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Study of microhardness and electrical properties of proton irradiated polyethersulfone (PES)

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Abstract. **Polyethersulfone (PES) films were irradiated with 3 MeV proton beams in the fluence range 10^{13}–10^{15} ions/cm^2. The radiation induced changes in microhardness was investigated by a Vickers' microhardness tester in the load range 100–1000 mN and electrical properties in the frequency range 100 Hz–1 MHz by an LCR meter. It is observed that microhardness of the film increases significantly as fluence increases up to 10^{14} ions/cm^2. The bulk hardness of the films is obtained at a load of 400 mN. The increase in hardness may be attributed to the cross linking effect. There is an exponential increase in conductivity with log frequency and the effect of irradiation is significant at higher fluences. The dielectric constant/loss is observed to change significantly due to irradiation. It has been found that dielectric response in both pristine and irradiated samples obey the Universal law and is given by $\varepsilon \propto f^{n-1}$. These results were corroborated with structural changes observed in FTIR spectra of irradiated samples.**

Keywords. **Polyethersulfone; microhardness; conductivity; dielectric response; FTIR.**

1. Introduction

The modification of polymer properties by energetic ions is a subject of widespread importance due to the increasing use of polymers in radiation environments encountered in nuclear power plants, space-crafts, sterilization irradiators, high energy particle accelerators etc (Woods and Pikaev 1994; Grossman and Gouzman 2003). The deposited energies effectively modify the chemical structures of the polymers resulting in changes to the dielectric, microhardness and thermal stability (Apel *et al* 2001). The energy transfer from bombarding ions to the target material results in a complex combination of polymer chain scission, covalent bond breaking and crosslinking. The absorption of radiation energy in sufficient amounts will affect the number of charge carriers in insulating materials to an extent as determined by its molecular structure and chemical composition. The dielectric property of the insulating material is dependent on the number and mobility of the charge carriers present in its structure. The best dielectric materials are those which contain a minimum of charge carriers and potential charge carriers which may be formed by the splitting of covalent, atomic or molecular bonds under the influence of the energetic ions. The dielectric response of a material provides information about the orientational and translational adjustment of mobile charges present in the dielectric medium in response to an applied electric field. The most important property of dielectric materials is its ability to be polarized under the action of the field. The dielectric loss behaviour of polymer films is very important because of their possible applications for insulation, isolation and passivation in micro-electronic circuits (Dang *et al* 2002). Polyethersulfone (PES) is finding extensive use in electronics due to its excellent dielectric property. There are only a few reports which mention the effects of low and high energy ions on PES. Wang *et al* (1991) studied the dose rate effects on the electrical properties of several polymers (PES, PEEK, PS, PAN and PSA) implanted by 50 keV atomic and molecular nitrogen ions. They have reported that the electrical conductivity of these polymers shows significant changes with varying dose rates. Bridwell *et al* (1991) studied the effects of 50 keV ions of He, C, B, Ar and As on PET, PAN, PES and PEEK polymers. They have reported that aliphatic or partially aliphatic polymers such as PET and PAN have lower resistivity than polymers that have more fully aromatic structures such as PEEK and PES. Evelyn *et al* (1999) irradiated stacks of thin films of PES, PS and PVC by 5 MeV helium ions and studied the radiation induced changes in chemical structure of the polymers. They observed a complex reorganization of the chemical structure. It was also reported that the disorder increases in the

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*Author for correspondence (singhnl_msu@yahoo.com) deeper irradiated layers of the polymer films due to the nuclear stopping power which increases in the deeper layer. In the present work, radiation induced changes in microhardness and electrical properties of PES at different fluences have been studied. The changes in these properties of the polymer have been corroborated with structural modifications.

2. Experimental

Four pieces of PES [$(C_{12}H_8O_{35}S)_n$; density: 1·41 g/cm^3], each of thickness, 275 μm and size, 1·5 × 1·5 cm^2, were cut from a sheet supplied by Gharda Chemicals, India. The samples were irradiated by a 3 MeV proton beam at the Physics Department, Panjab University, Chandigarh, India. The current density of the proton beam was 30 nA/cm^2 and the irradiation was carried out at fluences of 10^{13}, 10^{14}, $0·5 \times 10^{15}$ and 10^{15} ions/cm^2. The proton beam of diameter, 6 mm, was incident perpendicular to the target. The irradiation was carried out under vacuum at a pressure of 10^{-6} Torr. Consistency of data was checked by irradiating another set of films at the above fluences. To study the structural changes, including the alteration in position and intensity of characteristic bands, the FTIR spectra of all samples were recorded in the wave number range 4000–500 cm^{-1} (Bomem, Canada, model-104) with a resolution of 4 cm^{-1}. Vickers' microhardness indentation was carried out on the surface of pristine and irradiated films at different loads in the range 100–1000 mN at room temperature using a Carl Zeiss Axiotech microscope and its accessories. The electrical properties of all samples were studied after irradiation. The resistance, dielectric loss (tan δ and capacitance measurements were carried out using an LCR meter (Hewlett Packard 4284A) over a frequency range 100 Hz–1 MHz at room temperature. The a.c. conductivity was calculated using the relation

$$\sigma = (2\pi f C_p D t) A^{-1} (\Omega^{-1}\ \mathrm{cm}^{-1}).$$

The dielectric constant was calculated using the relation

$$\varepsilon = C_p/C_o,$$

where C_p is capacitance measured using the LCR meter, f the frequency, D the dielectric loss and $\varepsilon = \varepsilon_o A/t$, where ε_o is the permittivity of vacuum and A and t are the cross-sectional area and thickness of the sample.

3. Results and discussion

The electronic $(dE/dx)_e$ and nuclear $(dE/dx)_n$ stopping power profiles for 3 MeV ions transiting polymer material show that $(dE/dx)_e$ dominates at shallower penetration depths compared with $(dE/dx)_n$ which is maximum at the end of the ion track. The projected range and the electronic and nuclear stopping powers were calculated using SRIM-2000 (Ziegler 2000) code. The projected range of a 3 MeV proton beam in PES was calculated to be 115 μm, which is 2·4 times less than the thickness of PES film. The electronic stopping power $(dE/dX)_e$ and nuclear stopping power $(dE/dX)_n$ were found to be $1·07 \times 10^{-1}$ eV/Å and $6·371 \times 10^{-5}$ eV/Å, respectively.

3.1 *FTIR analysis*

Figure 1 shows the spectra of pristine and irradiated PES samples. The absorption bands as obtained from the pristine spectrum are identified as (A) 720 cm^{-1}: CH_2 absorption bands, (B) 890 cm^{-1}: C–H bending vibration, (C) 1080 cm^{-1}: C=S stretching vibration, (D) 1730 cm^{-1}: C=O stretching vibration, (E) 1950 cm^{-1}: C=C stretching vibration and (F) 3000 cm^{-1}: C–H stretching vibration. It is observed that there is no change in overall structure of the polymer but a minor change in intensities was observed up to the fluence of 10^{14} ions/cm^2. It may be concluded that PES is resistant to radiation atleast up to the fluence of 10^{14} ions/cm^2. The spectrum corresponding to the fluence of 10^{15} ions/cm^2 indicates a very significant change in the structure of polymer. This might be due to the breakage of bonds in the structure as well as formation of unsaturated structure. Further at this fluence, the surface became dark brown as seen with naked eyes and surface roughness increased (as observed under optical microscope). This may also contribute in reduction of transmitted intensity.

3.2 *Vickers' microhardness*

For microhardness tests, the indenter employed was a Vickers' pyramidal diamond indenter supplied with the

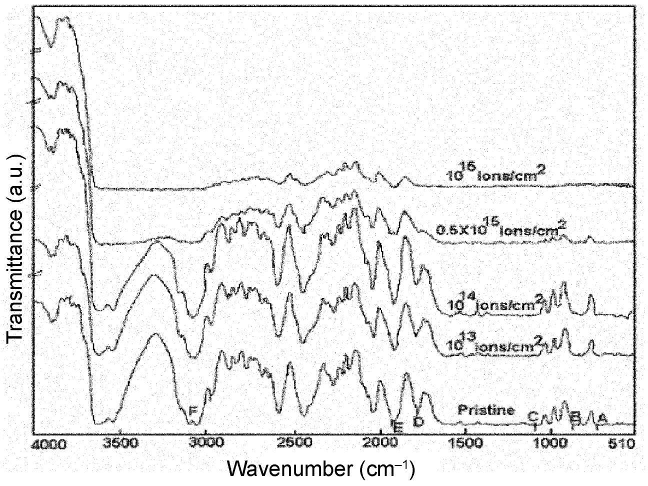

Figure 1. FTIR spectra of pristine and irradiated polyethersulfone films.

microhardness testing accessory of a Carl Zeiss optical microscope. The microhardness indentations were carried out on the surface of the pristine and irradiated films at room temperature under different applied loads from 100–1000 mN and a constant loading time of 30 s. The Vickers' diamond pyramidal hardness, H_V, is the quotient of the applied load, P and the pyramidal surface area, d^2, of the impression and is given by

$$H_\mathrm{V} = \frac{1{\cdot}854\times P}{d^2},$$

where P is the applied load in mN obtained as the product of load in g and gravitational acceleration ($g = 9{\cdot}8$ m/s^2), d the average of the two indentation marks having diagonal length in μm and H_V = Vickers' hardness in MPa. Figure 2 shows the plot of Vickers' microhardness (H_V) vs applied load (P) for pristine and irradiated films. It is evident from the figure that the H_V value increases with load up to 200 mN, and then decreases. It shows saturation beyond a load of 400 mN. The increase of H_V with load can be explained on the basis of the strain-hardening phenomenon. On applying the load, the polymer is subjected to some strain hardening and beyond certain loads the polymer exhausts its strain hardening capacity and the hardness tends to become constant. The rate of strain hardening is greater at low loads and decreases at higher loads (Singh *et al* 2004a). As can be seen, the hardness becomes independent of the loads for loads more than 400 mN. The value obtained from the saturation region, therefore, represents the true hardness of the bulk materials. Since at high loads the indenter penetration depth is also high and surface effects become insignificant. It is also observed that the hardness increases as fluence increases. This may be attributed to the cross-linking phenomenon (Lee *et al* 1997). At the fluence of 10^{15} ions/cm^2, the indentation marks were not seen because of changes in colour of sample. It became dark brown in colour. Hence, hardness could not be measured at this fluence.

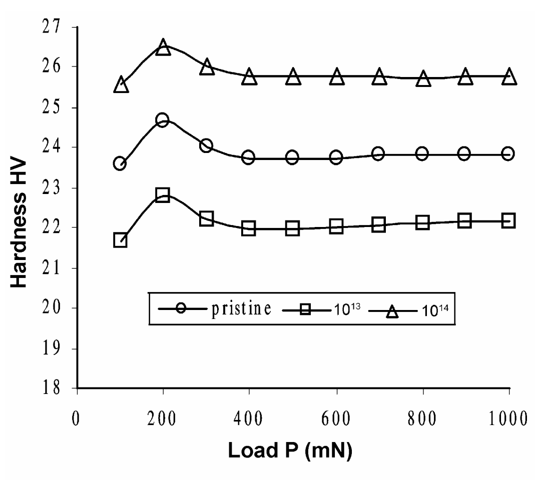

Figure 2. The plots of Vickers' hardness vs applied load for pristine and irradiated polyethersulfone films.

3.3 *A.C. conductivity*

A.C. conductivity measurement was performed for pristine and irradiated PES samples and is shown in figure 3. A sharp increase in conductivity has been observed in pristine as well as irradiated samples. It is also observed that conductivity increases as fluence increases. The increase in conductivity at a given frequency due to irradiation may be attributed to scissioning of polymer chains, resulting in an increase of free radicals, unsaturation, etc. An a.c. field of sufficiently high frequency may cause a net

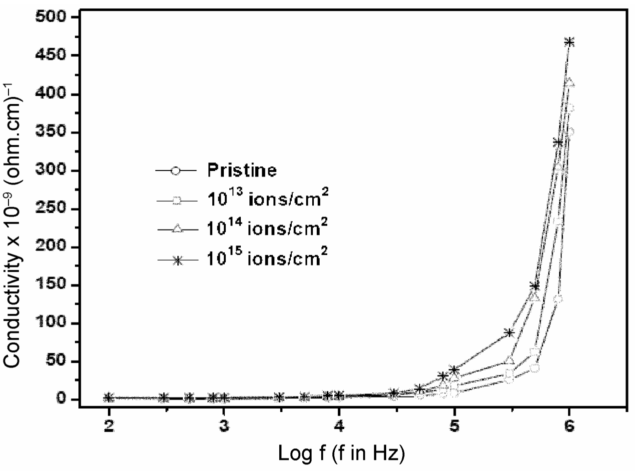

Figure 3. A.C. conductivity vs log frequency plot for pristine and irradiated polyethersulfone films.

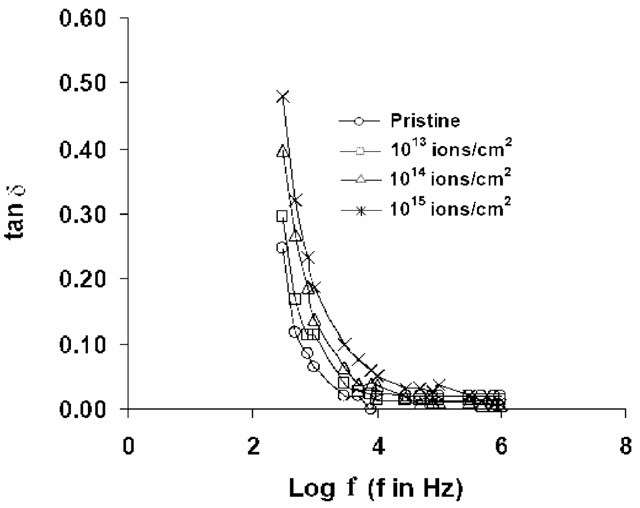

Figure 4. Variation of tan δ with log frequency for pristine and irradiated polyethersulfone films.

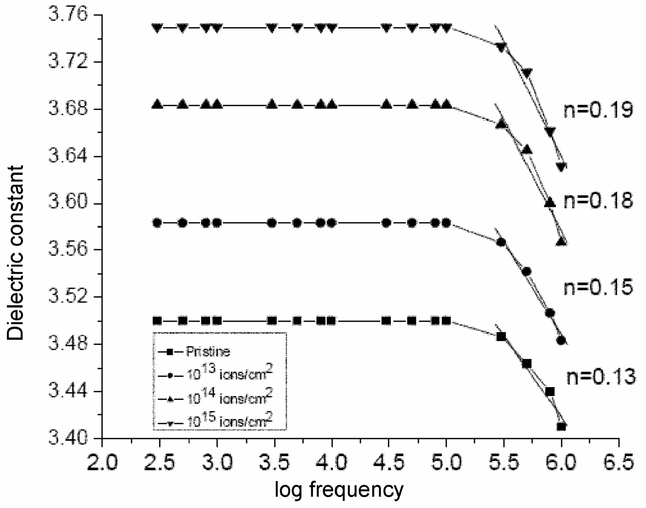

Figure 5. Plot of dielectric constant vs log frequency for pristine and irradiated polyethersulfone films.

polarization, which is out of phase with the field. This results in a.c. conductivity and it appears at frequencies greater than that at which traps are filled or emptied (Jonscher 1977; Singh *et al* 2004b). Figure 4 shows a plot of tan δ (dissipation factor) vs log frequency for pristine and irradiated PES films. It is observed that loss factor decreases as frequency increases. It is also observed that the loss factor increases moderately with fluence. The increase in loss factor with fluence may be due to scissioning of polymer chains, resulting in an increase of free radicals, unsaturation, etc. Figure 5 shows a plot of dielectric constant (ε) vs log frequency at ambient temperature for pristine and irradiated samples. As evident from the graph, the dielectric constant remains almost constant up to 100 kHz and then decreases at higher frequencies. At lower frequency, the mobility of the free charge carriers is constant and thus the dielectric constant is constant. As the frequency increases the charge carriers migrate through the dielectric and get trapped against a defect site and induce an opposite charge in its vicinity. At these frequencies, the polarization of trapped and bound charges cannot take place and hence the dielectric constant decreases. The decrease in dielectric constant at higher frequency can also be explained by Jonscher's power law i.e. $\varepsilon \propto f^{n-1}$, where n varies between zero to one ($0 < n < 1$). It is observed that the value of n increases from 0·13–0·19 on increasing the fluence (Singh *et al* 2007).

4. Conclusions

The FTIR spectra revealed that PES is a structurally radiation resistant polymer. The minor change in the intensity of functional groups of irradiated samples may be due to breakage of few bands in the ladder structure, but this will not change the overall structure of the polymer. The Vickers' microhardness of the polymer increases as fluence increases and this might be attributed to hydrogen depleted carbon network which make the polymer harder. The increase in dielectric properties due to irradiation may be attributed to scissioning of polymer chains, resulting in an increase of free radicals, unsaturation etc.

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References

Apel P Y, Blonskaya I V, Oganessian V R, Orelovich O L and Traitman C 2001 *Nucl. Instrum. Meth.* **B185** 216

Bridwell L B, Giedd R E, Wang Y Q, Mohite S S, Jahnke T, Brown I M, Bedell C J and Sofield C J 1991 *Nucl. Instrum. Meth.* **B56–57** 656

Dang Z M, Shen Y and Nan C W 2002 *Appl. Phys. Lett.* **81** 4814

Evelyn A L *et al* 1999 *Nucl. Instrum. Meth.* **B148** 1141

Grossman E and Gouzman I 2003 *Nucl. Instrum. Meth.* **B208** 48

Jonscher A K 1977 *Nature* **267** 673

Lee E H, Rao G R and Mansur L K 1997 *Mater. Sci. Forum* **248–249** 135

Singh N L, Shah N, Desai C F, Singh K P and Arora S K 2004a *Rad. Eff. Defects Sol.* **159** 475

Singh N L, Sharma A, Shrinet V, Rakshit A K and Avasthi D K 2004b *Bull. Mater. Sci.* **27** 263

Singh N L, Qureshi A, Singh F and Avasthi D K 2007 *Mater. Sci. Eng.* **A457** 195

Wang Y Q, Bridwell L B, Giedd R E and Marphy M J 1991 *Nucl. Instrum. Meth.* **B56/57** 660

Woods R J and Pikaev A K 1994 *Applied radiation chemistry: Radiation processing* (New York: John Wiley & Sons) p. 341

Ziegler J F 2000 *SRIM-2000 code, The stopping range of ions in matter* (New York: IBM Research) pp 1–28