Surface characterization of polyvinyl chloride membranes modified by plasma treatment

P. ANURADHA[*], A. ANU KALIANI[a]

P.G.Department of Physics,Vellalar College For Women, Erode, India
[a]P.G and Research Department of Physics, Kongunadu Arts and science college, Coimbatore, India

Surface-modified polymers play a substantial role in various aspects of science and technology. Many physical as well as chemical methods are available for modifying polymer surfaces. Surface modification of polymers by plasma treatment is a facile approach which offers flexibility, effectiveness, safety and environmental friendliness. By plasma treatment bulk properties of the material remains unchanged whereas the surface properties may be tailored to the need of the application. Commercial polyvinyl chloride membrane purchased from Malaysian Sun Cool Shade Sails is used as modification material. The membrane is treated in the D.C. glow discharge plasma chamber for different exposure times. The changes in chemical structure and topology of the membrane surface after plasma treatment were investigated using FTIR, XRD and SEM studies in correlation with that of the untreated membrane. According to the result, there is a change in crystalline nature, grain size and surface roughness after plasma treatment. The predominant result of this study was longer the plasma treatment, rougher the membrane surface.

1. Introduction

Polymer based industrial applications require materials with very good bulk properties and precisely controlled surface chemistries. Plasma treatment of polymers provides a novel method of surface treatment without affecting the bulk properties. Commercial polyvinyl chloride (PVC) membrane purchased from Malaysian Sun Cool Shade Sails, is used as modification material. Plasma contains various active particles such as electrons, ions and free radicals etc, which interact with the polymer surface and cause surface modification.

According to Barton et al. [1] the key feature of plasma treatment is that the bulk properties of the polymer remains unchanged while the surface properties may be tailored to the application. Denes and Manolache [2] have concluded that cold plasma treatment represents an unusually convenient and versatile surface modification Technique. Dejun et al. [3] reported that the modification of polymer surface by means of plasma treatment is an effective method. Surface modification of a PVC membrane by UV irradiation for reduction in sludge adsorption was studied by Kim et al. [4]. Boria et al. [5] related plasma surface modification to polymer characteristics. Topala [6] studied in depth the application of atmospheric and low pressure plasma in materials science. In the proceedings of the TTT2005 academic conference Li and Hsueh [7] concluded that the surface roughness increases with increase of plasma treatment time.

2. Experimental

The experimental set up consists of a plasma chamber, electrodes, substrate holder, vacuum system and power supplies (Fig. 1). The plasma chamber is made up of stainless steel with internal diameter 25 cm and length 50 cm It consists of two flanges and disc (diameter 25cm, thickness 0.6 cm) that is made up of stainless steel and polished to prevent any air leak. Provisions are there on each side of the disc for inserting electrodes and substrate holder. Four holes are there on the flanges and discs so that they can be joined together by nuts and bolts. On either side of the discs, brass extension of length 3cm was fixed using Wilson joints.
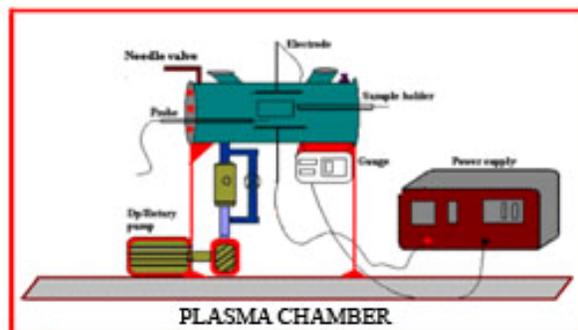

Fig. 1. Schematic diagram of plasma chamber.

On either side of the glass tube, flanges were fixed using araldite paste. By keeping a neoprene ring of suitable size between the frame and disc, they were shielded using nuts and bolts. The pressure gauge heads, rotary pump and air admittance valve, were connected to the chamber through thick walled PVC tubes. Electrodes and substrate holder were then inserted into the chamber. The chamber was cleaned with water and then with distilled water. It was dried and then cleaned with acetone. Any oxide formation on electrode was cleaned using an alkali. Once the chamber was put into the vacuum system, electrodes and substrate holder were cleaned by a discharge current of about 1μA for about 15 minutes. PVC membrane, was cut into 5 x 5 cm pieces and used as modification material. The membrane was placed inside the plasma chamber using a stainless steel specimen holder between the electrodes. The electrode distances were fixed to be 5 cm apart and the specimen was placed 2 cm apart from the cathode. The chamber was firmly closed. Then the vacuum pump was switched on. When the required pressure of 0.8 mbar was inside the chamber, the power supply was switched on and a voltage of 350 V was applied between the electrodes. The membrane was placed between the electrodes and plasma treated for 10, 15 and 20 minutes. The plasma treated membranes were taken out of the plasma chamber and the characterization studies were performed.

3. Results and discussion

3.1 FTIR analysis

The Fourier Transform Infra Red (FTIR) spectroscopy of the untreated and treated membrane exposed for 10, 15 and 20 minutes in plasma were performed using Thermo Nicollet Avatar 370, spectrophotometer in 4000-400 cm^{-1} wave number range.The FTIR spectrum of untreated membrane is shown in Fig. 2 (i). In the untreated sample the peaks at 2920 cm^{-1}and 2840 cm^{-1} corresponds to C-H stretching. The CH$_2$ bending was observed by a prominent peak at 1470 cm^{-1}. The C-Cl stretching can be interpreted by the presence of two peaks at 727 cm^{-1} and 685 cm^{-1}. After 20 minutes of plasma treatment the peak observed at 2920 cm^{-1} was shifted to a higher wave number range of 2923 cm^{-1} as shown in Fig. 2 (iv).The peak observed at 2840 cm^{-1} in the untreated sample has shifted to a higher frequency range of 2850 cm^{-1} in plasma treated samples as shown in Fig. 2(ii), Fig. 2 (iii) and Fig. 2(iv). There is no variation in the peak observed at 1470 cm^{-1} in the untreated sample, except for 15 minutes exposure time, where it was shifted to lower wave number range of 1460 cm^{-1} as shown in Fig. 2 (iii). The peak observed at 727 cm^{-1} in the untreated sample, shifted to a lower wave number range of 720 cm^{-1} for 10 minutes plasma treated sample as shown in Fig. 2(ii) and 723 cm^{-1} for 15 and 20 minutes plasma treated samples as shown in Fig. 2 (iii) and 2 (iv). The peak observed at 685cm^{-1} in the untreated sample was shifted to a lower wave number range of 681 cm^{-1} for 10 minutes plasma treated sample as shown in Fig. 2 (i) and

to a higher wave number range of 698 cm^{-1} for 15 and 20 minutes plasma treated samples as shown in Fig. 2 (ii) and (iii).
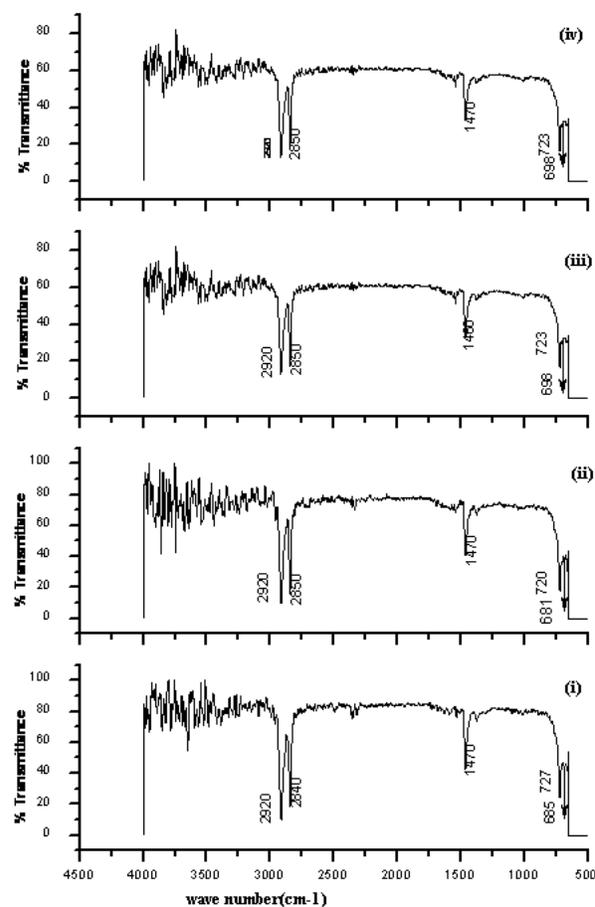

Fig. 2. FTIR spectrum of (i) Untreated membrane (ii) Plasma treated membrane for 10 minutes. (iii) Plasma treated membrane for 15 minutes. (iv) Plasma treated membrane for 20 minutes.

New functional groups were not identified in the case of plasma treated membranes within the limits of errors [6]. Unlike high energy materials polymers have little free energy on the surface. With the plasma treatment the polymer expands and produces free volume in between the polymeric chains. Thus the ions or polymer segments on the surface move into the free volume. This may be the reason for shifting in IR absorbance of some chemical groups.

3.2 X-ray diffraction studies

The XRD spectra of untreated and treated membrane exposed for 10, 15 and 20 minutes were analyzed using AXS D8 Advance X-ray diffractometer. In the untreated sample a sharp peak is found around 21.4º, followed by another small peak around 23.73º with maximum intensity as shown in Fig. 3(i). The two peaks observed exhibit different intensity which confirms the semi crystalline

nature of the membrane. Further, the sharp peak observed at 21.4º and the small peak around 23.73º was found to have a continuous decrease in intensity with increase of plasma treatment time as shown in Fig. 3(ii), (iii) and (iv).
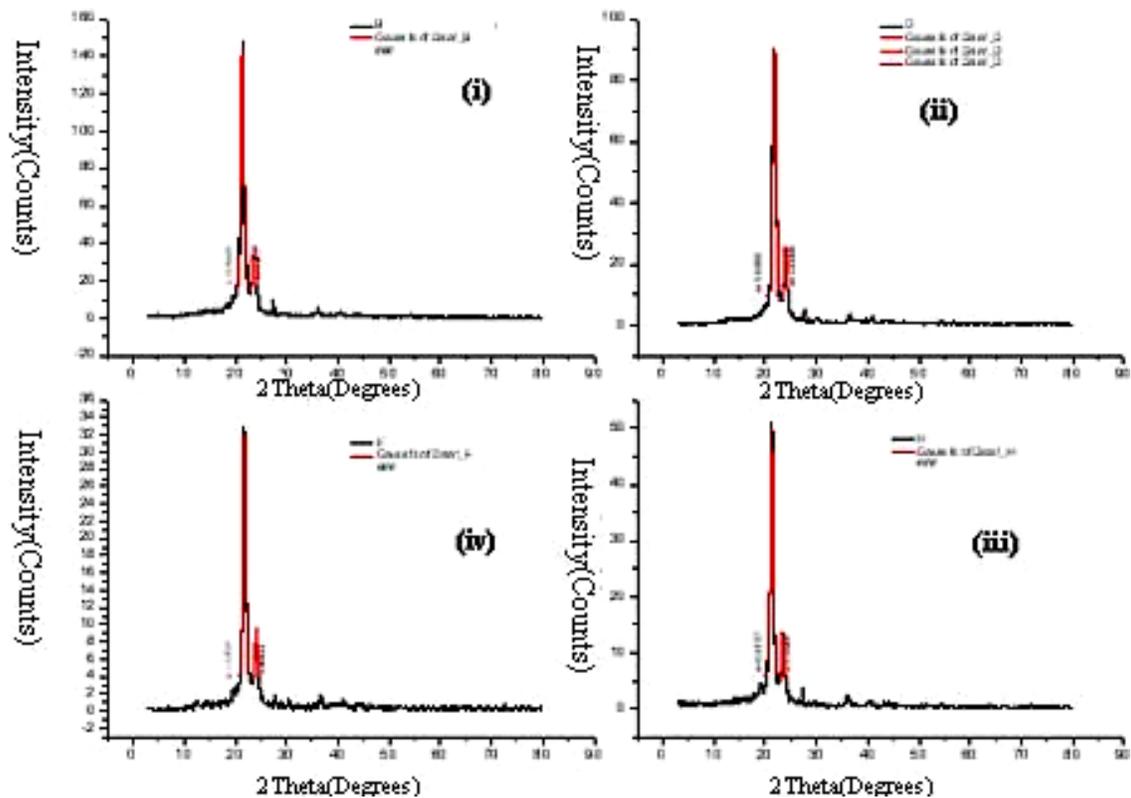

Fig. 3. XRD patterns of (i) Untreated membrane (ii) Plasma treated membrane for 10 minutes. (iii) Plasma treated membrane for 15 minutes and (iv) Plasma treated membrane for 20 minutes.

Table 1. Grain size calculated from Scherrer's formula.

S.NO	Exposure Time	Grain Size(nm)
1	0 minutes	13.61
2	10 minutes	13.69
3	15 minutes	13.73
4	20 minutes	16.27

The above changes reveal the decrease in the crystalline nature of the specimen, which is also confirmed by the SEM analysis. This result could be interpreted in terms of the Hodge et al. [8] criterion which has established a correlation between the height of the peak and the degree of crystallinity. Grain size was calculated from the Scherrer formula and is tabulated in Table 1.The particle size (iv), from Scherrer formula is given by $D = (K \lambda)/(\beta \cos \theta)$ where K is the shape factor which has a typical value of 0.94, λ is the X-ray source wavelength (1.54 Å), β is the full width at half maximum value in radians and θ is the Bragg angle. The grain size calculated using this formula for the untreated specimen is 13.61 nm which has gradually increased to 16.27 nm, with the increase of the plasma exposure time as tabulated in Table (i).

The increase in grain size is also confirmed by SEM analysis. This effect may be due to the covalent bonding of neighboring atoms in the polymer membrane during plasma treatment.

3.3 SEM analysis

The SEM studies were performed using JEOL model JSM-6390LV scanning electron microscope. The morphologies of the untreated and plasma treated membrane for various exposure times is shown in Fig. 4(i), 4(ii), 4(iii), 4(iv).

The surface morphology of the untreated membrane show definite arrangement of grains on the surface. The change in surface chemistry of the membrane is obvious immediately after 10 minutes of plasma treatment as shown in Fig. 4(i). This clearly indicates that the surface layers have been modified due to interaction with plasma. The increase in roughness of the surface with increase in plasma treatment time [8] can be clearly seen from the SEM micrographs shown in Fig. 4 (ii), (iii) and (iv). The energetic species in the plasma react with the surface of the polymer and the energy transferred to the membrane surface, was dissipated with in the membrane, which resulted in the roughening of the surface. There is a predominant increase in the grain size of the specimen after plasma treatment, which may be attributed to the coalescence of neighboring grains after plasma treatment.

Fig. 4 (iv) clearly shows small holes on the membrane surface. So we can optimize the maximum plasma treatment time at 15 minutes to obtain good surface modification without damaging the membrane. According to Kochkodan et al. [9] criterion the susceptibility of the membranes to microbiological fouling reduces with a decrease in the roughness of the membrane surface and the research paper of Emerson *et al.* [10] confirms the decrease in bacterial growth with increased surface roughness when nano-micrometer scales are considered. As the increase in surface roughness was clearly indicated after plasma treatment, the treatment can be used for antimicrobial activity.
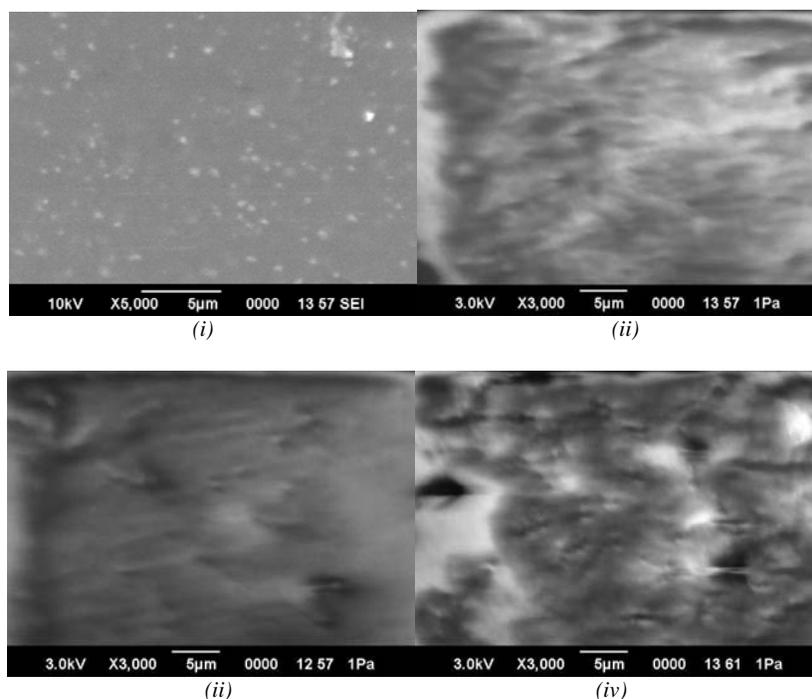

Fig. 4. SEM images of (i) Untreated membrane (ii) Plasma treated membrane for 10 minutes. (iii) Plasma treated membrane for 15 minutes. and (iv) Plasma treated membrane for 20 minutes.

4. Conclusions

The Glow Discharge DC plasma treatment is an effective and environmental friendly technique in the surface modification of poly vinyl chloride membrane because there is no disposal or personal safety issues commonly associated wet chemistry or other conventional methods. FTIR studies confirm the change in absorbance of some chemical groups after plasma treatment. New functional groups were not identified after plasma treatment. XRD studies showed a decrease in crystallinity and an increase in grain size after plasma treatment.

The SEM micrographs show an increase in surface roughness and in grain size, of the membrane after the plasma treatment. Plasma treatment time plays a vital role in deciding the surface modification of the polyvinyl chloride polymer membrane. The plasma treated polymer membrane can be tailored to the need of theapplication, in different fields of modern technology, especially in the field of biomedicine for improvement of anti-bacterial properties. The simplicity of this process and required equipment makes it attractive for industrial applications. The process becomes closer to clean room environments due to inherent cleanliness.

References

[1] D. Barton, J. W. Bradley, D. A. Steele, R. D. Short, J. Physical. Chemistry **B**, 103 (1999).

[2] F. S. Denes, S. Manolache, Progress in Polymer Science **29**, 815 (2004).

[3] Li Dejun, Zhao Jie, G. U.Hanqing, L. U. Mozhu, D. Fuquing, Chin. Phys. Letter **9,** 1992.

[4] D. S. Kim, J. S. Kang, K. Y. Kim, Y. M. Lee, Desalination **146**, 301 (2002).

[5] C. Boria, G. Boria, N. Dumitrascu, Applied Physics **A90**, 2008.

[6] I. C. Topala in Atmospheric and low pressure plasma applications in material sciences, Single phase materials, Aachen, Germany, 2005.

[7] S. Y. Hsin Li, T.-H. Hsueh, Proceedings of the TTT2005Academic Conference, 2005.

[8] JR. M. Hodge, Graham. H. Edward, George.P. Simon, Polymer **37**, 1371 (1996).

[9] V. M. Kochkodan. Hilal, V. V. Goncharuk, L. Al-Khatib, T. I. Levadana, Colloid Journal **68**, 267 (2006).

[10] R. J. Emerson, S. Bergstorm, Y. Liu, E. R. Soto, Langmuir **22**, 11311 (2006).

_____

[*]Corresponding author: anusham_33@ yahoo.co.in