 9.58 nm for 30 min treatment duration.

For nitrogen and SF_6 plasma treatment, the higher values of roughness were observed only for over-expositions (80 min. or more) as in Fig. (7e,g), whereas the R_{rms} increased up to 29.79nm and 30.25nm for treatment time of 80 min, et.at reported the direct dependence between the degree of crystallinity of polymer and surface roughness after the plasma treatment [5,6]. Plasma predominantly etches the amorphous regions than the crystalline ones which are bonded with higher energy. Hence, after plasma treatment, these crystalline regions will remain present, while amorphous are etched away which is leading to rougher surface, because our samples were amorphous. These results have been corroborated by SEM measurements as described in next section.

The results discussed in the preceding paragraph were further confirmed by SEM analysis The SEM image in Fig. (8a) shows the pristine PC film has smooth surface structure without any changes on surface morphology. It can be observed from Fig. (8b,e) that after 10min of argon and nitrogen plasma treatment some uneven granular like defect spots began to appear on the surface. It seems that the PC film begin rough due to the nucleation process during the plasma treatment. It was observed that defective spots increased in density as well as became larger with longer treatment time as shown in Fig. (8c,d,f). Consequently, for SF_6-Plasma treatment, the 18.3X magnification image in Fig. (8g) shows newly formulated SC–layer in aggregation form. The 3.1X magnification image in Fig. (8h) shows PC surface looking shinier with higher reflectance due to treatment with SF_6 gas for longer duration as in Fig. (8h).

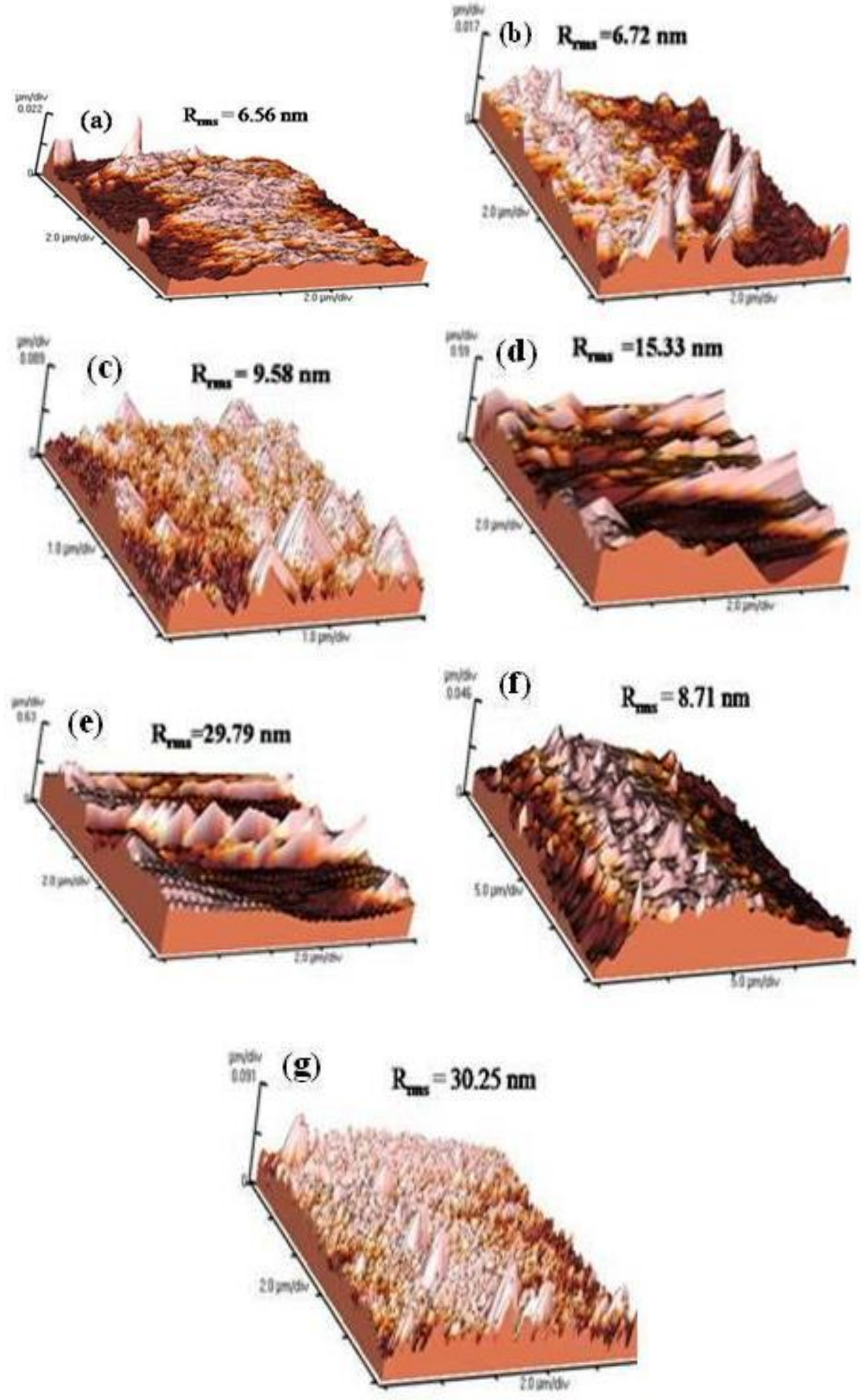

Fig. (7) AFM images of Polycarbonate films with different plasma treatment (a) pristine (b) Ar-plasma for 10 min (c) Ar-plasma for 30 min (d) N_2-plasma for 10 min (e) N_2-plasma for 80 min (f) SF_6-plasma for 10 min and (g) SF_6-plasma for 80 min

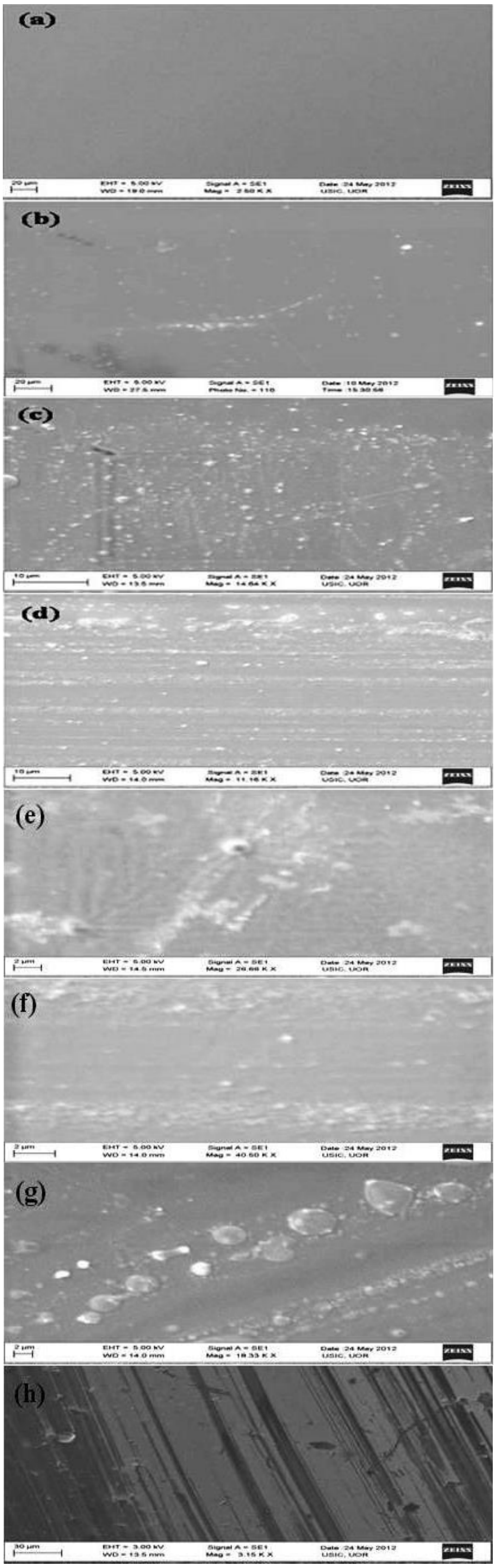

Fig. (8) SEM micrographs of polycarbonate film (a) Pristine (b) Ar-plasma for 10 min (c) Ar-plasma for 30 min (d) Ar-plasma for 60 min (e) N_2- plasma for 10 min, (f) N_2-plasma for 80, (g) SF_6-plasma for 10 min and (h) SF_6-plasma for 80 min

4. Conclusion

In this work, a low-pressure dc glow discharge plasma was generated and diagnosed using the electric probing method. Three different gases (Ar, N_2, and SF_6) were used to generate the discharge plasma. The generated plasma was used to treat the surfaces of thin films of polymeric materials (polycarbonate and polymethyl metha acrylic) prepared by solution cast method. The treatment process was performed at different treatment times. The morphological and topographical characteristics of the treated surfaces were introduced and compared to untreated surfaces. Results showed reasonable modifications in the surfaces as their roughness has increased. Also, the surfaces treated with SF_6 gas showed better characteristics than those treated with Ar and N_2.

References

[1] S.D. Lin, M. Bollinger, and M.A. Vannice, Catal. Lett. 17, 245 (1993).
[2] O.A. Hamadi, K.Z. Yahiya and O.N.S. Jassim, J. Semicond. Sci. Technol., 5(3) 182-186 (2005).
[3] M. Valden X. Lai, and D.W. Goodman, Science 281, 1647 (1998).
[4] M.M. Shubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Pluzak, and R.J. Behm, J. Catal. 197, 113 (2001).
[5] O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 1(2) 3-8 (2008).
[6] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J.K. Nørskov, J. Catal. 223, 232 (2004).
[7] Z. Yan, S. Chinta, A.A. Mohamed, J.P. Fackler, and D.W. Goodman, Catal. Lett. 111, 15 (2006).
[8] O.A. Hamadi, B.A.M. Bader and A.K. Yousif, Eng. Technol. J., 26(8) 995-1001 (2008).
[9] T.V.W. Janssens, B.S. Clausen, B. Hvolbæk, H. Falsig, C.H. Christensen, T. Bligaard, and J.K. Nørskov, Top. Catal. 44, 15 (2007).
[10] B. Hvolbæk, T.V.W. Janssens, B.S. Clausen, H. Falsig, C.H. Christensen, and J.K. Nørskov, Nanotoday 2, 14 (2007).
[11] O.A. Hamadi, N.J. Shakir, F.H. Hussain, Bulg. J. Phys., 37(4), 223-231 (2010).
[12] Y. Zhou, N.J. Lawrence, L. Wang, L. Kong, T-S. Wu, J. Liu, Y. Gao, J.R. Brewer, V.K. Lawrence, R.F. Sabirianov, Y-L. Soo, X.C. Zeng, P.A. Dowben, W.N. Mei, and C.L. Cheung, Angew. Chem. Int. Ed. 52, 6936 (2013).
[13] B. Hammer and J.K. Nørskov, Nature 376, 238 (1995).
[14] O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 3(1) 23-26 (2010).
[15] B. Hammer and J.K. Nørskov, Adv. Catal. 45, 71 (2000).
[16] T. Bligaard and J.K. Nørskov, Electrochem. Acta 52, 5512 (2007).
[17] O.A. Hammadi and N.E. Naji, Iraqi J. Appl. Phys., 10(2) 27-31 (2014).
[18] J.G. Wang and B. Hammer, Phys. Rev. Lett. 97, 136107 (2006).
[19] D. Matthey, J.G. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Lægsgaard, B. Hammer, and F. Besenbacher, Science 315, 1692 (2007).
[20] O.A. Hammadi, W.N. Raja, M.A. Saleh and, W.A. Altun, Iraqi J. Appl. Phys., 12(3), 35-42 (2016).
[21] T. Fujitani and I. Nakamura, Angew. Chem. 50, 10144 (2011).
[22] O.A. Hammadi, W.N. Raja, M.A. Saleh and W.A. Altun, Iraqi J. Appl. Phys., 12(4), 19-28 (2016).
[23] I.X. Green, W. Tang, M. Neurock, and J.T. Yates, Jr., Science 333, 736 (2011).
[24] D. Widmann and R.J. Behm, Angew. Chem. Int. Ed. 50, 10241 (2011).
[25] O.A. Hammadi, J. Optoelectron. Phot., 7(5), 21 (2016).
[26] O.A. Hammadi, J. Laser Micro/Nanoeng., 11(6), 151 (2016).
[27] A. Visikovskiy, H. Matsumoto, K. Mitsuhara, T. Nakada, T. Akita, and Y. Kido, Phys. Rev. B 83, 165428 (2011).
[28] O.A. Hammadi, J. Biomed. Nanotechnol., 12(8), (2016).
[29] N.S. Phala and E. van Steen, Gold Bulletin 40, 150 (2007).
[30] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[31] O.A. Hamadi, Iraqi J. Appl. Phys., 12(2) 9-13 (2016).
[32] R.L. Kurtz, R. Stockbauer, T.E. Madey, E. Román, and J.L. de Segovia, Surf. Sci. 218, 178 (1989).
[33] Z. Zhang, S-P. Jeng, and V.E. Henrich, Phys. Rev. B 43, 12004 (1991).
[34] S. Wendt, P.T. Sprunger, E. Lim, G.K. Madsen, Z. Li, J.Ø. Hansen, J. Matthyiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, and F. Besenbacher, Science 320, 1755 (2008).
[35] O.A. Hammadi, Phot. Sens., 6(4) 345-350 (2016). DOI: 10.1007/s13320-016-0338-4
[36] C.M. Yim, C.L. Pang, and G. Thornton, Phys. Rev. Lett. 104, 036806 (2010).
[37] Z. Dohnálek, I. Lyubinetsky, and R. Rousseau, Prog. Surf. Sci. 85, 161 (2010).
[38] Y. Kido, H. Namba, T. Nishimura, A. Ikeda, Y. Yan and A. Yagishita, Nucl. Instrum. Methods B 136-138, 798 (1998).
[39] H. Matsumoto, K. Mitsuhara, A. Visikovskiy, T. Akita, N. Toshima and Y. Kido, Nucl. Instrum. Methods B 268, 2281 (2010).
[40] L.P. Zhang, M. Li, and U. Diebold, Surf. Sci. 412/413, 242 (1998).
[41] O.A. Hammadi and N.E. Naji, Phot. Sens., 8(1) 43-47 (2018).
[42] U. Diebold, Surf. Sci. Rep. 48, 53 (2003).
[43] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, and M. Haruta, J. Catal. 202, 256 (2001).
[44] J.S. Muenter, J. Mol. Spectroscopy 55, 490 (1975).
[45] Z. Wang, Y. Zhao, X. Cui, S. Tan, A. Zhao, B. Wang, J. Yang, and J.G. Hou, J. Phys. Chem. C 114, 18222 (2010).
[46] A.A. Hadi and O.A. Hamadi, Iraqi J. Appl. Phys. Lett., 1(2) 23-26 (2008).
[47] M. Klimenkov, S. Nepijko, H. Kuhlenbeck, M. Bäumer, R. Schlögl, and
[48] H.-J Freund, Surf. Sci. 391, 27 (1997).
[49] J.T. Miller, A.J. Kropf, Y. Zha, J.R. Regalbuto, L. Delannoy, C. Louis, E. Bus, and J.A. van Bokhoven. J. Catal. 240, 222 (2006).
[50] O.D. Häberlen, S. Cheong, M. Stener, and N. Rösch, J. Chem. Phys. 106, 5189 (1997).
[51] Y. Xu and M. Mavrikakis, J. Phys. Chem. B 107, 9298 (2003).
[52] R.V. Hardeveld and F. Harog, Surf. Sci. 15, 189 (1969).
[53] Z. Huang, P. Thomson, and S. Di, J. Phys. Chem. Solids 68, 530 (2007).
[54] A. Bongiorno and U. Landman, Phys. Rev. Lett. 95, 106102 (2005).

[55] A.K. Yousif and O.A. Hamadi, Bulg. J. Phys., 35(3) 191-197 (2008).
[56] O.A. Hammadi, Mater. Res. Exp., 8(8), 085013 (2021)
[57] F.J. Kadhim, O.A. Hammadi, and N.H. Muthesher, J. Nanophot., 16(2), 026005 (2022).
[58] Z.H. Zaidan, K.H. Mahmood, O.A. Hammadi, Iraqi J. Appl. Phys., 18(4), 2730 (2022)
[59] O.A. Hammadi, Optik, 208, 164147 (2020).
[60] B.T. Chiad, O.A. Hammadi, F.J. Kadhim, and M.K. Khalaf, Iraqi J. Appl. Phys., 12(3), 17-26 (2016).
[61] O.A. Hammadi, Adv. Sci. Eng. Med., 11(5), 346-350 (2019).