Modification of microstructure of the surface and the bulk in ion-irradiated membrane studied using positron annihilation spectroscopy

S.K. Sharma, P. Maheshwari, D. Dutta, K. Sudarshan, P.K. Pujari *

Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

ABSTRACT

The effect of ion irradiation and etching on the microstructure of polyethyleneterephthalate (PET) membrane has been studied using positron annihilation spectroscopy. PET membrane of 25 μm thickness was irradiated by 100 MeV ^{35}Cl beam (7×10^7 ions/cm^2) and then etched with NaOH for 45 min. The modification in the microstructure at the surface of the membrane was probed by depth-dependent Doppler-broadened S-parameter and positronium 3γ–2γ annihilation ratio using a slow positron beam, while the free volume properties in the bulk of the membrane were studied using the conventional positron lifetime technique. Positron annihilation parameters were found to be very sensitive to the microstructural changes occurring in the polymer at such a low fluence. It was observed that on ion-irradiation, the surface of the membrane is modified in a different way than the bulk. While the ion-irradiation produces large fraction of excess free volumes at the surface of the membrane due to chain scission, the free volumes are reduced in the bulk of the membrane due to cross-linking. FTIR and XRD measurements were also carried out to investigate the changes occurring in the chemical structure and crystallinity of the polymer samples on ion-irradiation and etching.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The spatial arrangement of long chain molecules influences many properties in polymers, including mechanical stability, conductivity, optical properties, transport properties and porosity. The irradiation of polymeric materials by energetic heavy ions leads to modification in porosity or transport properties of the polymers, which are further modified by etching the irradiated polymers in acidic or alkaline medium (Itoh and Tanimura, 1994; Trautmann, 1995). These track-etch polymeric membranes having controlled and well defined pores are widely used as templates for the synthesis of nano-materials (Apel et al., 2006) and in nano-filtration (Ferain and Legras, 1994). They are also useful as *in vitro* substrates in cell biology (Sergent-Engelen et al., 1990; Ferain and Legras, 1994) and in the development of new sensor devices (Tahara et al., 1997; Zhang et al., 1997; Singh and Prasher, 2006). It is, therefore, important to study the microstructural properties of the track-etch membranes under different experimental conditions for their technological applications.

There are various techniques viz. positron annihilation spectroscopy (PAS), infrared (IR) spectroscopy and X-ray diffraction (XRD) that are employed to characterize the effect of

ion-irradiation and etching in polymeric membranes (Singh et al., 2003, 2008; Zhu and Kelley, 2005; Sun et al., 2003; Hsu and Hadely, 1971; Suzuki et al., 1992; Kobayashi et al., 1995; Dlubek et al., 2000; Saito et al., 2007). The sensitivity of these techniques to the changes in the polymer microstructure varies. Most of the studies on changes in the polymer microstructure by ion beam irradiation have been carried out at the fluences of 10^{10}–10^{16} ions/cm^2 and changes in film properties like absorbance, crystallinity, capacitance and mechanical properties have been monitored (Singh et al., 2003, 2008; Sun et al., 2003; Singh and Prasher, 2006). The present study aims at monitoring of the microstructural changes at lower fluence (7×10^7 ions/cm^2). Hence a more sensitive technique is required to probe the microstructural changes starting at lower fluence.

Positron annihilation spectroscopy (PAS) is one of the most sensitive techniques to study the changes in microstructure even at lower fluence of ions. It has been extensively used to characterize polymers in terms of available free volume, chemical vicinity of annihilation site as well as effects of gamma as well as ion-irradiation on the microstructure of polymers (Hsu and Hadely, 1971; Suzuki et al., 1992; Kobayashi et al., 1995; Dlubek et al., 2000; Saito et al., 2007; Schultz and Lynn, 1988). When the positrons are injected into a polymer matrix, a substantial fraction of thermalized positrons may form positronium (quasi-bound state of an electron and a positron), which diffuses and localizes in the available free volumes or the region of low electron density. The *pick-off* annihilation rate (lifetime) of Ps can be correlated to

* Corresponding author. Tel.: +91 22 25595326; fax: +91 22 25595151.
  E-mail addresses: sudarshankathi@gmail.com (K. Sudarshan),
pujari@barc.gov.in (P.K. Pujari).

the pore size i.e. larger the size, longer the o-Ps lifetime and vice versa. Positron annihilation studies with the conventional radioisotope source span the entire range (surface to a depth of few mm) of the sample due to the broad energy distribution of the emitted positrons (0–540 keV) and the lifetimes measured using the conventional positron annihilation technique give the average bulk properties.

Surface studies or depth-selective measurements of free volume in polymer membranes are carried out by a mono-energetic slow positron beam. The mean implantation depth $\langle Z \rangle$ of the mono energetic positron beam having incident energy E (keV) in a material of density ρ (g/cm^3) is given as

$$\langle Z \rangle = \frac{A}{\rho} E^n \tag{1}$$

where $\langle Z \rangle$ is expressed in nm. A and n are the material dependent constants (Schultz and Lynn, 1988; Coleman, 2002). For polymers, the values of A and n are generally taken as 40 and 1.6, respectively (Xie et al., 1995; Myler et al., 1998). Doppler broadening spectroscopy (DBS) using a slow positron beam has evolved as a useful technique to characterize the microstructure of a polymer membrane as a function of depth (Kobayashi et al., 1995; Dlubek et al., 2000; Saito et al., 2007). When the thermalized positron/o-Ps annihilates through two photons mode by taking an electron from the surrounding medium, the 511 keV energy of the annihilation photon is Doppler broadened due to the finite momentum of the electron. The broadening of the 511 keV peak is represented by line shape parameters, namely, S-parameter defined as the ratio of the counts in the central region of 511 keV peak to the total counts under the peak (Coleman, 2002). The depth-dependent S-parameter and the three photon to two photon ($3\gamma/2\gamma$) annihilation ratio measurements are sensitive probes to characterize the architecture of pores or free volumes, electron density and interconnectivity of the free volumes to the surface of a polymer (Coleman, 2002).

In this work, PET membrane has been irradiated by an 100 MeV ^{35}Cl beam (7×10^7 ions/cm^2). The conventional positron annihilation lifetime spectroscopy (PALS) is used to characterize the free volumes in the bulk of the polymer and depth-dependent Doppler broadening spectroscopy (DBS) using a slow positron beam to characterize the surface and near surface region of the polymer membrane. Fourier transform infra-red (FTIR) and X-ray diffraction (XRD) measurements have also been carried out to supplement the positron studies.

2. Experimental

Polyethyleneterephthalate (PET) polymer films of 25 μm thickness and 1.39 g/cm^2 density were irradiated by an 100 MeV ^{35}Cl beam (7×10^7 ions/cm^2) in the presence of air at BARC–TIFR pelletron accelerator facility in India. The beam energy was sufficiently high for the ions to pass through the polymer film. The ion-irradiated film was etched with 6 N NaOH solution for 45 min. The positron annihilation lifetime measurements were carried out using plastic scintillators coupled to a fast–fast coincidence system. The time resolution (FWHM) measured with a ^{60}Co source was 250 ps for the positron window settings. The measurements were carried out by taking a stack of films (sufficient thickness to stop positrons in the polymer) on either side of a ^{22}Na source (10 μCi) sealed in kapton foil of 6 μm thickness. Silicon single crystal was used as a reference material to correct for the fraction of positrons annihilating in the source. All the lifetime spectra containing more than 10^6 counts were analyzed using the PATFIT-88 (Kirkegaard et al., 1989) and CONTIN (Provencher, 1982a, 1982b) programs.

Depth profiling of the surface of the pristine, irradiated and etched samples, as the case may be, was carried out using the slow positron beam at Radiochemistry Division, Bhabha Atomic Research Centre, India. Positrons emitted from a sealed ^{22}Na source (iThemba labs) are moderated by 1 μm thick tungsten single crystal. The thermalized positrons come to the surface as tungsten has negative work function for positrons (Schultz and Lynn, 1988). These positrons are extracted and focussed by a symmetric Einzel lens to the entry point of a 90° bent solenoid. The positrons are guided to the target by Helmholtz coils at the end of the solenoid. The positron energy is varied by floating the target to different voltages.

The Doppler broadening measurements were carried out in the energy range 200–6 keV, which corresponds to a depth upto ~500 nm. S-parameter was evaluated as the fractional peak area in the region of 511 ± 0.75 keV. The S–E curves were fitted using the VEPFIT program to evaluate e$^+$/Ps diffusion length (van Veen et al., 1990). The o-Ps $3\gamma/2\gamma$ annihilation ratio was also calculated by taking the ratio of the integrated counts in the range 375–460 keV to the integrated counts under 511 keV full-energy peak.

All the samples studied were also characterized by FTIR (in transmission mode) using JASCO FT-IR-420 spectrometer and XRD using a Philips X'pert Pro XRD unit.

3. Results and discussion

3.1. FTIR result

FTIR spectra of the pristine, ion-irradiated and etched polymer samples are shown in Fig. 1. The observed characteristic peaks are as follows: (i) 727 cm^{-1}: deformation of phenyl ring and bending vibration of CH$_2$ group, (ii) 972 cm^{-1}: C–H deformation out of plane, (iii) 1024 cm^{-1}: C–O–C stretching, (iv) 1342 cm^{-1}: C–C stretching of phenyl ring and vibration band of para substituted benzene ring, (v) 1726 cm^{-1}: stretching vibration of C=O, (vi) 2967 cm^{-1}: C–H stretching of CH$_2$ group and (vii) 3430 cm^{-1}: O–H group. All these characteristic bands are present in the pristine, ion-irradiated and etched samples. No new peaks are observed after ion-irradiation and etching. It may be mentioned that there is a report of the formation of–C= C–double bonds when PET is irradiated with energetic Cu ions (120 MeV) (Singh et al., 2008) while similar chemical changes are not seen for energetic C ion (70 MeV) irradiation in the PET. Singh and Prasher (2006) have reported the IR transmittance through various functional groups changes after Li (50 MeV) ion-irradiation on the PET. In the present study too, we have observed a decrease in the transmittance of the peaks like 972, 2967 and 3430 cm^{-1} corresponding to C–H and C–OH groups, in the irradiated membrane. This might be due to chain scission upon irradiation, and reaction of oxygen (from air) with radicals. On etching, the polymer becomes translucent and transmittance in the range 1800–4000 cm^{-1} decreases considerably. We have not observed any new peak in the FTIR spectra, which indicates that no other major modification in the chemical structure has taken place after low fluence ion-irradiation and subsequent etching in our samples.

3.2. XRD characterization

X-ray diffraction spectra of the pristine, ion-irradiated and etched PET are shown in Fig. 2. XRD spectrum of the pristine sample shows that it is highly crystalline. Singh et al. (2008) reported a decrease in crystallinity of PET by irradiation with copper and carbon ions to the fluence of 10^{13}–10^{14} ions/cm^2.
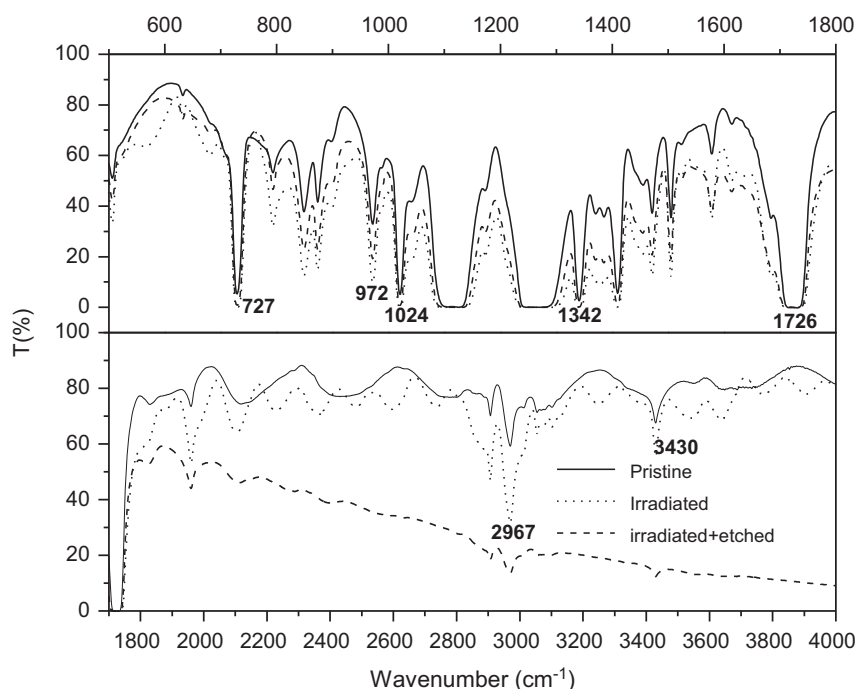
Fig. 1. FTIR spectra of the pristine, ion-irradiated and etched PET films in transmission mode. No major modification in the chemical structure on ion-irradiation is observed. Characteristic peaks have been marked in the figure.
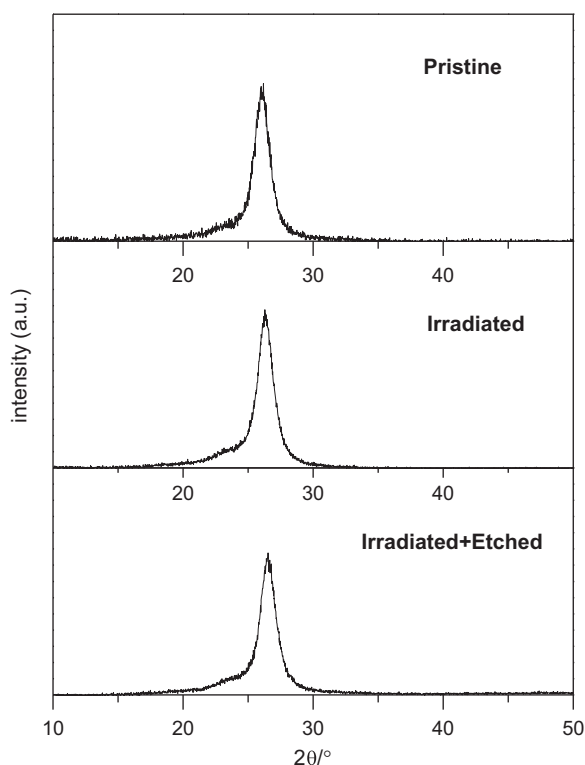

Fig. 2. XRD spectra of the pristine, ion-irradiated and etched PET films showing the negligible change in crystallinity of the PET films on ion-irradiation and etching.

In the present study, no new phase formation is observed in XRD spectra on ion-irradiation and etching probably due to the low fluence. Also, FWHM of XRD peak shows that there is no change in crystallinity of the sample after ion-irradiation and etching.

Table 1
o-Ps *pick-off* lifetime (τ_3) and intensity (I_3) evaluated from PATFIT.

Sample	PATFIT analysis	
	τ_3 (ns)	I_3 (%)
Pristine	1.95	15
Ion-irradiated	1.68	10
Etched	1.61	13

3.3. Positron annihilation lifetime spectroscopic (PALS) result

The o-Ps *pick-off* lifetime (τ_3) and the corresponding intensity (I_3) in the pristine, ion-irradiated and etched PET films are listed in Table 1. On irradiation, τ_3 decreases, indicating the reduction in size of free volumes in the bulk of the polymer. On ion-irradiation, the degree of cross-linking increases in the polymer due to the formation of radicals, which participate in new bond formation. As a result of cross-linking, size of the free volumes decreases, which results in the reduction of τ_3. The intensity I_3 decreases on ion-irradiation of the polymer, which indicates the overall reduction in the fraction of available free volumes in the bulk. The presence of some inhibitor species in the irradiated polymer sample is also possible, which may be responsible for the inhibition of Ps formation and hence the reduction in I_3.

On etching, no significant change in τ_3 was observed as compared to ion-irradiated PET. This shows that etching by NaOH has not changed the average microstructure of the bulk of the polymer. The *pick-off* intensity I_3, on the other hand, is observed to increase on etching of the ion-irradiated PET films. The increase in I_3 can be attributed to either the increase in fractional free volume or the removal of scission products and the inhibitor species due to the etching. The nature of the pore size distribution shows that the latter is more probable.

The free volume size distribution as shown in Fig. 3 has been evaluated from the Tao–Eldrup equation (Eldrup et al., 1981; Tao, 1972) using the o-Ps *pick-off* lifetime distribution obtained
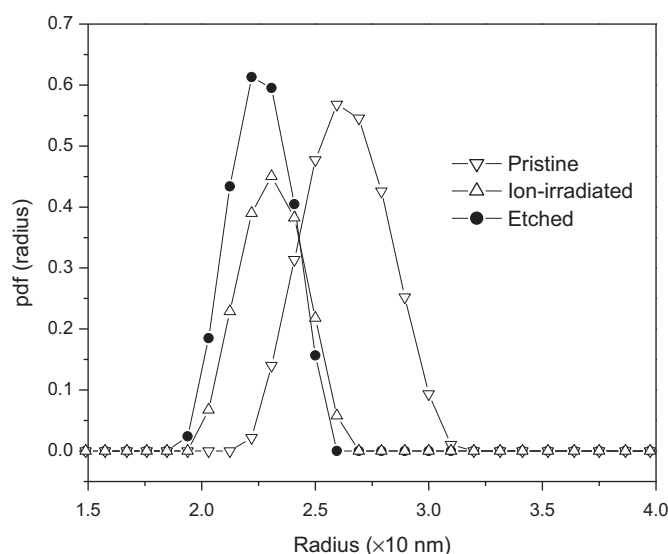
Fig. 3. Free volume radius (× 10 nm) distributions in the bulk of the pristine, ion-irradiated and etched PET films showing the reduction in free volumes on ion-irradiation.

from the CONTIN analysis. Peak positions of the size distribution are in agreement with the values obtained from the PATFIT (Table 1). FWHM of the size distribution curves for the pristine, ion-irradiated and etched polymer were observed to be 0.36, 0.24 and 0.23 nm, respectively, which illustrates that the free volume size distribution becomes narrower on ion-irradiation.

3.4. Doppler broadening spectroscopic (DBS) results using slow positron beam

The modification in the surface and near surface region due to ion-irradiation and etching on the PET membranes was probed by Doppler-broadened S-parameter measurement and $3\gamma/2\gamma$ annihilation ratio using the slow positron beam. The plots of positron implantation energy (E) vs S-parameter and $3\gamma/2\gamma$ ratio of the pristine, ion-irradiated and etched PET films are shown in Figs. 4 and 5, respectively.S–E curves of the pristine, ion-irradiated and etched PET were fitted using the VEPFIT and diffusion lengths of Ps were evaluated. The Ps diffusion lengths for the pristine, ion-irradiated and etched PET are 34.2 ± 9.3, 3.4 ± 0.5 and 4.3 ± 0.5 nm, respectively. The dramatic reduction of diffusion length on irradiation shows the formation of excess free volumes in the surface of the film caused due to the chain scission. A number of positron annihilation spectroscopic studies (Hsu and Hadely, 1971; Suzuki et al., 1992; Kobayashi et al., 1995; Dlubek et al., 2000; Saito et al., 2007) have been carried out to observe the effect of irradiation on polymer membranes. All these studies have reported (i) the formation of excess free volumes or the change in size of the free volumes due to the fragmentation of long molecular chains along with the formation of new chemical bonds (change in degrees of cross-linking) and (ii) the formation of radicals and ions (paramagnetic species) due to the breaking of bonds, which finally get converted into peroxides and carboxy groups in the presence of oxygen. The attendant changes in the polymer are reflected in the positron annihilation characteristics. In the present study, the surface S-parameter for the irradiated polymer is observed to be higher than for the pristine PET (Fig. 4) and dramatically reduces even below the pristine value in the case of the etched sample. The higher value of S-parameter for the irradiated polymer membrane indicates the presence of excess free volume or defects created as a result of chain scissioning due
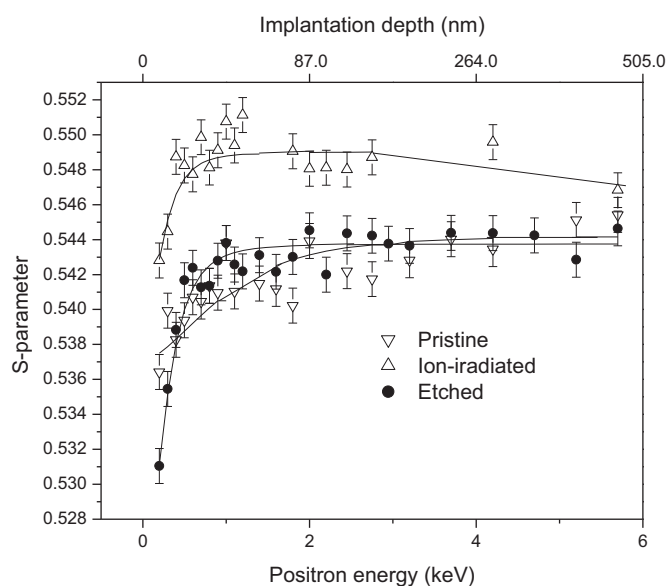

Fig. 4. Positron implantation energy (keV) vs S-parameter. Top axis shows positron implantation depth and solid lines are eye guides. Variation of S-parameter as a function of implantation energy shows the free volume fraction at the corresponding depth.
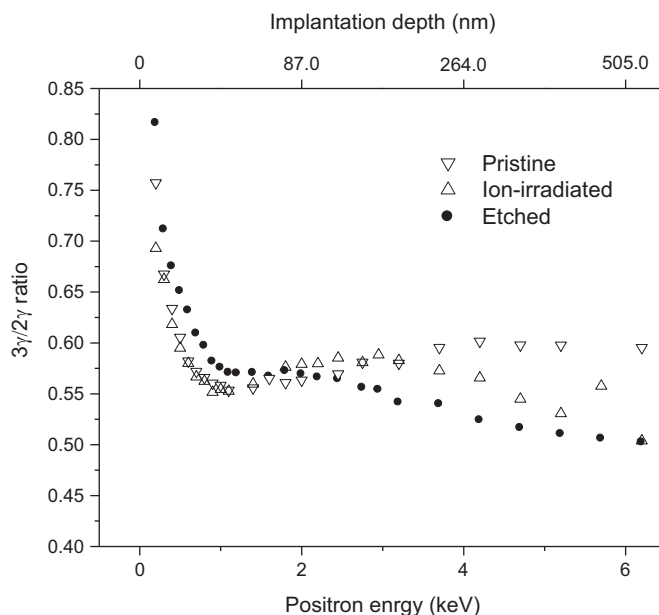

Fig. 5. Positron implantation energy (keV) vs $3\gamma/2\gamma$ ratio. Top axis shows positron implantation depth. variation of $3\gamma/2\gamma$ as a function of implantation energy shows the o-Ps re-emission from the corresponding depth.

to the irradiation. However, for the etched membrane, the surface S-parameter reduces dramatically even below that of the pristine membrane. The reduction of the surface S-parameter as compared with that in the irradiated membrane can be understood from the $3\gamma/2\gamma$ profiles for the membranes. The $3\gamma/2\gamma$ ratio (Fig. 5), signifying the Ps re-emission probability, is found to be the highest in the case of the etched sample and the lowest in the ion-irradiated sample. The increase in $3\gamma/2\gamma$ ratio at the surface reflects high surface open porosity, which may be due to the removal of chemical species formed during the irradiation by etching treatment. The re-emission of Ps from the surface of etched samples due to the surface open porosity resulted in the

decrease of surface *S*-parameter in this case. However, effect of the etching is more predominant at the surface and near surface regions, which is reflected in the large difference in *S*-parameter and $3\gamma/2\gamma$ ratio at the surface and in the bulk. The $3\gamma/2\gamma$ ratio decreases from the surface to the bulk, showing the decrease in Ps re-emission from deep inside the membranes.

It is noticeable that the effect of ion-irradiation and etching is different on the surface from that in the bulk. From the positron lifetime studies using isotope source, where the contribution to the spectra is principally from the bulk of the polymer, the free volumes were seen to decrease on irradiation. On the other hand, the free volume and porosity of the surface is increased as seen by the enhanced Ps re-emission from the etched sample. These results together show that chain scission is the principal mechanism on the surface and near surface regions on ion-irradiation while cross-linking seems to be the major effect in the bulk of the polymer. Chain scission in the surface layers might be favored due to the presence of air during the irradiation of the membrane.

4. Conclusion

The effect of energetic Cl ion irradiation and etching on PET membrane has been studied using FTIR, XRD and positron annihilation spectroscopic methods. There is neither new phase formation initiated in the membrane nor any change in crystallinity after irradiation. FTIR studies showed that no other major modification in the chemical structure has taken place after low fluence ion-irradiation and subsequent etching. The changes seen are primarily in the free volume fraction and size. It is observed through the positron annihilation characteristics that the ion-irradiation and etching result in microstructure changes of the polymer membrane but the effect of etching on irradiated membranes is more pronounced at the surface. Positron annihilation spectroscopy is seen to be a very sensitive technique to evaluate the microstructural changes selectively on the surface as well as bulk of the membrane even at very low fluence.

Acknowledgements

References

Apel, P.Yu., Blonskaya, I.V., Dmitriev, S.N., Orelovitch, O.L., Sartowska, B., 2006. Structure of polycarbonate track-etch membranes: origin of the paradoxical pore shape. J. Membr. Sci. 282, 393–400.
Coleman, P.G., 2002. Experimental techniques in positron spectroscopy. In: Jean, Y.C., Mallon, P.E., Schrader, D.M. (Eds.), Principles and Applications of Positron and Positronium Chemistry. World Scientific Publishing Co. Pvt. Ltd., Singapore, pp. 54–55.
Dlubek, G., Borner, F., Buchhold, R., Sahre, K., Krause-Rehberg, R., Eichhorn, K.-J., 2000. Damage–depth profiling of ion-irradiated polyimide films with a variable-energy positron beam. J. Polym. Sci. 38, 3062–3069.
Eldrup, M., Lightbody, D., Sherwood, J.N., 1981. The temperature dependence of positron lifetimes in solid pivalic acid. Chem. Phys. 63, 51–58.
Ferain, E., Legras, R., 1994. Track-etched membrane: dynamics of pore formation. Nucl. Instrum. Method Phys. Res. Sect. B 84, 331–336.
Hsu, F.H., Hadely Jr, J.H., 1971. Positron annihilation in irradiated Teflon. Phys. Lett. 34A, 317–318.
Itoh, N. and Tanimura, K. (Eds.), 1994. In: Proceedings of the Special issue of the Seventh International Conference on Radiation Effect in Insulator (REI-7), 1993, Nagoya, Japan, Nucl. Instrum. Methods Phys. Res. Sect. B 91, 1–700.
Kirkegaard, P., Pedersen, N.J., Eldrup, M., 1989. PATFIT-88: a data-processing system for positron annihilation spectra on mainframe and personal computers. RISO-M-2740. RISO National Laboratory, Denmark.
Kobayashi, Y., Kojima, I., Hishita, S., Suzuki, T., Asari, E., Kitajima, M., 1995. Damage–depth profiling of an ion-irradiated polymer by monoenergetic positron beams. Phys. Rev. B 52, 823–828.
Myler, U., Xu, X.L., Coleman, M.R., Simpson, P.J., 1998. Ion implant-induced change in polyimide films monitored by variable energy positron annihilation spectroscopy. J. Polym. Sci. 36, 2413–2421.
Provencher, S.W., 1982a. A constrained regularization method for inverting data represented by linear algebraic or integral equations. Comput. Phys. Commun. 27, 213–227.
Provencher, S.W., 1982b. CONTIN: a general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. Comput. Phys. Commun. 27, 229–242.
Saito, F., Yotoriyama, T., Fujji, Y., Nagashima, Y., Nakao, A., Iwaki, M., Nishiyama, I., Hyodo, T., 2007. Study of ion-irradiated polystyrene using slow positron beam. Radiat. Phys. Chem. 76, 200–203.
Schultz, P.J., Lynn, K.G., 1988. Interaction of positron beams with surfaces, thin films, and interfaces. Rev. Mod. Phy. 60, 701–779.
Sergent-Engelen, T., Halleux, C., Ferain, E., Hanot, H., Legras, R., Schneider, Y.-J., 1990. Improved cultivation of polarized animal cells on culture inserts with new transparent polyethylene terephthalate or polycarbonate microporous membranes. Biotechnol. Tech. 4, 89–94.
Singh, N., Sharma, A., Awasthi, D.K., 2003. Effects of high energy (MeV) ion beam irradiation on polyethylene terephthalate. Nucl. Instrum. Method Phys. Res. Sect. B 206, 1120–1123.
Singh, R., Samra, K.S., Kumar, R., Singh, L., 2008. Microstructural modifications in swift ion irradiated PET. Radiat. Phys. Chem. 77, 575–580.
Singh, S., Prasher, S., 2006. A comparison of modifications induced by Li^{3+} and O^{6+} ion beam to Makrofol-KG and CR-39 polymeric track detectors. Nucl. Instrum. Method Phys. Res. Sect. B 244, 252–256.
Sun, Y., Zhu, Z., Wang, Z., Jin, Y., Liu, J., Hou, M., Zhang, Q., 2003. Swift heavy ion induced amorphisation and chemical modification in polycarbonate. Nucl. Instrum. Method Phys. Res. B 209, 188–193.
Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Knodo, K., Ito, Y., 1992. Positron annihilation in irradiated and unirradiated polyethylenes. J. Polym. Sci. B 30, 517–525.
Tahara, H., Kawabata, T., Zhang, L., Yasu, T., Yoshikawa, T., 1997. Exposure of spacecraft polymers to energetic ions, electrons and ultraviolet light. Nucl. Instrum. Method Phys. Res. Sect. B 121, 446–449.
Tao, S.J., 1972. Positronium annihilation in molecular substances. J. Chem. Phys. 56, 5499–5510.
Trautmann, C., 1995. Observation and chemical treatment of heavy-ion tracks in polymers. Nucl. Instrum. Methods Phys. Res. Sect. B 105, 81–85.
van Veen, A., Schut, H., Vries, J. de Hakvroot, R.A., Ijpma, M.R., 1990. Analysis of positron profiling data by means of "VEPFIT". In: Proceedings of the Fourth International workshop on slow-positron beam techniques for solids and surfaces, AIP Conf 218, 171–198.
Xie, L., DeMaggio, G.B., Frieze, W.E., DeVries, J., Gidley, D.W., 1995. Positronium formation as a probe of polymer surfaces and thin films. Phys. Rev. Lett. 74, 4947–4950.
Zhang, L., Yasui, T., Tahara, H., Yoshikawa, T., 1997. X-ray photoelectron spectroscopy study of the interactions of O^+ and N^+ ions with polyimide films. Jpn J. Appl. Phys. 36, 5268–5274.
Zhu, Z., Kelley, M.J., 2005. IR spectroscopic investigation of the effect of deep UV irradiation on PET films. Polymer 46, 8883–8891.