



Polymer Treatment Using Atmospheric Glow Discharge

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THE treatment of inorganic and organic surfaces is widely examined by plasma treatment, deposition of thin films and processing of materials. The plasma treatment for surface modification of polymer films is the most effective way of uniform and controlled treatment. Atmospheric Pressure Glow Discharge (APGD) has been understood by using a plasma needle of argon. The uniform plasma increases in scale from a small region near the needle tip to a plasma plume with a length of about 20 mm with increasing the applied voltage. In this work, a polymer film (Makrofol) was modified using atmospheric glow discharge at different treatment times. Scanning electron microscope (SEM), atomic force microscopy (AFM) and X-Ray Diffraction (XRD) measurements were used to investigate and characterize the surface-treated polymer. It was found that the change in surface properties depends on the treatment time. Also, it was found that the plasma treatment modifies the polymer surface in both morphology and composition. These behaviors originated from ablation by Ar plasma treatment.

Keywords. Atmospheric Pressure Glow Discharge (APGD); plasma polymer treatment; Makrofol polymer film; SEM microscopy and AFM microscopy.

Introduction

The plasma treatment at different processing conditions can be used to modify the surface of polymer films [1,2]. Therefore, different techniques such as chemical oxidation [3], flame [4], grafting [5,6], laser [7], UV irradiation [8] and plasma treatments for surface modification attracted more attention [9,10]. The subsequent and significant reactions on materials, which are subjected to plasma treatments based on free radical chemistry.

Glow discharge plasma is efficient at creating a high density of free radicals by dissociating molecules through electron collision and photochemical processes. These gas-phase radicals have sufficient energy to disrupt chemical bonds in polymer surfaces on exposure, which results in the formation of new chemical species [11].

Operating at atmospheric pressure (atmospheric pressure glow discharge, APGDs), the linear dimension over which the discharge develops is reduced. Stable APGDs used for technological applications have developed,

differing with respect to the structure of electrodes, carrier gas and operating frequency. Typically, APGD systems are characterized by having one electrode covered with a dielectric with the discharge operating in alternating voltage.

Kropke et al. [13] presented a new approach for the surface treatment of polymer films at atmospheric pressure. The DC glow discharge generated by applying a high voltage between two electrodes, which are placed in a channel with a high flux of air. The airflow removes charge carriers from the plasma zone, which prevents the formation of sparks. In the almost homogeneous plasma, a comparably high electrical power is converted, forming a high concentration of active species. The flowing air transports them to the polymer surface. The resulting alterations in the surface structure of the polymers are characterized by XPS and contact angle geometry.

Vijayalakshmi et al. [14] treated the polycarbonate film (PC) surface using glow discharge low-pressure air plasma. The modified surface was characterized by contact angle, FTIR, XRD, AFM and XPS analysis. It was found that,

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after plasma treatment, the root mean square (RMS) roughness of the PC film gradually increased with exposure time and plasma treatment modified the chemical composition of the polymer surface.

ATTA et al. [15] investigated the morphology and wettability of semi crystalline polyethylene terephthalate (PET) foils using argon plasma and argon ions produced from cold cathode ion source. The induced effects in the structure, surface morphology and surface wettability were analyzed by using the Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and by using the contact angle method. The results showed that, there are a change in surface free energy of polymer surface after argon plasma treatment.

Hassouba and Dawood [16] examined the surface properties of the plasma-treated samples by microscopy techniques include contact angle measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM), infrared (IR) spectroscopy and refractive index measurements. It is found, the plasma treatment modifies the polymer surface in both composition and morphology.

The aim of the present work is to measure the electrical measurements of the applied voltage

and discharge current at different experimental conditions. The polymer film (Makrofol) modified using the atmospheric glow discharge at different treatment time. The surface properties of the plasma-treated polymer are examined using X-ray diffraction (XRD) measurements, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Experimental setup

The discharges formed between two circular plane parallel electrodes, 40 mm in diameter. The upper electrode is covered by a ceramic plane with a thickness of 2 mm and a diameter of 70 mm as dielectric barriers and surrounding by Teflon as an insulator. The other electrode made of stainless steel and connected to the earthed. The air gap between the two electrodes varied in the range of 1 to 4 mm. A 0-30 kV, 20-50 kHz power-frequency high voltage is used as a voltage supply as shown in Fig. 1.

Electrical measurements of discharge current and the applied voltage are measured using Tektronix voltage probe (model P6015A), while the current flowing in the circuit is measured using current monitor (model 6585 Pearson electronics, USA). The applied voltage on the two electrodes and the discharge current through the reactor monitored using a four-channel digital phosphor oscilloscope type (Tektronix model DPO 4054).

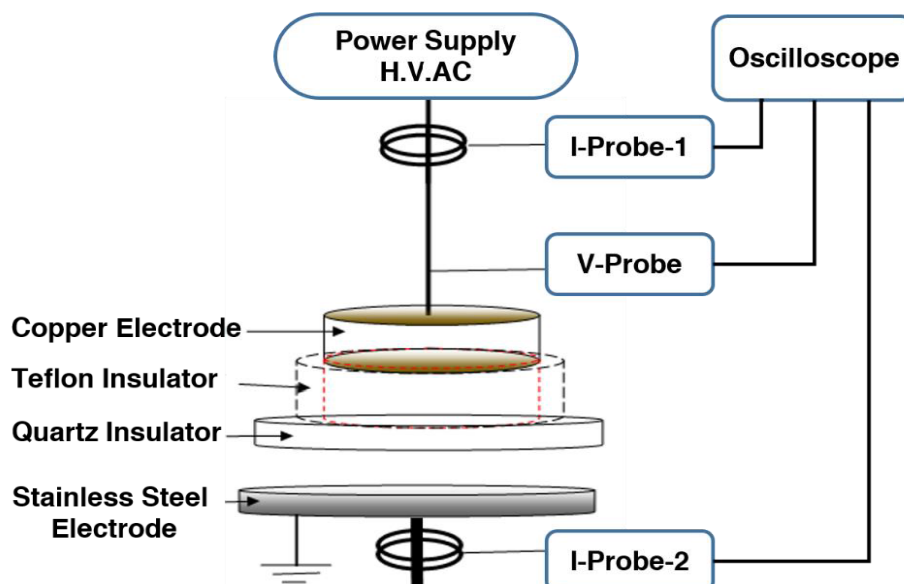


Fig. 1. Schematic diagram of the experimental set-up.

The polymer film (Makrofol, Makrofol films have been developed by Farbenfabriken Bayer A.G. (Leverkusen, Germany). which has a chemical composition of), as shown in Fig. 2, with an average thickness and density of, treated is placed on the lower plate. It has high resistance to heat, excellent elasticity, and good electrical insulation, resistance to abrasion, weather and chemical products. The changes in its surface properties were examined using X-ray diffraction XRD (SHIMADZU 6000, 60 kV, 80 mA, Cu-X-ray TUBE --Japan), scanning electron microscopy SEM (JSEM 7400F, Joel, Japan) and atomic force microscopy AFM (CP-11 SPM, Veeco, USA).

Results and Discussion

Uniform atmosphere glow discharge plasma is beneficial in optimizing the conditions for

plasma formation and its surface treatment applications. The main advantage of APGDs is the absence of vacuum conditions, which greatly reduces the cost and complexity of the glow discharge operation.

A typical oscillogram of the applied voltage and discharge current in APGD is shown in figure 3. Spike currents are observed in the current waveform in the rising portion of each half cycle of the applied voltage from the start to the time of voltage peaking. The spikes caused by the filament discharges. As the two electrodes are of the same size and shape, the discharge current in the positive half-cycle is about the same as that in the negative half-cycle. The APGD is characterized by a single current pulse per half-cycle of the applied voltage with the same periodicity.

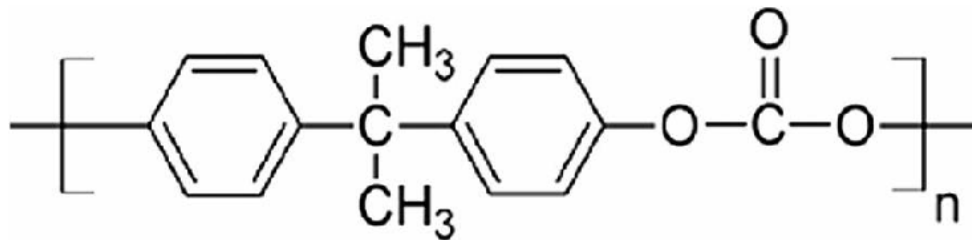


Fig. 2. Monomer unit of Makrofol.

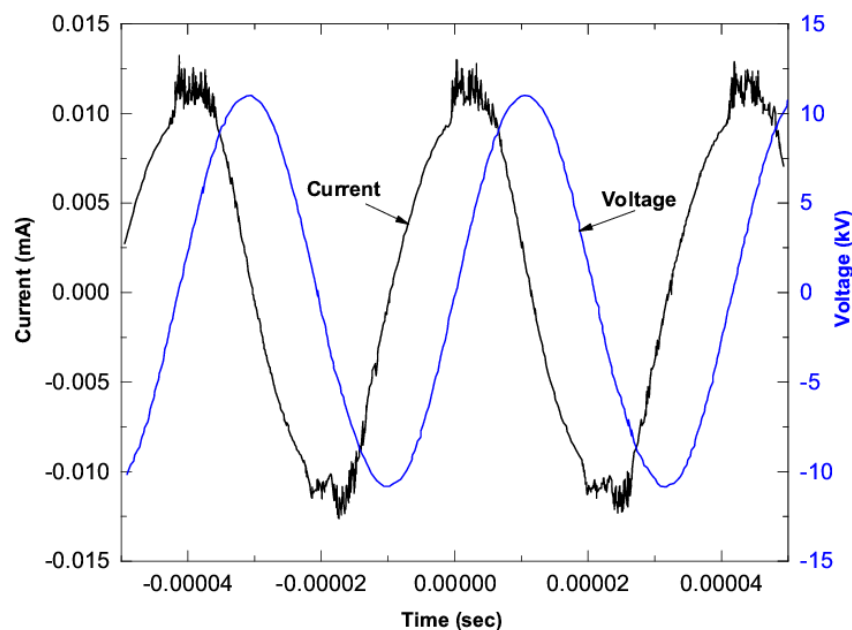


Fig.3. V-I waveforms for APGD Ar gas.

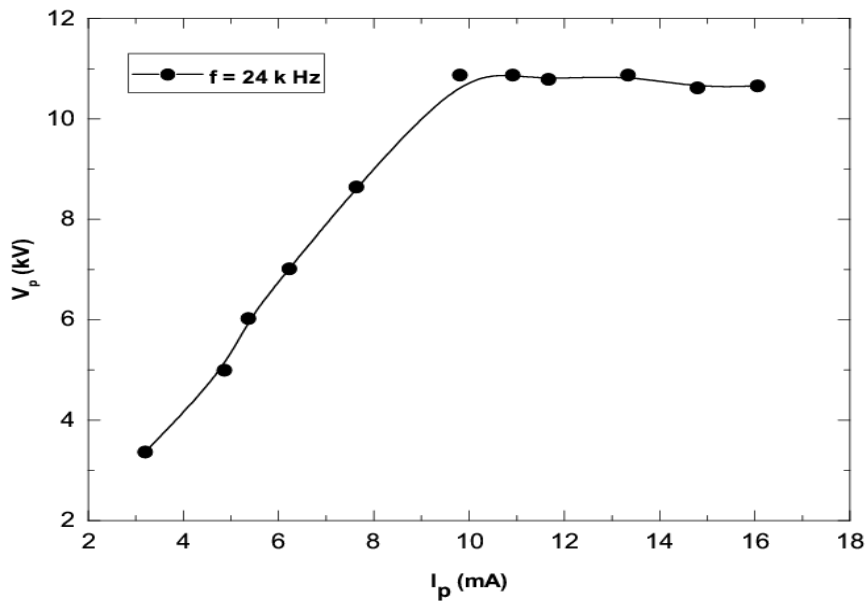


Fig. 4.Relation between V_p and I_p .

Figure 4 shows the relation between the peak values of the applied voltage and discharge current at constant frequency(). In addition, it increases with increases until at then saturation is occurring.

In addition, Fig. 5 shows the relation of the gap distance between the two electrodes of APGD as a function of the breakdown voltage. It is clear that, the breakdown voltage increases with increases the gap distance. Surface treatments performed by setting the air gap fixed at and the applied voltages at. The changes in the surface determined by varying the treatment time and observed using XRD.

Figure 6 shows the X-ray curves of the polymer after the treatment at different treatment times. The XRD analysis can be used to assessment and quantification of the crystalline phases (polymorphism), polytypic and all types of solid-state molecular arrangements. The diffraction pattern indicates that this polymer is amorphous in nature. It is also shows broadening of this XRD peak with increasing the treatment times [17,18]. Table 1 shows the calculated FWHM (Full width at half maximum) with the plasma treatment times.

The broadening of peak points out an evolution of the polymer towards a more disorder state and a change in crystallite size by irradiation of

ions [19, 20]. The contribution of the amorphous region to the XRD pattern increases and there are changing in width position of the peaks resulting from the crystalline region. As seen in Fig. 6, a strong peak was observed at $2\theta = 19^\circ$, showing the semicrystalline nature of Makrofol polymer.

On the other hand, Fig. 7 shows the relation between the calculated areas under the curves of the X-ray for the samples of polymer treated by plasma as a function of the treatment time. It is found that the change in surface properties depends on the treatment time. This figure shows that the integral intensity increases up to a maximum value at sample of treatment time, then decreases on increasing the treatment time.

The increase in integral intensity indicates an increase in ordering in the Makrofol samples due to degradation. Then, the free radicals cause, cross-linking, this cross-linking destroys the crystallinity, giving the resilience to the polymer. The figure shows that the integral intensity increases up to a maximum value at 10 min. treatment sample, indicating an increase in ordering due to chain scission, then decreases on increasing the plasma treatment exposure time. This shows that the polymer crystallinity decreases with increasing treatment exposure time and undergoes amorphization [21-23].

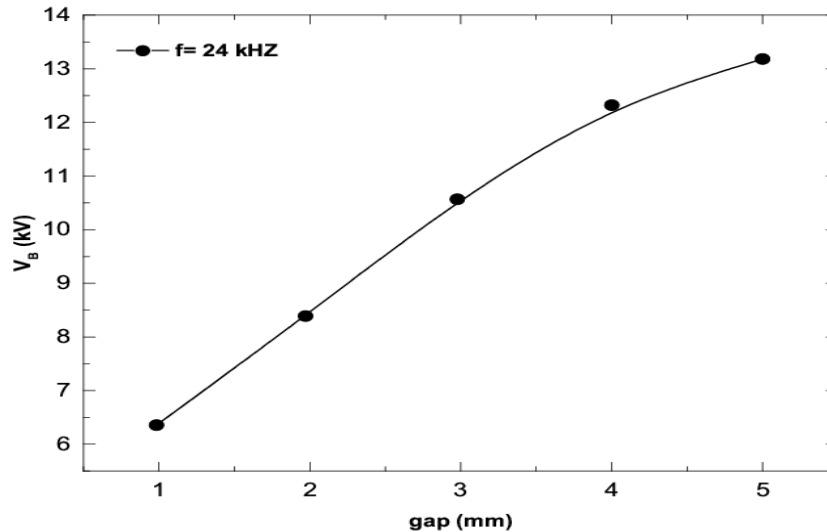


Fig. 5.The relation between gab distance and breakdown voltage.

Table 1.

(Treatment time(min	FWHM
1	7
5	7.5
10	8
15	7.5
20	7.25

On the other hand, the interaction of energetic ions with polymeric materials creates reactive radicals on the polymer surface, which in turn can form cross-links, and new functional groups, which is effective because no special additives are require.

Science the surface functionality of polymeric materials plays an important role in improving cell, tissue, the scanning electron microscopy (SEM) are performed, and an atomic force microscope (AFM) are examined. In this meaning, plasma grafting and immobilization techniques to prepare polymeric materials with specific functionalities are appropriate means as mentioned earlier.

Figure 8 shows the cross-sectional SEM images of the Makrofol film. The pristine sample showed relatively smooth surface, the SEM micrographs of irradiated samples by argon display small voids on the surface. There was clear roughness on the surface of the irradiated sample and voids becomes large size with increasing time treatment. The untreated and treated SEM images had taken at the same magnification power and accelerating voltage.

In addition, Figure 9 shows the topographical changes of Makrofol film due to Argon plasma treatment, AFM images taken at different treatment time. It is clear that, the plasma treatment can change the Makrofol surface topography.

For polymers, the surface irregularities increase with the increases of plasma treatment time. An energetic ion passing through the polymer transfers its energy into highly localized regions in a very short time interval through elastic and inelastic collisions [23]. Consequently, the surface topography and roughness changed as the plasma treatment time increased.

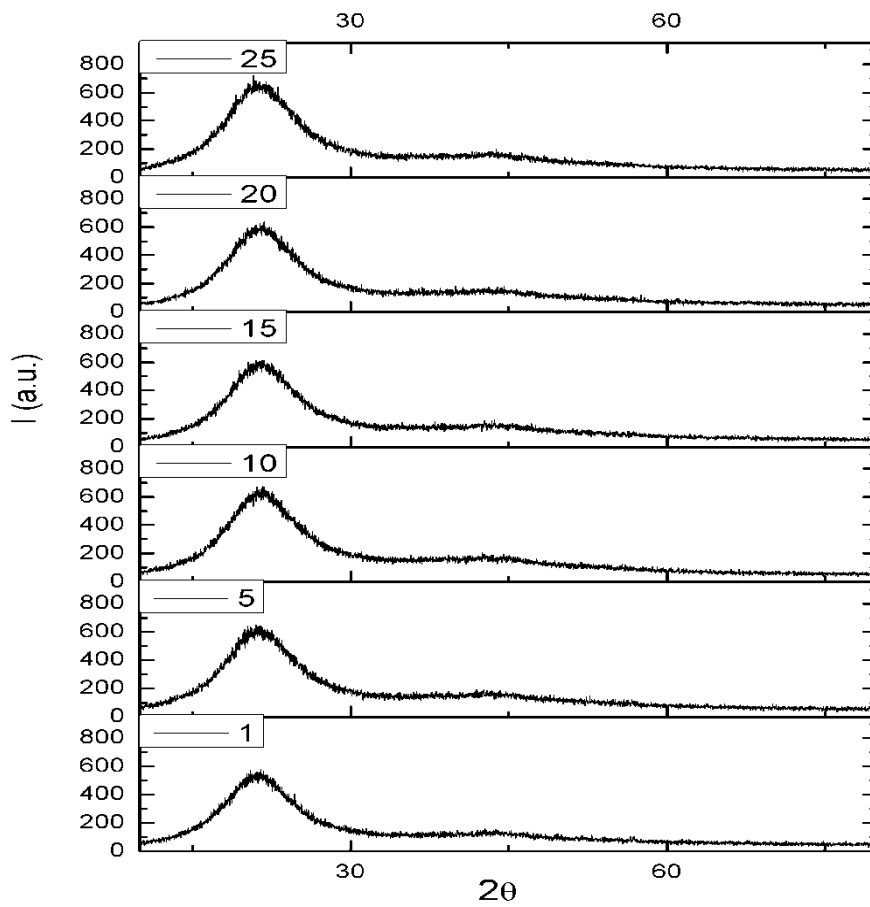


Fig. 6. X-ray diffraction (XRD) patterns of the Makrofol film at different treatment times (1-25 min).

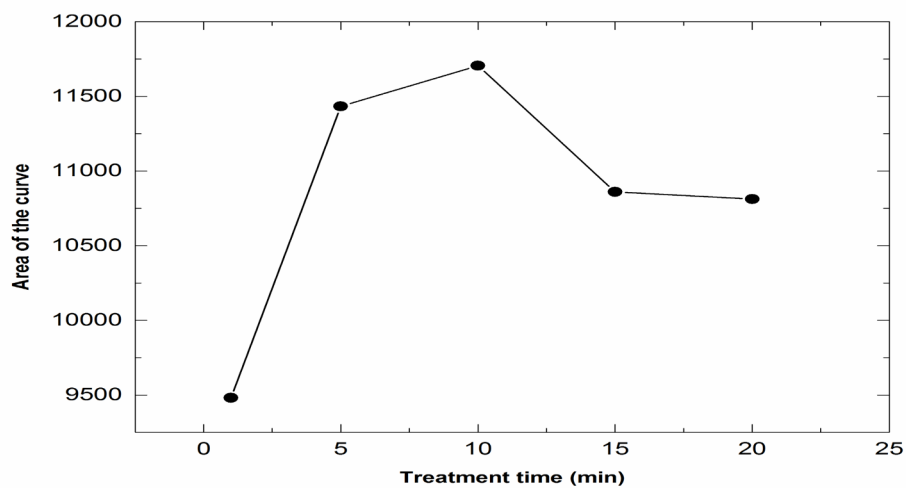


Fig. 7. The relation between the area under the x-ray curve and treatment time

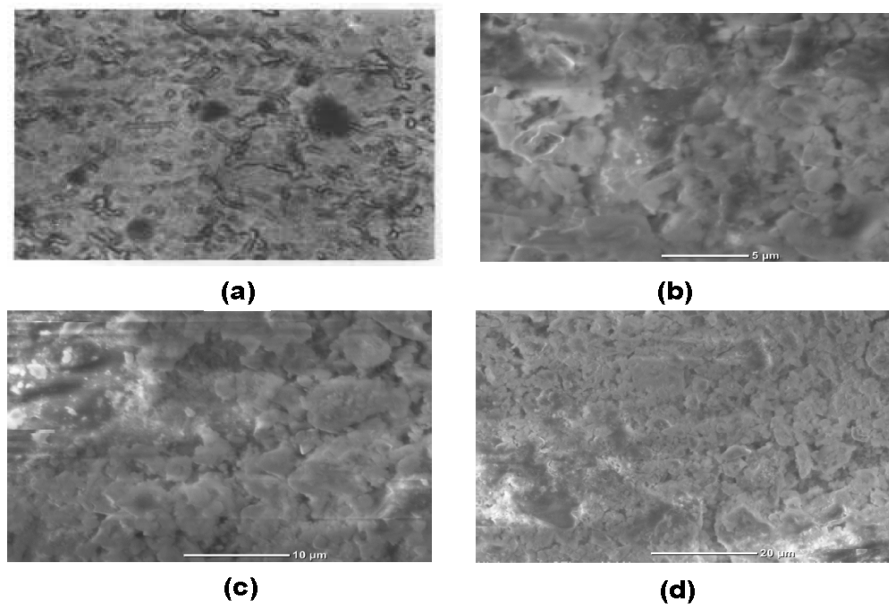


Fig.8. SEM micrographs for irradiated Makrofol film by using argon plasma: (a) pristine, (b) at 1 min, (c) 5 min and (d) at 10 min.

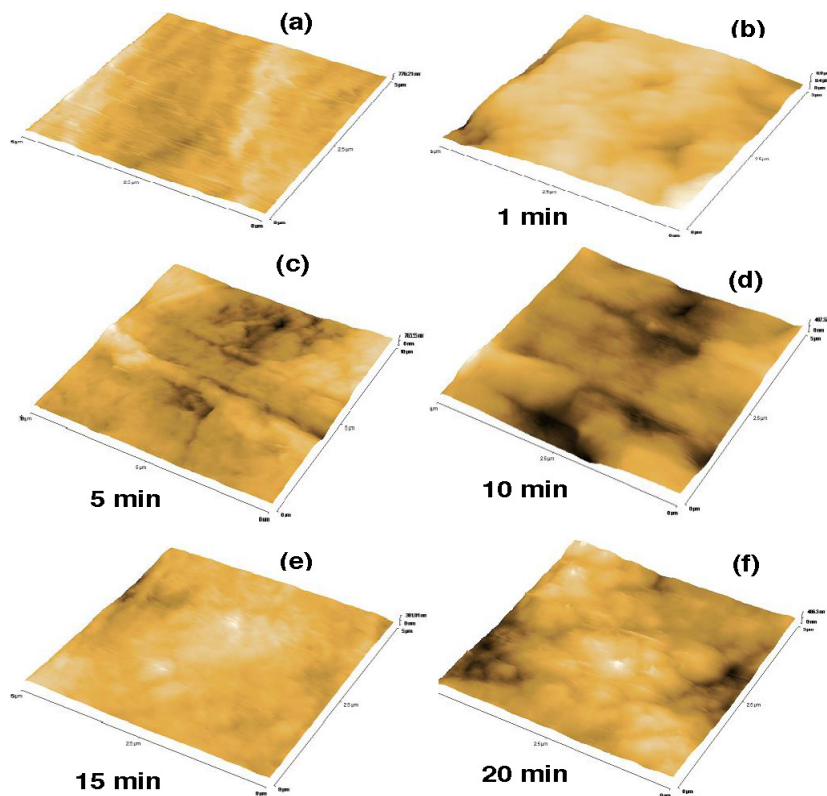


Fig. 9. Atomic force microscope (AFM) images: (a) pristine (b), (c), (d), (E) and (F) are Ar-plasma treated for 1, 5, 10, 15 and 20 min, respectively.

Conclusion

Wave forms of the applied voltage and discharge current in APGD measured at different experimental conditions. In addition, the relation of the gap distance between the two electrodes of APGD as a function of the breakdown voltage is measured. The APGDargon plasma used to modify the surface of polymer film (Makrofol). Plasma treatment carried out at different treatment time.

It is clear that the breakdown voltage increases with increases the gap distance of APGD. Surface treatments of polymer films performed by setting the air gap fixed at 3 mm and the applied voltages at 15 kV. The changes in the surface are determined by varying the treatment time and observed the surface changes using XRD. Degradation of the Makrofol samples occurs. Then, the free radicals'causes' crosslinking, this crosslinking destroys the crystallinity of the treated polymer samples. The APGD is more effective in polymer surface modification where it is able to modify the surface more uniformly.

Also, found that the Makrofol film surface became rougher when increasing the treatment time as clear in SEM and AFM images.

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معالجة البوليمر باستخدام التفريغ الكهربائي عند الضغط الجوي

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يتم فحص معالجة الأسطح غير العضوية والعضوية على نطاق واسع عن طريق معالجة البلازما وترسب الأغشية الرقيقة ومعالجة المواد. إن معالجة البلازما لتعديل سطح أغشية البوليمر هي الطريقة الأكثر فعالية للمعالجة المنتظمة والأكثر تحكما. تم دراسة التفريغ الكهربائي عند الضغط الجوي (APGD) باستخدام إبرة بلازما من الأرجون. يزداد حجم البلازما المنتظمة من منطقة صغيرة بالقرب من طرف الإبرة إلى عمود بلازما بطول حوالي ٢٠ ملم مع زيادة الجهد المطبق. في هذا العمل، تم تعديل البوليمر، فيلم (Makrofol) باستخدام التفريغ الكهربائي في أزمنة معالجة مختلفة. تم عمل مسح مجهر إلكتروني (SEM)، مجهر القوة الذرية (AFM) وقياسات حيود الأشعة السينية (XRD) المستخدمة لفحص وتوصيف البوليمر المعالج بالسطح. ووجدت أن التغيير في خصائص السطح يعتمد على وقت المعالجة. ووجدت أيضًا أن معالجة البلازما تعدل سطح البوليمر في كل من المورفولوجيا والتكوين.