

Indian J. Phys. **83** (7), 955-961 (2009)



Spectroscopic studies of copper and carbon ion irradiated polypropylene

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Abstract : The samples of polypropylene (PP) have been irradiated with 120 MeV $^{64}\text{Cu}^{9+}$ and 70 MeV $^{12}\text{C}^{5+}$ ion beams, with the fluence ranging from 1×10^{13} to 1×10^{11} ions/ cm^{-2} . UV-VIS and FTIR techniques have been used to study the chemical and optical properties of these irradiated polymers. UV spectra revealed that the optical-gap energy decreases by 54 % with copper ion irradiation at the fluence of 1×10^{13} ions/ cm^2 , whereas at the same fluence, carbon beam decreases the optical-gap energy by 20%. FTIR analysis of ion irradiated samples revealed the presence of $-\text{OH}$, $\text{C} = \text{O}$ and $\text{C} = \text{C}$ bonds. Alkyne formation has been observed only in the case of copper ion irradiation.

Keywords : Polypropylene, optical-gap energy, UV-VIS and FTIR techniques.

PACS No. : 71.20.Rv

1. Introduction

When a swift heavy ion enters a polymer target, it loses most of its energy in exciting and ionizing the atoms along its trajectory. The high value of energy deposited in a very small cylindrical region around the ion path, called latent track, leads to dramatic modifications in the target material [1-3]. The changes induced are dependent upon the material, parameters of ion beams and the environment of irradiation process. The induced effects are responsible for altering the properties of the material, which can be determined by different analytical techniques. The UV-visible absorption studies of ion-irradiated polymers provide information regarding the variation in optical band gap [4]. The chemical changes caused by ionizing radiations involve the main-chain scission, cross-linking, creation of free radicals and formation of saturated and unsaturated groups with stimulated evolution of gasses [5-7].

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In the present work, PP film samples have been irradiated with carbon (70 MeV) and copper (120 MeV) ion beams. The electronic energy loss of carbon (70 MeV) and copper (120 MeV) ions in PP are 2.52×10^2 and 5.11×10^3 keV/ μm respectively. We expect that large difference in energy deposition would lead to different response of PP towards these beams. So, the induced modifications have been analyzed with regard to the optical and structural properties.

2. Experimental details

Polypropylene (PP) specimen in the form of flat polished film was procured from Good Fellow Ltd. (England). Without any further treatment, a set of samples of the size (1×1 cm²) samples was irradiated with copper (120 MeV) ion beam available from the 15UD Pelletron accelerator at the Inter University Accelerator Center (IUAC), New Delhi, India. Another set of similar samples was irradiated with carbon (70 MeV) ion beam. The fluence was varied from 1×10^{11} to 1×10^{13} ions cm⁻². A vacuum of the order of $\sim 4 \times 10^{-6}$ Torr was maintained during the irradiation. The beam current was kept low to suppress thermal decomposition and was monitored intermittently with a Faraday cup. Two techniques have been employed to study the irradiation-induced effects in PP. The samples were analyzed with UV-VIS spectroscopy in transmission mode using Hitachi Modal U-3000 spectrophotometer in the range 200-800 nm to observe the variation in optical band gap (E_g). The chemical-changes were studied using Nexus 870 FTIR Spectrometer in the range 4000-500 cm⁻¹.

3. Results and discussion

The results of this study are discussed in two parts.

3.1. UV-VIS analysis :

The study of the optical absorption particularly the absorption edge, is a useful method for investigating the optically induced transitions. It provides information about both the band structure and optical energy gap in materials. The polymer irradiation leads to a shift in the optical absorption edge towards longer wavelengths, which indicates a lowering of the energy gap. This is related to the formation of clusters with rings or due to the formation of conjugated double bonds or quinonic structures [4]. This shift can be correlated with optical band gap E_g by expression [8] :

$$\omega^2 \varepsilon_2(\lambda) = (\hbar\omega - E_g)^2. \quad (1)$$

Here $\varepsilon_2(\lambda)$ is the imaginary part of the complex refractive index *i.e.* the optical absorbance, and λ is the wavelength. E_g is usually derived from the plot between $\sqrt{\varepsilon_2/\lambda}$ and $1/\lambda$. The intersection of the extrapolated spectrum with the abscissa yields the gap wavelength

λ_g , from which the gap energy is derived to be

$$E_g = hc/\lambda_g \quad (2)$$

UV-Vis absorption spectra of ion irradiated polypropylene film samples are represented in Figures 1 and 2.

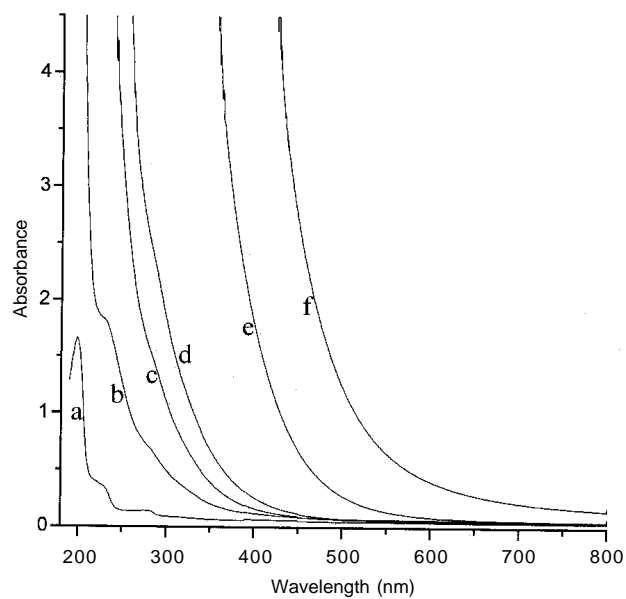


Figure 1. UV-VIS spectra of PP irradiated with 120 MeV copper ions at the fluence of (a) 0, (b) 1×10^{11} ; (c) 5×10^{11} , (d) 1×10^{12} , (e) 5×10^{12} , (f) 1×10^{13} ions cm^{-2} .

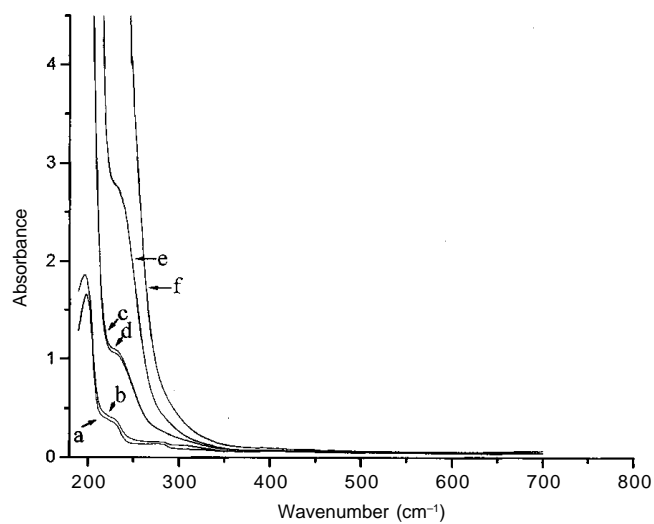


Figure 2. UV-VIS spectra of PP irradiated with 70 MeV carbon ions at the fluence of (a) 0, (b) 1×10^{11} , (c) 5×10^{11} , (d) 1×10^{12} , (e) 5×10^{12} , (f) 1×10^{13} ions cm^{-2} .

The value of absorption edges and the corresponding optical band-gap energies are given in Table 1. The virgin sample has absorption edge at 196 nm with corresponding optical energy-gap energy as 6.33 eV. The pronounced shift in absorption edge is observed with Cu-120 MeV ion beam, and optical edge shifted to 424 nm, with optical band-gap energy 2.93 eV. Thus a change of $\sim 54\%$ is there in the optical gap energy at the highest fluence of 1×10^{13} ions cm^{-2} . Carbon beam showed a very feeble shift up to the fluence of 1×10^{12} ions cm^{-2} , as the edge shifts up to 216 nm. At the highest fluence (1×10^{13} ions cm^{-2}), this absorption edge shifted to 245 nm, with corresponding optical-gap energy of 5.07 eV. So, there is a change of $\sim 20\%$ in the optical-gap energy with carbon ion irradiation at the highest fluence of 1×10^{13} ions cm^{-2} .

Table 1. Absorption edge and optical-gap energy in virgin and irradiated samples of polypropylene (PP).

Ion Beam	Fluence	Absorption edge (λ_g) (nm)	Optical-gap energy (E_g) (eV)
Virgin Sample	–	196	6.33
	1×10^{11}	206	6.04
	5×10^{11}	238	5.22
Cu (120 MeV)	1×10^{12}	258	4.82
	5×10^{12}	355	3.51
	1×10^{13}	424	2.93
	1×10^{11}	198	6.28
C (70 MeV)	2.5×10^{11}	204	6.08
	1×10^{12}	206	6.03
	5×10^{12}	216	5.74
	1×10^{13}	245	5.07

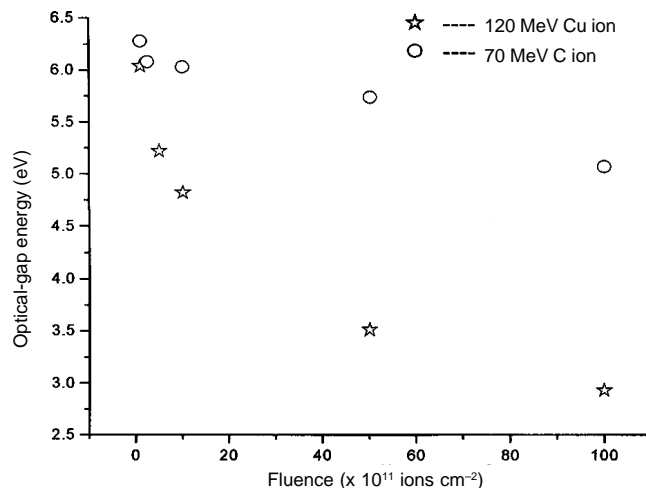


Figure 3. Variation of optical gap energy with respect to ion fluence.

The variation in optical energy gap of PP with ion fluence for the two ion beams has been presented in Figure 3. We observe that the effect of the copper (120 MeV) ion beam is very pronounced in modifying the optical gap as compared to carbon ion beam (70 MeV). This might be attributed to very high energy-loss of copper ions in comparison to that of carbon ions.

3.2. FTIR analysis :

FTIR spectrum of the virgin PP sample (Figure 4) reveals strong absorption in the range $2840\text{--}3000\text{ cm}^{-1}$ due to sp^3 C-H stretch, along with strong bands near 1458 and 1376 cm^{-1} due to bending absorptions of CH_2 and CH_3 groups, respectively, which are characteristics of polypropylene.

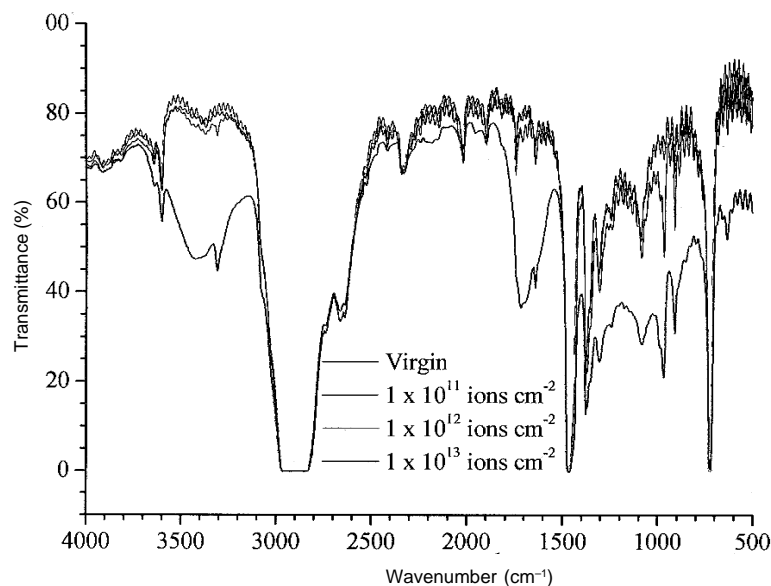


Figure 4. FTIR spectra of PP irradiated with 120 MeV copper ions.

FTIR spectra of 120 MeV copper ion irradiated samples (Figure 4) reveal that with the increase in ion fluence, there appears a new band near 3422 cm^{-1} , which is attributed to O-H stretching. Also, a band starts growing near 1715 cm^{-1} that indicates the presence of C = O bonds. These might have been formed due to the reaction of the polymer with atmospheric oxygen/ H_2O (moisture). The reaction might have taken place in the chamber during irradiation as the vacuum of few micro-torr is not sufficient to remove all the oxygen/ H_2O (moisture) contents. In addition to this post irradiation factor is also a probable factor for the formation of such bonds. Similar results have been reported in case of heavy ion irradiated polymers [9-10]. Another significant observation is the growth of band near 3310 cm^{-1} on irradiation, which is characteristic sp -hybridized C-H stretching mode of alkyne end group. In addition to above, sp^2 -hybridized C-H stretch occurring at 3074 cm^{-1} , along

with = C–H out of plane bending at 910 cm^{-1} and C = C stretch at 1640 cm^{-1} suggests the formation of unsaturations in the polymer chains (double bonds).

Figure 5 shows the FTIR spectra of 70 MeV carbon ion irradiated PP samples, with the fluence ranging from 1×10^{11} to 1×10^{13} ions cm^{-2} . It is observed that there are no significant changes in the polymer on irradiation. Weak band of sp^2 -hybridized C–H stretch at 3074 cm^{-1} , out of plane = C–H bending at 910 cm^{-1} and C = C stretch at 1640 cm^{-1} , are observed suggesting a little presence of chain-unsaturations in the carbon ion irradiated PP samples. Alkyne formation has not been observed with carbon beam irradiation. So, it is expected that the formation of alkyne requires remarkable reorientation of the polymer which can be possible with the ion transferring high energy within a very short time while traversing the polymer.

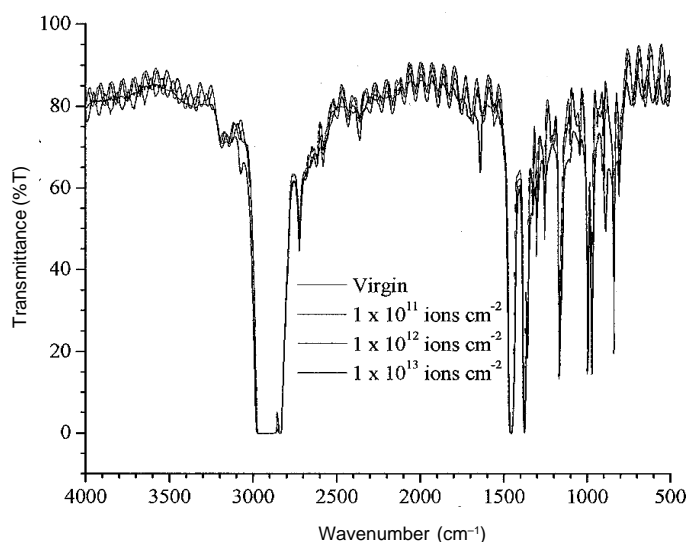


Figure 5. FTIR spectra of PP irradiated with 70 MeV carbon ions.

4. Conclusion

UV-VIS and FTIR studies reveal that there are significant modifications in the optical and structural properties of PP on carbon and copper ion irradiation. The optical absorption studies reveal that the optical energy gap decreases by 20% on carbon irradiation at fluence of 1×10^{13} ions cm^{-2} , whereas with the copper beam, at the same fluence, a decrease of 54% has been found. FTIR analysis reveal the formation of O–H, C=O and C=C bonds on ion irradiation. But the effect of copper beam has been more pronounced both in reducing the optical-gap and the formation of new bonds. Alkyne formation has been observed only in the case of copper irradiated PP. The difference in the response of PP towards these ion beams might be owing to the large difference in energy loss of the ions in the polymer. Moreover, the formation of alkyne appears to be phenomenon of the

swift heavy ion losing high amount of energy to the PP sample within a very short time span, which lead to remarkable reorientation of the polymer.

Acknowledgments

The authors are thankful to Mr. Sandeep Chopra, Mr. Fauran Singh and the other staff members of IUAC (Inter University Accelerator Centre), New Delhi, India for their help during irradiation. Thanks are also due to Dr. M.P.S. Isher, Deptt. of Pharmaceutical Sciences, G.N.D.U. Amritsar for his valuable suggestions in the FTIR analysis.

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