

Structural, optical, thermo-mechanical and transport properties of ion irradiated polymer membranes

Vaibhav Kulshrestha^a (✉), Kamendra Awasthi^a, N.K. Acharya^a, M. Singh^a,
P.V. Bhagwat^b, Y.K. Vijay^a (✉)

^a Department of Physics, University of Rajasthan, Jaipur-302 004, INDIA

^b Nuclear Physics Division, BARC, Trombay, Mumbai-400 085, INDIA

E-mail: vaibhav_phy@rediffmail.com, yk_vijay@sancharnet.in; Fax: +91-141-2707728

Received: 18 October 2005 / Revised version: 27 December 2005 / Accepted: 10 January 2006
Published online: 27 January 2006 – © Springer-Verlag 2006

Summary

The modifications in PET induced by swift heavy ion irradiation are analyzed. PET membrane of 15 μm was irradiated by Cl^{9+} ions of 100 MeV at TIFR Mumbai. The changes due to exposure to high-energy ions were investigated by Fourier Transform Infrared (FTIR) and Ultraviolet/ Visible absorption (UV/VIS) spectroscopies, X-Ray diffraction technique, Dynamic mechanical analysis and by the Gas permeation. A significant loss of crystallinity is observed by the XRD data. Particle size or grain size calculated using Scherrer formula indicates measurable change in particle size of irradiated samples. The polymer chain scissions and structure degradations are expected to occur for irradiated samples. Optical properties of the films were changed due to irradiation that could be clearly seen in the absorption and FTIR spectra. Gas permeation through these membranes before and after irradiation using hydrogen and carbon dioxide gases shows that permeability for both gases increased after irradiation but permeability for hydrogen is higher than carbon dioxide due to its small molecular size.

Introduction

High energy ion bombardment induced modifications in polymeric materials have been attracting much attention, now a days. The energy loss mechanism of an energetic ion in solid is described via two independent processes, i.e. ion-atomic nucleus interaction which dominates at lower energies and ion-electron interactions prevalent at higher energies [1,2]. The interaction of the ions with polymer leads to bond breaking, formation of free radicals and various phenomena that are induced by the complex secondary chemical processes along the trajectory of the ions [3,4]. The ionization and electronic excitation processes are known to lead in polymers to both, chain scission and cross-linking, their ratio depending on the system. Chain scission leads to decreasing molecular weight and cross-linking to its increase. Both effect changes the polymer phase, chemical structure, crystallinity and also the molecular weight. The breaking of atomic bonds and the rearrangements of polymer structure around the ion path result in a heavily modified cylindrical area, which is called latent track [5,6]. In such a small cylinder, the energy deposited along the ion path is

extremely high and can reach several hundred eV/Å. Taking into account that the energy of carbon bonds is only few eV, this high energy deposition is sufficient to break all bonds in the track core. At lower distances, the ionization and excitations are caused by energetic electrons. The maximum range of the electron cascade depends on the ion velocity and may up to 1000 nm. The tracks of energetic ions can be used to modify the physical and chemical properties of polymers. It has been observed that the irradiation effect depend not only on the target properties but also on ion beam parameters such as ion current, fluence and energy, etc. Experiments showed that semi crystalline polymers are also amorphous after irradiation by suitable ions [7,8], resulting from scission process of the main chains of the trans configuration of the ethylene glycol residue. In this case amorphization does not mean that an atom leaves the lattice site and moves to other neighbors, in this process the long molecular chains are damaged but are not completely destroyed by the ion impacts. The localized energy deposition activates the movement of molecular chain and thus the atoms leave their position in the crystalline lattice, although the close neighbors in the chain are partially reserved [9,10]. The glass transition (T_g) is one of the most important properties exhibited by a polymer, determining its physical state and influencing other properties such as mechanical stiffness and toughness. Dynamic mechanical analysis is a good technique to study the variation in the transition regions due to the high-energy irradiation treatment of the polymers.

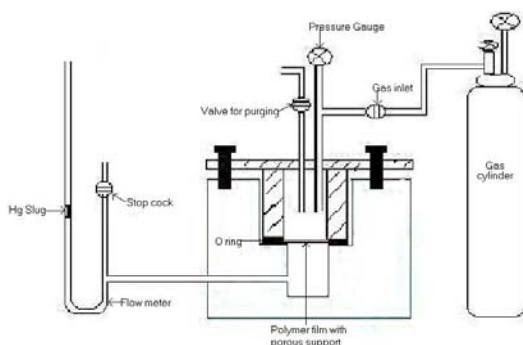
In present work chemical modifications induced by Cl^{9+} ions of 100 MeV at the ion fluences from 2×10^{10} to 3×10^{12} ion/cm², have been studied using optical spectroscopy, XRD, thermo mechanical and gas permeation measurements. The choice of Cl^{9+} ion of 100 MeV due to its lower mass number but corresponding higher electronic energy loss, which essential for track formation and the range of the of Cl^{9+} ion of 100 MeV is also much higher than the thickness of the membrane. The study of the detailed structure of ion track and its dependence on irradiation parameters is still on focus.

Experimental

The poly (ethyleneterephthalate) PET ($[-C_{10}H_8O_4-]$) membrane of thickness (15 μ m) used for the present study is commercially available. These membranes were irradiated at the fluence 2×10^{10} ion/cm², 4×10^{11} ion/cm² and 3×10^{12} ion/cm² by Cl^{9+} ion of 100 MeV. The irradiation was performed under high vacuum of order 10^{-6} torr at TIFR Mumbai. The membranes were irradiated by the scanned beam of dimension, width 1 cm. and 10 cm of length.

Permeability of hydrogen and carbon dioxide has been measured for the pristine and irradiated membranes. The gas permeability for various membranes was measured using permeability cell and the schematic diagram is illustrated in scheme 1. The pressure used for the study was 30 psi. Pressure gradient across the membrane was kept constant for a single measurement. The permeate side of cell was connected with a glass capillary of 2 mm diameter and 80 cm of height. Gas permeability was calculated by Fick's sorption-diffusion-desorption formula [11].

X-ray diffraction patterns were obtained by means of a standard PW 1840 diffractometer, working at 40 kV and 25 mA, and equipped with a scintillation counter with single channel pulse height discriminator associated counting circuitry. The $FeK\alpha$ radiation ($\lambda = 1.93604 \text{ \AA}$) was collimated with soller slits. The X-ray diffraction patterns were collected in a step-scanning mode with $\Delta 2\theta = 0.020^\circ$ Steps.



Scheme 1. The schematic of gas permeability set up

Chemical modifications have also been analysed by Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy was performed in transmission mode using NICOLET-550 FTIR spectrometer. The spectra were recorded in the wave number range of $1000-3000\text{ cm}^{-1}$. Dynamic mechanical properties were studied using a rheometric dynamic mechanical thermal analyzer. Samples were cut into strips of $20 \times 8\text{ mm}^2$, and their dynamic loss tangent ($\tan \delta$) were measured within the range of $40-150^\circ\text{C}$ at a heating rate of $3^\circ\text{C}/\text{min}$. The spectra were recorded in the tensile mode, obtaining the dynamic loss tangent ($\tan \delta$), at a frequency of 1 Hz , as a function of time. The UV/VIS measurements were carried out on a HITACHI-330 spectrophotometer in absorption mode in the wavelength range of $700-250\text{ nm}$.

Results and discussion

Gas Permeation Measurements

The effect of Swift Heavy Ions (SHI) irradiated polymeric membranes is the creation of permanent damage, the damage region was characterized by gas permeability measurements. Permeability of irradiated membranes depends on operating conditions such as temperature, pressure and composition as well as on structural features of the material.

Table 1. Permeability of H_2 and CO_2 for virgin and irradiated PET, samples

S. No.	PET (Fluence ion/ cm^2)	Permeability (barrer)*	
		H_2	CO_2
1.	Virgin	0.045	0.027
2.	2×10^{10}	0.14	0.09
3.	4×10^{11}	0.24	0.19
4.	3×10^{12}	0.36	0.28

*[1 barrer = $10^{-10}\{\text{cm}^3(\text{STP})\text{ cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cm-Hg}\}$]

Electronic energy loss corresponding to selection of ion and material in present case is 2.77 keV/nm . The tracks present in an irradiated polymer membrane are very small in size of the order of $2-6\text{ nm}$ [12] which are not visible optically. In polymers,

the permeability decreases as the permeate size increases [13]. Permeability of hydrogen for untreated PET membrane is found to be 0.045 barrer and that for carbon dioxide it is 0.027 barrer, which is well agreed with reported values [14]. But after irradiation the permeability for membrane increases, the permeability of hydrogen is found to be 0.14 barrer and that for carbon dioxide is 0.09 barrer for the 2×10^{10} ion/cm² irradiated film, which goes to 0.36 barrer for hydrogen and 0.28 barrer for carbon dioxide at the 3×10^{12} ion/cm² irradiated film, shown in table 1. The changes in the permeability for irradiated membranes are due to increase in the radii of the free volume holes [15]. As the ion fluence increases, the free volume increases, facilitating gas transport through the membrane. The permeability of the H₂ and CO₂ are different due to the difference in the kinetic diameter of the gas molecules, 2.89 Å and 3.3 Å for H₂ and CO₂ respectively.

XRD Measurements

The crystallinity loss in PET sample irradiated using Cl⁹⁺ ions was also confirmed by XRD measurements.

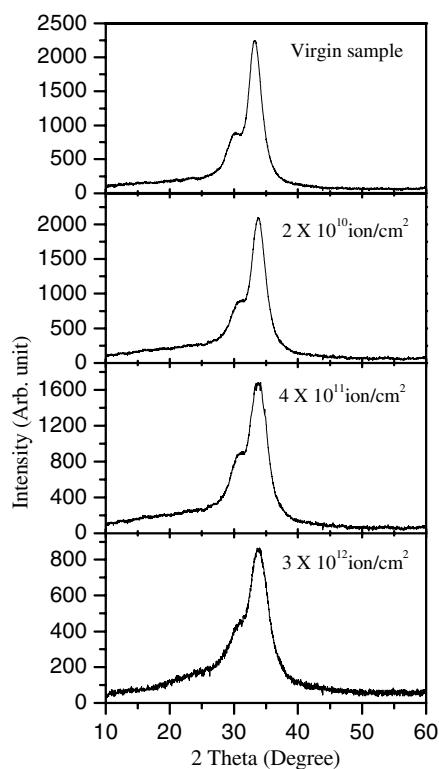


Figure 1. X-ray diffraction pattern of virgin and irradiated PET membranes

Figure 1 shows the diffraction pattern of the virgin and irradiated samples at different energies. The measurement shows that there are two well-resolved diffraction peaks. The strong peak occurs at $2\theta=33.68^\circ$ and the weak peak takes place at $2\theta=31.24^\circ$,

which corresponds to diffraction from (100) and (200) planes for strong weak peak respectively [16, 17]. It is found that after irradiation the intensity of peaks decreases, indicating the decrease of crystallinity of PET. No significant shift of peak position is observed, this implies that the lattice parameters do not change significantly [18]. The broadening of peaks suggests an evolution of polymer toward a more disorder state and also change in crystallite size on irradiation by the chlorine beam of 100 MeV.

The crystallite size of virgin and irradiated samples has been calculated using Scherrer's equation;

$$b = K\lambda / L \cos \theta$$

where, λ is the wavelength of X-ray beam, L is the crystallite size in Å, K is the constant and b the full width at half maxima (FWHM) of the peak. The crystallite size in the case of virgin sample is calculated to be 43.27 Å, but in the case of 3×10^{12} ion/cm² irradiated film, the crystallite size decreases and goes to 30.59 Å, it shows that the particle size L reduces by 29% compared to the virgin sample. The detail is shown in table 2.

Table 2. X-ray diffraction results on particle size and loss in particle size, for virgin and irradiated PET membranes

S. No.	PET (Fluence ion/cm ²)	Particle size (Å)	Loss in particle size
1.	Unirradiated	43.27 Å	--
2.	2×10^{10}	40.21 Å	7%
3.	4×10^{11}	31.31 Å	27%
4.	3×10^{12}	30.59 Å	29%

FTIR Analysis

The nature of the chemical bonds of polymers can be studied through the characterization of the vibration modes determined by infrared spectroscopy. In figure 2, the transmission spectra of PET before and after irradiation at two different doses are presented in the range 1000-3000 cm⁻¹. The findings are in detail the following,

1. The absorption of the bands at 975 and 1470cm⁻¹ due to the CH₂ bending vibration, which correspond to the crystalline phase seem to decrease with ion fluence. This may be attributed to the destruction of crystalline lamellar structure of polymer in our case.
2. However, the absorbance band at around 1100, 1375 and 1455 cm⁻¹ (attributed to the amorphous) are found to increase with the ion fluence as shown in figure 2. This probably shows amorphization.
3. An interesting result is the remarkable decrease in the absorbance of the 2360 cm⁻¹ vibration band, which corresponds to the CO₂ vibration. At the 1740 cm⁻¹ the absorbance of the band at higher fluence also decreases due to C=O stretching.
4. Further, the absorbance band at around 1850, 2880 and 2941 cm⁻¹ decreases corresponds to C-H stretching, at 2880 and 2941 cm⁻¹ bands methyl and methylene group superimposed upon O-H stretching, at the higher fluences.

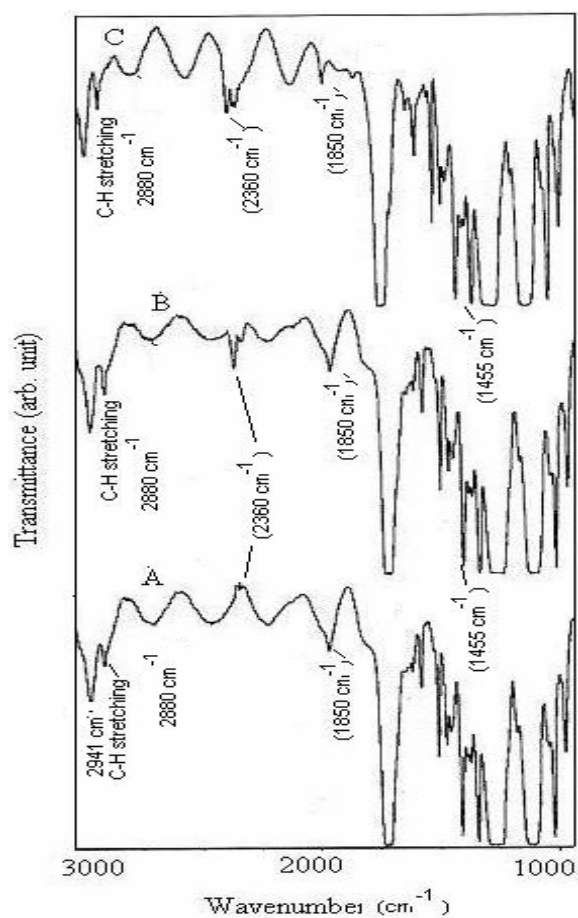


Figure 2. FTIR spectra of (A) virgin (B) irradiated with 4×10^{11} ion/ cm^2 (C) irradiated with 3×10^{12} ion/ cm^2 PET membranes

UV-VIS Measurements

Figure 3 gives the UV/VIS spectra of pristine and irradiated PET membranes. It can be seen from the figure that a strong increase in absorbance appears in the ultraviolet and visible region at high fluence.

A shift of absorption edge towards longer wavelength with increasing ion fluence can be readily observed. The shift may be produced by the creation of free radicals, ions and hot molecules due to ion irradiation and thus increases the capability of polymers to conduct. The increase in absorption may be attributed to the formation of a conjugated system of carbon bonds as a consequence of bond breaking and reconstruction include by irradiation [9]. For comparison between the pristine and irradiated samples, the spectra for high fluence are shifted along Y-axis by regular displacement [17]. The modifications in absorption are found with the change in colour of PET samples, which is transparent for the pristine film, cream colour at fluence 2×10^{10} ion/ cm^2 irradiated film, yellowish for the 4×10^{11} ion/ cm^2 irradiated film and goes to dark brown for the 3×10^{12} ion/ cm^2 irradiated film.

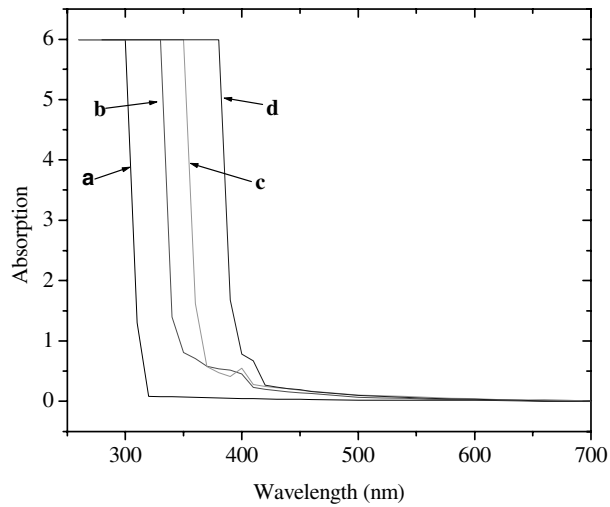


Figure 3. Graph of absorption versus wavelength for (a) virgin (b) irradiated with 2×10^{10} ion/cm² (c) irradiated with 4×10^{11} ion/cm² (d) irradiated with 3×10^{12} ion/cm² PET membranes

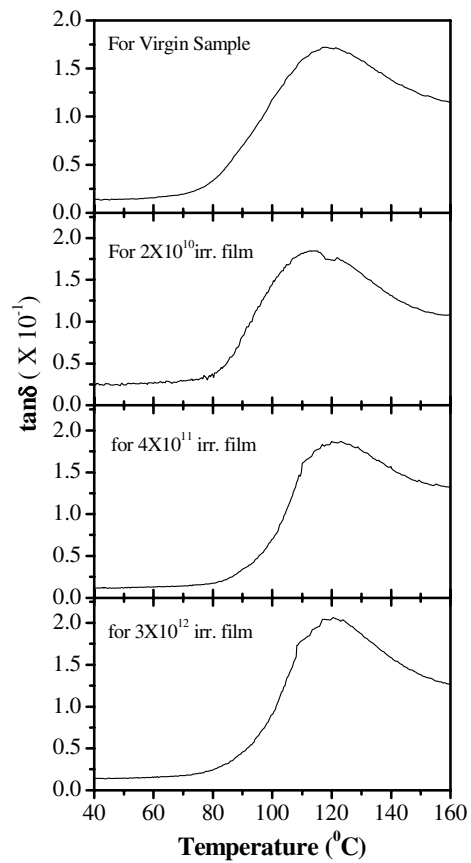


Figure 4. Temperature versus dynamic loss ($\tan \delta$) curve for PET membranes

Thermo mechanical analysis

The results of the dynamic mechanical analyzer (DMA) measurements are shown in Table 3 and Figure 4.

The $\tan \delta$ value of irradiated PET in Table 3 suggests the preferential formation of the cross-linking structure. The peak width have increased with ion fluence, in ion-irradiated PET membranes, increasing of the $\tan \delta$ was confirmed and showed a cross-linking structure induced by the ion irradiation. The $\tan \delta$ of Cl ion irradiated membrane is approximately 120% higher than that of pure PET membrane at the fluence of 3×10^{12} ions/cm² shows the decrease in crystallinity, which is due to the chain scissions and structure degradations in polymer membranes.

Table 3. Dynamic characterization by DMA

S. No.	PET (Fluence ion/cm ²)	$\tan \delta$	$T_{\tan \delta}$
1.	Unirradiated	0.172	117.7
2.	2×10^{10}	0.184	115.2
3.	4×10^{11}	0.187	123.2
4.	3×10^{12}	0.206	120.7

Conclusion

Techniques like gas permeation, X-Ray diffractometer, fourier-transform infrared transmission spectroscopy, thermo mechanical analysis and UV-VIS measurements, show the change in the crystalline and chemical structures of PET after the irradiation by the chlorine ions. Gas permeation through polymer membranes increases with increases ion fluence, due to enhancement in free volume. XRD measurements show the decrease of the peak intensity with increasing the ion fluence. Progressive loss of crystallinity is observed with increasing fluence traced by XRD measurements. FTIR and DMA results also support the increasing of the amorphisation and reduced the density of irradiated polymers, due to chain scissions and structure degradations.

Acknowledgements. Authors are indebted to TIFR, Mumbai for ion irradiation. Authors are grateful to Mrs. Prerana Mudgal & Mr. Manoj Kumar for XRD and FTIR analysis, Authors are also thankful to NSC-New Delhi, for providing financial assistance for the work.

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