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N_2, N_2-Ar and N_2–He DC Plasmas for the improvement of Polymethylmethacrylate surface wettability

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ABSTRACT

The objective of the present work is to investigate the effect of low power, low pressure DC glow discharge plasma of N_2, N_2-Ar and N_2–He gases on the surface free energy and the morphology of the surface of PMMA films. For this purpose lab-prepared PMMA samples were exposed to three gas environments under the same discharge conditions (discharge power, pressure, and sample electrode spacing). Changes in the surface hydrophilicity, morphology, and chemical composition of the treated samples were characterized by contact angle measurements, scanning electron microscopy (SEM), and FTIR- spectroscopy. Treatment of PMMA with N_2, N_2-Ar, and N_2–He gases showed an increase in the surface free energies. The SEM and FTIR detected changes in the treated surfaces morphology and the formation of new functional groups.

Key words: DC plasma surface treatment, PMMA, Hydrophilicity, Surface energy.

INTRODUCTION

Polymer materials are successfully used in virtually any industry in the world including aerospace. For instance polymethylmethacrylate (PMMA) has many applications in the field of medicine, due to its biocompatibility, It had used as bone cement, intraocular lenses, contact lenses, fixation of articular porstheses, denture syringes hard tissue replacement, and blood pump [1,2]. Also it can be used in the field of semiconductor, the computer microstructures, and in the automotive industry. Generally polymers have excellent bulk physical, chemical and weather resistance properties, they are relatively inexpensive and easy to process. Polymers are known to be hydrophopic materials due to low surface energy and wettability, the defect which limits its applications when strong bonding is required between polymer surface and adhesive. It is well known that permanent bonding, potting coating printing on the surface of many plastics is impossible without some special treatment of the surface.

For the last 50 years different polymer surface modification techniques have been proposed and used to alter polymer surfaces without affecting bulk properties of the materials. Plasma treatment is one of the most universal techniques [3,4]. Plasma, in general consists of partially ionized gas or gas mixture. The plasma species accelerate in the electrical field to the energies that are comparable or exceed the bonding energies of the polymer surface. When polymer surfaces exposed to such environment, active sites may be created on the polymer surfaces through bond scission resulting from the energetic ion bombardment. Active sites can interact with the gas species to form functional groups such as C-O, C=O, O-H, -NH, etc., which results in a change in surface polarity and hence improving their surface energies, keeping the volume properties of the materials [5].

Nitrogen containing plasmas are widely used to improve wittability, printability, bondability, electrical conductivity and biocompatibility of polymer surfaces [3,6]. Nitrogen plasma characterized not only by the appearance of highly vibrationally excited molecules but also their molecules can have a variety of electronically excited states, most of them are metastable, that make the plasma a rich source of excited nitrogen molecules[7]. As it was reported, changing the plasma gas or gas composition can be a possible option to improve the analytical performance of the glow discharge plasma [8,9,10]. Nobel gases such as (He, Ar) were used to generate free radicals in surfaces followed by cross-linking or the generation of active sites for further reaction [11]

This paper is devoted to study the influence of nature of working gas and treatment time on the properties of a polymeric material. Pure PMMA were treated by different gases namely pure nitrogen, 3:2 N_2-Ar and 3:2 N_2-He gas mixtures. The operational conditions, i.e., power, pressure and inter-electrode distance were the same for all plasma treatment.

MATERIALS AND METHODS

Experimental and methods

Fig. 1 represents a schematic diagram of the DC glow discharge setup used for surface treatment of the PMMA substrates. The setup consists of a Pyrex tube of (18 cm) long and (13 cm) diameter closed at each end with aluminum plate. Two planes circular copper plates of (5 cm radius) represent the two electrodes are connected to each other with four isolated rods keeping the spacing constant at (7 cm). The two electrodes move axially forward and backward as a unit controlled by a handle outside the tube. The base pressure is attained into the tube at (10^{-3} Torr) by using a rotary pump (Edwards H. vacuum pump, model ED 200) then the gas (gases) is allowed to inter the tube throw a controllable needle valve. Plasma properties were kept constant during the experiment, as the gas pressure was 0.4 Torr, and the input power was about 3 W.

The plain PMMA films with thickness (0.175 mm) were prepared in the lab by the cast method and when dried they have been cut to give sample size (1.5x2 cm) The films of PMMA were supported on a glass rode and put in front of the cathode at the edge of the negative glow. The plasma parameters, such as, electron and ion densities and electron temperature were determined using Langmuir probe as a diagnostic method.

Surface analysis

1. Contact angle measurements

Surface energy of polymers play a kye role in wetting and coating processes. The behavior of colloidal dispersion, adhesion, and friction is influenced by surface tension. The surface tension of a polymer can be determined by the contact angle measurements. Using the sessile drop technique [12], the contact angle (the wetting angle) of distilled water and glycerol on the surfaces of plasma treated and untreated PMMA samples were measured using a travelling microscope equipped with cross-head eyepiece. The vertical and horizontal reference lines of the eyepiece were positioned so as to measure the height *h* and the radius *r* of the spherical segment of the drop, and then the contact angle calculated using the following equation [13,14]:

$$\theta = \sin^{-1}\left[\frac{2rh}{r^2+h^2}\right] \qquad (1)$$

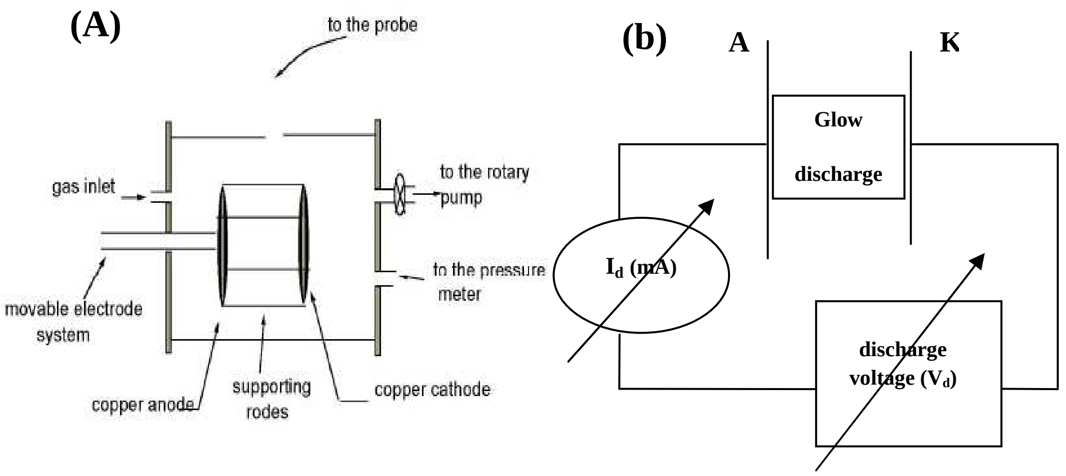

Figure (1): A schematic diagram for (a) The experimental equipment and (b) The electrical circuit.

We applied the Owens-Wendt model which considered one of the most common methods for calculating the surface free energy (SFE) of polymeric materials. According to the model, the SFE can be obtained using the following equation [15]:

$$0.5\,\gamma_L(1+\cos\theta) = (\gamma_S^D\,\gamma_L^D)^{\frac{1}{2}} + (\gamma_S^P\,\gamma_L^P)^{\frac{1}{2}} \tag{2}$$

where γ_S^D and γ_L^D are the dispersion part of the solid and liquid SFE. γ_S^P and γ_L^P are the polar part of the solid and liquid SFE. γ_L is the total liquid SFE, and θ is the contact angle between the sample and the liquid.

By using the information given in Table1 about the two measuring liquids (deionized water and glycerol) and substituting the values of their contact angles with the samples one can obtain a set of two equations of the form of Equ.2, when solved simultaneously one can get the unknowns γ_S^D and γ_S^P. Finally the total surface energy has been estimated by the following equation [16]:

$$\gamma_S = \gamma_S^D + \gamma_S^P \tag{3}$$

Table 1: Values of the polar, dispersion and total surface energies of the measuring liquids [17]

Liquid	γ_L^P (mN/m)	γ_L^D (mN/m)	γ_L (mN/m)
Deionized water	50.2	22.6	72.8
Glycerol	22.8	40.6	63.4

2. FTIR-analysis

Infrared spectroscopy can be used in reflection or attenuated total reflection mode for surface investigation it allows quantitative determination of composition via vibrational modes and is powerful analytical tool for the detection of the new functional groups formed due to plasma treatment, in addition to the intensity of the pre-existing groups.

3. Scanning electron microscopy (SEM)

For surface morphology investigation, the electron microscope is used in scanning mode. SEM is revealed images of the surfaces before and after treatment with plasma.

RESULTS AND DISCUSSION

Figure (2) shows a dramatic decrease of the contact angle measured with the scissel drop technique, as a function of the exposure time for fixed discharge power. The contact angle decreased from 78^o to 41^o for water through 6 hrs of treatment time, while it decreased from 67^o to 32^o for glycerol through the same time interval.

The PMMA surface energy have been calculated using the contact angle measurements, and the dependence of the surface energies on the exposure time to plasma is depicted in Fig.(3). It is clear that the effect of time on the disperse component γ_S^D of surface energy and the increase in the total surface energy γ_S refers to the increase in the polar γ_S^P component.

Upon investigating the effect of type of plasma's working gas on the total surface energy γ_S, the variations of γ_S^D of PMMA with different gases are relatively much less than those for γ_S^P under similar conditions, as shown in Fig. (5). It has been observed that the use of N_2-Ar gas mixture results in relatively larger increase in the total surface energy of the PMMA followed by those treated with N_2-He and then pure N_2. This result was a consequence of the lowest contact angle observed for the sample treated with N_2-Ar gas mixture as shown in Fig.(4). The addition of inert gas like Ar and He to the reactive N_2 gas helps in increasing the surface roughness which confirmed by SEM and agree with the literature [3, 10].

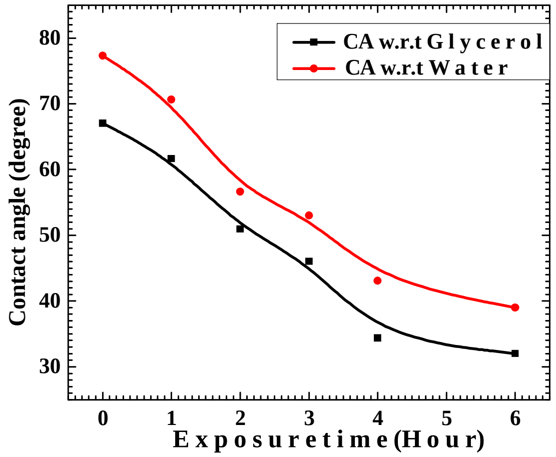

Figure (2): Variation of contact angle of PMMA film as a function of exposure time.

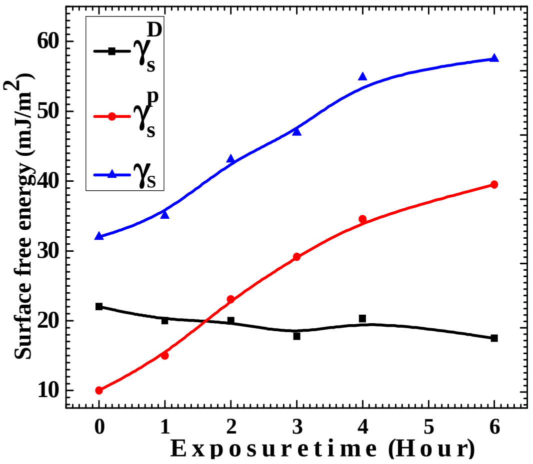

Figure (3): Surface energy of the plasma-treated PMMA film as a function of exposure time.

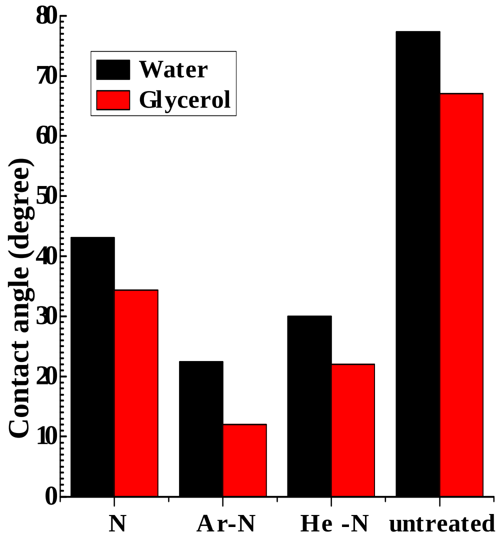

Figure (4): Contact angle for untreated sample beside treated samples for 4 hours in N_2, N_2-Ar and N_2-He plasma.

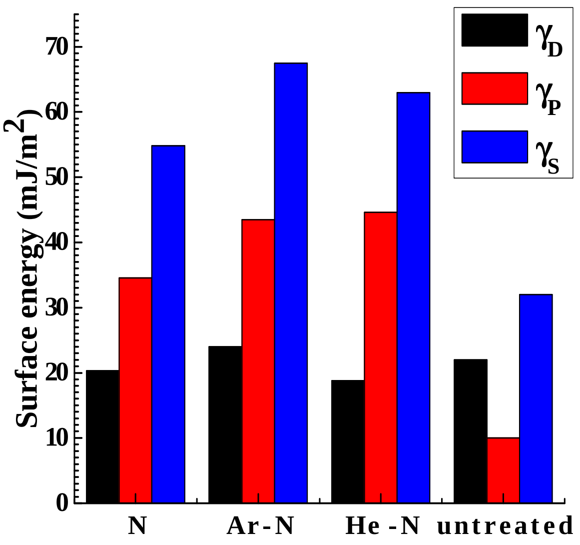

Figure (5): Surface energy for untreated sample beside treated samples for 4 hours in N_2, N_2-Ar and N_2-He plasma.

Fourier transform infrared (FTIR) spectroscopy was applied in the reflectance mode to detect any changes in the chemical structure of the surface which can be determined by functional groups present on the sample surface, either pre-existed or newly formed. Fig.(6) shows a typical peaks of conventional PMMA in comparison with the treated samples with N_2 plasma for different exposure times. A characteristic peaks of carbonyl (C=O vibrations) in the pendant group (-$COOCH_3$) of the PMMA at 1723 cm^{-1}, (C-H bending vibration) at 1447 cm^{-1}, and (C-O ester bond stretching) were observed at 1141 cm^{-1}. These peaks decreased as the treatment time increased until the time is 3 hrs the intensities started to increase back to the original. (C-H stretching) appeared at 2924cm^{-1}. –NH group has been observed on the treated surfaces at 3416 $cm^{-1}$and showed an increased intensity with treatment time. The decrease of C-O and C=O functionalities with treatment time is may be due to side chain degradation combined with cross-linking effects [18, 19].

The FTIR spectra of untreated, N_2, N_2-Ar and N_2-He plasma-treated samples at the same discharge conditions (discharge voltage and exposure time) are presented in Fig.(7). According to this analysis, we note that the addition of Ar and He add new functional groups to the PMMA surface. The addition of Ar to N_2 adds oxygen containing groups, O-H (broad band around 3568 cm^{-1}) [20, 21] besides nitrogen containing group. Meanwhile the addition of He to N_2 adds only oxygen containing groups, O-H (broad band around 3568 cm^{-1}). The resulting changes in film chemical composition are in accordance with the Langmuir probe measurements. The addition of Ar to N_2 increases ion density in nitrogen plasma. Meanwhile the addition of He to N_2 decreases ion density in nitrogen plasma.

The presence of oxygen functionalities are always incorporated in nitrogen plasma treated polymers during or after non-oxygen plasma treatment, may be attributed to the free radicals species created on the PMMA surface due polymer chain scission or hydrogen abstraction by bombardment of plasma species. The free radicals on the polymer surface can react with oxygen during a plasma treatment. In addition free radicals that remain on a polymer surface after a plasma treatment will react with oxygen when the surface exposed to the atmosphere [3]. Free groups as polar groups may be formed due the interaction of these radicals with the air oxygen as soon as the films come out from the discharge chamber, or due to the oxygen already exist in the discharge tube as a residual [3,18].

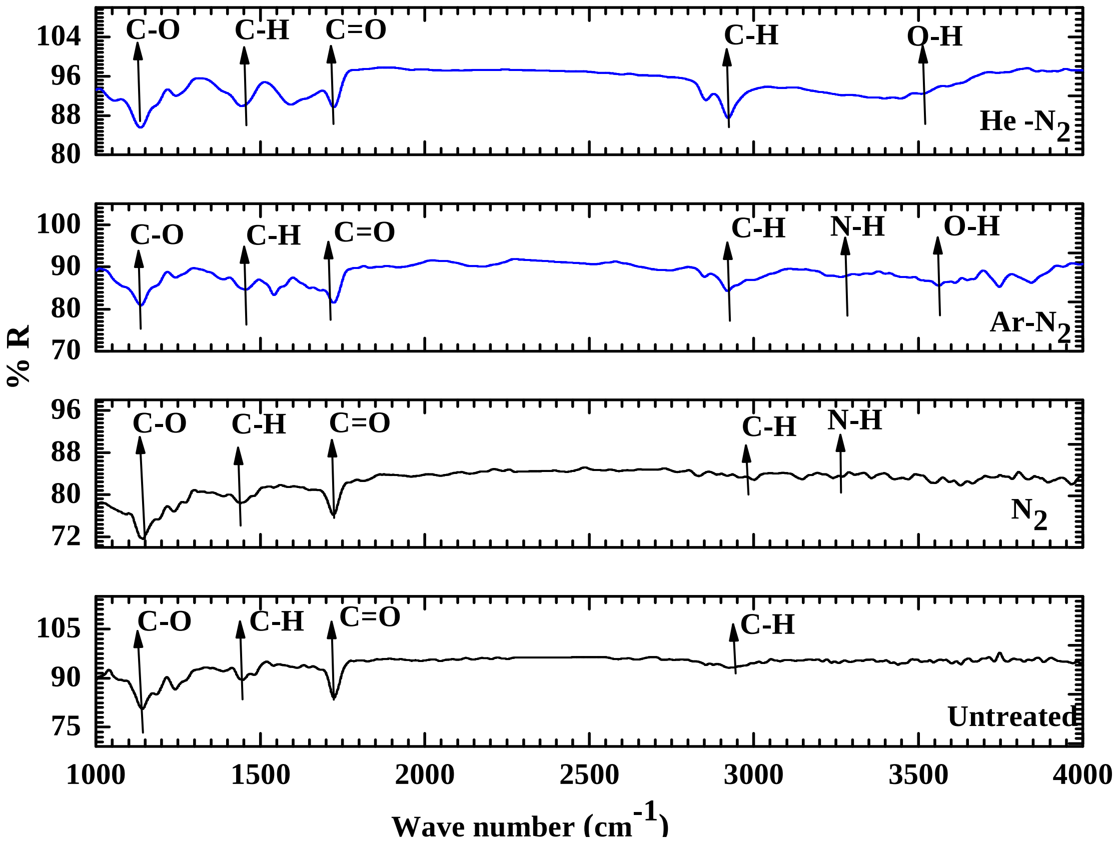

Figure (7): FTIR spectrum for untreated sample beside treated samples for 4 hours in N_2, N_2-Ar and N_2-He plasma.

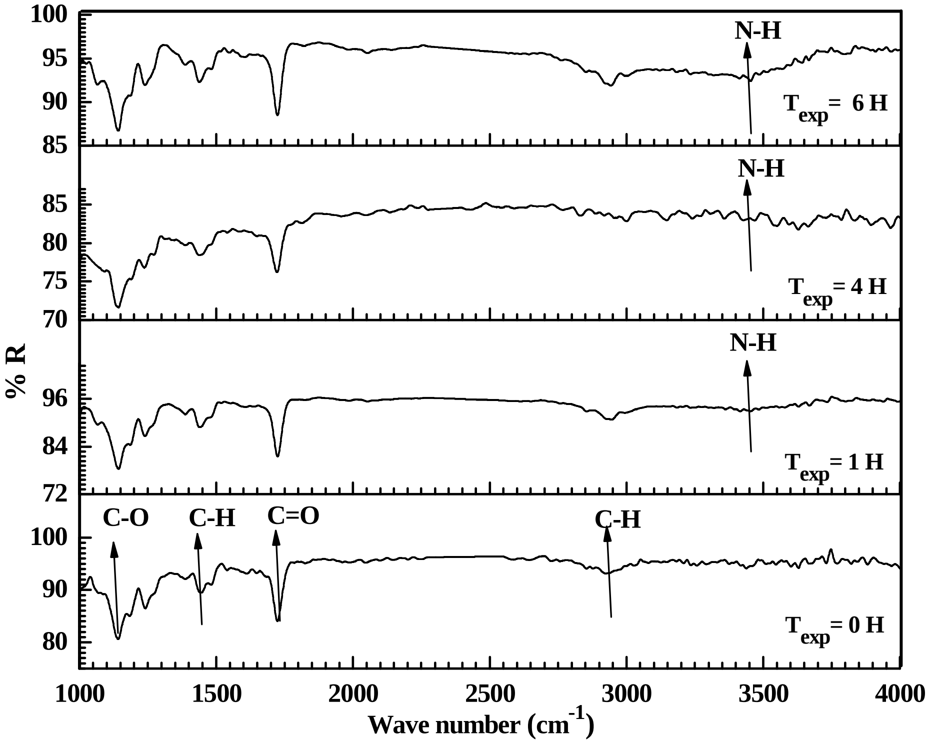

Figure (6): FTIR spectrum for untreated sample beside treated samples for 1, 4 and 6 hours in N_2-plasma.

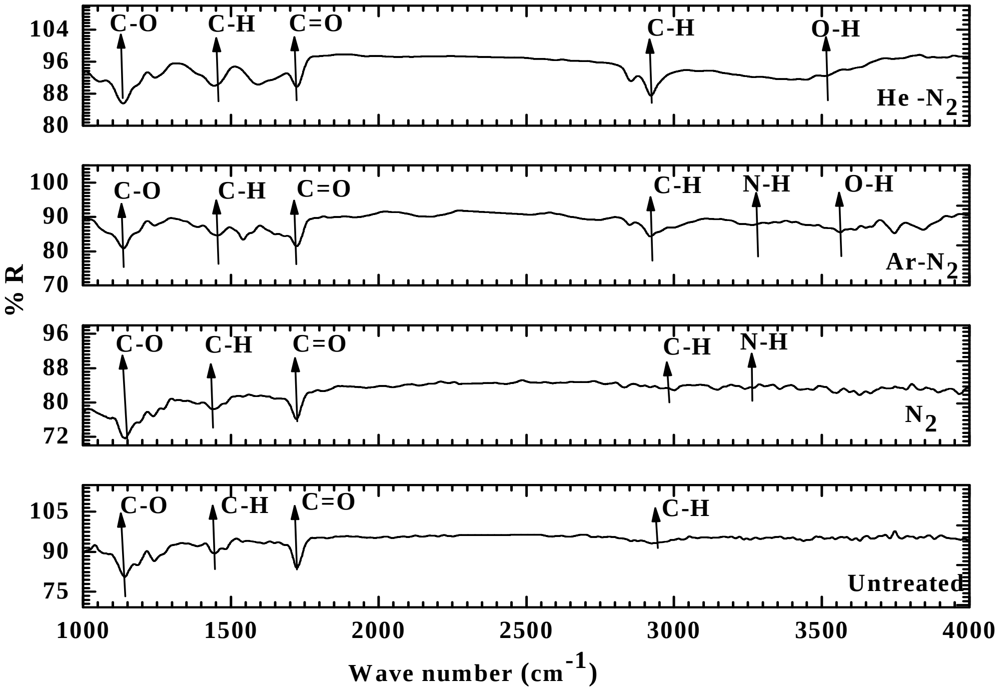

Figure (7): FTIR spectrum for untreated sample beside treated samples for 4 hours in N_2, N_2-Ar and N_2-He plasma.

Morphological investigation was carried out by imaging the PMMA films by SEM. Fig. (8) represent micrographs for samples untreated and treated with N_2, N_2-Ar, and N_2-He plasmas for four hours at the same discharge conditions. Fig.(8 a) shows that the pristine sample is smooth, while considerable morphological alterations were observed in Fig. (8 b, c, and d). In Fig.(8 b) negligible damage can be seen, since only two mounds appeared on the surface after treating with pure nitrogen. Many mounds and scratches can be seen on the surface after treatment with N_2-Ar gas mixture with ratio, while large damage of the surface appeared, represented with a great crack, after treatment with N_2-He gas mixture. It is well known that He and Ar in the gas mixtures cannot bring about chemical reactions but they only increase the roughness structure. It is noticeable that the effect of He is more than that of Ar this may be attributed to the larger excitation energy of He (20.96eV) than Ar (11.72 eV) [22, 23]**.**

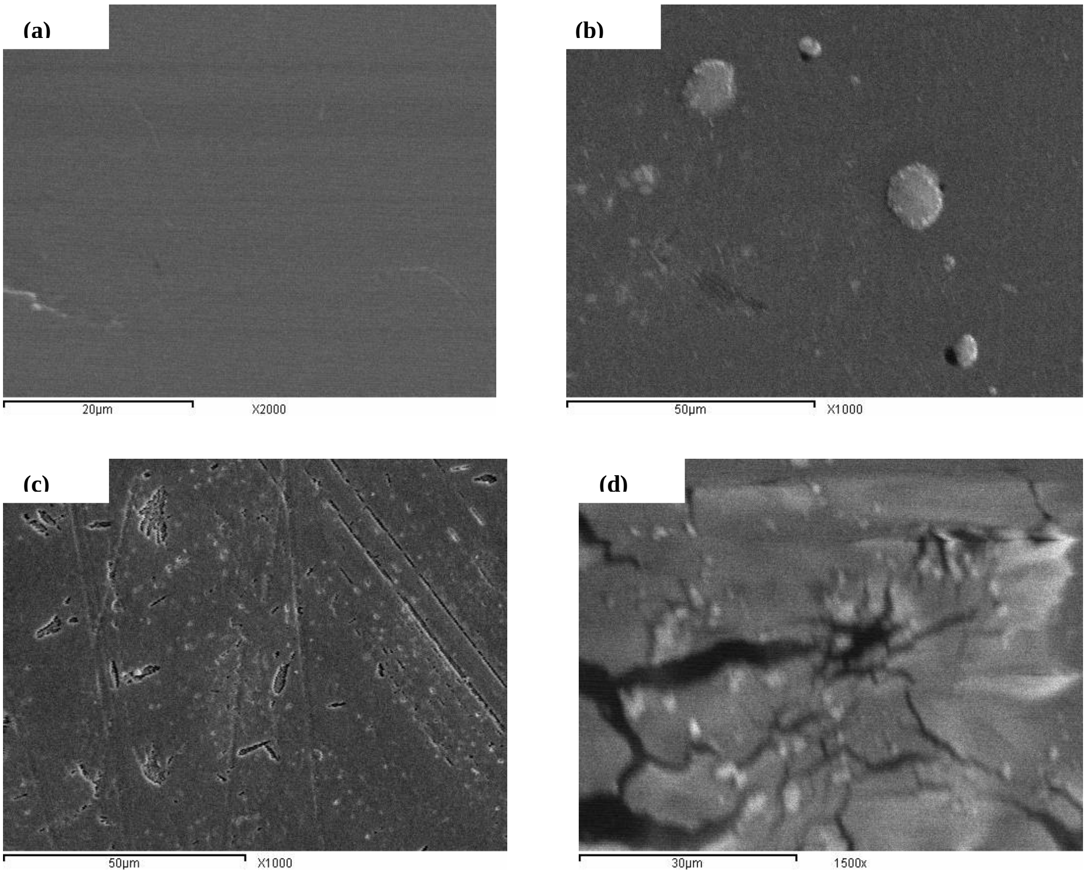

Figure (8): SEM image of PMMA film, untreated (a) treated for 4 hours in N_2 (b) in N_2-Ar (c) and in N_2-He plasma (d).

CONCLUSION

Low power, low pressure DC plasma has been used to modify the surface of PMMA films, precisely increasing its wettability or hydrophilic property. Samples prepared and exposed to N_2 plasma for varying treatment time. Contact angle measurements showed that their values decreased, consequently increase in SFE, as the treatment time increases, which, in turn, enhance the surface wettability. A comparison was carried out to investigate the effect of adding Ar and He to N_2 plasma on the surface characteristics. The results showed that the increase in surface energy is more efficient with the addition of Ar more than He and both are better than pure N_2. Although FTIR spectrum recorded a decrease of the oxygen content (decrease of the C=O and C-O intensities) which may be due to occurrence of crosslinking on the top surface, newly formed -NH and OH functional groups were also detected which can increase the hydrophilic properties of the film's surface. Considerable changes in the surface morphology, seen by SEM, would increase the surface area and hence results in more moisture adsorption.

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