SHI induced nano track polymer filters and characterization

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Abstract : Swift heavy ion irradiation produces damage in polymers in the form of latent tracks. Latent tracks can be enlarged by etching it in a suitable etchant and thus nuclear track etch membrane can be formed for gas permeation / purification in particular for hydrogen where the molecular size is very small. By applying suitable and controlled etching conditions well defined tracks can be formed for specific applications of the membranes. After etching gas permeation method is used for characterizing the tracks. In the present work polycarbonate (PC) of various thickness were irradiated with energetic ion beam at Inter University Accelerator Centre (IUAC), New Delhi. Nuclear tracks were modified by etching the PC in 6N NaOH at 60 (±1) ºC from both sides for different times to produce track etch membranes. At critical etch time the etched pits from both the sides meet a rapid increase in gas permeation was observed. Permeability of hydrogen and carbon dioxide has been measured in samples etched for different times. The latent tracks produced by SHI irradiation in the track etch membranes show enhancement of free volume of the polymer. Nano filters are separation devices for the mixture of gases, different ions in the solution and isotopes and isobars separations. The polymer thin films with controlled porosity finding it self as best choice. However, the permeability and selectivity of these polymer based membrane filters are very important at the nano scale separation. The Swift Heavy Ion (SHI) induced nuclear track etched polymeric films with controlled etching have been attempted and characterized as nano scale filters.

Keywords : Nanofilters, Gas permeability, Selectivity

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1. Introduction

The membranes are used because of their low cost and easy processability into a variety of shapes. Polymeric membranes are also widely used for the research purpose. In the last few decades, the researchers have shown a lot of interest concerning the applications of polymeric membranes in biotechnology, medicine and electronics. Polymeric membranes are also extensively used for commercial gas and ion separation [1].

Several applications of the polymer membrane could be further extended by modification of the physical and chemical properties of the polymers. The mechanical, chemical, optical and structural properties of polymer membrane can be modified by depositing the energy of ions in the polymeric material by ion irradiation [2]. Some unique modifications in polymers are accomplished by heavy ion bombardment like alternation in the polymer structure, which is never observed by using electrons and gamma rays. Dense electronic excitation in heavy ion tracks provides the creation of various unsaturated products ranging from isolated allenes and alkynes to relatively big molecules. When the energetic ion passes through the polymeric films, it loses its energy *via* atomic collisions and electronic excitation. In electron excitation, the energy lost from the irradiant is mostly transferred to the electrons. A passage of energetic projectile through polymeric membranes produces cylindrical zones of irreversible chemical and structural changes. These zones have a diameter of a few nanometers and known as latent tracks surrounding by a halo. The formation of latent track is related with the electronic energy loss $(dE/dx)_e$ [3]. In polymers, the chemical changes are quite significant because of the macromolecular structure of these materials. The kind of changes, which predominantly depends on the type of polymer and irradiation conditions. The tracks create molecular chains breaking (scissioning), crosslinks, free radicals and other radiolytic processes [4]. Chain scission leads to decreasing molecular weight and increase in cross-linking. Both effects produced changes in the polymer phase, chemical structure, crystallinity and also in the molecular weight. The breaking of atomic bonds and the rearrangement of polymer structure around the ion path result in a heavily modified cylindrical area, called as latent track [5,6]. The damage caused by the passage of energetic ion modifies the free volume properties of polymeric material. Positron annihilation spectroscopy (PAS) has been developed as a useful tool in probing the microscopic and local properties of polymers. One of the great success in this area of research is the determination of micro-structural properties of the defects, such as free volumes and holes, on an atomic scale (2-20 Å) in polymers. The high sensitivity of PAS in probing defect properties arises from the fact that the positronium atom (Ps)-an atom consisting of a positron and an electron- is preferentially localized in atomic-scale free volume and holes. The average free volume is found to be increase with ion fluence in low fluence regime while it decreases for higher fluence. The increase in average free volume can be attributed to chain scission along the tracks. With the increase in ion fluence, the scissioned segments crosslink randomly, decreasing the average free volume, because of overlapping of tracks. The increase in gas permeability and selectivity also indicates the increase in the available free volume due to SHI irradiation [7].

The tracks are enabled to pass the gas molecules or liquids so it is required to preferentially etch to enlarge the size. Damaged zones can be converted in to useful ion track pore by controlled chemical etching. Both the track and bulk etching takes place in irradiated membrane, etching temperature having an important role to determine the formation of permeating tracks [8, 9]. The size of ion tracks increase with etching time [8,10].

Meeting the increasing interest in the production of pores with diameter down to the nanometer scale, new methods have been developed by using one side etching procedure. In an electrolytic cell, the chemical solution serves as well as etchant and as an electrolyte. In the very moment breakthrough of a track the beginning and increasing electrical current provides information of the "birth and growing of the track" [11].

Very narrow pore size distribution and low sorption ability are the distinctive properties of track-etched membrane, which is especially important for the filtration of gas mixtures. Their pore size, shape and density can be varied in a controlled manner [12]. It is based on the fact that the damaged region possesses a higher chemical activity than the undamaged matrix, so the etching process makes tracks be observable directly by optical or Scanning Electron Microscopy (SEM) [13]. This technique has numerous applications in applied science ranging from Solid State Nuclear Detector (SSND) to micro machining such as growth of nanostructure. The membranes used can be seen as model systems acting as interconnects between two separate liquids. Electric fields are preferred over pressure gradients as driving force in nanochannels, because very large pressure drops would be required to drive flow in small channels. By applying an external electric field over the interconnects, a potential difference is created across the membrane, which makes it is possible to selectively drive charged species from one liquid into the other through the pores [14].

The important challenges for the researchers are of bio- adoptability, stability, degradation and durability for these membranes under different conditions of operation arises. The artificial membranes have been successfully demonstrate their importance in drug delivery system for diabetic patients dialysis, blood purification, food packing and preservation, chemical and food industries *etc*. The controlled permeation of asymmetrically shaped nanopores has recently attracted a big interest to novel studies of translocation of biomolecules [15, 16].

In this paper, we have used ion, irradiation of polymeric membranes and applications of these membrane for gas separation, ion permeation and biological applications were also discussed.

2. Experimental

2.1. Irradiation :

The polymers were obtained in granular form and membranes of varying thickness from 1 to 50 μm were prepared by solution cast method [17]. The swift heavy ion irradiation was performed in General Purpose Scattering Chamber (GPSC) at Inter University Accelerator Center, New Delhi under high vacuum of 10^{-6} torr [18]. The irradiated samples were etched chemically in suitable etchant under standard conditions, *i.e.* temperature, concentration and pH value of etchant. The gas permeability for hydrogen and carbon dioxide of these membranes was measured [19].

2.2. Positron Annihilation :

A Na[22] source ($\approx$ 5μCi) deposited on a rhodium foil was sandwiched between the stacks of two layers of film. The PAL spectra were obtained using conventional fast fast coincidence system [20]. The BaF$_2$ scintillators coupled to Phillips XP2020 photomultipliers were used. Ortec constant friction differential discriminators were used for selecting energy and providing timing signal to time to amplitude converter. The time resolution (FWHM) of Co-60 prompt was 270 ps with Na-22 gate.

2.3. Chemical etching :

A computer-controlled electrolytic cell is used to etch the ion tracks and measure their electrical properties [14]. During etching, a chosen voltage across the cell was applied while monitoring the electrical current. The etching process was interrupted by a stopping medium after breakthrough. Etching was performed at room temperature by filling one compartment of the cell with 9M NaOH. The selection of this temperature represented a compromise between efficient track etching and preventing NaOH from rapid decomposition. Earlier studies have shown that a strongly basic pH value of the etchant ensure the formation of conical pores with large opening angles [21]. We therefore used a NaOH solution of intially high pH value 12.6. This leads to a narrow cone. The other compartment of the cell was filled with 1M KC1 or with a mixture of 2M KCl and 2M HCOOH (1:1) volume that served as a neutralizing agent.

2.4. Conduction measurements :

Transport properties of etched membranes have been examined using the same conductivity cell, in which the foils were etched. This set up offers a convenient way to perfuse both sides of membrane with different media [22].

2.5. Gas permeability :

The flux was estimated by the gas flow rate through the membrane, measured by the flow rate meter. A 38 mm diameter membrane with porous support was placed in the cell. The details are given elsewhere [23].

3. Results and discussion

The PALS has been used in the present study to characterize the effects induced by the ion bombardment in the polymers. The polymeric materials contain local free volumes, which have the size of few Å. These are the favourable sites where positorn and Ps atoms are localized prior to annihilation [7]. The positron in the polymeric material has following possible states at the time of annihilation : (i) free (delocalized) and/or localized positron state and (ii) free and/or localized Ps state. The localization sites are free volume holes, which are more favourable sites than the bulk for positrons and Ps. The Ps probes only free volume regions are not interfered by the bulk properties of the polymeric material.

The lifetime parameters of the unirradiated and irradiated samples of PS are shown in Table 1. The simple component, attributed to free annihilation of positrons is between 0.438–0.466 ns. This matches well with the value (0.3–0.5 ns) reported in the literature. The intensity of this component is around 35-40% and shows marginal variation with increasing fluence. The complex component of the spectra consists of one simple component, attributed to p-Ps and one continuous component, attributed to o-Ps. The lifetime of the component corresponding to p-Ps is found between 0.166–0.170 ns. The intensity of this component is around 60%, which is much higher than the theoretical value.

Table 1. Lifetime parameters of plane component of PC

Sample	Variance of Fit	Plane component			
		I_2	x^2 (%)	τ_2 (ns)	x^2 (ns)
Pristine	1.14	35.50	1.60	0.466	0.024
5×10^6	1.10	40.40	1.60	0.466	0.021
4×10^8	1.29	36.78	1.73	0.438	0.019
1×10^{12}	0.98	36.80	1.50	0.453	0.019

The o-Ps lifetime, τ_3, for PC increases for the fluence of $5 \times 10^6 - 4 \times 10^8$ ions cm^{-2} and then decreases for 1×10^{12} ions/cm^2. For PC, the variation in the lifetime and intensity with dose is shown in the Figure 1. The intensity of this component does not vary significantly with dose.
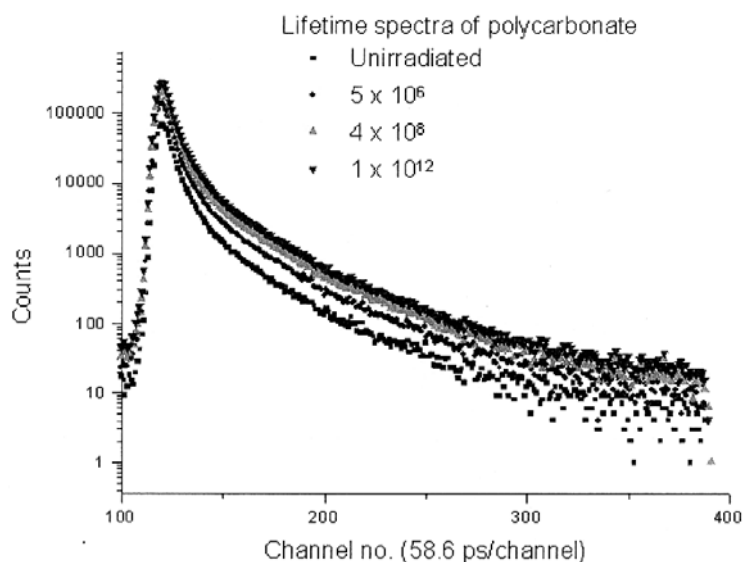
Figure 1. Life time spectra of polycarbonate.

The nanofabrication technique is based on the irradiation of polymeric membrane with swift heavy ions. The damaged zone by SHI of the material along the straight ion path is selectively removed by chemical etching, leaving the pristine material almost intact. By a proper choice of etchant and its composition, temperature and the etch time, the diameter of pore can be adjusted up to micron order. For obtaining, conical shape of pore, the membrane is placed between the two chambers of the electrolyte cell and etched from one side while another is protected by a stopping medium. The etching is controlled by ion current. When the pores are etched through, the current increases confirm the opening of the pore as shown in Figure 2.
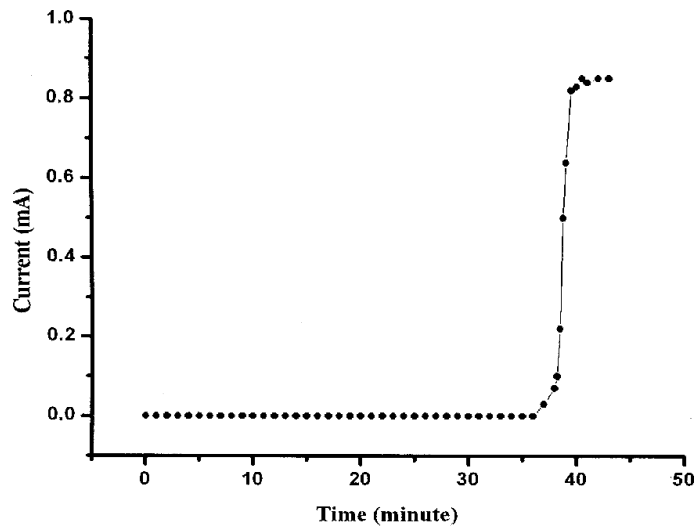
Figure 2. Current monitored etching.

After, the washing polymeric membrane in distilled water, the V-I characteristics are examined in the same cell by putting same electrolyte. Figure 3 presents the electrical conduction nature of electrolyte (FeCl$_3$) through the conical pores in the etched membrane.
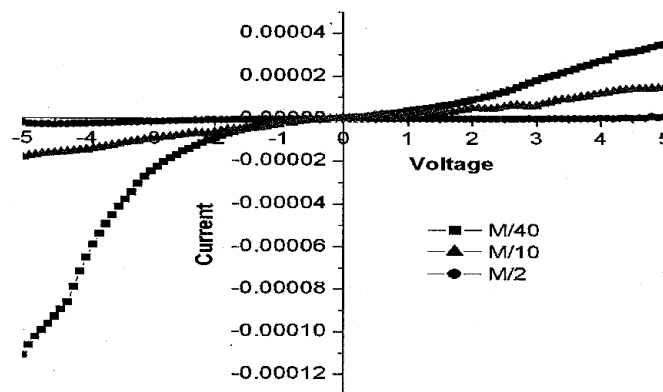
Figure 3. V-I characteristics of nanopores.

The obtained V-I characteristics are similar to an electrical diode and further lowering the concentration of electrolyte the rectifying nature is omitted. Such behavior is attributed due to the conical shape of the pore.

Current rectification provides an additional indication for nanometer scale of the pore opening [11, 12]. For lower salt concentrations, the electrical double layer at the pore wall is thicker *i.e.* fewer counter ions are screening the surface charges, whose effect is therefore more pronounced. So it is expected that lowering the electrolyte concentration would enhance the rectification effect. At concentration M/40, there is large difference is forward and backward current and have a rectification nature while at concentration M/2 and M/10 there is no rectification of ion current.

The stopping range of Ni^{7+} ion of 100 MeV in polycarbonate is 22 μm. For 18 μm thick membrane, the critical etching time (τ_c) is less than that of 38 μm thick membrane for both the gases. In 38 μm thick and 10^8 ions/cm^2 irradiated membrane τ_c is 20 minutes and for 25 μm and same fluence τ_c is 3 minutes as shown in Figure 4.

This large difference can be attributed to the difference in the bulk and track etching rate in various irradiated membranes. At this stage the gas passes

(a)

(b)

(c)
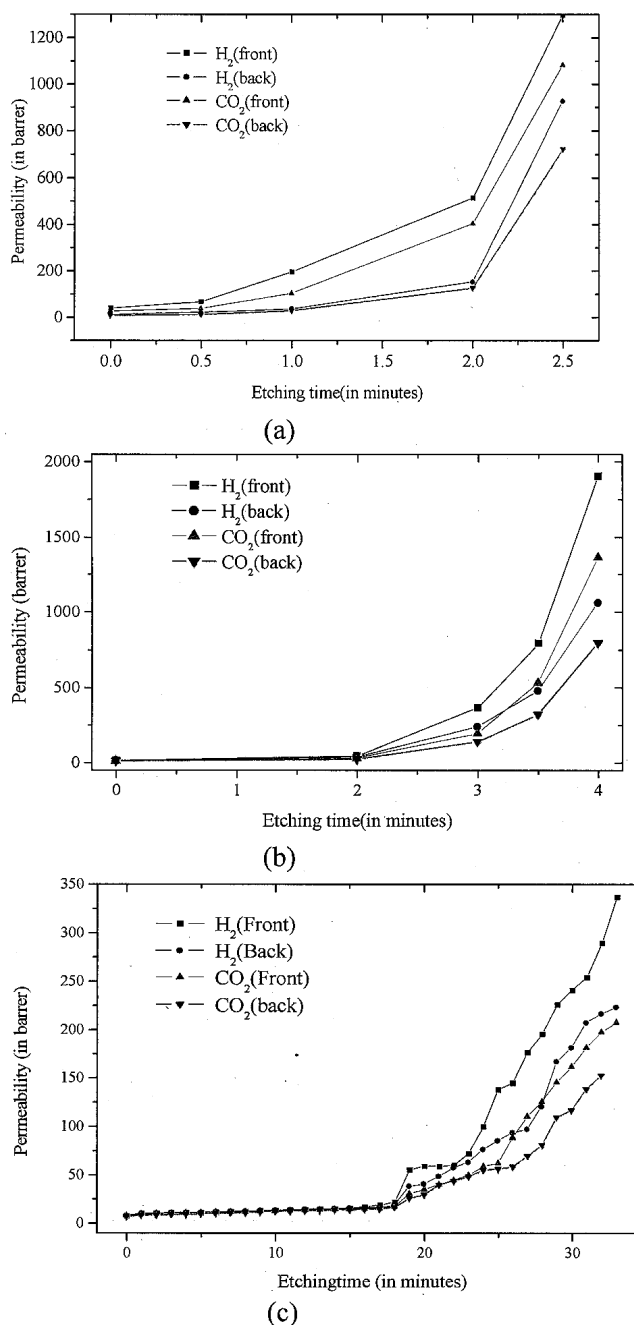
Figure 4. Etching time *vs* gas permeability for (a) 18 μm (b) 25 μm (c) 38 μm PC.

through the conical tracks that are just meeting at their vertices. In case of asymmetric membrane the gas passes through the conical tracks formed at ion incidence side. The gas permeability from the ion incidence side (front) is more than that of ion emergence side (back) due to the shape of the etched track as shown in Figure 4. So, the polarity of the membrane is important for production of an asymmetric membrane.

The gas permeability of the same membrane for hydrogen is greater than that of carbon dioxide due the difference in their molecular sizes [7]. The ion fluence also alters gas permeation rate. The higher fluence membranes having less critical etching time than the lower fluence membranes due to variation in the number of tracks that are overlapped [17]. In case of 18μm thick membrane, the critical etching time for 10^8 ions/cm^2 irradiated membrane is found to be 2 minute, whereas for 10^6 ions/cm^2 irradiated membrane it is found to be 4 minutes.
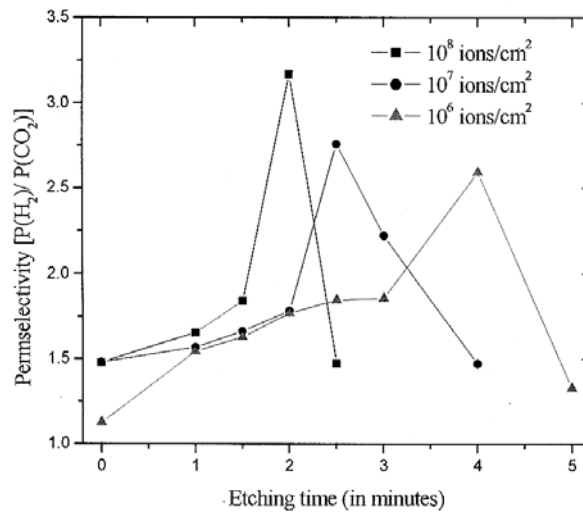
Figure 5. Permselectivity of PC membrane.

The permselectivity of hydrogen over carbon dioxide is also found to increase with increasing etching time and reached to a maximum value and on further increment in etching time it reduces, which shows that after critical etching the membrane allows to pass both the gases as shown in Figure 5, at this time the diameter of tracks is more than the diameter of particular gas molecules.

4. Conclusion

The latent tracks produced by SHI irradiation in the track etch membranes show enhancement of free volume of the polymer. Nano filters are separation devices for the mixture of gases, different ions in the solution. The polymer thin films with controlled porosity is finding itself as the best choice. However, the permeability and selectivity of these polymer based membrane filters are very important at the nano scale separation.

Acknowledgment

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