# EFFECT OF ION BEAM ON STRUCTURAL AND THERMAL PROPERTIES OF POLYMER THIN FILM

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***Abstract***

***Polycarbonate (PC) films were prepared by a solution mixing method. The Electroactive properties of the ion beam irradiated single layer polycarbonate samples were illustrated by means of UV-Vis spectroscopy FTIR, XRD, AFM, thermally stimulated discharge current, DSC to understand change in polymer morphology and relaxation properties. For XRD we conclude that the effect of carbon beam irradiation on polycarbonate film that crystallite size in polycarbonate is decreased by 11.31%. For UV–Visible absorption spectra we have illustrated the energy band gap and found that the energy band gap of polycarbonate decreases with ion fluence rate.***

***Keywords: Polycarbonate, glass transition temperature, DSC.***

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**Introduction**

Swift heavy ion beam irradiation is an effective technique to the modification of various properties of the polymeric material such as electrical, optical and thermal properties etc [1-5]. The organic polymer materials have attracted tremendous attention to their large potential application in the field of telecommunications, optics switching, electronics and mechanics [6-11]. Organic polymers generally have long-term stability and good process ability, outstanding optical, catalytic, electronic and magnetic properties, which are significantly different, their bulk states. Organic polymer, PC are considered promising material due to its excellent properties such as light weight, color less, toughness and wide band gap material while inorganic zinc oxide is a transparent, wide band gap material of particular interest due to its optical, electrical, catalytic, gas sensing, thermal properties and great technological applications in various fields [12-15]. Filling of nanoparticles in polymers plays very important role to improve the optical, electrical and thermal properties of polymeric insulating materials.

In this paper, we investigate the effects of 55 MeV $C^{+5}$ beam on structural and thermal properties of polycarbonate/ films. The structural and thermal properties were investigated by using Scanning electron microscopy (SEM), Energy dispersive X-ray (EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC) measurement. The analyses of these results are discussed in detail.

**Experimental**

Polycarbonate (PC) pellets were procured from Redox, India and dichloromethane (DCM) were procured from Merck Pvt. Ltd. India. The polymeric films were prepared by

solution mixing method. PC pellets (5 gm) was dissolved in 50 mL of DCM (solvent) and then kept for 3 h in magnetic stirrer to become homogeneous and transparent solution at 333 K. After 1/2 h, Now the final solution was kept in sonicator at a frequency of 30 kHz for 15 min. Thus the prepared solution was poured on optically plane glass and the solvent was then allowed to evaporate inside vacuum oven at room temperature for 24 h to yield circular films shape. All films of same thickness about 25 μm were selected for ion beam irradiation. The details of ion beam irradiation are reported in our earlier publications [3, 4, 5, 14, 15]. Desperation of the nanoparticles and surface Morphology of polymeric nanocomposites films were observed by Scanning Electron Microscopy (SEM, Hitachi S - 4800) and Energy dispersive X-ray (EDX, ZEISS EVO 40) spectra were recorded the chemical constitutes of polymer nanocomposites films. The percentage of crystallinity and crystallite size of nanocomposites films were investigated by The X-ray diffraction (XRD) patterns were carried out on PC/ZnO nanocomposites films using the Cu Kα radiation (λ=1.541Å) by Brukar AXS D8 diffractometer with diffraction angle has been varied from 5 to 40 degree. The chemical changes were investigated by using Fourier transform infrared spectroscopy (FTIR, Nexus - 670) in the wavenumber range from 500–3500 $cm^{-1}$. The glass transition temperature ($T_g$) were investigated by differential scanning calorimetry (DSC, 2910 MDSC). The pristine and SHI beam irradiated nanocomposites films were cut into small pieces and these pieces put into the empty aluminum pans and weighed in micro-balance up to an accuracy of 10 ppm. The mass of the nanocomposites films was kept in 10–12 mg while mass of the empty aluminum pan was 0.002 mg. DSC thermograms were taken under a nitrogen atmosphere with a constant heating rate of 10 K/min from 330 to 460 K.

## Preparation of the samples

The circular samples of PC 25μm thickness and 5 cm in diameter have been used in the present study. The solution of particular concentration was prepared in a glass beaker by dissolving PC (5gm) in 100 ml toluene at room temperature ($30^0$C). The solution was kept for 24h to give homogeneous and transparent solution. The solution thus prepared was poured onto an optically plane glass plate floating in mercury pools and the solvent was then allowed to evaporate inside an oven at $40^0$C for 24h to yield the desired samples. The dried sample was subjected to room temperature outgassing at $10^{-5}$ torr for a further period of 24 h to remove any residual solvent.

**Coating of samples**

The samples prepared having diameter 5 cm and thickness 25μm. For good ohmic contact, both the surface of the samples were vacuum aluminized usingVacuum Equipment Co (VEQCO) Delhi. Vacuum coating unit with Penning and Pirani pressure gauges, ST-A6P3; over central circular area of diameter 3.5 cm. both sides vacuum aluminized samples have been used for electrical conductivity measurements.

**Irradiation of samples:**

Polycarbonate films of size 1x1 $cm^2$ were irradiated with $C^{+5}$ ion beam of 55 Mev in the General Purpose Vacuum chamber (GPSC) ($3x10^{-6}$ mbar) at IUAC New Delhi. The line current has been maintained at 1 pna and differences fluence rate $1x10^{11}$to $1x10^{13}$.

# Results and discussion

**Short-Circuit TSDC:**

The samples were thermally charged at $150^0$C with different value of poling field and constant time. The TSDC was recorded by means of electrometer (Scientific Roorkee, India) at a heating rate of $3^0$C/min. In order to avoid the effect of ground loop and extraneous electrical noise the electrometer was carefully shielded and grounded.

The short circuit TSDC spectra are recorded in range of 280-480 K. The short-circuit TSDC spectra of PC (Pristine) show one peak at 418 K approximate temperature.

The peak current increases with temperature and poling field. The position of PC (Pristine) peak is shifted towards higher temperature side with increasing poling field. The peak current for all samples has been found to be the function of poling field.

The TSDC peak in pristine PC is due to the motion of main chain segment and trapping of charge carriers in surface traps. The charge carriers of energy 0.6eV shows that surface traps are more dominant. The TSDC results of pristine samples are well reproducible. The TSDC of carbon ion beam irradiated samples are under observation.

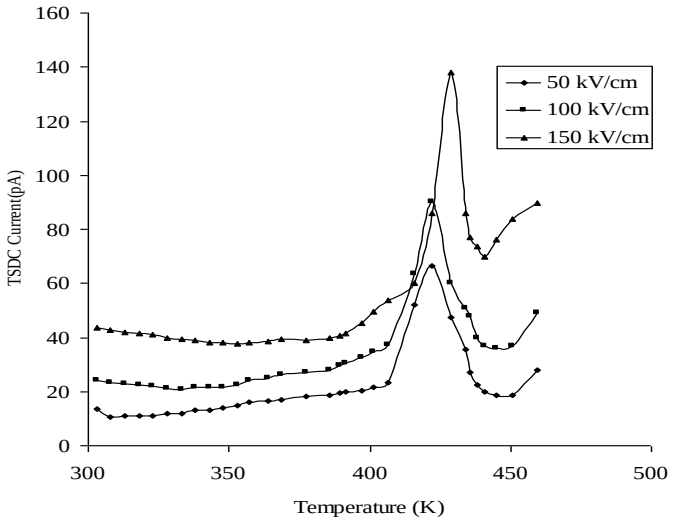



**Fig.1**. TSDC spectra of PC (Pristine) samples with different poling fields (i.e. 50kV/cm, 100kV/cm and150 kV) at 150°C.

**XRD analysis:**

The XRD spectra of pristine and ion beam irradiated 25 μm thick polycarbonate samples with fluence rate of $1\times10^{11}$ to $1\times10^{13}$ ions/cm$^2$ is shown in Fig.2. The XRD characteristics of pristine PC is characterized by one prominent and three small peaks at 26.67˚ (d≈ 5.35 Å, d=λ/2 sin θ is the lattice spacing or crystalline interplaner distance), 26.67˚, 29.50˚, 35.16˚ respectively. XRD pattern shows that the peak intensity and full-width at half maximum (FWHM) increases with increase in fluence rate**.** The observed decrease in peak intensity and FWHM is generally associated with decrease in crystallinity of the polymer. The larger are the crystals of a given component, the sharper are the peaks on the XRD pattern for each crystal plane. Thus the breadth of the peak can

be related to the crystal size. The average crystallite size L, have been calculated by Scherer formula.

$$L = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where β is the FWHM of the peak (in radian) and k is the shape factor whose value is equal to 0.9. Assuming k =0.9 in the above equation, the crystallite sizes of pristine and irradiated polycarbonate were calculated and these results are shown table1. The crystallite size in polycarbonate is decreased by 11.31% on $C^{5+}$ (55 MeV) irradiation.

**Table 1**

**XRD spectra data of pristine and ion beam irradiated polycarbonate**

| Fluence (ion/cm$^{-2}$) | 2θ (degree) | β( degree) | L (Å) | d (Å) | Intensity |
|---|---|---|---|---|---|
| Pristine | 16.78 | 4 | 0.34 | 5.27 | 1158.54 |
| $1\times10^{11}$ | 16.76 | 3.27 | 0.42 | 5.28 | 1069.08 |
| $3\times10^{12}$ | 16.74 | 2.80 | 0.49 | 5.29 | 1023.21 |
| $1\times10^{13}$ | 17.03 | 2.80 | 0.49 | 5.20 | 725.01 |

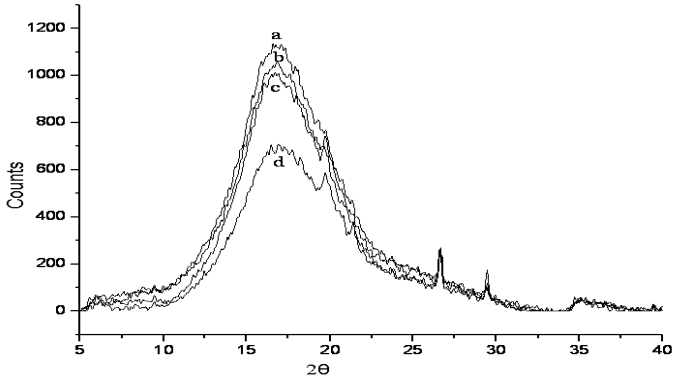



Fig. 2. XRD Spectra (a)pristine (b) 1×1011 fluence(c)3×1012 fluence (d) 1×1013 fluence carbon (55 MeV) ion beam irradiated polycarbonate film

**Energy band gap analysis**

UV–Visible absorption spectra of pristine polycarbonate and irradiated with carbon ($C^{5+}$) ion beam 55 Mev in fluence rate of $1\times10^{11}$-$1\times10^{13}$ ions/cm$^2$ shown in the figure. It is shown that the fundamental absorption band is shifted towards higher wavelength side with increase in fluence rate. The optical band gap has been determined at different fluence rate from the fundamental absorption edge of UV-VIS spectra.

In order to evaluate the indirect band gap of pristine and irradiated samples the absorption Coefficient ($\alpha$) and photon energy ($hv$) were calculated by the relation using UV-VIS absorption spectra:

The values of $(\alpha hv)^{1/2}$ were plotted as a function of photon energy ($hv$). From the intercept of the best-fit lines in the plots of $(\alpha hv)^{1/2}$ versus $hv$, the values of indirect band gap for the pristine and carbon($C^{+5}$) ion beam-irradiated samples with different fluance rate were determined . Similar procedure was followed for the determination of direct band gap except for the fact that $(\alpha hv)^{1/2}$ values were replaced by $(\alpha hv)^2$. The values of indirect and direct band gaps are presented in table 2 along with their standard errors for the pristine and carbon ($C^{5+}$) ion beam irradiated polycarbonate samples.

Fig. 3 shows that band gap reduces with increase in fluence rate of high energy carbon ion beam due to addition of ionic species in polymer matrix during irradiation and due to formation of nanoclustures in polymer matrix, so that it become behave as a semiconductor. These ionic species causes the creation of nanostructured crystalline boundaries in polymeric material, which provide the sufficient space for charge carries for residing between conduction and balance band. The data provides new information for interaction of high energy carbon ion beam with polycarbonate at high fluence rate and it is not yet been reported in literature.

**Table 2**

**Relevant data of UV-Vis spectra of pristine and carbon (55 MeV) ion beam irradiated polycarbonate film**

| Fluence (ion/cm$^2$) | Direct band gap (eV) | Indirect band gap (eV) |
|---|---|---|
| Pristine | 4.27 | 4.24 |
| $1\times10^{11}$ | 4.09 | 4.16 |
| $3\times10^{12}$ | 3.76 | 3.48 |
| $1\times10^{13}$ | 3.47 | 3.19 |

**4 FTIR Analysis**

Fig.4 shows the Fourier transform infrared (FTIR) spectra of pristine and high energy carbon ion beam irradiated samples of PC. The vibration modes of chemical bonds are characterized by the absorption bands of FTIR spectra. The various absorption bands are indicated in pristine and ion beam irradiated samples under different fluence rate. The comparison of absorption band position was made with respect to FTIR spectra of pristine PC. It has been observed that at wavelength 828.96, 888.49, 1653.30, 2332.38 and 2362.37 cm$^{-1}$ shows cross linking and 1688.29 cm$^{-1}$ shows chain scissoring due to polar polymer.

**Table 3**

**Relevant data of FTIR spectra of pristine and carbon (55 MeV) ion beam irradiated polycarbonate film**

| PC (Pristine) $\nu$ $cm^{-1}$ | PC $1\times10^{11}$ Fluence $\nu$ $cm^{-1}$ | PC $1\times10^{13}$ Fluence $\nu$ $cm^{-1}$ | Source of Origin |
|---|---|---|---|
| 634.67 | 634.67 | 635.67 | Phenyl ring vibration |
| 708.24 | 708.24 | 707.24 | C-H out of plane bending |
| 731.43 | 731.43 | 731.43 | C-H out of plane bending |
| 767.81 | 767.81 | 770.61 | CH deformation |
| 828.96 | 828.96 | - | Para in plane aromatic CH waging |
| 888.49 | 888.49 | - | C-$CH_3$ stretching |
| 919.05 | 919.05 | 916.57 | C-$CH_3$ stretching |
| 943.04 | 943.04 | 943.04 | C-H in plane bending |
| 961.35 | 961.35 | 958.86 | C-H in plane bending |
| 1013.41 | 1013.41 | 1013.41 | Para in plane aromatic CH waging |
| 1081.29 | 1081.29 | 1081.29 | C-C Stretching/ $(CH_3)_2$ rocking |
| 1105.99 | 1105.99 | 1105.99 | C-O-C stretching |
| 1215.00 | 1215.00 | 1215.00 | C-O-C stretching |
| 1363.97 | 1363.97 | 1363.97 | $CH_3$ symmetric |
| 1386.22 | 1386.22 | 1386.22 | $CH_3$ symmetric |
| 1501.37 | 1501.37 | 1501.37 | Para in plane aromatic ring semicircle stretching |
| 1653.30 | 1653.30 | - | C=O stretching |
| - | - | 1688.29 | C=O stretching |
| 1763.92 | 1763.92 | 1763.92 | C=O stretching |
| 2231.38 | 2231.38 | 2233.09 | overtone and combination band |
| 2332.38 | 2327.27 | - | overtone and combination band |
| 2362.37 | - | - | overtone and combination band |
| 2827.58 | 2827.58 | 2827.58 | - |
| 3039.18 | 3039.18 | 3039.18 | Aromatic CH stretching |
| 3058.72 | 3058.72 | 3058.72 | Aromatic CH stretching |

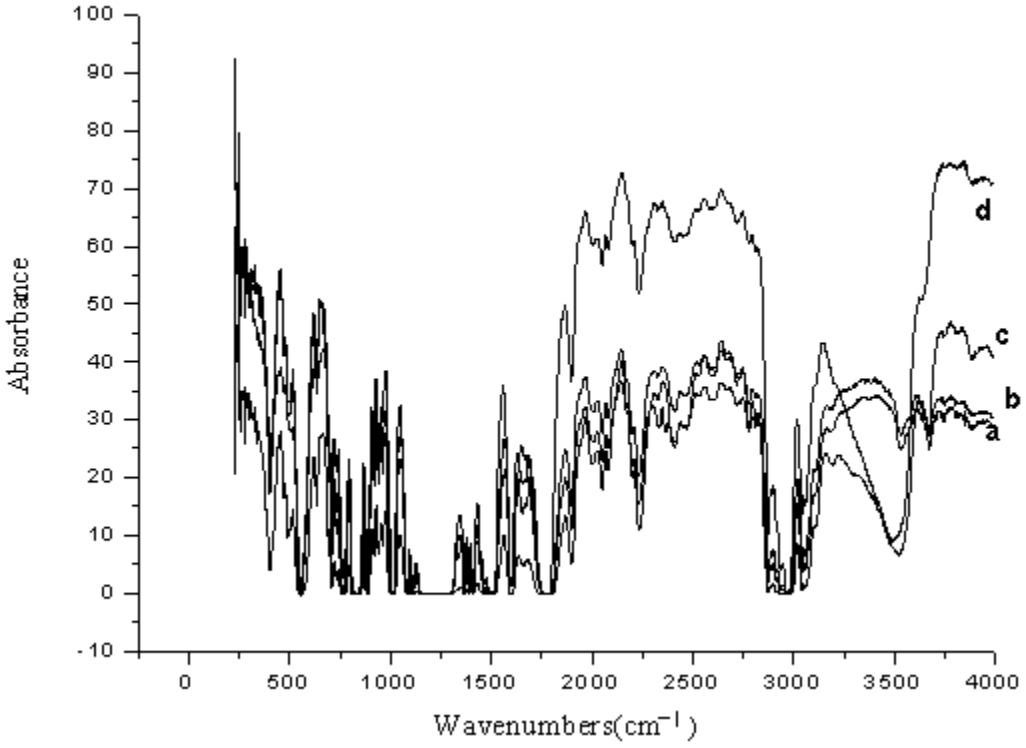



**Fig. 4.** FTIR Spectra of (a) pristine (b) $1\times10^{11}$ fluence (c) $3\times10^{12}$ fluence (d) $1\times10^{13}$ fluence carbon (55 MeV) ion beam irradiated polycarbonate film

**Differential scanning calorimetry Analysis**

The DSC scans for the PC (Pristine) sample DSC thermograms were obtained in the range of 330-450 K by heating at of the 283 K/min with liquid nitrogen medium in UGC-DAE Consortium Indore (M. P.) – India. The Figure 5 shown that glass transition temperature of PC (Pristine) is 414.83 K.

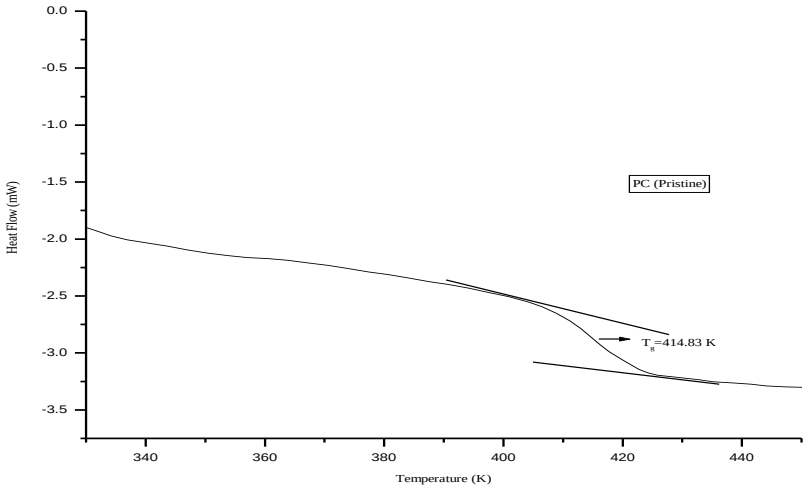
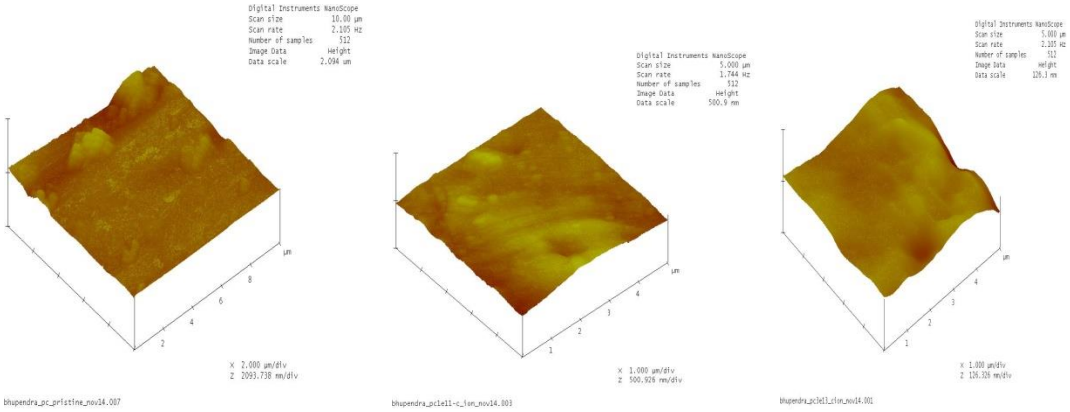



**Fig. 5.** DSC curve of PC (Pristine)

**Atomic force microscopy**

AFM was performed to examine the surface morphology and to measure roughness values for pristine and irradiated polycarbonate with fluence rate of $1\times10^{11}$-$1\times10^{13}$ .Figure 6, 7 and 8 show three dimensional topographic scan of the samples respectively. Results reveal that ion beam irradiated surface was rougher as compared to the pristine sample surface. After irradiation the polymer film shows a remarkable change in yellow mounds with diameter from 1000-200 nm and topography (height) up to 5 nm. Results also shows large amount of pits of the order of 2.5nm-25 nm depth. The variation of rms roughness and dimension of the hills (average height and diameter) with fluence, measured from the manufacturer's software available with the microscope. The increase in the roughness is due to the change in cross linking density and degradation of a polymer surface. This result is consistent with other published works that report that ion beam irradiation can significantly change surface morphology.



## Conclusions

The TSDC characteristics of pristine PC indicate the distribution of energetic traps at different depth. This is due to the fact that the activation energy is different for TSDC peaks appeared with different polarizing field and temperature. The differential scanning calorimetry spectra of PC gives the temperature position of phase change (i.e glass transition temperature), which is well agreed with the position of TSDC peak. However the TSDC measurement on irradiated samples in underway, therefore, it difficult to say anything about the effect of ion beam in TSDC characteristics of PC. FTIR results reveal that the effective change in intensity of absorbance peak according to fluence rate is due to the bond scissions and cross link-ages followed by formation of nanoclusters. It is concluded that irradiation of PC using high energy carbon ion beam created the nano clustures and reduces the energy band gap. The remarkable results are that the band gap energy is found to be a function of fluence rate and density of nano clusters. The decrease in crystallnity is an evidence for growth of nano clusters in PC after irradiation. Present investigation motivates the application of high energy carbon ion beam irradiated PC as a semiconductor and it is first time very low band gap observed by our research group. It is also observed that the surface roughness is highly influence by ion beam irradiation as presented in AFM study.

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