Polymer Bulletin 57, 723–728 (2006)
DOI 10.1007/s00289-006-0625-0

Polymer Bulletin

Conduction nature of conical pores in PET membrane

Kamlendra Awasthi[1] (✉), V. Kulshrestha[1], Rashi Nathawat[1], N. K. Acharya[1], M. Singh[1], D. K. Avasthi[2] and Y. K. Vijay[1] (✉)

[1]Department of Physics, University of Rajasthan, Jaipur-302 004, India
[2]Inter University Accelerator Centre, New Delhi-110 067, India

E-mail: kamlendra_awasthi@yahoo.co.in, yk_vijay@sancharnet.in; Fax: +91-141-3295402

Received: 29 December 2005 / Revised version: 4 May 2006 / Accepted: 14 June 2006
Published online: 29 June 2006 –

Summary

The preparation of conical pores in polyethylene terepthlate (PET) membrane is described. The conical pores prepared in PET by track etching technique. For this purpose, Cl^{9+} ion irradiated film was placed into an electrolytic cell and etched from one side while other side of membrane was protected by a stopping medium. During etching, current was recorded as a function of time, which shows a sudden change, indicating the pores breakthrough. After breakthrough, the etch process is interrupted by replacing the etching solution. After etching, the current voltage characteristics were determined under symmetric bath conditions. The resulting conical pores show non ohmic behavior, similar to that of an electronic diode.

Introduction

The basic process of track membrane is based on the irradiation of polymer films with swift heavy ions (SHI) and subsequent chemical etching in an appropriate etchant. Recently some qualitatively new results regarding polymer modifications induced by high-energy heavy ions have been reported [1-3]. Some unique modifications in polymers are only detected by heavy ion bombardment like alternation in the polymer structure, which is never observed by using electrons and gamma rays. Dense electronic excitation in a heavy ion tracks provides the creation of various unsaturated products ranging from isolated allenes and alkynes to relatively big molecules [1, 3]. Swift heavy ions transfer energy to the polymer essentially by inelastic (electronic) process while elastic (nuclear) energy transfer is, in general negligible for pristine polymers. But nuclear energy loss gains importance with proceeding polymer destruction, when tracks start overlapping. The energy transfer leads to excitation and ionization of molecular chains leading to radical formation to side or main chain bond scissioning and also to cross linking of polymer chains. Due to the electrostatic repulsion, these ions repel each other, thereby creating vacancies and interstitials. The range of this atomic collision cascade defines the core of latent track and has a diameter of less than 10nm. The track core is surrounded by a much larger halo of about 100-1000 nm [4, 5]. Thus the bombardment of energetic ions results in the change in the free volume properties of material [6]. Ion irradiated polymeric membrane can be preferentially etched to dissolve the damaged material. By the

technique of selective etching, it is possible to dissolve the chemically modified material, in the track at a higher rate than the undamaged matrix.
Track etched membranes offer distinct advantage over conventional membrane due to their precisely determined structure. The structure of ion track membrane such as size, shape, density of tracks and aspect ratio of pores can be controlled not only by the material properties but also irradiation conditions like ion, ion energy, fluence etc. and etching conditions like etchant concentration, etching temperature etc. [7].
Novel biotechnological filtration and sensing process required small pores with diameters similar to those of biochannels [8]. This goal is easier with conical pores than cylindrical pores. For generating conical pores, asymmetric track etching technique is used. This technique has already been used for single pore nuclear track filter [9]. The results suggest that one sided etched pore membrane could serve as a model of biological channels [10].
For requirement of conical nanopores, the etching is done from one side in a conductivity cell and controlled by monitoring the electric current and to be stopped shortly after the membrane is etched through, which is observed as sudden increase in current. In this paper, we used the same technique for multipore nuclear track filter using different concentration of electrolyte.

Experimental details

Sample and ion irradiation:

In present study, commercial available foil of polyether terepthlate (PET) having thickness 15µm is used. The membrane was irradiated by Cl^{9+} ion of 120 MeV (fluence 10^6 ions/cm^2) utilizing the General Purpose Scattering Chamber (GPSC) under high vacuum of order of 10^{-6} torr at Nuclear Science Centre, New Delhi, INDIA [11]. The projectile range of ion in PET is around 41µm. The electronic energy loss value across the sample thickness is 38.66. After ion irradiation, the samples were stored in air conditions.

FTIR measurements:

The nature of the chemical bonds of polymers can be studied through the characterization of vibration modes determined by infrared spectroscopy. The

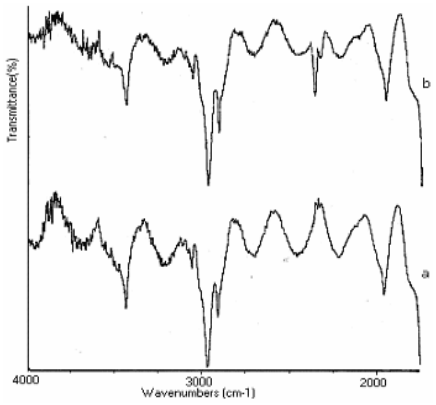

Figure 1: FTIR Graph for (a) virgin (b) irradiated PET film

transmission spectra of PET before and after irradiation in the range 1750-4000 cm^{-1} are recorded.

Current –monitored etching:

Conical pores in the irradiated PET samples were generated by using asymmetric etching technique. To etch the track from one side, the irradiated membrane was clamped between the two chambers of conductivity cell [12]. One chamber of the cell was filled with the etchant (9M, NaOH) at room temperature while the other side of membrane was protected by a stopping medium (mixture of 2M KCl +2M, HCOOH). Platinum electrodes are used in conductivity cell. In this technique, etching starts from one side and as soon as it reaches the other side of sample, the moment of breakthrough (when the membrane is etched through) is observed, characterized by a sudden increase of the current as shown in figure2. Application of the chemical and electrical stopping procedures ensured a slow increase of opening diameter of the conical pore after the breakthrough.

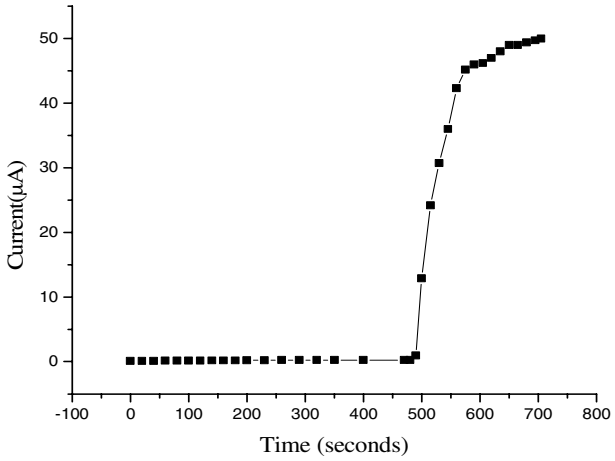

Figure 2: Graph of Ion current versus time

Voltage- current characteristic:

The electrolytic conduction studies through etched pores were also carried out in conductivity cell, under symmetric bath conditions, which measure the ion current across the membrane. The polymeric membrane separates the electrolytes and platinum electrodes are dipped in the cell. By applying the voltage, the permeation of particular ion depends upon the characterization of membrane i.e. the available free volume in the form of tracks. The electrolytic solution of $FeCl_3$ of different concentration is used for conduction measurements through etched pores of PET. Double distilled and carrier free de-ionized water will be used as a standard solvent, which obtained from Millipore ultra pure water system. The voltage current characteristics were measured by stepping 0.1V between -5 to + 5V. The ion current is recorded corresponding to the voltages with help of Keithley 238 high current source measure unit [9].

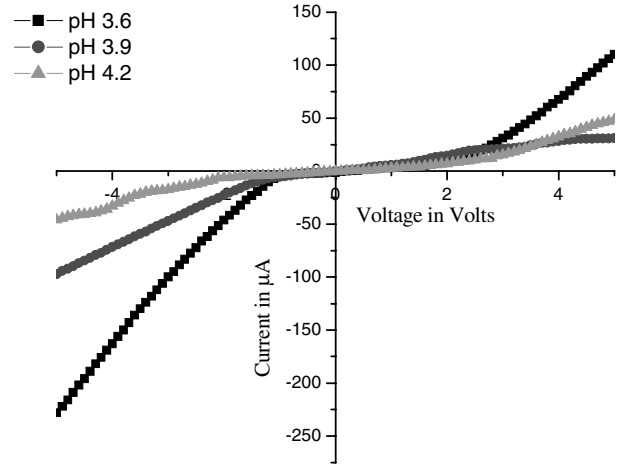

Figure 3: Voltage-Current characteristics of PET

Micrograph of etched membrane:

The optical microphotograph of etched membrane is recorded by LABOMED optical micrograph at 400 times magnification. The figure shows etched pits of etched side.

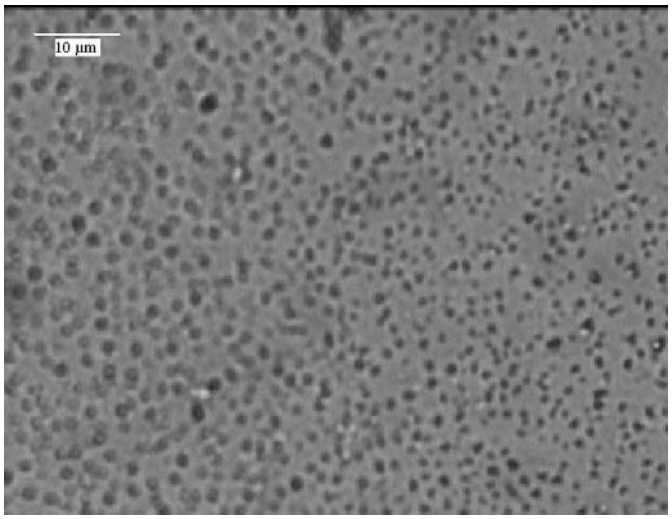

Figure 4: Optical micrograph of etched membrane of PET

Results and Discussion

FTIR spectra of irradiated samples show considerable changes [13], where modifications are clearly evident, the intensity of absorption peaks at 3060 cm^{-1} and 1950 cm^{-1} decreases and intensity at 2880 cm^{-1} increases (C-H stretching) on irradiation. A peak at 2360 cm^{-1} deform in the irradiated samples. Change after the irradiation in the region 2950-2850 cm^{-1} (C-H stretching) (methyl & methylene

group), superimposed upon (O-H stretching) have also observed. This indicated that chain scission may be taking place at the primary amine site.
The etching is controlled by monitoring the current. Because the tracks left in material by energetic heavy ions are not permeable to ions, the current in beginning of etching process is zero. When the pore is etched through, the current increases gradually, showing the opening of the pore as well as reflecting the increase of pore diameter as shown in figure 2. After the breakthrough, the current typically exhibits some instability, most probably due to redox reaction occurring at the tip of conical pore, which influences the current recorded by the electrode.
Conduction measurements were carried out for conical pores by electrical conduction (V-I characrestics) behavior of electrolytes in PET. At an alkaline pH of electrolyte solution forming the bulk phases of the membrane, the internal surface of conical pores carries negative charges formed by ionic group [9]. It is expected that, as a result of etching, the surface of PET contain carboxylic groups (COOH). These charges are covalentaly bound either directly to the internal surface and /or to polymer chains forming a layer of a hydrophilic gel. As a result a mobile counter ion layer close to surface is formed. The change in thickness of layer may lead to instabilities such as current fluctuation or transition between an open and closed state. The V-I characteristics obtained are that of an electronic diode. Such a behavior of pores due to their conical geometry [14]. Conduction a measurement shows the nature of etched conical pores, which depend on the concentration of electrolyte. At pH 3.6, the pores rectify the ion current while at pH 4.2 pore losses its rectifying nature. Due to conical shape of pores, there is a large difference in forward and backward resistances.

Conclusion

The preparation of asymmetric pore in PET has been presented. The rectification behavior observed for the pores in PET was an additional indication of the nanometer size of the pore opening. We have shown that the effect of ion current rectification strongly depends on the surface charge of the pore, which has been modified by the concentration of electrolyte. A conically shaped, charged pore is cation selective and acts as a diode with a preferential direction for the cation flow. This technique encourages developing a device based on nanostructure.

Acknowledgements. The authors are indebted to Nuclear Science Centre, New Delhi, India for ion irradiation and Ministry of Non –Conventional Energy Sources, New Delhi, India for providing financial assistance for the work. Gratitude is expressed to Prof. Reimer Spohr, GSI, Germany, Dr. Zuzanna Siwy, University of California, Irvine, Canada and Prof. R H Iyer, BARC Mumbai India for their help and suggestions.

References

1. Balanzat B, Bouffard S, LeMoel A, Betz N, Nucl. Instr.and Meth.B 91(1994) 140.
2. Ferain E, and Legras R, Nucl. Instr.and Meth.B 82(1993) 539.
3. Chadderton L T, Fink D, Gamaly Y, Moeckel H, Wang L, Omichi H, Hosoi F, Nucl. Instr.and Meth.B 91(1994) 71.
4. Krammer M, Nucl. Instr.and Meth.B 105(1995) 14.
5. Bouff S et al., Nucl. Instr.and Meth.B 105(1995) 1.
6. Ferry J.D., Viscoelastic properties of Polymers 3rd Edition (John Wiley & Sons Inc. NewYork) 1990.

7. Fleischer R.L., Price P.B., Walker R.M., Nuclear Tracks in Solids: Principals & Applications, Univ. of California Press, Berkeley, (1975).
8. Li J, Stein D, McMullam C, Branton D, Aziz M J, Golovchenko J A, Nature412 (2001) 337.
9. Apel P., Korchev Yu.E., Siwy Z., Spohr R., Yoshida M., Nucl. Instr. and Meth. in Phys.Res.B (2001); 184: 337-346.
10. Siwy Z, Apel P, Baur D,. Dobrev D, Korchev E., Neumann R, Spohr R, Trautmann C, Voss Kay-Obbe, Surface Science (2003); 532-535: 1061-1066.
11. Mehta G K, Nucl. Instr. and Meth. in Phys.Res.A 382 (2001)335.
12. Awasthi Kamlendra, Kulsreshtha V, Acharya N K, Singh M, Vijay Y K, European Polymer Journal 42(2006)883.
13. Biswas A, Lotha S, Fink D, Singh J P, Avasthi D K, Yadav B K, Bose S K, Khating D T, Avasthi A M, Nucl. Instr.and Meth.B 159(1999) 40.
14. Apel P Yu, Radiat. Meas.34 (2001) 559.