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Structural, optical and gas evolution studies of 60 MeV Si^{5+} ion irradiated PoT-PVC blends

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ABSTRACT

Swift Heavy Ion (SHI) irradiation induces chemical and structural changes in polymers by evolving various gases and gaseous fragments. The evolution of gases as a result of chain scissoring and bond breaking leads to cross-linking and cluster formation. Study of the evolved gases helps in understanding the various chemical and structural changes occurring within the polymer under the effect of SHI irradiation. In the present work, Poly (o-toluidine) (PoT), a derivative of polyaniline, is prepared by chemical oxidation polymerization and is blended with polyvinylchloride (PVC) to achieve self supported films. These PoT-PVC blend films were irradiated by 60 MeV Si^{5+} ions at different fluences and evolved gases were monitored on-line by Residual Gas Analyzer (RGA). Pre and post irradiation FTIR, UV-Visible absorption and XRD studies have been carried out on these films to observe the changes in chemical/structural and optical properties. An effort has been made to correlate the evolved gases and structural properties after irradiation. Copyright © 2011 VBRI press.

Keywords: RGA studies; poly(o-toluidine); XRD; FTIR; UV- visible absorption.

G.B.V.S. Lakshmi is presently a research associate at Inter University Accelerator Centre, New Delhi, India. She received her Ph.D. degree in Physics from Jamia Millia Islamia, New Delhi on the topic “Effects of Swift Heavy ion irradiation on conjugated polymers”. Her present research interest in synthesis of various conducting polymers and conducting polymer nanofibers and study the effects of irradiation and their applications in various sensors. She has experience in chemical synthesis and characterization of conducting polymers.

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Saif A. Khan is Scientist D at Inter University Accelerator Centre, New Delhi, India. His major interests are - Electronic sputtering studies specially utilizing online-ERDA facility; Simulation of Ion irradiation induced modifications in materials using Molecular Dynamics method and Synthesis and modification of metal nanostructures by energetic particles and its atomistic simulations.

Introduction

Conducting polymers are an important class of organic polymers, which have many applications in optical, electronic, optoelectronic and sensory devices [**1-3**]. Polyaniline is the most studied polymer because it exhibits high conductivity and environmental stability. Substituted polyanilines are important due to their solubility and processability. The protonic acid doped poly (o-toluidine) (PoT) emaraldine salt phases were studied and it was concluded that HCl doped PoT showed higher conductivity and less thermal stability [**4**]. Electrical and structural properties of p-toluene sulphonic acid doped poly(o-toluidine) are studied recently; an increase in conductivity is reported after doping due to structural changes in the polymer [**5**].

Irradiation of polymers also plays an important role in modifying the various properties of the polymers [**6-8**]. These modifications in the macro-properties like structural, electrical, optical and thermal properties can be traced to transformations in the micro-level through cross-linking, chain scissoring, bond breaking and cluster formation due to the energy deposited by Swift Heavy Ion (SHI) beam [**9-11**]. Triple bond formation and new crystallite formation were found to occur due to C ion irradiation in poly(o-toluidine)-PVC blends [**12**]. The new bond formation and change in crystallinity may lead to a decrease in conductivity and optical band gap in these blends after irradiation [**13**]. The recrystallization of PmT-PVC blends due to irradiation with 60 MeV C^{5+} ions has been reported recently [**14**]. The irradiation of polymers promotes the formation of carbon clusters, which sometimes may result in nano-clusters [**15, 16**]. In polymers chain scissoring and bond breaking leads to release of various gasses from the ion track. Study of these released gasses helps in understanding the changes in structural and chemical properties of the polymer. Avasthi et al. studied various gas evolutions from mylar under irradiation [**17**]. Jai Prakash et al. have studied the evolved gases to understand the interface mixing of Ni on PTFE bilayer system [**18**].

In the present work, we have prepared poly(o-toluidine) powder by chemical oxidation polymerization and blended with PVC. These self-supported films were irradiated by 60 MeV Si^{5+} ions at different fluences as 10^{11}, 3.3×10^{11} and 10^{12} ions/cm^2. The paper discusses the experimental results from Fourier transform infrared spectroscopy (FTIR), online residual gas analysis (RGA), X-Ray diffraction (XRD) and Ultraviolet-visible (UV-vis) absorption spectroscopy in order to get information about changes in optical and structural properties due to irradiation.

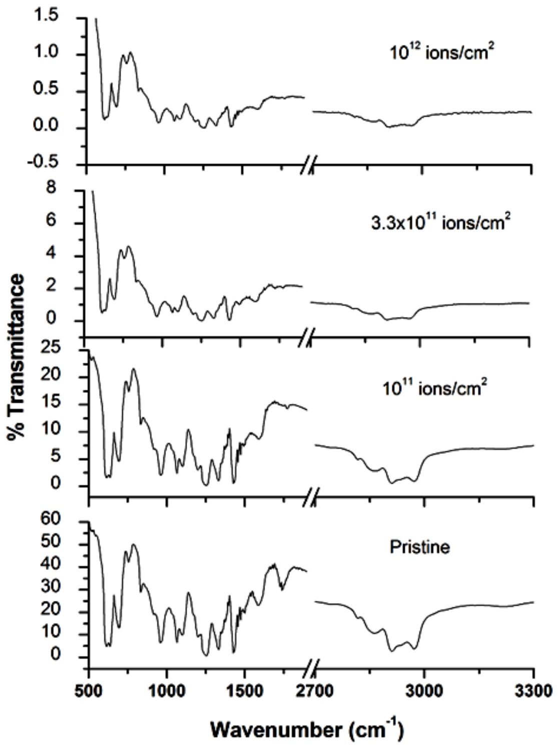


Fig. 1. FTIR of pristine and irradiated PoT-PVC blends.

Experimental

The PoT-PVC blend films having thickness of 25 μm were prepared by chemical method as explained in ref. [**5**]. Samples have been irradiated by 60 MeV Si^{5+} ions, generated from the 15 MV Pelletron Accelerator at the Inter University Accelerator Center (IUAC), New Delhi. Energy range calculations are performed using TRIM code [**19**] and the thickness of samples was so chosen that the range of SHI beam is larger than the film thickness. The range of 60 MeV Si^{5+} ions in PoT-PVC blends has been estimated to be 30.26 KeV/μm. Irradiations were carried out at different fluences of 10^{11}, 3.3×10^{11} and 10^{12} ions/cm^2.

FTIR spectroscopy has been carried out on pristine and irradiated films using NEXUS-670 FTIR spectrometer to get functional group information in the wave number range 400-4000 cm^{-1}. UV-Visible absorption spectroscopy has been carried out on pristine and irradiated films using Hitachi U-3300 UV-Visible Spectrometer to get optical information in the wavelength range 300-800 nm. Online RGA measurements were carried out using PFEIFFER Vacuum CP400– QMG 442 quadrupole mass analyzer attached to ultra high vacuum chamber (low 10^{-7} torr) at IUAC. In order to get the information about the crystallinity, XRD studies were carried out using Bruker AXS, D-8 Advance X-ray diffractometer on pristine and irradiated samples.

Results and discussion

FTIR studies

FTIR transmission spectra of pristine and irradiated PoT-PVC blend films are shown in **Fig. 1**. After irradiation the overall transmission intensity of the polymer blend decreases which indicates some disturbance in the structure of polymer blend films. The C-Cl stretch intensity at 625 cm^{-1} drastically decreases after irradiation. The intensity of substituted benzene ring vibration at 680 cm^{-1} also decreases after irradiation. The C-N stretch intensity at 971 cm^{-1} decreases and the peak broadens after irradiation. The C-H in-plane deformation stretch at 1065 cm^{-1} almost disappears with increase in fluence. The intensity of ring vibrations of benzenoid and quinoid groups at 1602 and 1427 cm^{-1} decreases, which may be due to the deformation in ring structure of polymer blend after irradiation. The C-H stretch vibration at 2850 – 3000 cm^{-1} deforms after irradiation. The drastic changes in the FTIR vibration peaks after irradiation are due to the chain scissoring and bond breaking in the polymer chains.

RGA studies

Online Residual Gas Analysis (RGA), which is basically a quadrupole mass analyzer, studies have also been carried out on PoT-PVC blends to observe various gases evolved during irradiation. The mass spectra were recorded before and during irradiation with 60 MeV Si^{5+} ions in the ultra high vacuum chamber at a pressure of 10^{-7} torr for a number of cycles ranging from mass 1 amu to 100 amu. **Fig. 2**. shows the mass spectra of the irradiation chamber before irradiation (background) and during the ion irradiation (after the beam on PoT-PVC) of the blend film. Various gaseous molecules or radicals evolved during ion irradiation can be seen from the mass spectra.

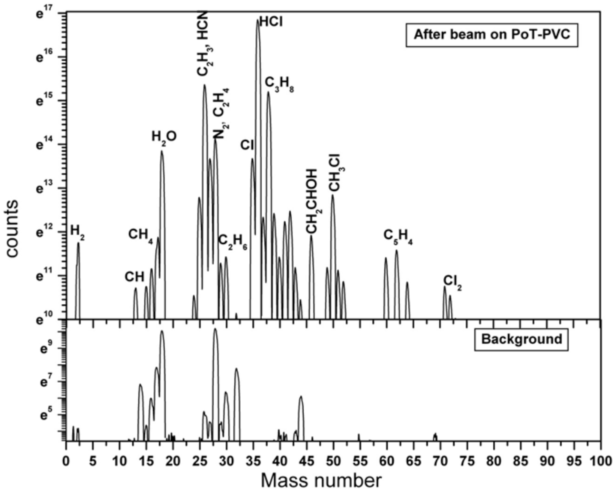


Fig. 2. RGA spectrum showing mass number vs. counts.

It is well known that a heavily ionized charged particle passing through a solid material creates microscopic trails of radial damage along its path. In polymers, thermal spike along the ion trajectory together with excitations due to Coulomb interaction causes localized melting. This leads to chain breaking and production of new chain ends which in turn leads to release of gaseous fragments.

The evolution of H_2 can be seen from the peak at 2 amu. The peaks of CH_4 occur at 16 amu NH_3 and OH at 17 amu. OH peak shows the presence of some moisture in the blend films. The evolution of H_2O contributes to the peak at 18 amu. The peak at 13, 15 amu represents the CH and CH_3 radical evolution. The peaks at 24 and 25 amu are due to C_2 radical evolution. The peak at 26 amu represents the evolution of C_2H_2 and 27 amu is due to the release of C_2H_3 and HCN. The increased intensity of peak at 28 amu may be due to the combined effect of evolution of N_2 and C_2H_4. The peaks at 29 and 30 amu correspond to $C_2H_{5,}$ and C_2H_6 evolution respectively. Peaks at 35, 36 amu correspond to Cl and HCl respectively. The peaks at 37, 38, 39, 40, 41, 42 and 43 amu represent the evolution of various C_3H_8 fragments. A small peak at 44 shows the evolution of C_3H_8 and CO_2. The peak at 46 amu is due to the hydroxyl ion combined with hydrocarbons (CH_2CHOH). The peaks at 49, 50, 51 and 52 amu are due to release of fragments of CH_3Cl (50 amu) from PVC. The peaks at 60, 62 and 64 amu are due to ring breaking as shown in **Scheme 2**. The peaks at 71 and 72 amu are due to release of Cl_2. The assignment of various mass numbers to evolved molecules or radicals is also given in **Table 1**.

The time vs. counts of different mass numbers spectrum is shown in **Fig. 3**. Each cycle lasts for 50 sec. The background is collected for few cycles before irradiation and then the ion impingement started on PoT-PVC at 120 sec in spectrum, with 0.5 pnA current, 0.1 cm^2 spot size and fluence of 3.47×10^{10} ions/cm^2. The evolution of all gasses increases up to fluence 3.47×10^{11} ions/cm^2 and then decreases except C_2H_3 and HCN. This particular gaseous fragments show an increase up to higher fluences.

Table 1. Identification of various mass numbers from RGA.

Mass number	Molecules or radicals
2	H_2
13	CH
15	CH_3
16	CH_4
17	NH_3, OH
18	H_2O
24,25	C_2
26	C_2H_2
27	C_2H_3, HCN
28	C_2H_4, N_2
29	C_2H_5
30	C_2H_6
35	Cl
36	HCl
37,38,39,40,41,42 and 43	Evolution of various (C_3H_8) fragments
44	C_3H_8, CO_2
46	(CH_2CHOH)
49, 50, 51 and 52	Fragments of CH_3Cl
60, 62 and 64	Ring breaking (C_5H_4) fragments
71 and 72	Cl_2

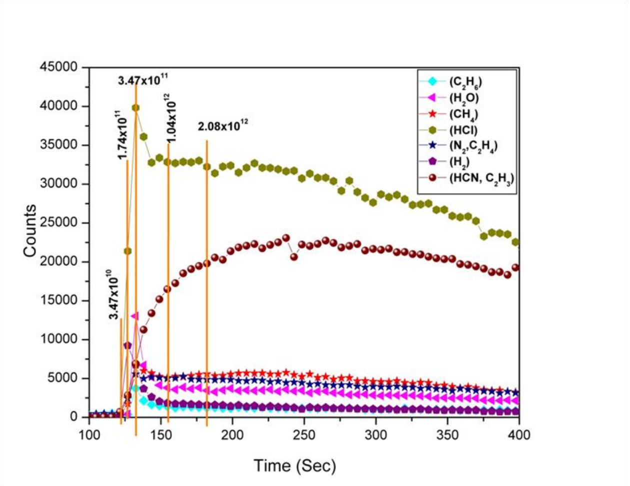
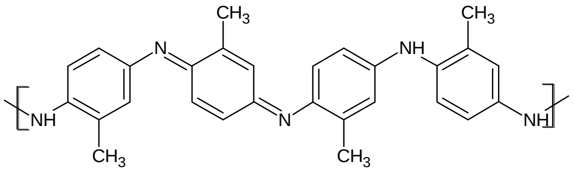


Fig. 3. RGA spectrum showing time vs. counts for different mass numbers.

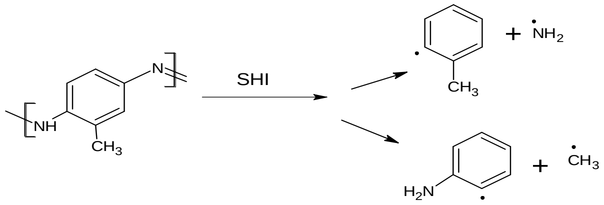
There is no peak at the higher masses (>72 amu) in the mass spectrum, which indicates that a complete aromatic ring evolution does not take place. But the aromatic ring breaking is evident from the evolution of higher mass hydrocarbons (masses near 60 amu) and also confirmed by the decrease in IR intensity of benzenoid and quinoid ring vibrations. There are many peaks in RGA mass spectrum which are due to the chemical combination of different gaseous fragments from these two polymers: aromatic (PoT) and aliphatic (PVC). Some of the mass numbers have been discussed here.

The possible free radical formation which may occur in PoT when exposed to swift heavy ion is shown below in **Scheme 1**. Along with methyl groups (-CH_3) the polymer also loses nitrogen and hydrogen which lead to chain scissoring and ring breaking.

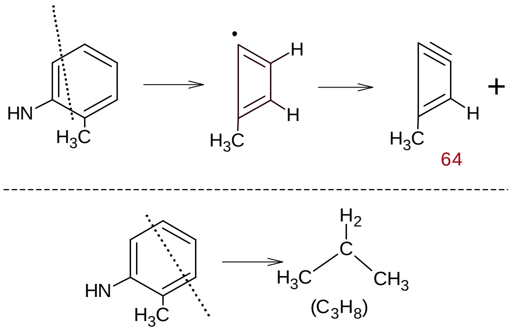
The peaks at 64, 60 and 62 amu are due to ring breaking and further evolution of hydrogens from the ring fragments as shown in **Scheme 2**. Radiation sensitive methyl group (-CH_3) undergoes the homolytic fission and gets separate with one odd electron called the free radical producing methyl free radical and another free radical in form of ring with odd electron positioned at ortho to NH group. These free radicals thus formed from different chains undergo recombination.



Chemical structure of poly (o-toluidine)



Scheme 1. Free radical formation.



Scheme 2. Possible mechanism of ring breaking.

$$\dot{NH}_2 + \dot{H} \rightleftharpoons NH_3$$

$$\dot{CH}_3 + \dot{CH}_3 \rightleftharpoons C_2H_6$$

$$\dot{CH}_3 + \dot{H} \rightleftharpoons CH_4$$

$$\dot{H} + \dot{H} \rightleftharpoons H_2$$

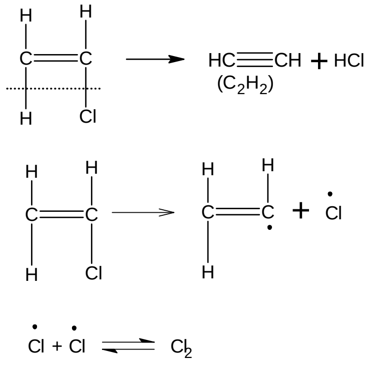
$$\dot{N} + \dot{N} \rightleftharpoons N_2$$

Scheme 3. Possible mechanism for recombination and evolution of gases.

The recombination of free radicals with self or other radicals produced during irradiation, results in evolution of different gases as shown in **Scheme 3**. In PVC the possible changes are given in **Scheme 4** due to irradiation. Along with this the chain scissoring also takes place in aliphatic polymers.

XRD studies

The X-ray diffraction patterns of PoT-PVC blends before and after irradiation at different fluences are given in **Fig. 4**. In pristine polymer blend no crystalline peak appears. It is clear from the figure that after irradiation formation of crystallite zone is taking place. Two crystalline peaks are observed at 28.4^o and 32^o, which correspond to PoT and PVC respectively (from JCPDS data).



Scheme 4. Possible mechanism of evolution of gases from PVC.

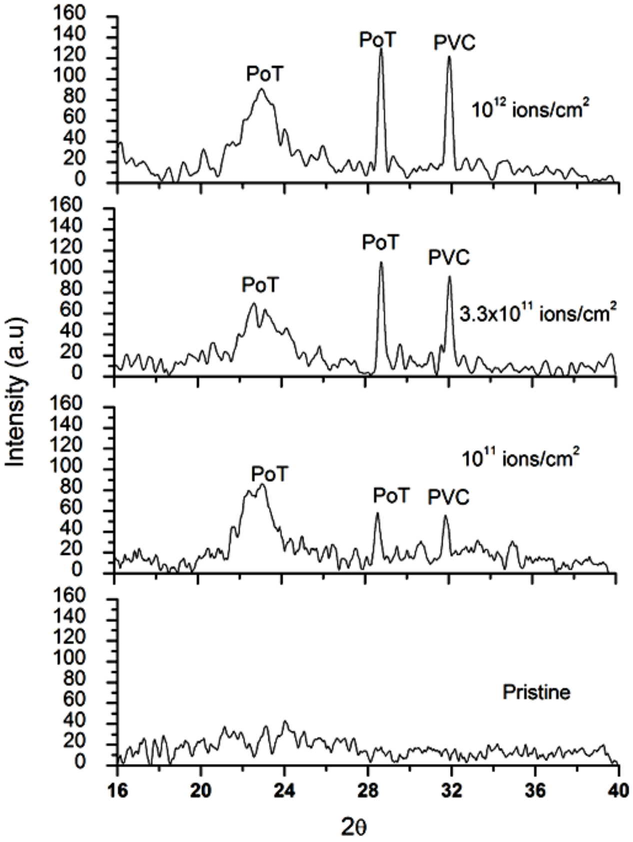


Fig. 4. XRD of pristine and irradiated PoT-PVC blends.

The intensity of these peaks increases on irradiation. A combination of two peaks around 22^o also forms after irradiation, which represents PoT peaks. It is clear from these results that after irradiation with Si ions, both PoT and PVC are getting crystallized. During SHI irradiation a lot of energy is deposited to the polymer along the path of the ion beam. This energy is converted into heat and dissipates away from the track which facilitates the formation of crystalline zones by creating annealing effect away from the track. Also it was observed that the polymer blend shrinks after irradiation and becomes brittle in nature which indicates the increase in the density of the polymer.

UV-visible studies

The UV-visible absorption spectra of pristine and silicon irradiated PoT-PVC blend films are shown in **Fig. 5**. The absorption intensity of the polymer blends increases after irradiation. The absorption in aromatic compounds is due to π - π^* transition. The absorption peak at 550 nm in spectra of pristine and irradiated samples is the signature of the insulating phase of the polymer blends. Since the blend films exhibit an insulating phase, the absorption process in this case may be by excitons. The $\pi - \pi^*$ transition is very sensitive to the change in environment around phenyl ring [**20**]. The phonon absorption in many amorphous materials is found to obey the Tauc relation [**21**], which is of the form:

$$\alpha h\nu = B\,(h\nu - E_g)^n \qquad \text{---------------} \ (1)$$

where, α is the absorption coefficient given by:

$$\alpha = O_d / t \qquad \text{---------------} \ (2)$$

where, O_d is the optical density and t is the thickness of the film. B is a constant, $h\nu$ is the photon energy, E_g is the optical band gap and n is related to the density of states. The index n has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden, respectively. In the direct and allowed cases, the index n is 1/2 whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed cases n = 2 and for the forbidden cases it will be 3 or more. In the present case the photon energy is plotted against $\alpha h\nu$ and for n = 2, a good straight line fit is observed which indicates that the samples obey indirect transition.

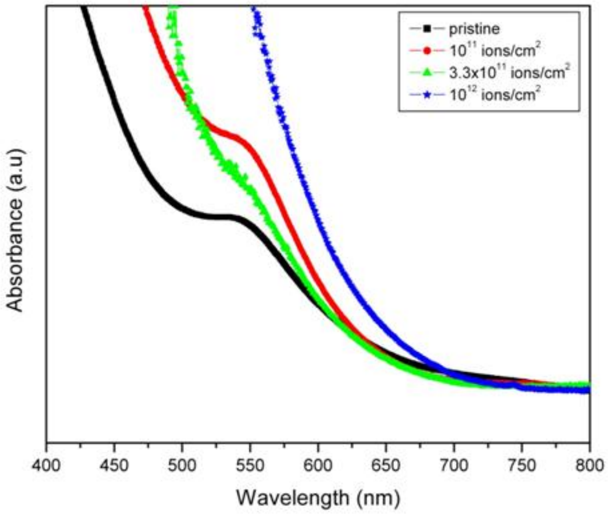


Fig. 5. UV-visible absorption spectra of pristine and irradiated PoT-PVC blends.

The optical band gap vs fluence has been plotted in **Fig. 6**. It is clear from the figure that the optical band gap of the polymer blends increases after irradiation with increase in fluence. During irradiation some gases are released from the organic polymeric materials, which cause the enrichment of carbon atoms leading to the formation of carbon rich clusters whose optical band gap depends on the C/H ratio [**22**]. Irradiation results in bond breaking conformed from RGA data and bond rearrangements leading to destruction of some bonds and formation of new bonds. This new bond formation is responsible for the change in optical band gap.

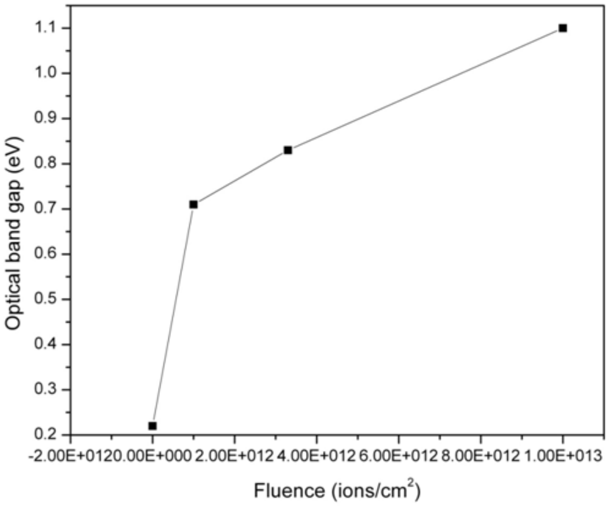


Fig. 6. Optical band gap vs. fluence.

PoT-PVC blend films have also been irradiated with 60MeV C^{5+} ions earlier [**12, 13**] and found that the structural and optical changes are different from that of present case. In C irradiated films there is only one crystalline peak which appears at 32°. The optical band gap decreases after irradiation when compared to pristine films. Where as in Si irradiated films we found two crystalline peaks in XRD patterns and increase in optical band gap after irradiation. The difference is due to the difference (approximately one order of magnitude) in electronic energy loss of the two ion beams.

Conclusion

Poly (o-toluidine)-Polyvinyl chloride (PoT-PVC) blends were prepared by chemical method. The blend films were irradiated with 60 MeV Si^{5+} ions and the structural and optical properties were studied before and after irradiation. RGA studies show the release of gases like H, CH_4, C_2H_6, N_2 and various fragments of hydrocarbons during SHI irradiation. The release of gases in turn causes the change in C to H ratio leading to the formation of carbon rich clusters. The optical band gap of the polymer blend is found to increase after irradiation. From XRD it is found that crystallization of the polymer blend is taking place after irradiation. The crystallization causes the increase in optical band gap. The increase in density also plays a role in the increase in the optical absorption and band gap. The electronic energy loss plays a crucial role in the modification of properties of polymers after irradiation.

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