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Characterization of Optical Modification in Polyethersulfone due to Irradiation with Si and Ne ions

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Irradiation of the polymeric materials with radiation results into the modification of their physico-chemical properties due to the transfer of high value of energy by the heavy ions causing unusual density of electron hole pairs close to the ion path. Films of 250 μm thickness of the polymer, polyethersulphone (PES) were irradiated to Si^{8+} ions of energy 100 MeV to the fluences of 1×10^{10}, 1×10^{11}, 1×10^{12} and 5×10^{12} ions/cm^2 and Ne^{6+} ions of energy 145 MeV to the fluences of 1×10^{12} and 1×10^{13} ions/cm^2. Optical modifications were characterized by UV-Vis. Spectroscopy is found to decrease with transferred energy density of the ion beams. The energy band gap (E_g) values were computed from the absorption edge in the 200-800 nm region. E_g varied from 2.68 to 1.63 eV in Si^{8+} irradiated PES samples and from 2.68 to 1.61 eV Ne^{6+} irradiated PES samples. The cluster size varied in a range of 6 to 11 carbon atoms per cluster.

Key Words: Polyethersulfone polymer, Si^{8+} ion irradiation, Ne^{6+} ion irradiation, Ion beam modification, UV-visible spectroscopy.

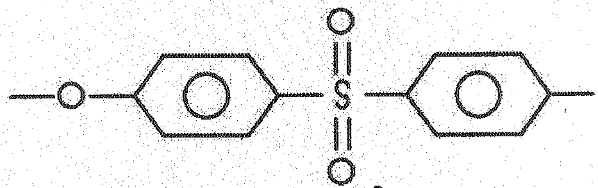
INTRODUCTION

A wide variety of material modifications in polymers have been studied by using ion irradiation technique[1-4]. Extensive researches have focused onto Swift Heavy Ions (MeV's energy), probably because of good controllability and the large penetration length in polymers. High energy ion irradiation tends to damage polymers significantly by electronic excitation and ionization. It may result into the creation of latent tracks and can also cause formation of radicals such as ablation, sputtering, chain scission and intermolecular cross-linking, creation of triple bonds and unsaturated bonds and loss of volatile fragments[2, 3]. The nature of the defects and the relative radiative sensitivity of different polymers depend on the properties such as the composition and molecular weight, on the mass and energy of the impinging ion and also on the environmental conditions during irradiation. The use of ion beam irradiation is getting high impetus as chemical composition and the related physical properties of the polymers can be modified in a controlled way by easy to control parameters like the ion fluence. Availability of heavy ions from the accelerators has brought new impetus to the field of ion beam modifications as dramatic modifications have been observed as a result of irradiation of polymers with heavy ions. The effect of ionizing radiation on polymers is generally classified into main chain scission (degradation) and cross linking. At very high fluences of ions carbonization may also take place[5]. Free radicals are created due to chemical changes caused by ionizing radiation in the polymers. These may initiate modifications such as formation of chemical bonds between different molecules; inter molecular cross linking; irreversible cleavage of bonds (scission) in the main chain, resulting into the fragmentation of molecules and the formation of saturated and unsaturated groups with stimulated evolution of gases[6].

Aromatic polymers such as Polyethersulphone (PES) are finding extensive use in electronics, particularly in sensor applications. The physical properties of these films may be tailored as has been shown that ion irradiation improves the sensor properties of PES films[7,8]. In the present comparative study of 100 MeV Si^{8+} ion and 145 MeV Ne^{6+} ion induced modifications in the optical properties of PES films and their dependence on ion fluence are investigated through UV-Vis spectroscopy.

EXPERIMENTAL

PES in the form of flat films of thickness 250 μm was procured from Good Fellow, Cambridge Ltd., England (UK) and has the structure:



The specimens of the size (1.5 × 1.5 cm^2) were prepared for irradiation. Samples were mounted on a vertical vacuum shield ladder and irradiated in General Purpose Scattering Chamber (GPSC) by 100 MeV Si^{8+} ion beam from 15 UD Pelletron accelerator at Inter-University Accelerator Centre, New Delhi to the fluences of 1×10^{10}, 1×10^{11}, 1×10^{12} and 5×10^{12} ions/cm^2. From the 145 MeV Ne^{6+} ion beam at Variable Energy Cyclotron Centre (VECC), Kolkata, irradiation was carried out to the fluences of 10^{12} and 10^{13} ions/cm^2. XY scanner was used for uniform irradiation of the film. At VECC ion beam was defocussed using a magnetic scanning system so that the film may be uniformLy irradiated. Optical, modifications have been characterized by UV-Vis spectroscopy analyses. UV-Vis spectroscopy is performed in the wavelength range 200–800 nm by Shimadzu, UV-1601 PC (Japan), UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

UV-Vis spectroscopy is an important tool for investigation as it gives an idea about the value of optical band gap energy (E_g). The absorption of light energy by polymeric materials in UV and Visible regions involves promotion of electrons in σ, π and η orbitals from the ground state to higher energy states which are described by molecular orbitals[9, 10]. Ion beam interaction with polymer generates damage which leads to the formation of new defects and new charge states.

The formation of new bands due to ion irradiations have been studied by UV-Vis spectroscopy. The results of absorption studies with UV-Vis spectrophotometer carried out on virgin and irradiated samples at higher fluences are illustrated in Fig. 1 and 2. The optical absorption spectrum of the virgin sample (Fig. 1(a)) shows a sharp decrease with increasing wavelength upto *ca.* 425 nm, followed by a plateau region. Fig.1 also shows the optical spectra for PES polymer samples after irradiation with Si^{8+} ions to the fluences of 1×10^{10}, 1×10^{11}, 1×10^{12} and 5×10^{12} ions/cm^2. Fig. 2 shows the spectra of virgin and Ne^{6+} ion irradiated samples to the fluences of 10^{12} and 10^{13} ions/cm^2. It is evident that optical absorption increases with increasing fluence and this absorption shifts from UV-Vis towards the visible region for irradiated samples. The increase in absorption may be attributed to the formation of a conjugated system of bonds due to bond cleavage and reconstruction[11].

The optical absorption method can be used for the investigation of the optically induced transitions and can provide information about the bond structure and energy gap in crystalline and non-crystalline materials[12]. The shift in absorption edge is correlated with the optical band gap energy, E_g given by: $E_g = hc / \lambda_g$

Where h is the Planck constant and c is the velocity of light. The wavelength λ_g can be determined using Tauc's expression[13] from the intersection with the abscissa of the plot of $(\varepsilon^{1/2} / \lambda)$ vs $(1 / \lambda)$ where ε is the optical absorbance and λ is the wavelength.

The number of carbon atom per conjugation length (N), for a linear structure is given by[14] $N = 2\beta\pi / E_g$

Here 2 β gives the band structure energy of a pair of adjacent π sites. The value of β is taken to be – 2.9 eV as it is associated with $\pi \rightarrow \pi^*$ optical transmission in –C=C– structure.

The values of λ_g and the corresponding results of energy gap (E_g) and the number of carbon atoms per conjugation length (N) for pristine as well as irradiated samples are reported in Table 1 and 2. Errors in optical measurements may be ± 3 %. It is observed that energy gap decreases with the increase in ion fluence. For Si ions optical band gap decreases by almost 39 % at the highest fluence of 5×10^{12} ions/cm^2.

TABLE-1

VARIATION OF ABSORPTION EDGE (Λ_G), ENERGY GAP (E_G) AND NUMBER OF CARBON ATOMS (N) PER CONJUGATION LENGTH IN PRISTINE AND Si^{8+} ION IRRADIATED SAMPLES OF PES TO DIFFERENT FLUENCES

Fluence (ions/cm^2)	Absorption edge (λ_g) (nm)	Band gap energy (eV)	N
0	463.22	2.68	6
1×10^{10}	497.21	2.50	7
1×10^{11}	498.30	2.49	7
1×10^{12}	681.05	1.82	10
5×10^{12}	762.19	1.63	11

TABLE-2

VARIATION OF ABSORPTION EDGE (Λ_G), ENERGY GAP (E_G) AND NUMBER OF CARBON ATOMS (N) PER CONJUGATION LENGTH IN PRISTINE AND Ne^{6+} ION IRRADIATED SAMPLES OF PES TO DIFFERENT FLUENCES

Fluence (ions/cm^2)	Absorption edge (λ_g) (nm)	Band gap energy (E_g) (eV)	N
0	463.22	2.68	6
1×10^{12}	698.03	1.78	10
1×10^{13}	771.54	1.61	11

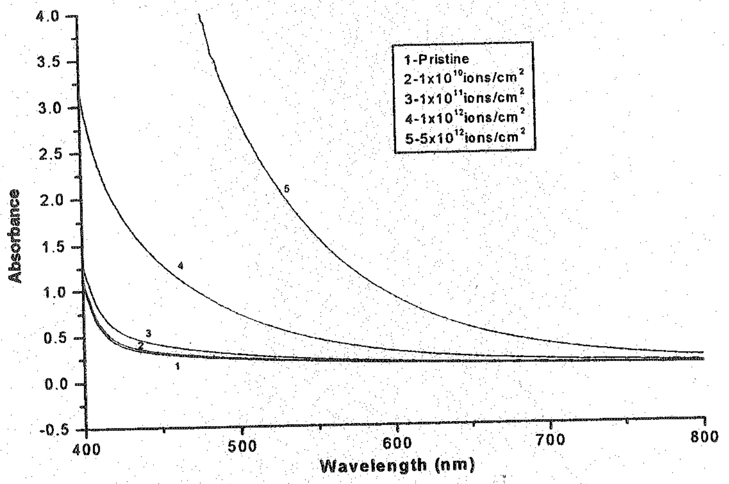


Fig. 1. Optical absorption spectra of Polyethersulphone (PES) irradiated with 100 MeV Si^{8+} ion beam

For Ne ion irradiation to the fluence of 1×10^{13} ions/cm^2, the optical band gap decreases by almost 40%. Earlier studie[15-18] on different polymers have indicated that the carbon enriched domains created in polymers during irradiation are responsible for the decrease in band gap.

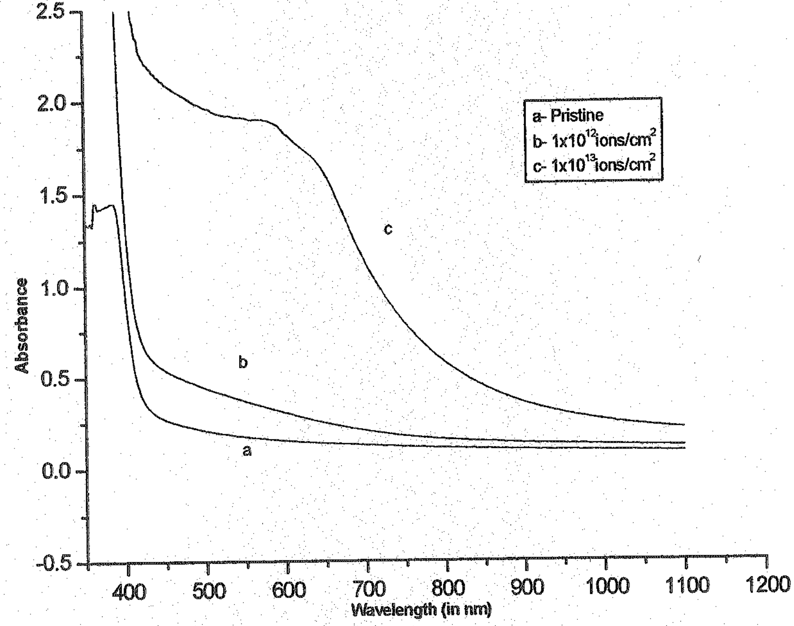


Fig. 2. Optical absorption spectra of Polyethersulphone (PES) irradiated with 145 MeV Ne^{6+} ion beam

Conclusion

It is observed that energy gap decreases with the increase in ion fluence. Optical band gap decreases by almost the same amount for both the ions irradiation. It is found that cluster size increases with transferred energy density for both the ions.

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REFERENCES

1. E. Balanzat and S. Bouffard, A. Le Moel and N. Betz, *Nucl. Instr. Meth.B*, **91**, 140 (1994).
2. E.H. Lee, *Nucl. Instr. Meth. B*, **29**, 151 (1999).
3. S. Bauffard, B. Gervais and C. Leray, *Nucl. Instr. Meth. B*, **1**, 105 (1995).
4. D.M. Ruck, *Nucl. Instr. Meth. B*, **602**, 166 (2000)
5. J.P. Durand, A.L. Moel. *Nucl. Instr. Meth. B*, **105**,71(1995).
6. D. M. Ruck, J. Schulz, N. Deusch, *Nucl. Instr. Meth. B*, **131**,149(1997).
7. R. Buchhold and B. Gassensoren, Dresden University Press, Dressden and Munich, (1999).

8. M. Guenther, K.Sahre, G. Suchaneck, G.Gerelach K.J. Eichhorn, *Surf. Coat. Tech.*, **482**, 142 (2001).
9. R. Kumar, R. Prasad, Y.K. Vijay, N.K. Acharya, K.C. Verma and U. De, *Nucl. Instr. Meth. B*, **212**, 221 (2003).
10. J.R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, NJ: Prentice-Hall Inc. (1994).
11. L.S. Farenza, R.M. Papaleo, A. Hallen, M.A. Araujo, R.P. Livi and B.U.R. Sundqvist, *Nucl. Instr. Meth. B*, **105**, 134 (1995).
12. R. Mishra, S. P. Tripathy, D. Sinha, K.K. Dwivedi, S.Ghosh, D.T. Khating. M. Muller, D. Fink, W.H. Chung, *Nucl. Instr. and Meth., B*, **168**, 59 (2000).
13. J. Tauc, R. Grigorovici and A. Vaneu, *Phys. Status Solids*, **15**, 627 (1996).
14. D. Fink, W.H. Chug, R. Klett, A. Schmoidt, J. Cardosa, R. Montiel, M.H. Vazquez, L. Wang, F. Hosoi, H.Omichi and P. Oppelt-Langer, *Radiat. Eff. Defects Solids*, **133**, 193 (1995).
15. D. Fink, R. Klett, L.T. Chaddertan, J. Cardosa, R. Montiel, M.H. Vazquez and A. Karanovich, *Nucl. Instr. Meth. B*, **111**, 303 (1996).
16. Saha, V. Chakaraborty and S.N. Chintalpudi, *Nucl. Instr. Meth. B*, **168**, 245 (2000).
17. H.S. Virk, P.S. Chandi and A.K. Srivastava, *Nucl. Instr. Meth. B*, **183**, 329 (2001).
18. T. Phukan, D. Kanjilal, T.D. Goswami and H.L. Das, *Radiat. Measur.*, **36**, 611 (2003).