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Surface Modifications of High Density Polycarbonate by Argon Plasma

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***Abstract*— The polycarbonate (PC) membranes were implanted to 16 W argon ions plasma. The samples were treated for different exposure time 10 min, 30 min and 60 min. The effect of argon ions implantation on optical and chemical properties of PC membrane has been investigated. The observed changes have been correlated with the induced structural changes in the implanted layer using UV-Visible spectroscopy. The Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were employed to study the surface characteristics of the membrane. The AFM results indicate significant changes in the surface morphology of the polymer membranes before and after plasma treatment.**

***Keywords*— Polycarbonate (PC), Plasma treatment, AFM, SEM, UV-Visible spectroscopy.**

I. INTRODUCTION

For several past decades, polymers have been used in different fields such as adhesion, biomaterials, protective coatings, friction and wear, composites, microelectronic devices, and thin-film technology. 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. Most Polymers do not have the surface properties required 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 [1,2].

Surface modifications, such as plasma treatment, corona discharge and flame treatment, are frequently employed to enhance the surface properties of thin films. Actually, a simple way to modify the chemical and physical states of the polymer surface, without altering the bulk properties, is by plasma treatment. The plasma treatment of polymers leads to the creation of new chemical groups, cross-linking, degradation, branching of the macromolecules and formation of low-molecular weight oxidized structures like free radicals [3-8]. The rates of these processes being a function of the plasma reactivity which depends strongly upon the structure of polymers and deposited energy by the ion irradiation. Therefore, appropriate plasma treatment can be applied to improve the modifications occur in surface layer only and polymer bulk saves the same unchanged mechanical properties. Furthermore, the modified surface layer can be affected by composition of ambient atmosphere, and the modified surface layer will able to have a good homogeneity.

Argon plasma treatment can enhance sputtering of the PC surface layer, which increased surface roughness, and the sputtering depth is up to tens of nanometers [9]. Furthermore, argon plasma causing a cross-linking of polymer matrices which can improve the chemical resistance, optical density, hardness, cohesive strength of the surface and other surface properties[10,11]. The argon plasma treatment can also induce the direct energy transfer of the surface, due to vacuumed- ultra violet radiation (VUV) emitted by plasma glow [12]. The kinetic energy of argon ions, fast neutrals, and UV-radiation from DC-discharge also causing a significant rearrangement of the surface structure. Surface roughness can be depending on ion implementation, gas composition and treatment conditions such as using an ions, electrons, fast neutrals and radicals. These species can contribute to the polymer treatment, resulting in etching, activation and /or cross-linking [13,14]. A synthetic polymer like Polycarbonate (PC) is considered an important polymer due to its various desirable properties. It is transparent about 90% in the visible range of the electromagnetic spectrum, which make it an excellent substitute of glass substrate in different optical applications like solar cells, antireflective coatings, optical lenses, etc. The monomer structure of PC is shown in Figure 1.

The surface properties like etching, roughness, transmission and absorption so as mechanical properties can be modified depending on type of gas used [15]. Consequently, ions flow current i.e. the number of ions passing through plasma discharge channel per unit time, or the energy deposited in molecules matrix, depend basically on the accelerated molecular charges of specific gas used in plasma treatment. Furthermore, surface treatment properties can be chosen according to type of required application, and can very well optimized by selecting type of gas or the ions current [16]. In the present work the effect of Ar-ion plasma treatment on surface properties for PC membranes under different treatment time was studied at discharge power of 16W.

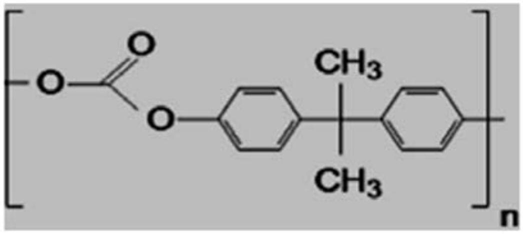

Fig. 1 Monomer structure of polycarbonate (PC)

II. MATERIALS AND METHOD

A. Sample preparation

The 30µm thick PC membranes were prepared by solution cast method. The PC granular has dissolved in dichloromethane (CH_2C1_2) solution 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 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 [17].

B. Plasma Treatment

The schematic diagram of set up for plasma treatment is shown in Figure 2.Typical configuration of a complete plasma processing system is constituted by a stainless-steel cylinder with 40 cm length and 30 cm diameter, electromagnetic energy (DC generator). 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 1x1 mm metal mesh shown in Figure (2) were used to repel the electrons and accelerates the positive ions to impact PC membrane. The plasma chamber was evacuated to 10^{-4} mbar pressure. Samples of PC were treated by Ar-plasma at various exposure times and 16 W discharge power. The PC samples were located at the midpoint of the chamber using a glass support.

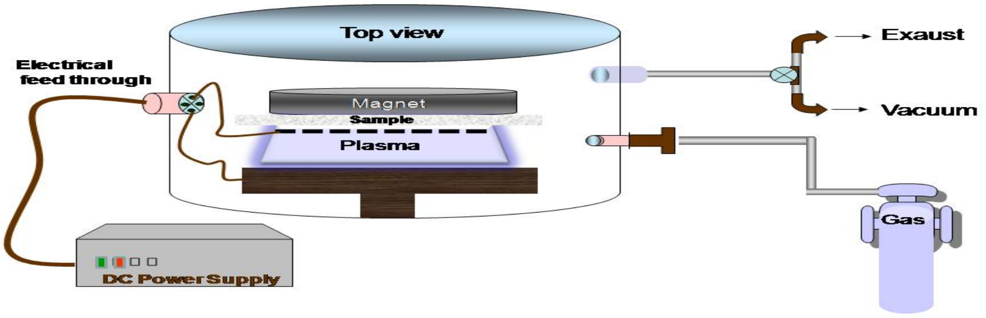

Fig. 2. Experimental set-up for plasma treatment system

C. Characterizations

The Atomic Force Microscope (AFM) type (Veeco,diCp-II) was used for surface morphology. The Scanning Electron Microscope (SEM) manufactured by ZEISS, EVD 18 to study the surface properties. We use the UV-visible spectroscopy for optical properties manufactured by HITACHI model U-2900 spectrophotometer in the wavelength range of 200 to 500 nm. The Fourier Transform Infrared Spectroscopy (FTIR) model IRAffinity-1 (SHIMADZU) was used to study the chemical structures of the polymeric membrane surface.

III. RESULTS AND DISCISSION

A. Atomic Force Microscope

Fig. 3(a) shows the corresponding AFM topographical images of the untreated membrane, and Fig. 3(b), (c) and (d) for treated membranes by argon plasma at 10 min., 30 min. and 60 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 [18]. The AFM measurements show clearly, that the short time argon plasma treatment does not influence the surface morphology as in Fig. 3(b), whereas the root mean square value of roughness (R_{rms}) for treated film within 10 min time is 9.58 nm. The Higher values of roughness were observed only for over-expositions (30 min. or more) as in Fig. 3(c) and 3(d), whereas the R_{rms} increased up to 15.33 nm and 29.79 nm for treatment time of 30 min and 60 min, et.at reported the direct dependence between the degree of crystallinity of polymer and surface roughness after the plasma treatment [19-20]. 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.

B. Scanning Electron Microscope (SEM)

The results discussed in the preceding paragraph were further confirmed by SEM analysis. The SEM images, Fig.4 shows that the image of the pristine PC film has smooth surface structure without any changes on surface morphology. It can be observed from Fig.4 (b) that after a treatment time of 10 min, some uneven granular like defect spots began to appear on the surface. It seems that the PC film begins 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.4(c) and (d).

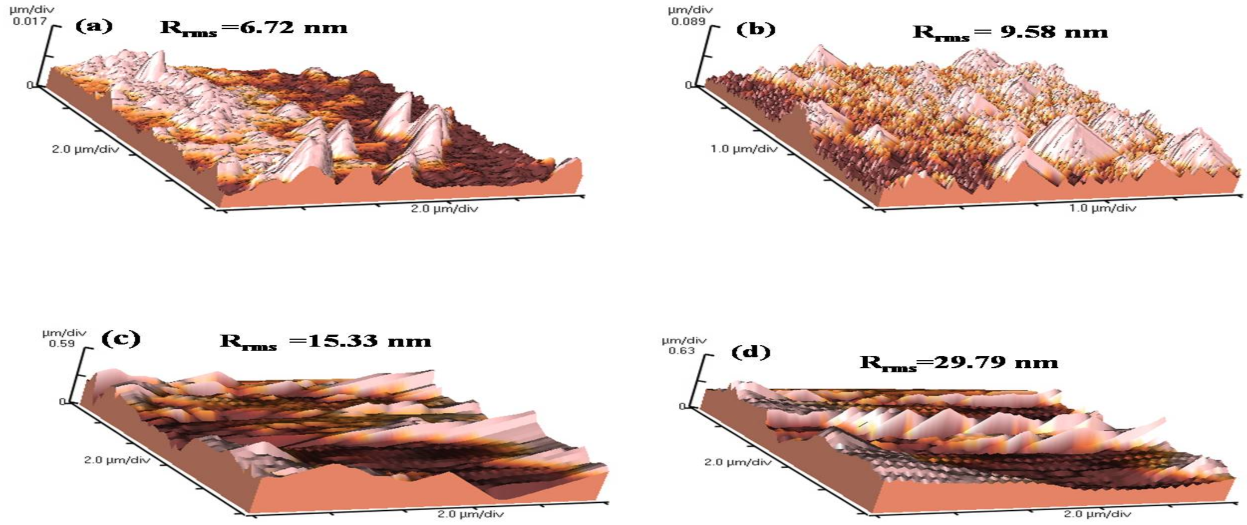

Fig.3. AFM images of Polycarbonate film with different plasma treatment time (a) untreated, (b) 10 min, (c) 30 min, and (d) 60 min.

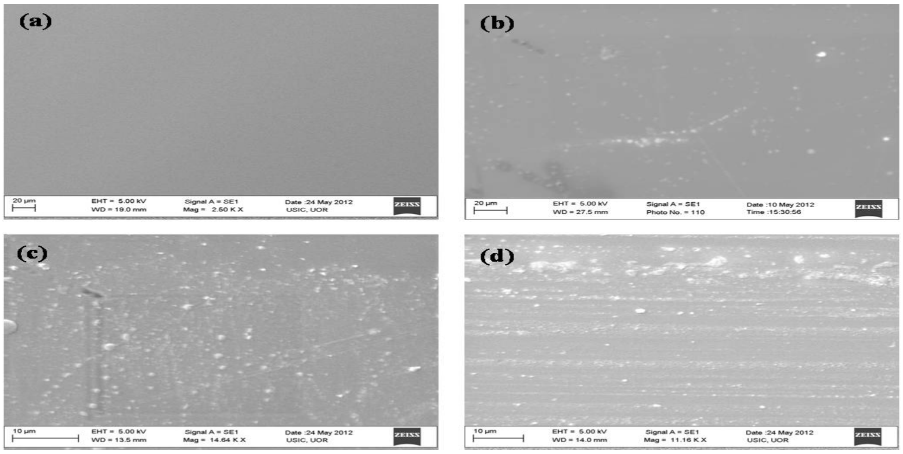

Fig. 4. SEM micrographs of polycarbonate film (a) untreated, (b) 10 min, (c) 30 min and (d) 60 min.

C. UV-Visible Spectroscopy

The optical transparency for treated PC films was evaluated by recording the UV-visible transmission spectra for various argon plasma glowing duration as shown in Fig.5, the reference used for transmission measurements is untreated PC film. It is well known that the transparency of a bulk film strongly depends on the surface roughness and an increase in the average roughness will result in a decrease in transmittance due to light scattering effects, but the action of some species present in the plasma promotes chain scission (as described in introduction), and this could lead to etching and material removal, thus promoting changes in surface roughness which in most cases positively contributes to a transparency decrease. The increased roughness may be envisioned as the increase in the concentration and sizes of the degradations on surface, which leads to higher light scattering [20]. This effect shown clearly in PC membrane treated with argon gas for higher treatment time such as 30 min. and 60 min. as in Fig.5 and also corroborated by Atomic Force Microscopy images shown in Fig.3.

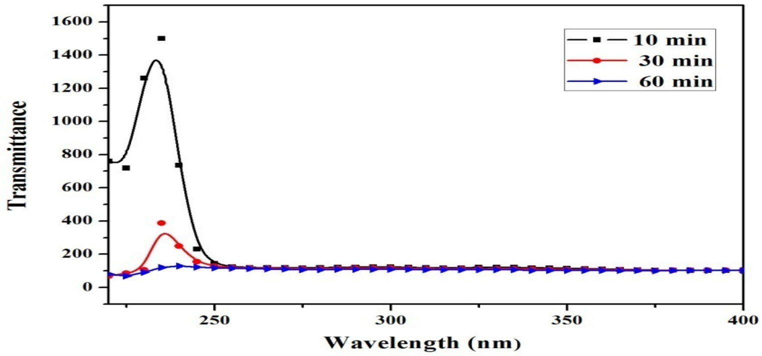

Fig. 5. UV-Visible spectrum for polycarbonate treated membrane for different irradiation time (a) 10 min (b) 30 min (c) 60 min.

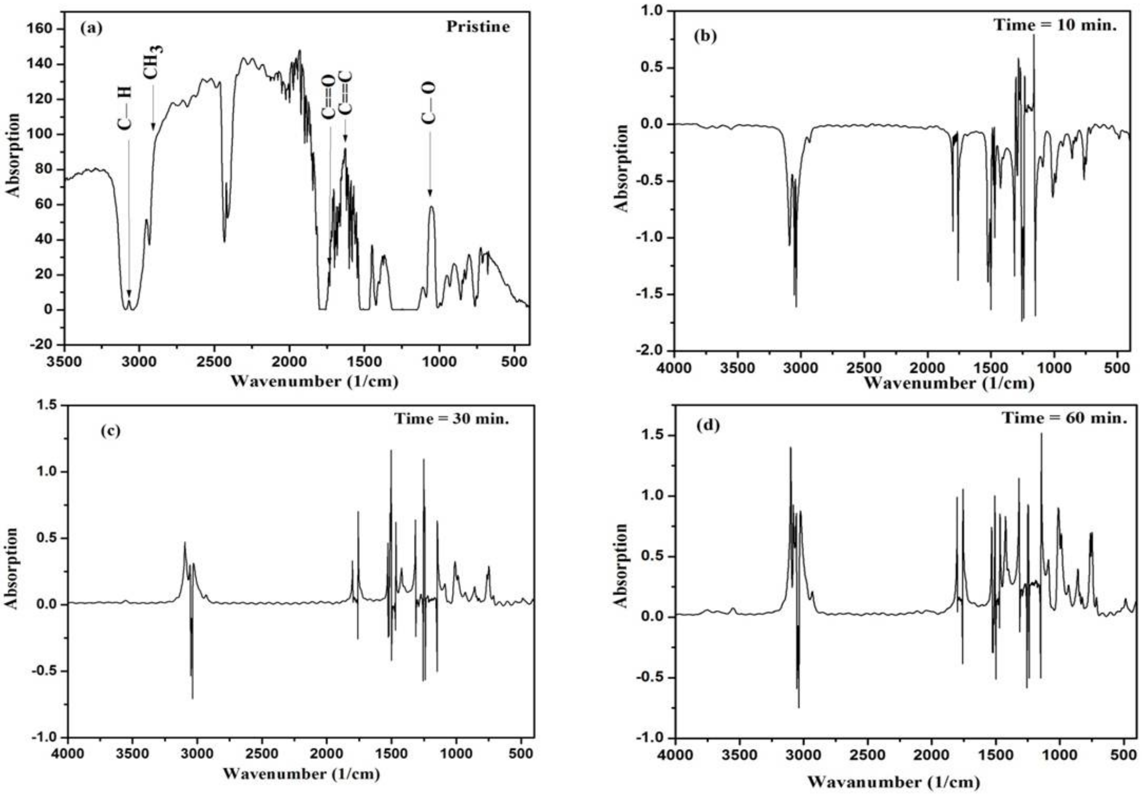

Fig. 6. FTIR spectrum for polycarbonate film (a) untreated, (b) 10 min, (c) 30 min and (d) 60 min.

D. Fourier Transform Infrared Spectroscopy (FTIR)

Plasma treatment by argon ions can break chemical bonds in PC 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 [21]. Consequently, recombination process or cross-linking can occur when these free radicals start moving, this interaction can produce high-molecular weight structures. The absorption bands as obtained from the untreated film are classified as (A) 1030 cm-1 ,C-O stretching vibration (B) 1645 cm-1 ,C=C unsaturated (C) 1770cm^{-1} , C=O stretching vibration (D)2890 cm^{-1}, CH3 stretching vibration and (E) 3070 cm^{-1} C-H stretching vibration of aromatic compound. The enhancement in the absorption bands of C-O and C=O at 1030 cm^{-1} and 1770 cm^{-1} for 10 min,30 min and 60 min treatment duration has been attributed to the creation of unsaturated – C=C− bonds at 1645 cm^{-1} . It is also observed from FTIR spectra that there is decrease in C-C and C-H bands after plasma treatment. It indicates that cross linking phenomenon enhance during plasma treatment.

IV.CONCLUSIONS

Polymer membrane of PC were prepared by solution cast method and the effect of argon ions, neutrals, free radicals and other plasma species were studied after plasma treatment by argon gas for different treatment time. It was observed that an Ar-plasma treatment can change surface properties of PC membrane like: optical transmittance, surface roughness and surface energy due to surface cross-linking, degradation, functionalization and free radical formation. The AFM and SEM images shows enhancement in surface roughness related to longer argon plasma treatment time. The plasma treatment by argon ions leads to decrease the optical transparency in PC due to high surface roughness and consequently high light scattering effect. The FTIR spectroscopy results indicate to decrease in C-C and C-H absorption bands after argon plasma treatment. In other hand, a creation of new functional groups like unsaturated – C=C− bonds has been observed.

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