

Characterization of N₂ Plasma Treated Nano Composites Polymer Membranes

N. K. Agrawal¹, R. Agarwal², Y. K. Vijay³ and K. C. Swami¹

¹Department of Physics, Malaviya National Institute of Technology, Jaipur 302017, India

²Centre for Converging Technologies, University of Rajasthan, Jaipur-302004, India

³Department of Physics, University of Rajasthan, Jaipur-302004, India.

Article history

Received: 6-Oct-2013

Revised: 13-Nov-2013

Available online 20 Dec. 2013

Keywords:

Synthetic Membrane, Plasma Treatment, Ion Energy, Plasma Etching Time.

Abstract

Systematic study was carried out to characterize the effects of Nitrogen ion plasma on nano composite polymer membrane. Using solution casting and spin coating method, nano composite polymeric membranes in the range of 20 micron were prepared. Nitrogen ion plasma treatment was done for these membranes. Variable treatment time was used to modify the membrane surface and its characteristics. These membranes were characterized before plasma treatment and after plasma to make comparative study by different technique such as AFM, UV-Vis Spectrometry and Fourier transform infrared spectroscopy. Results show the Plasma treatment is a quite effective tool for improving the properties of composite membranes with unique characteristics. These results are discussed in this paper.

© 2013 JMSSE All rights reserved

Introduction

The increased demands for polymers, due to their important properties and ability to be recycled, make it very valuable materials, since polymers have high strength to weight ratio, resistance to corrosion, and their relatively low cost are being increasingly used for different purposes¹. Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial applications such as adhesion, biomaterials, protective coatings, friction and wear-resistant composites, microelectronic devices and thin film technology²⁻³. To increase the range of applications for polymers, several techniques have been developed to modify the polymer surfaces for improve or change some of the surface properties without altering the bulk properties. These techniques involve ion and electron beams bombardment, UV light, laser irradiation, and X-ray exposure⁴. Among all the methods of modifying polymer surfaces low pressure plasma treatment has proved to be one of the most effective, ensuring uniformity, as well as being non-polluting technique⁵. Plasma is an ionized gas including both charged and neutral particles, such as electrons, ions, atoms, molecules and radicals. The interaction between charged and neutral particles as well as photons with polymer membrane can significantly affects the optical, electrical, and mechanical properties like cross-linking, functionalization degradation and radical formation⁶. The plasma is capable to effect on polymer membranes by many ways like surface cleaning, surface ablation or etching, surface cross-linking, and modification of the surface chemical structure⁷. These effects depend on a presence of the active species in plasma (electrons, ions, radicals, photons) which interact with polymer surfaces and modify their chemical and physical properties. In general, the surface modification techniques can be divided into three categories: cleaning and etching by removal of material from the surface, surface reactions producing functional groups,

cross- linking and deposition of thin films on the surface⁸. The principle effect of low-pressure glow discharge plasma treatment depends on the strict control of the treatment conditions such as the kind of plasma (DC, radio frequency RF or microwave (MW)), the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time⁹.

Furthermore, plasma treatment can be applied to improve modifications occur in surface layer only and polymer bulk saves the same unchanged mechanical properties, the modified surface layer can be affected by composition of ambient atmosphere, and the modified surface layer will able to have a good homogeneity¹⁰.

Plasma treatment is a very effective way to enhance the hydrophilicity of polymer surface by adopting two processes which are usually responsible for surface ageing: the first one is the reorientation of the polar groups into the bulk polymer, and the second is the mobility of small polymer chain segments into the matrix, both leading to a decrease in surface energy¹¹. Plasma can interact with the polymers through the formation of cross-linkages between adjacent polymer chains or by chain scission. The improvement of surface hydrophilicity is induced by formation of new oxygen containing groups on the surface, such as carbonyl, carboxyl or hydroxyl depending on the treatment conditions and gas composition like ions, electrons, fast neutrals and radicals which contribute to the polymer treatment, resulting in etching, activation and/or cross-linking¹².

The main aim of this work is to make characterization of low pressure Nitrogen plasma to improve roughness of a polycarbonate film surface, and study functionalization/activation phenomena as well as surface roughness changes induced by the plasma-etching mechanism for different treatment time and for 16W dc-discharge power using different experimental techniques¹³⁻¹⁴.

Experimental

Polycarbonate (PC) granules were used to prepare flat sheet membranes by solution cast method. They were obtained as commercial grade from Loxim Polymers, Jaipur. Dichloromethane of extra pure grade was used as a solvent for preparing 10% polymer solution¹⁴.

Preparation of Membranes

Solution-casting method was used for preparation of polycarbonate membranes. Polycarbonate granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution¹². The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution. The process is carried out at room temperature for around 2-3 hours till a clear solution is formed then pour in flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10–12 h.

Nitrogen Ion Plasma Irradiation

Plasma treatment consists of a source chamber with the complete power supply, connected to a vacuum system. The magnet is positioned to get a magnetic field inside the source chamber. Nitrogen gas used for containing plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes in magnetic field. The confined plasma in the chamber is used for surface modification. Applying a high voltage between two electrodes with magnetic field generates the DC glow discharge^{9,11}.

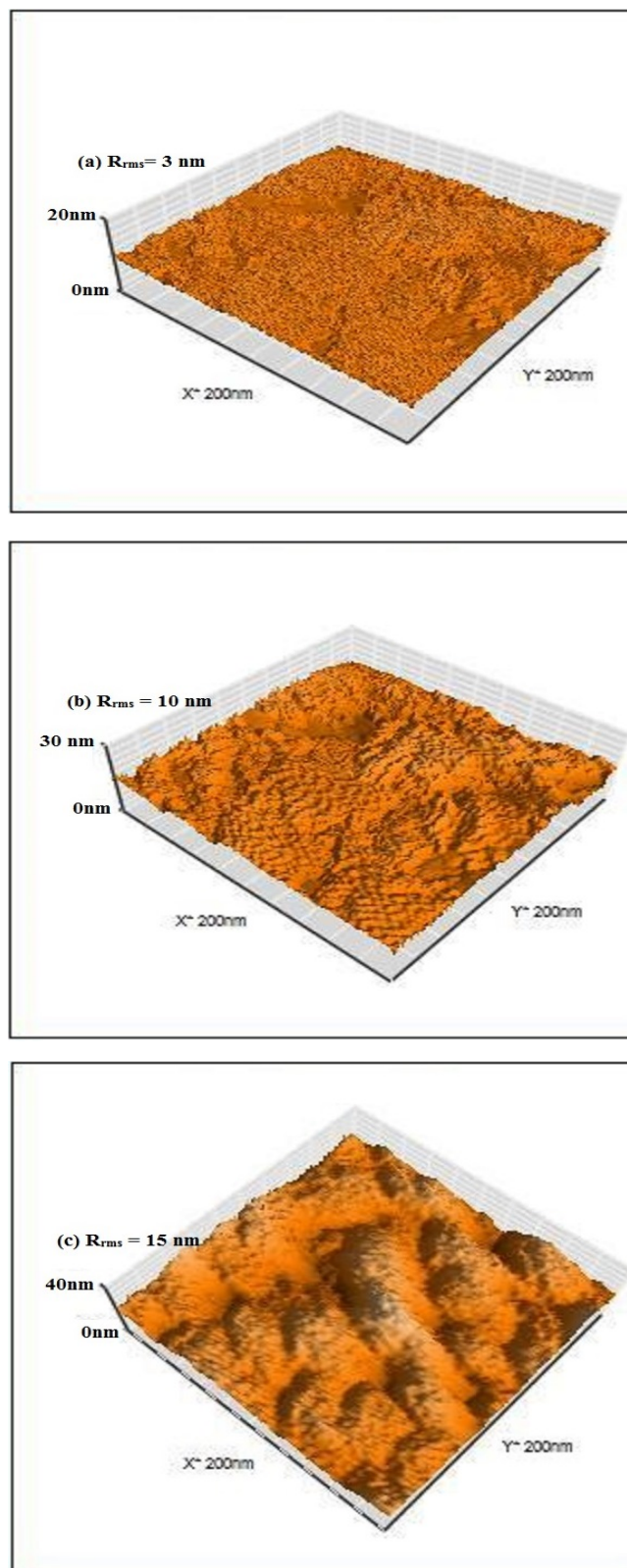
In this study we have used Nitrogen plasma. The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and then refilled with low-pressure Nitrogen gas to create glow discharge plasma. The gas is then energized by direct current. The energetic species in plasma include ions, radicals, electrons and meta-stable photons in short-wave UV range. DC glow discharge is generated by applying a high voltage between two electrodes in the presence of magnetic field. The measurement for all PC treated films was accomplished shortly after plasma exposures due to highly unstable free radicals and polar groups newly formed after plasma treatment. These structures can be degraded quickly to be more stable as explained later. The PC films were treated by Nitrogen plasma treatment for 10, 30, 60 and 80 min respectively.

Surface topography and roughness analysis of the plasma-treated surfaces for different exposure times was carried out by means of atomic force microscopy (AFM) was performed on a multimode AFM Microscope. From the analysis of the images, the root-mean-squared roughness (R_{rms}) and different topographic profiles measured. To study the optical properties for plasma treated PC membrane, A UV-visible spectroscopy from (HITACHI, U-2900 spectrophotometer) was used in the wavelength range of 200 nm to 500 nm. The pristine PC membrane was used as a reference film for all measurements. The characterization of the chemical structure of the pristine and modified polymers films was carried out by Fourier transform infrared spectroscopy (FTIR) IRAffinity-1 from (SHIMADZU).

Results and Discussion

Figure 1 shows the corresponding AFM topographical images of the untreated membrane and treated membranes by Nitrogen plasma at 10, 30, 60 and 80 min, respectively. Here 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 samples were amorphous. The UV-

visible transmission spectra of pristine PC membrane and the treated film by Nitrogen plasma at different time duration (10, 30, 60 and 80min) have been shown in Figure 2, the reference used for transmission measurements is untreated PC film. To study and analyse the effects of plasma treatment on chemical structure of PC membrane, FTIR measurements was carried out. Figure 3 shows the IR spectra of untreated and treated membrane.



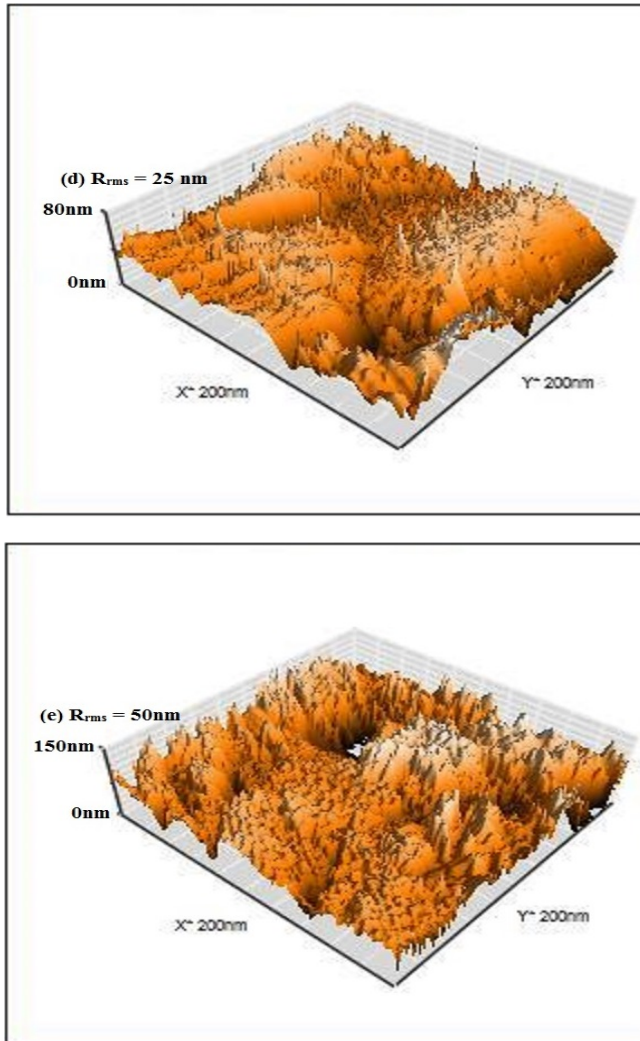


Figure 1: AFM images of Polycarbonate film with different plasma treatment time (a) untreated, (b) 10 min, (c) 30 min, (d) 60 min and (e) 80 min, respectively.

The absorption bands as obtained from the untreated film are classified as (A) 1030 cm⁻¹, the C-O stretching vibration (B) 1645 cm⁻¹, the C=C unsaturated (C) 1770 cm⁻¹, the C=O stretching vibration (D) 2890 cm⁻¹, the CH₃ stretching vibration and (E) 3070 cm⁻¹, the C-H stretching vibration of aromatic compound. The increments in the absorption bands of C-O and C=O at 1030 cm⁻¹ and 1770 cm⁻¹ has been attributed to the creation of unsaturated -C=C- bonds at 1645 cm⁻¹ after plasma treatment. Obviously, it is also observed from FTIR spectra that the C-C and C-H bands have been decreased after plasma treatment. It indicates that cross linking phenomenon enhanced during plasma treatment.

Summary and Conclusions

As polycarbonate membrane is prepared without the help of any support, it can be concluded that polycarbonate has considerable strength as compared to other polymeric materials like polyamide which cannot be prepared without the help of support. It was observed from the analysis of the results that by plasma treatment using Nitrogen gas for different irradiation periods one can change surface properties of polymer membrane surface like optical transmittance, surface roughness and surface energy due to surface cross-linking, degradation, and functionalization.

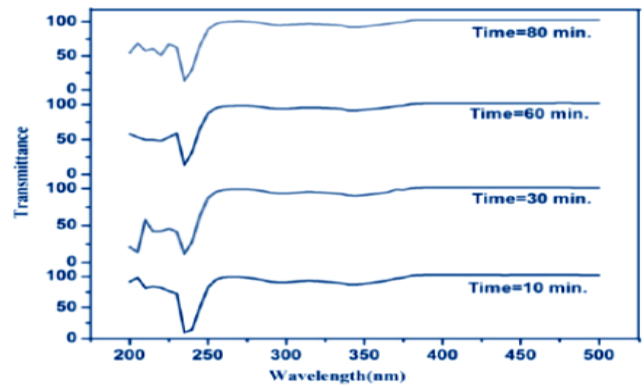


Figure 2: UV-Visible spectra for plasma treated PC membranes for different irradiation time.

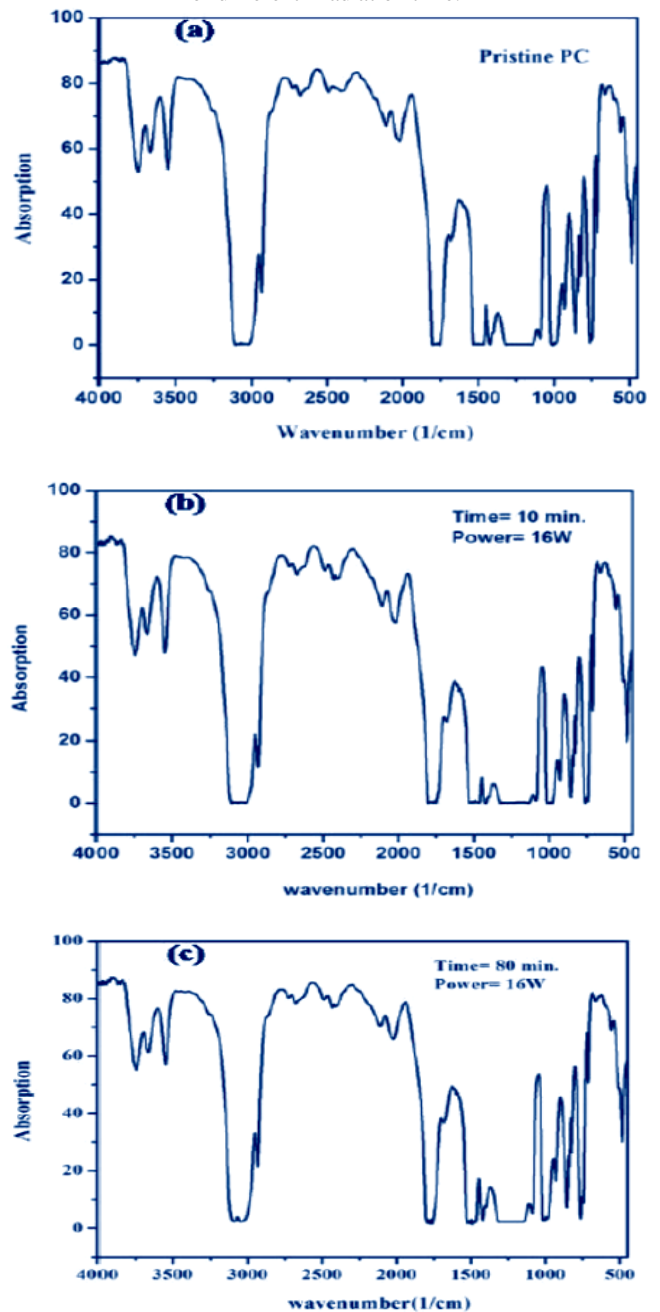


Figure 3: FTIR spectra for plasma treated PC membranes for different irradiation time (a) untreated, (b) 10 min and (c) 80 min.

These modifications can be controlled by plasma operational conditions like discharge power, time of treatment, and type of gas used. The AFM images show increased surface roughness along with increased of irradiation duration. The decline value of refractive index of the Nitrogen-plasma treated films can attribute to formation of low density surface layer. The optical transparency of the treated films has been increased due to degradation effect of the PC molecules on the surface by chain scissoring effects. FTIR analysis shows increasing in the absorption bands of C-O and C=O for treated films due to creation of unsaturated – C=C– bonds, also decreasing in C-C and C-H bands because of cross linking phenomenon enhancement during plasma treatment.

Acknowledgement

The authors wish to acknowledge to Department of Physics, University of Rajasthan for providing AFM measurement facility.

References

1. Y. Sanchuan, L. Xuesong, L. Jingqun, W. Dihua, L. Meihong and G. Congjie, Surface modification of thin-film composite polyamide reverse osmosis membranes with thermo-responsive polymer (TRP) for improved fouling resistance and cleaning efficiency; *Separation and Purification Technology*: 76, 2011, 283-291.
2. B. Bagra, P. Pimpliskar and N. K. Agrawal, Bio-Compatibility, Surface & Chemical characterization of glow discharge plasma modified ZnO Nanocomposite Polycarbonate; proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings: India, 2013, Dec. 17-21.
3. P. Pimpliskar, B. Bagra, A. Sharma, S. Khandwal and N. K. Agrawal, An Innovative Approach for Efficient and Reusable Catalization for Synthesis of α , β -Unsaturated Compounds Using Polymer - NPs Composites as Catalyst; proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings: India, 2013, Dec. 17-21.
4. L. Zou, I. Vidalis, D. Steele, A. Michelmore, S.P. Low and J.Q. Verberk, Surface hydrophilic modification of RO membranes by plasma polymerization for low organic fouling; *Journal of Membrane Science*: 369, 2011, 420-428.
5. N. K. Agrawal, N. A. Kumar, M. Singh, Y.K.Vijay and K.C.Swami, Plasma Surface Modification of Nano Composite Polymer Membranes: An Innovative Approach for Synthesis of Nano-Bio Materials; proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings: India, 2013, Dec. 17-21.
6. L. Meihong, Y. Sanchuan, Q. Ming, P. Qiaoming and G. Congjie, Impact of manufacture technique on seawater desalination performance of thin-film composite polyamide-urethane reverse osmosis membranes and their spiral-wound elements; *Journal of Membrane Science*: 348, 2008, 268-276.
7. P. Agarwal, R. Agarwal and N. K. Agrawal, Morphology and Crystallization of Size-Controlled Spherical Silver Nanoparticles Synthesized Using *Coriandrum sativum*: A Greener Approach; proceedings of 58th DAE- Solid State Physics Symposium, AIP proceedings: India, 2013, Dec. 17-21.
8. W.M. King, P.A. Cantor, L.W. Schoellenback and C.R. Cannon, High-retention reverse-osmosis desalination membranes from cellulose acetate, *Membranes from Cellulose Derivatives*; Interscience Publisher: New York, 2001, 203-207.
9. P. Agarwal, A. Mehta, S. Kachhwaha and S. L.; Kothari, Cicer arietinum Leaf Extract Mediated Synthesis of Silver Nanoparticles and Screening of Their Antimicrobial Activity; *Advanced Science, Engineering and Medicine*: 5 (7), 2013, 709-714.
10. J.K. Beasley, The evaluation and selection of polymeric materials for reverse osmosis membranes, *Desalination*; Interscience Publisher: New York, 1997, 181–189.
11. R. Agarwal, N. K. Agrawal and Ramvir Singh, Cicer arietinum Leaf Extract Mediated Synthesis of Silver Nanoparticles and Screening of Its Antimicrobial Activity; *Advanced Science, Engineering and Medicine*: 6 (2), 2014, 203-207.
12. N. K. Agrawal, K. Awasthi, Y. K. Vijay and K. C. Swami, Synthesis and characterization of plasma treated TiO₂ Nano composites polymer membranes; *Journal of Advanced Electrochemistry*: 2, 2013, 31-35.
13. K. Hyun and K. S. Soo, Plasma treatment of thin film composite reverse osmosis membrane; *Journal of Membrane Science*: 286, 2009, 193–201.
14. N. K. Agrawal, M Singh, Y. K. Vijay and K. C. Swami, Synthesis and Characterization of Colloidal TiO₂ Nanoparticles: Acquire Through Titanium Chloride Rich Solutions; *Advanced Science, Engineering and Medicine*: 7, 2014, 1–5.