

Indian J. Phys. **83** (7), 969-976 (2009)



Study of optical band gap and carbon cluster sizes formed in 100 MeV Si⁸⁺ and 145 MeV Ne⁶⁺ ions irradiated polypropylene polymer

Rajesh Kumar^{1*}, S Asad Ali¹, A. H. Naqvi¹, H. S. Virk², Udayan De³,
D K Avasthi⁴ and Rajendra Prasad¹

¹Department of Applied Physics, Z. H. College of Engineering & Technology,
Aligarh Muslim University, Aligarh-202 002, Uttar Pradesh, India

²360 Sector-71, SAS Nagar (Mohali), Chandigarh-160 071, Punjab, India

³Variable Energy Cyclotron Centre, 1/AF, Bidhan Nagar, Kolkata-700 064, India

⁴Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110 067, India

E-mail : drrajesh04@rediffmail.com

Abstract : A wide variety of material modifications in polymers have been studied by using ion irradiation techniques. Extensive research has focused on to 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 volatile fragments. Polypropylene polymer films of thickness 50 μm were irradiated to the fluences of 1×10^{10} , 3×10^{10} , 1×10^{11} , 3×10^{11} , 6×10^{11} and 1×10^{12} ions/cm² with Si⁸⁺ ions of 100 MeV energy from Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi and Ne⁶⁺ ions of 145 MeV to the fluences of 10^8 , 10^{10} , 10^{11} , 10^{12} and 10^{13} ions/cm³ from Variable Energy Cyclotron Centre, Kolkata. Optical modifications were characterized by UV towards the red end of the spectrum with the increase of the fluence. Value of optical band gap E_g shows a decreasing trend with ion fluence irradiated with both kinds of ions. Cluster size N , the number of carbon atoms per conjugation length increases with increasing ion dose. Cluster size also increases with the increase of electronic stopping power.

Keywords : Polypropylene polymer, silicon and neon ions, ion beam modification, carbon clusters, band gap energy.

PACS Nos. : 42.88+h, 78.70.Bj, 71.20.Rv

* Corresponding Author

1. Introduction

The potential of polymers has been proved in all fields of life and especially in medical sciences, electronics and space research. The intensified interest in polymers stems from their low cost, easy processability and light weight, besides, some special physico chemical properties exhibited by polymers such as ion transport, redox behavior, electrochemical effects, photo activity, catalytic agents and electronic junction effects. When a polymer target is bombarded with highly energetic charged ion, it loses most of its energy in exciting/ionizing the atoms along its trajectory. 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 [1–3]. Target ionization may cause bond cleavages and formation of free radicals, which are responsible for most of the chemical transformation observed in the polymer films [4]. 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. 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. Carbonaceous cluster, which are supposed to be carriers in electrical conductivity, are formed along the latent tracks of energetic ions in polymers. The formation of these clusters in polymer films with ion irradiation has been investigated extensively [6–8].

In the early years, ion beam modification was brought about by using low ionizing beam comprising mainly of fast electrons, low energy ions, gamma rays, X-rays *etc.* The availability of heavy ion accelerator has brought new impetus to the field of ion beams modification as dramatic modifications in polymeric material have been observed [9–14]. It has been reported that swift heavy ion irradiation in polymers leads to an increase in light absorption mainly in shorter wavelength region [15]. In the present investigations comparative study of 100 MeV Si⁸⁺ ion and 145 MeV Ne⁶⁺ ion induced modifications in the optical properties of polypropylene (PP) films and their dependence on ion parameters are carried out through UV-Vis spectroscopy.

2. Experimental details

Polypropylene (PP) in the form of flat films of thickness 50 μm was procured from Good Fellow, Cambridge Ltd. England (U K). The specimens of the size (1.5 \times 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 Si⁸⁺ ion beam from 15 UD Pelletron accelerator at Inter University Accelerator Centre, New Delhi to the fluences of 1×10^{10} , 3×10^{10} , 1×10^{11} , 3×10^{11} , 6×10^{11} and 1×10^{12} ions/ cm^2 . Irradiation with 145 MeV Ne⁶⁺ ion beam was carried out at Variable Energy Cyclotron Centre (VECC), Kolkata to the fluences of 10^8 , 10^{10} , 10^{11} , 10^{12} and 10^{13} ions/ cm^2 . The ion

beam was defocused using a magnetic scanning system so that the film may be uniformly irradiated. The beam current was kept below (10 nA) to suppress thermal decomposition. Optical modifications are characterized by UV-Vis spectroscopy analyses. Ultraviolet-Visible (UV-Vis) spectroscopy is performed in the wavelength range 200–800 nm by SHIMADZU, UV-1601 PC (Japan) UV-Visible spectrophotometer.

3. Results and discussion

Ultraviolet-Visible (UV-Vis) spectroscopy is an important tool for the investigation which gives us an idea about the value of optical energy gap (E_g) and is thus an ideal tool for the investigation of carbonaceous clusters. The absorption of light energy by polymeric materials in UV and Visible regions involves promotion of electrons in σ , π and n orbitals from the ground state to higher energy states which are described by molecular orbital [16]. 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 has been studied by UV-Visible spectroscopy. The results of absorption studies with UV-Vis spectrophotometer carried out on virgin and irradiated polypropylene (PP) samples are shown in Figures 1 to 4.

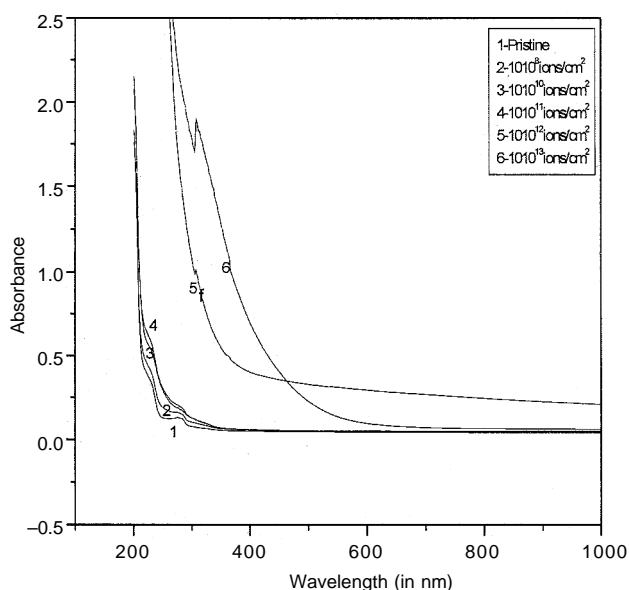


Figure 1. Optical absorption spectra of polypropylene (PP) polymer, pristine and irradiated with 145 MeV Ni^{8+} ion beam.

The optical absorption spectrum of the virgin sample shows a sharp decrease with increasing wavelength followed by a plateau region. Figure 1 show the optical spectra for PP polymer samples after irradiation with Si^{8+} ion to the fluences of 1×10^{10} , 3×10^{10} , 1×10^{11} , 3×10^{11} , 6×10^{11} and 1×10^{12} ions/cm² and Figure 2 shows the optical spectra of PP polymer samples after irradiation with Ne^{6+} ion to the fluences of 10^8 , 10^{10} ,

10^{11} , 10^{12} and 10^{13} ions/cm² respectively. 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 [17].

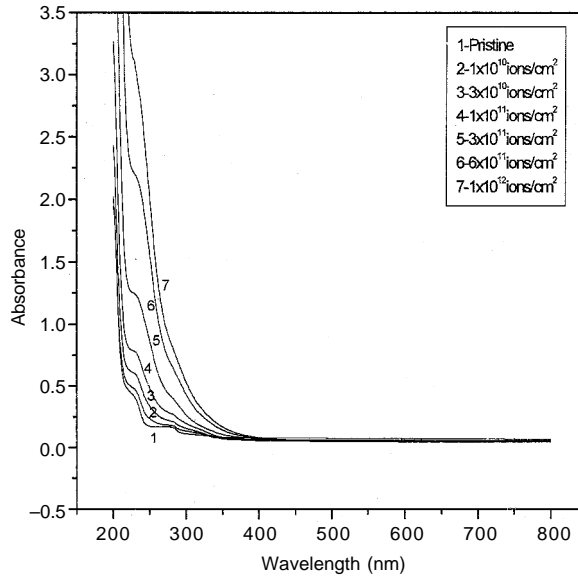


Figure 2. Optical absorption spectra of polypropylene (PP) irradiated with 100 MeV Si⁸⁺ ion beam.

The damage of sharpness decreases with increasing dose which indicates towards the increased damage in the films as the fluence is increased. 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 matter [18]. Optical band edge can be correlated to energy band gap E_g by Tauc equation [19] :

$$\omega^2 \varepsilon_2(\lambda) = (\hbar \omega - E_g)^2$$

where $\varepsilon_2(\lambda)$ is the optical absorbance, λ the wavelength and $\omega = 2\pi\nu$ is the angular frequency of the incident radiation. From the plot of $\sqrt{\varepsilon_2} / \lambda$ vs $1/\lambda$ value of E_g can be found. The intersection of the extrapolated spectrum with the abscissa yields the gap wavelength λ_g from which the energy gap $E_g = hc/\lambda_g$ is derived. The number of carbon hexagon rings in the cluster 'N' can be found from the Robertson relation [20] :

$$E_g = \frac{2\beta}{\sqrt{N}} \text{ eV} .$$

Here 2β is the band structure energy of a pair of adjacent π sites and its value is taken as -2.9 eV for a six numbered carbon ring Fink *et al* have pointed out that the Robertson equation under estimates the cluster size in irradiated polymers. Thus the structure of the cluster was assumed to be like a buck minister fullerene, that is, a C_{60} ring instead of C_6 and the relation emerges :

$$E_g = \frac{34.3}{\sqrt{N}} \text{ eV}$$

where N is the no. of carbon atoms per cluster in the irradiated polymer. Above relation has been used to calculate obtained the no. of carbon atoms per cluster in the irradiated samples.

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 presented in Tables 1 and 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 100 MeV Si^{8+} ion irradiated samples of PP to different fluences.

Fluence (ions/cm ²)	Absorption edge (λ_g) (nm)	Band gap energy (eV)	N
0	225.32	5.52	38
10^{10}	227.43	5.47	39
3×10^{10}	233.85	5.32	41
1×10^{11}	242.78	5.12	44
3×10^{11}	246.10	5.05	46
6×10^{11}	260.38	4.77	51
1×10^{12}	286.79	4.33	62

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 PP to different fluences.

Fluence (ions/cm ²)	Absorption edge (λ_g) (nm)	Band gap energy (eV)	N
0	228.27	5.45	39
10^8	229.68	5.41	40
10^{10}	232.11	5.36	41
10^{11}	233.57	5.32	42
10^{12}	352.65	3.53	94
10^{13}	458.87	2.71	160

Errors in optical measurements may be $\pm 3\%$. It is observed that energy gap decreases with the increase in ion fluence. Optical band gap decreases by almost 21% at the highest fluence of 1×10^{12} ions/cm² for Si⁸⁺ ion irradiation whereas for Ne⁶⁺ ion irradiation

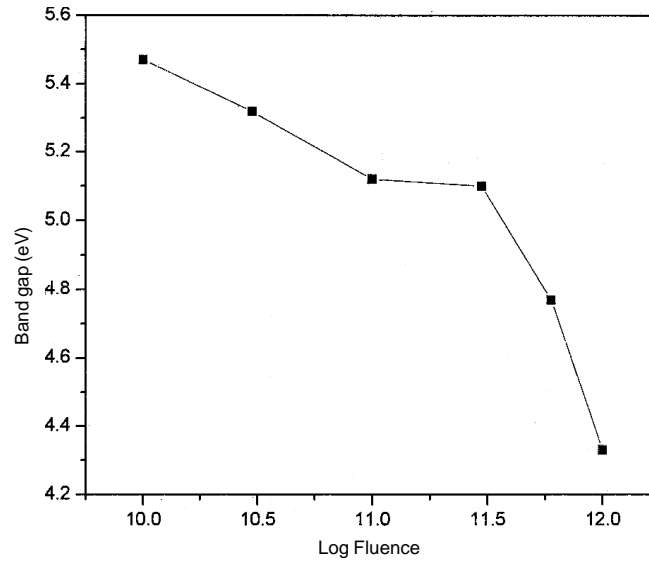


Figure 3. The variation in band gap energy with Si⁸⁺ ion irradiation fluences.

the change is 50% at the highest fluence of 10^{13} ions/cm² and earlier studies [21–23] have indicated that the carbon enriched domains created in polymers during irradiation are responsible for the decrease in band gap.

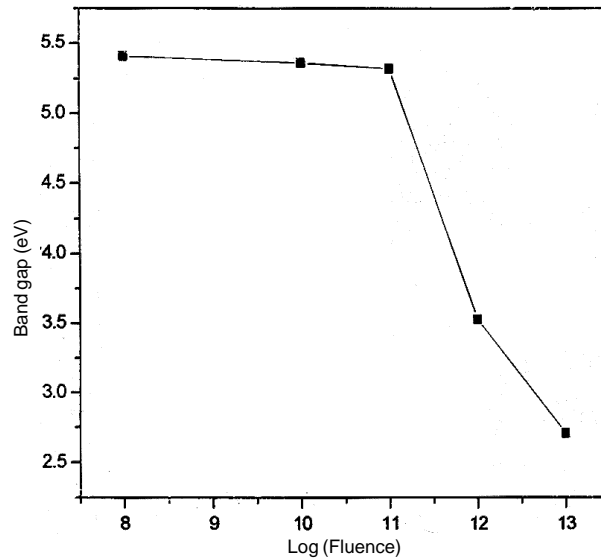


Figure 4. The variation in band gap energy with Ne⁶⁺ irradiation fluences.

4. Conclusions

UV-Vis analysis shows that there are significant modifications in optical properties of polypropylene irradiation with 100 MeV Si⁸⁺ ions and 145 MeV Ne⁶⁺ ions. UV-Vis studies reveal that optical energy gap decreases by 21% at the highest fluence of 1×10^{12} ions/cm² for Si⁸⁺ ion irradiation whereas for Ne⁶⁺ ion irradiation the change is 50% at the highest fluence of 10^{13} ions/cm². It is found that cluster size increases with transferred energy density for both the ions.

Acknowledgments

One of the authors, Prof. Rajendra Prasad is thankful to All India Council of Technical Education, Government of India for providing Emeritus Fellowship to carry out this work. Financial assistance provided by Department of Science & Technology (DST), Government of India to Dr. Rajesh Kumar as Young Scientist (Award No. SR/FTP/PS-31/2004) is gratefully acknowledged.

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