# Surface Roughening of Poly (methyl-methacrylate) Membranes by $SF_6$-Glow-Discharge Plasma Etching

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**Abstract:**
The (100 μm) thick of high density Polymethylmethacrylate PMMA membranes were prepared by solution cast method and treated by (42 W), low pressure, DC-discharge, $SF_6$-Plasma for different exposure time: 10,30,60 and 80 min. The observed changes in membranes surface properties have been characterized by Scanning Electron Microscopy(SEM).The optical properties for plasma treated membranes has been characterized by UV-Visible Spectroscopy. The chemical structure changes have been characterized by Fourier Transformation Infrared Spectroscopy (FTIR).The (SEM) results indicates to significant changes in surface morphology of the polymer membranes after plasma treatment. The UV-Visible spectroscopy results shows clearly reduction of light transmission due to plasma treatment, also the (FTIR) results shows the changes in molecular bonds for polymer chains in surface structure of polymer membranes.

**Keywords:** Polymers, Polymethylmethacrylate, Plasma Treatment, Vacuum Pump, SEM, FTIR, UV-Visible.

## Introduction:

Polymers have been used successfully in many scientific, biological and industrial fields such as thin-film technology, biomaterials, adhesion, protective coatings, friction and wear composites, and microelectronic devices. In general, special surface properties with regard to chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity, and cross-linking density are required for successful applications in various fields [1-3]. Polymers very often do not possess the surface properties needed for these applications. They have excellent bulk physical and chemical properties, and are inexpensive and easy to process. For these reasons, surface modification techniques which can transform these advantageous materials into highly valuable finished products have become an important part of the plastics industry [4-5].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 different from those of the bulk [6].

The plasma is capable to exert four major effects [7]: (i) surface cleaning, (ii) surface ablation or etching, (iii) surface cross-linking, and (iv) modification of the surface chemical structure, occurring both in situ or after subsequent exposure to the atmosphere. These effects depend on a presence of the active species in plasma (electrons, ions, radicals, photons) which interact with polymer surfaces and modify their chemical and physical properties [8].

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 [9]. Cross linking occurs when two radicals produce on the neighboring polymer units. 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 [10-11]. 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 [12].

Poly (methylmethacrylate) PMMA has been widely used in biomedical and optical applications for its advantages of chemically inert, transparent, excellent mechanical properties, low cost, and ease of fabrication. It has been widely used in applications such as tissue engineering [13]. PMMA is a hard, rigid, and transparent polymer with a glass transition temperature of (125)°C. Its average molecular weight is ($6\times10^{-4}$) so it is tougher than polystyrene. PMMA is a polar material and has a large dielectric constant. PMMA matrix is most preferred for designing components because of its better resistance to hydrolysis and its good outdoor weather resistance. It is a thermoplastic and can be molten and molded into any desired product [14-16].

This polymer also finds application in biomedical technologies, microelectronic, nano - microelectromechanical systems and micro fluidic devices[17]. At present time the PMMA is in the focus of many researchers for its possible applications in organic thin film transistors (OTFT) [18] or permanent memory devices where, for example the gold nano-particles can be attached to PMMA surface. A biocompatibility and excellent bulk properties designate PMMA to use in biomedical applications as a prosthetic material and PMMA is also an appropriate substrate for an immobilization of biomolecules enzymes, (DNA), proteins, or antibodies [19].

## Experimental:

The (100μm) thick PMMA membranes were prepared by solution cast method. The PMMA granular has

dissolved in dichloromethane ($CH_2C_{12}$) solution (Alpha-Aldrich) using magnetic stirrer for (10) hours. The solution was then pursed into flat-bottomed petrie-dish floated on mercury to ensure the uniformity in the membrane thickness. The solvent was allowed to evaporate slowly over a period of (12-14) 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 [20].The schematic diagram of set up for low-pressure, glow-discharge plasma treatment on polymer films is shown in Fig.(1). 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, 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 negatively-charged metallic grid shown in Fig. (1) was used to repelled the electrons and accelerate the positive ions to impact with PMMA membrane. 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 PMMA film due to uniform distribution of the activation species within discharge area which can produce good surface uniformity. The plasma generator chamber was evacuated to (0.1mbar) pressure, and then by purging of $SF_6$ gas inside the chamber, the working pressure to produce plasma plum increased up to (10mbar). The PMMA membrane was treated by $SF_6$-plasma at various exposure times and different output power. 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 pressure (0.1 mbar), working pressure (30 mbar), discharge voltage is (6kV), discharge current (7 mA), and the discharge power is (42 W). The polymer samples were located at the midpoint of the chamber with the help of glass support.

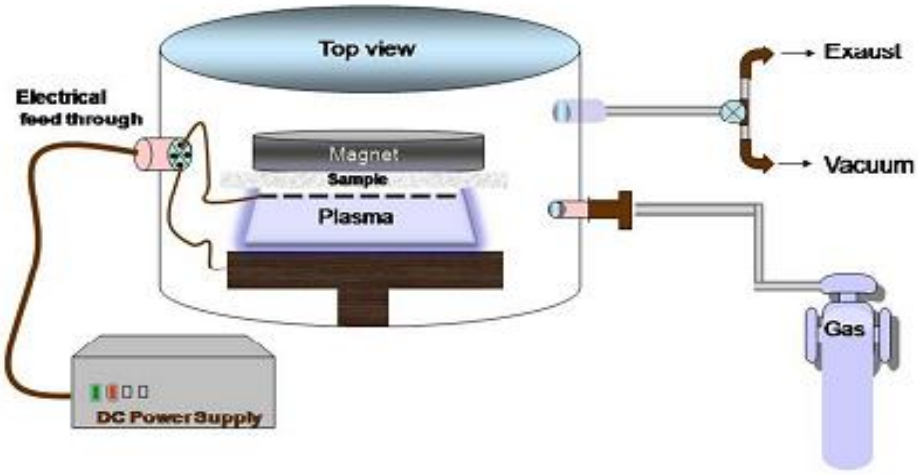


**Fig.(1) Setup of DC discharge plasma treatment system**

## Characterizations:

The Scanning Electron Microscope from ZEISS model (EVD 18) was attributed to study the surface properties of PMMA films. The UV-visible spectroscopy from HITACHI (U-2900) spectrophotometer in the wavelength range of (200 to 500nm) was used for characterization of optical properties of PMMA films. The characterization of the chemical structure of the pristine and modified polymers films was carried out by Fourier transform infrared spectroscopy (IRAffinity-1) from (SHIMADZU).

## Results and Discussion:

1. Scanning Electron Microscope (SEM)

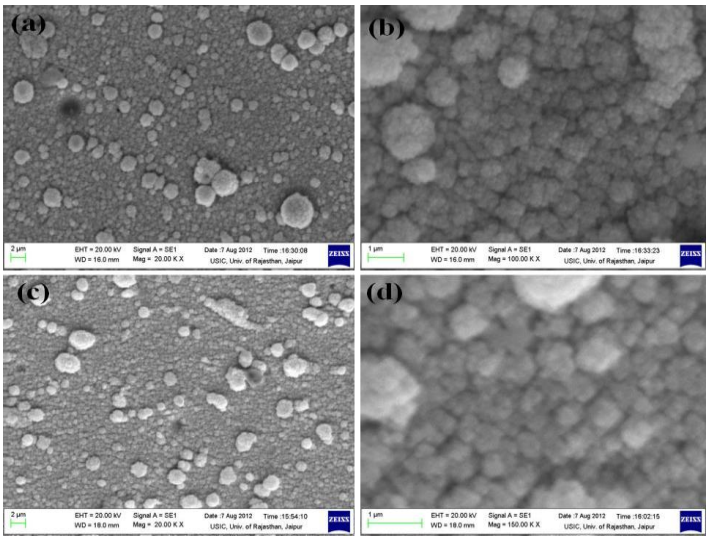


**Fig (2) SEM micrographs of PMMA film treated by (42W), $SF_6$ –Plasma**
**(a) 20kX- mag. for (30 min) treatment, (b) 100kX- mag. for (30min) treatment, (c) 20kX-mag. for (80 min) treatment and (d) 150kX-mag. for (80 min) treatment.**

Fig.(2) shows the SEM images of PMMA membranes treated by $SF_6$-plasma. The high magnification of SEM images (20kX and 100kX) for PMMA films treated for (30 min) are shown in figures (2a and b), it is describing clearly uniform distribution of degradations and etching effect in surface layers of PMMA. Furthermore, the density of granular spots and surface roughness are increased with higher treatment period (80 min) as shown in fig.(2c and d) with image magnification (20kX and 150kX). The images show also dependence of surface morphology on plasma operational parameters like plasma species energy and time of irradiation. Exposure to $SF_6$-plasma leads to a partial defluorination by (–C–F) bond scission or polymer chain breakage. The (–C–F) may arise from the ion interaction, which can react with other radical on polymer surface, also air oxygen, (–C=C–) bonds may be created on the plasma activated surface [21].

2. UV-Visible Spectroscopy

The optical transparency for treated PMMA films was evaluated by recording the UV-visible transmission spectra for various treatment time of $SF_6$-plasma as shown in fig. (3). The reference used for transmission measurements is untreated PMMA film. It is well known that the transparency of a bulk film strongly depends on the surface roughness, and an increasing in the average roughness will result decreasing in transmittance due to light scattering effects[22].The increased roughness may be envisioned as the increasing in the concentration and sizes of the degradations on membrane's surface [21], but the effects of some species present in the plasma promotes chain scission, and this could lead to etching and material removal. Thus promoting changes in surface roughness will-in most cases-positively contribute to decrease the transparency [23].

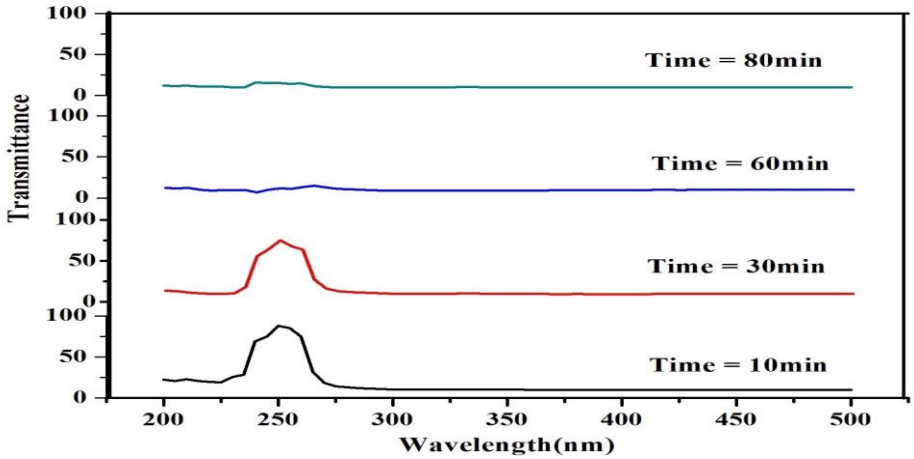


**Fig (3) UV-Visible spectrum for PMMA membranes treated by (42W), $SF_6$-plasma.**

For PMMA membranes which treated by $SF_6$-plasma, it can be observed from fig. (3) that the transparency decreased continuously with higher plasma irradiation period. This behavior can be explained by increasing of surface roughness along with irradiation process. Furthermore, for longer

treatment time and for higher plasma discharge power the surface properties of PMMA film will changed rapidly due to high thermal energy of incident plasma species which can cause a severe degradations in polymer chains, and later on blacking effect of sample side. The changes in membrane color leads to decreasing the transparency.

3. Fourier Transmission Infra-red Spectroscopy (FTIR)

Plasma treatment by $SF_6$ ions can break chemical bonds in PMMA matrix like (C-C) and (C-H), forming free radicals at or near the surface. These radicals tend to be stable by reaction with other radicals by chain-scissioning [24]. Consequently, recombination process or cross-linking can occur when these free radicals start moving, this interaction can produce high molecular weight structures. The most important characteristics of the surface of samples are determined by the functional groups present in the surface layer, (FTIR) spectroscopy is used for this purpose.

The (FTIR) absorption spectrum for PMMA polymer treated by $SF_6$-plasma is shown in fig. (4), absorption spectra of (C-O) and (C-H) bonds for pristine film are shown in fig. (4a). For treated films with $SF_6$-plasma for (10 min) as in fig.(4b), a noticeable change can be observed in the enhancement the (C-O) bonds at (1000 and 1250 $cm^{-1}$). For longer treatment time (80 min) as in fig (4c), the enhancement in absorption for (C-H) bands at (3100 $cm^{-1}$) and defluorination by (–C–F) bond scission or polymer chain breakage has been observed. These changes in absorption bands for PMMA is an evidence for cross linking and defluorination effects which have a different influence on polymer chain bonds according to plasma treatment time and powers.

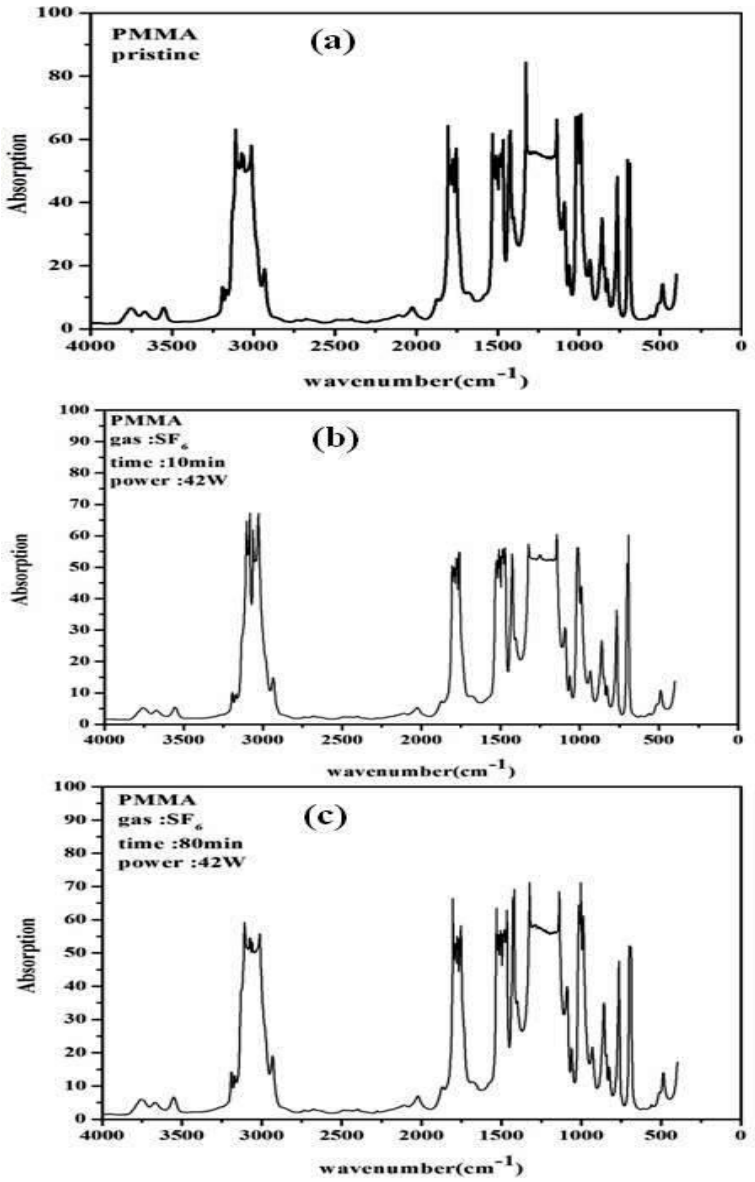


**Fig.(4) FTIR spectrum for PMMA film treated by $SF_6$- plasma(a) Pristine, (b) (42W) for (10 min) treatment, and (c) (42W) for (80min.) treatment.**

## Conclusions:

$SF_6$-plasma was employed to etch PMMA membranes. The morphological, optical and chemical surface properties were changed. A surface degradation with granular spots were observed by SEM images due to chain sissioning and cross-linking effects, this process produce highly surface roughness. The high roughness affected the optical properties of the plasma treated membranes as described in UV-visible spectra. The UV-visible spectroscopy shows that the optical transparency is decreased due to plasma treatment. The FTIR spectroscopy for treated membranes shows that the chemical molecular bonds like C-C, C-H and C-O were changed due to cross-linking and chain sissioning effects.

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# زيادة خشونة سطح غشاء البولي–ميثاكريلايت باستخدام بلازما التفريغ الكهربائي التوهجي لغاز سادس فلوريد الكبريت

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**الملخص:**

في هذا العمل تم تحضير أغشية بوليمر البولي – ميثاكريلايت عالي الكثافة بسمك (100µm) باستخدام طريقة ترسيب المذيب ، وتم معاملة هذه الأغشية ببلازما التفريغ الكهربائي لغاز سادس فلوريد الكبريت ($SF_6$) بضغط منخفض وبقدرة تفريغ كهربائي تبلغ (42W).وتم اختيار زمن معاملة يبلغ (10,30,60,80) دقيقة. وتم تسجيل التغييرات الحاصلة في خصائص سطح اغشية البوليمر باستخدام المجهر الإلكتروني الماسح. وتم تسجيل التغييرات الحاصلة في خصائص السطح البصرية نتيجة التعامل بالبلازما باستخدام المطياف الضوئي. وكذلك تم تسجيل التغييرات الجزيئية الكيمياوية في خصائص سطح غشاء البوليمر باستخدام مطياف فوريير للأشعة تحت الحمراء.

ولقد اشارت نتائج المجهر الإلكتروني الماسح الى حدوث تغييرات ملحوظة في خشونة سطح غشاء البوليمر بعد معاملته ببلازما التفريغ الكهربائي ذات الضغط المنخفض. وكذلك أظهرت نتائج المطياف الضوئي تناقص في نفاذية الضوء للغشاء المعامل بالبلازما. وكذلك أشارت نتائج مطياف فوريير للأشعة تحت الحمراء الى تغييرات في الاواصر الجزيئية لسلاسل البوليمر في سطح الغشاء نتيجة عملية كسر الاواصر وعملية الربط البيني في بنية سلاسل البوليمر.