Effects of Low Temperature Plasma Treatment on Poly Vinyl Chloride Film

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In this paper we have investigated the effects of low temperature Argon plasma produced by a cylindrical magnetron on properties of commercial Poly Vinyl Chloride (PVC) films. The films were tested at two different places (i.e. on the anode and cathode) and the treatments were performed under two different exposure times. The results show that the plasma treatment has changed the hydrophobic properties of PVC to hydrophilic of which the rate has been depended on the treatment time. Characterization of the functional changes of the samples has been carried out by means of Attenuated Total Internal Reflection spectroscope (ATIR) and their surface topography has been obtained by Atomic Force Microscope (AFM). It is shown that plasma treatment has caused an increase in the roughness and thus in the hydrophilicity of the samples which means that some properties of PVC such as poor biocompatibility and adhesion can be improved by this method. The optical changes of treated samples were investigated using Reflective Spectrophotometer. The results show that transmittance of untreated sample, which was about 30 % , has decreased to about 6 % and the absorption of treated samples increased from 63% to about 89%.

Keywords: Polymer, Poly Vinyl Chloride, Plasma, surface modification, Films.

1. Introduction

Polymeric materials have a wide range of application because of their attractive characteristics such as flexibility, softness, and a low cost. The applications include water tubes, window profiles and lenses for glasses which are of very frequent use. However polymers now becoming increasingly attractive for a series of applications have so far been dominated by metals, semiconductors and glasses. [1]

Polymers are also used in various applications due to their favorable mechanical properties such as flexibility and elasticity. [2]

Poly Vinyl Chloride (PVC) among polymers is the most widely used material for single use, pre-sterilized medical devices, and is employed in applications including blood storage bags, and as blood tubing in extracorporeal circuits. [3]

PVC is a relatively rigid and brittle polymer. Plasticizers are added to the PVC to facilitate processing and increase flexibility and toughness in the final product by internal modification of the polymer molecule. [4]

Hydrophobic biomaterials are considered as the initiation of the foreign body reaction. Ions and electrons present on material surfaces may interact with cell receptors to cause cell adhesion and growth, and to facilitate cell proliferation, leading to the foreign body reaction. [5]

It is shown that the modification of surface properties of commercial polymers can change their wettability, adhesion, adsorption, printability, chemical reactivity and sensitivity to light. [6-8]

Many techniques such as plasma, corona, electron beam, gamma ray irradiation, and ion irradiation have been reported to change hydrophobic polymer surfaces into hydrophilic ones for improving the adhesion to other materials. [9, 10]

The advantage of treating PVC by plasma is that, it acts only on thin surface layers, whereas the bulk of substance remains unchanged and modified material keeps the mechanical properties. [11]

In this study we have been interested in using a magnetron to treat the PVC surface and have used a low temperature Argon plasma magnetron for this purpose. The results are reported below.

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2. Experimental Part

2.1. Materials

PVC film was cut into several pieces of dimensions 1.5×1.5 cm^2. Prior to the experiment, the films were cleaned and pretreated by an ultrasonic system.

2.2. Plasma treatment

A cylindrical DC magnetron device was used as a Low Temperature Plasma source (LTP) for which the schematic diagram is presented in Fig 1. The device consists of two coaxial cylinders as cathode and anode. The diameter of cylinders is 3 and 10 cm respectively with a height of 20 cm. The chamber was pumped down to 10^{-5} torr using rotary and diffusion pumps and Argon was admitted to the system under 10^{-2} torr. Two different places (on the anode surface and on the cathode) were chosen for treating the samples. Samples were also treated under two different durations, i.e. 60 and 100 seconds.

The treated samples were analyzed with different instruments, as explained below:

2.3. Contact angle measurement

The measurements were carried out immediately after plasma treatment. The contact angle was measured by a contact angle meter. To lessen the effect of gravity, the volume of each drop was reduced to about 0.1 µl by a micro syringe. The average value of the angles of both sides of each drop was counted as one measurement. Each contact angle was determined by averaging 3 measurements.

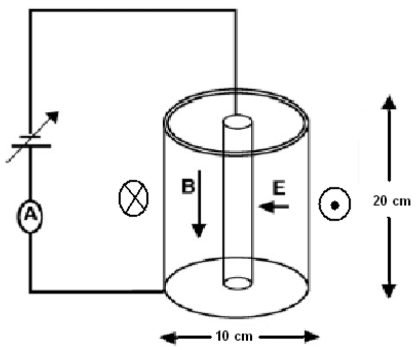

Fig.1 Schematic view of DC Magnetron sputtering setup

2.4. Atomic force microscopy (AFM)

The morphological and topographical changes of samples surface were obtained by Atomic Force Microscopy, (AFM, Park Scientific Instrument, Auto probe CP).

2.5. Reflective Spectrophotometery

For investigating the optical properties of PVC samples the optical reflectance measurements were performed using a UV–VIS–NIR Spectrophotometer, Varian, Cary 500 in the range of 100-3000 nm.

2.6. ATIR-FTIR Analysis:

A Thermo Nicolet Nexus 870 (made in USA) Attenuated total internal reflection Fourier Transform Infrared (ATIR-FTIR) spectrophotometer was used for examining the functional groups on the surface of samples. The IR spectra were in the range of 400–4000 cm^{-1}.

3. Results and discussion

Poly vinyl chloride (PVC) is a well known member of Vinyls family. The family of vinyls comprises a number of resins based on the vinyl radical, (CH2=CH-), or vinylidene radical (CH2=C>). PVC is a nearly hydrophobic polymer on which the contact angle of the water drop is around 90°. Contact angle is a measure of non-covalent forces between liquid and the first monolayer of material. So the low contact angles, indicate that the attraction of surface molecules has caused the liquid drop spreading on the solid layer and has wetted it. In this experiment we have shown that exposing a piece of PVC by a low temperature Argon plasma could change and decrease the percentage of its hydrophobicity.

Table.1 The contact angles of water drop for untreated and treated samples

Sample Position	Exposure Time	Contact Angle
Untreated	0s	90°
On the Cathode	60s	66°
On the Cathode	100s	60°
On the Anode	60s	74°
On the Anode	100s	63°

The results which are presented in Table 1 are obtained for different samples under different conditions.

As shown the change of contact angle is dependent on the duration of treatment and has decreased from 90° to 60°. The effect of treating the samples on anode and cathode is also shown in this table.

ATIR was used to examine the functional groups of the corresponding samples of which the results are shown in Figures 2and 3. As shown, an increase in absorbance at 1720 cm^{-1} (C=O) band and 3400 cm^{-1} (O-H) band has occurred after plasma treatment in accordance to those previously published [12-15].

This shows that, energetic particles of plasma have been accelerated towards the exposed samples and have broken the different bonds to form free radicals. After the polymer samples are brought out from the reactor, the reaction of the oxygen from the atmosphere with the free radicals takes place, and thus surface functionalization is obtained.

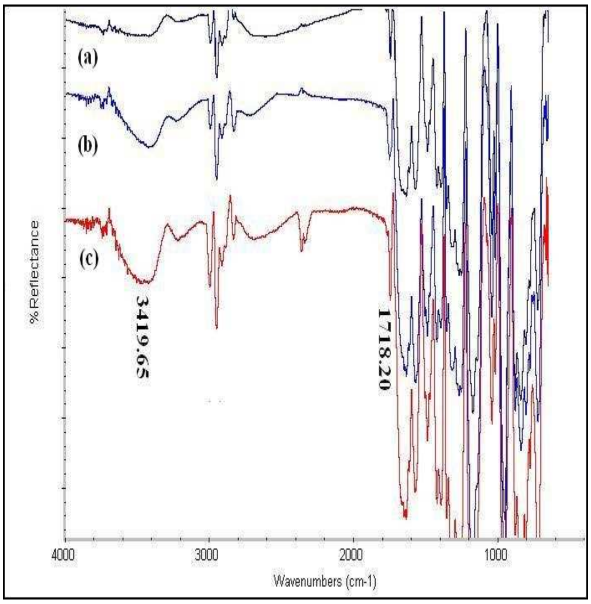

Fig.2. FTIR spectra for sample on the cathode (a) virgin sample, (b) plasma treated sample for 60s, (c) plasma treated sample for 100s

The results also show that the peaks have been increased by increasing the duration of treatment which in turn indicates the increase of hydrophilicity of samples by increasing the exposure time.

Detailed information of surface topography of the PVC samples are obtained by using an atomic force microscopy (AFM), of which the results are shown in Fig 4(a)–(c). As shown, the original surface of PVC film is characterized by the presence of wave like patterns, all oriented in parallel directions, while Fig. 4(b) which corresponds to 60s treated sample shows some pits and craters, almost uniformly distributed on the surface. This feature is more pronounced in Fig 4 (c) which presents the result of 100s exposure time.

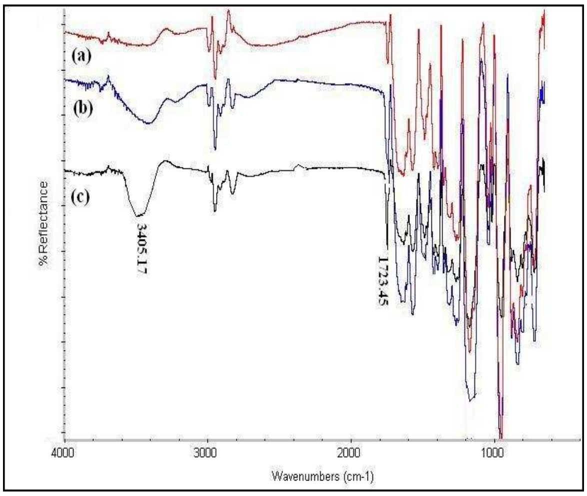

Fig.3 FTIR spectra for sample on the anode; (a) virgin sample, (b) plasma treated sample for 60 s, (c) plasma treated sample for 100 s

As seen, some porous area has been created on the surface after plasma treatment. Theses topological changes indicate an increase in hydrophilicity of the

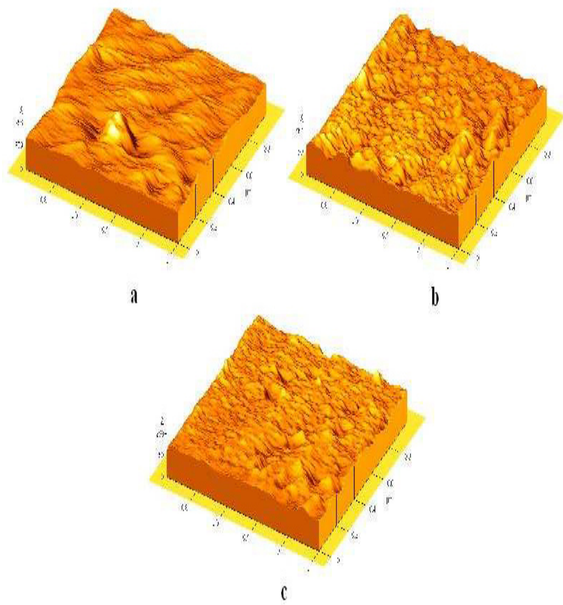

Fig.4 AFM images of samples on the anode (a) virgin sample, (b) plasma treated sample for 60s (c) plasma treated sample for 100s

Table 2. The average percentage of Absorption, Reflection and Transmission of untreated and treated samples

Sample Position	Exposure Time	T %	R %	A %
Untreated	0s	30	7	63
On the Cathode	60s	9	7	84
On the Cathode	100s	6	5	89
On the Anode	60s	14	7	79
On the Anode	100s	14	8	78

samples, in accordance to the results of contact angle measurements presented in Table 1 and FTIR spectra shown in Figure 2 and 3.

Optical properties of virgin and plasma treated samples are measured using a UV visible spectrophotometer, and the results which include reflectance, transmittance and absorption are shown in Table 2. As shown, by increasing the exposure time, the transmittance of the samples has fallen from 30% to about 6% and the absorption has increased from 63% to 89%. The reflectance is nearly constant and has remained around 7%. The reduction of transmittance might be a useful factor in packaging industry in which the lower transmittance of covers would result in a better protection of goods against light.

We should note that the results obtained for samples on anode and cathode show similar effects, though under equal exposure times, the results obtained on cathode are more pronounced. It seems that though magnetron produces a uniform medium, there are still some differences in energy of plasma particles near cathode in comparison to that of anode because of their different polarities.

4. Conclusion

The influence of low temperature Argon plasma magnetron on physical and chemical properties of PVC films has been investigated. The results of ATIR spectra and AFM images show that the hydrophilicity of the samples has increased. This has also been investigated by measuring the contact angle of water drop which shows a decrease from 90° to 63° under 60 seconds and to 60 ° under 100 seconds of treatment. It is also shown that the optical properties of the films such as transmittance and absorption coefficients have changed when exposed to Argon plasma. As shown the transmittance of the samples has fallen from 30% to 6% when treated under 100 seconds.

5. References

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