

EFFECT OF SWIFT HEAVY ION BEAM ON STRUCTURAL AND THERMAL PROPERTIES OF POLYCARBONATE FILMS

Bhupendra Singh Rathore^{1,2}, Satyendra Singh¹, Santosh Kumar Saxena³, Sandeep Sharma⁴ and Kripa Shanker Singh²

¹Department of Physics, Seth Gyaniram Bansidhar Podar College, Nawalgarh (Jhujhunu)- 333042 (Raj.), India

²Department of Physics, R. B. S. College, Agra (U.P.)-282002, India

³Department of Physics, S.N.K.P. Morarka Government College 332713, (Raj.), India

⁴Department of Physics, S. R. R. M. Government College, Nawalgarh Jhujhunu- 333042 (Raj.), India

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.

1. 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]. Ion beam irradiated thin film polymers plays very important role to improve the optical, electrical and thermal properties of polymeric insulating materials.

In this paper, we investigate 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. The analyses of these results are discussed in detail.

2. EXPERIMENTAL

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°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°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 using Vacuum 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 cm² 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 1x10¹¹ to 1x10¹³.

3. RESULT AND DISCUSSION

Short-Circuit TSDC:

The samples were thermally charged at 150°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 30°C/min. In order to avoid the effect of ground loop and extraneous electrical noise the electrometer was carefully shielded and grounded [1-4].

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 [7-10].

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.

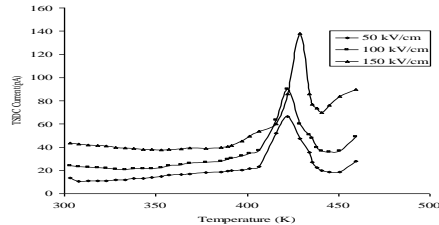


Fig.1. TSDC spectra of PC (Pristine) samples with different poling fields (i.e. 50kV/cm, 100kV/cm and 150 kV) at 150°C.

XRD analysis:

The XRD spectra of pristine and ion beam irradiated 25 μm thick polycarbonate samples with fluence rate of 1×10¹¹ to 1×10¹³ ions/cm² 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 [1-3] 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 [4-7].

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

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 C5+ (55 MeV) irradiation [5-7].

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
1×10 ¹¹	16.76	3.27	0.42	5.28	1069.08
3×10 ¹²	16.74	2.80	0.49	5.29	1023.21
1×10 ¹³	17.03	2.80	0.49	5.20	725.01

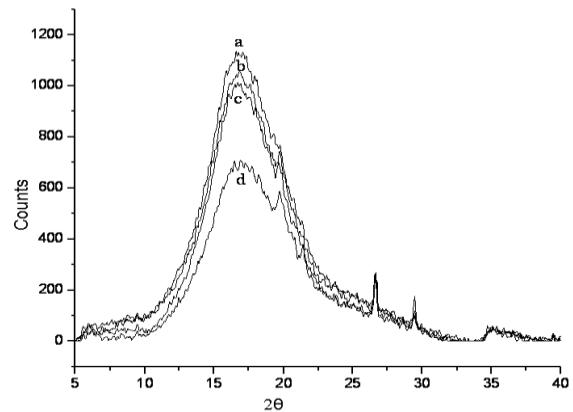


Fig. 2. XRD Spectra (a)pristine (b) 1×10¹¹ fluence (c)3×10¹² fluence (d) 1×10¹³ fluence carbon (55 MeV) ion beam irradiated polycarbonate film

Energy band gap analysis

UV-Visible absorption spectra of pristine polycarbonate and irradiated with carbon (C5+) ion beam 55 Mev in fluence rate of 1×10¹¹-1×10¹³ ions/cm² 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 [2-4].

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

The values of (αhν)^{1/2} were plotted as a function of photon energy (hν). From the intercept of the best-fit lines in the plots of (αhν)^{1/2} versus hν, the values of indirect band gap for the pristine and carbon(C+5) ion beam-irradiated samples with different fluence rate were determined. Similar procedure was followed for the determination of direct band gap except for the fact that (αhν)^{1/2} values were replaced by (αhν)². The values of indirect and direct band gaps are presented in table 2 along with their standard errors for the pristine and carbon (C5+) ion beam irradiated polycarbonate samples [1-4].

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 nanoclusters 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 [6-10].

Table 2

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

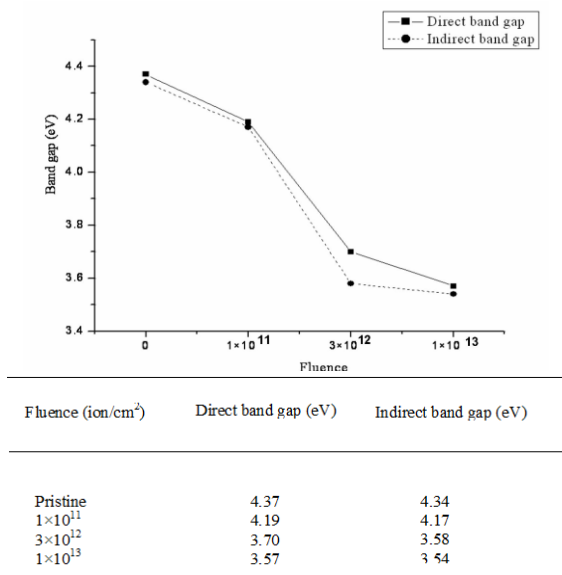


Fig. 3. Fluence versus band gap of pristine and irradiated polycarbonate film

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 [1-4].

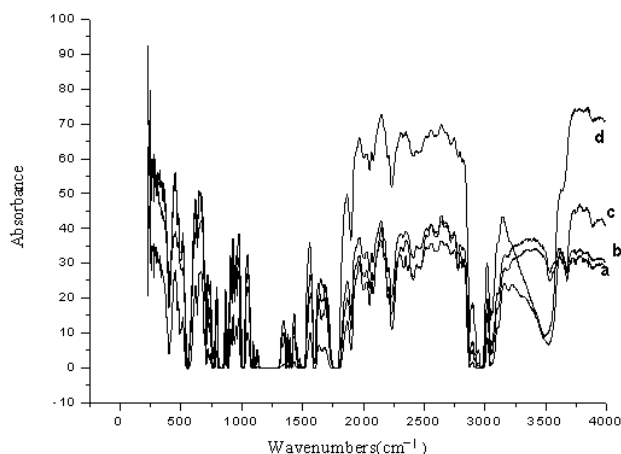


Fig. 4. FTIR Spectra of (a) pristine (b) 1×10¹¹ fluence (c) 3×10¹² fluence (d) 1×10¹³ fluence carbon (55 MeV) ion beam irradiated polycarbonate film

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 [3-4].

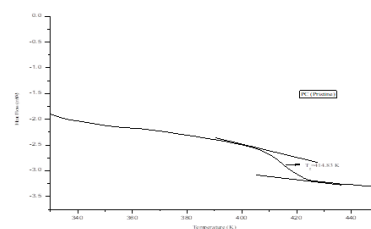
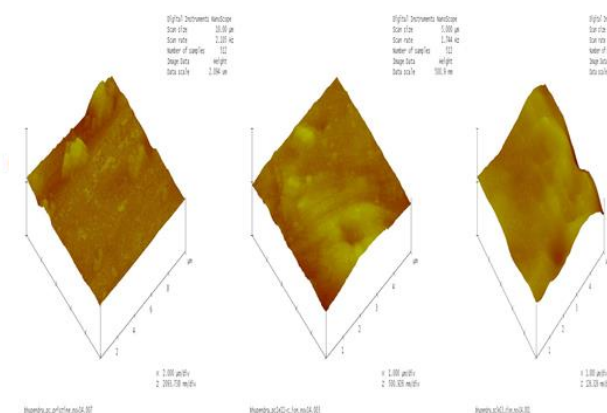


Fig. 5. DSC curve of PC (Pristine)

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 1×10¹¹-1×10¹³. 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 [5—11].



5. 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 clusters 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 crystallinity 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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