# The Effect of Oxygen Beam ($O^{+7}$,100 MeV) and Gamma Irradiation On Polypyrrole Thin Film.

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## ABSTRACT

Polypyrrole thin films doped with Para-toluene Sulphonic acid were prepared by electrochemical process and a comparative study of the effect of Swift Heavy Ions and Gamma rays irradiation on the structural and optical properties of Polypyrrole (PPY) has been carried out. For this study Oxygen ions (energy 100 MeV, charge state $O^{+7}$) fluence varies from $1X10^{10}$ to $3X10^{12}$ ions/cm$^2$ and the gamma dose varies from 6.8 to 67 gray. The polymer thin films were characterized by X-Ray diffraction (XRD), UV- Visible spectroscopy and Scanning Electron Microscopy (SEM). XRD pattern shows that after the irradiation the crystallinity was improved with increasing fluence, which could be attributed to cross-linking mechanism. The UV-visible spectra shows a shift in the absorbance edge towards the higher wavelength and significant decrease in the bandgap was found after irradiation. SEM study shows a systematic change in the surface of the polymer. A similar pattern was found with the Gamma irradiation.

***Key Words:*** Ppy, SHI, XRD, UV-Visible, SEM.

## 1 INTRODUCTION

Polypyrrole is an especially promising Inherently Conducting Polymers, as it is highly conducting, environmentally stable and relatively easy to synthesise. It has recently found applications in a wide range of fields, including chemical and biological sensors [1,2] lighting emitting diodes [3], electromagnetic interference shielding [4] and advanced battery systems [5,6]. Now research has been focused on the continuous monitoring for hazardous chemical vapors present in specified levels. Conducting polymers are good candidates for the sensors because of ease of fabrication, low cost and due to possibility of using the same polymer with the different modifications. The sensing properties of these conducting polymers are associated with detection of some hazardous gases like ammonia and chorine and organic solvent vapors [7,8,9,10]. The physical property of PPY films largely depends on the nature of dopant and methods of sample preparation and also low temperature of polymerization [11] that leads good electrical conductivity. Various dopants are used for synthesis of Ppy by electrochemical process [12,13]. Due to commercial uses polymers become a subject of scientific and commercial interest. The use of ion irradiation of these materials is of great importance to modify properties of these materials. Any modification of material depends on the structure and the ion beam parameters (ion mass energy and fluence) and the nature of target material itself. By using high-energy heavy ions, dramatic modifications in the polymer material have been observed. In general most of these modifications can be traced back to changes taking place in chemical structure of polymer. High energy ions by electronic excitation and ionization create the tracks in polymers. The latent tracks in the polymers can cause creation of triple bonds, unsaturated bonds and loss of volatile fragments [14]. Some other workers [15] studied the Polyvinyl alcohol (PVA) exposed by 16 MeV electrons and found that for the same transferred energy density heavy ions were more efficient for the damage in polymers than the low energetic ions. [16] studied the Polypyrrole irradiated by 160 MeV Ni $^{+12}$ ions and found that a sharp increase in the degree of crystallinity of polymer and also found a shift in the absorbance peak towards the higher wavelength.

## 2 EXPERIMENTAL METHOD

0.1 M Pyrrole monomer (Aldrich) and 0.1 M Paratolune sulphonic acid (Lancaster, UK) were distilled in double distilled water. The platinum plate used as counter electrode and electrochemical polymerization of the pyrrole was carried out on ITO, during the polymerization anodic potential was kept 0.8 V. Varying the deposition time controlled the thickness of the thin films. Self standing films of Ppy of size 1cm$^2$ were irradiated in Material Science Beam Line under high vacuum 5X $10^{-6}$ torr by using the 100 MeV $O^{+6}$ ion with a beam current of 1 pnA available from 15 UD Pelletron at Inter University Accelerator Centre, New Delhi using various fluences ranging from $1x10^{10}$ to $3x10^{12}$ ions/cm$^2$. The thickness in the present work was selected so as to be thin enough to allow the 100 MeV Oxygen ions to completely pass through it. XRD of the polypyrrole thin



NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

films were carried out by a Bruker AXS, X-ray diffractometer with Cu-Kα radiation (1.54 $A^0$) for a wide range of Bragg's angle 2θ (15<2θ<40). UV-Visible Spectra were obtained using a U-3300 Spectrophotometer. SEM images were obtained using a JEOL JSM 840 Scanning Electron Microscope.

# 3 RESULTS AND DISCUSSION

## 3.1 X-RAY DIFFRACTION

The XRD pattern of pristine and irradiated PPY irradiated by Oxygen beam is shown in Fig.1. The pristine polypyrrole shows the semi crystalline nature. After irradiation with SHI at low fluence, intensity of the peaks increases, which show the polymer crystallinity increases. This may be due to cross linking of the polymer chains or by the formation of single or multiple helices which produces more crystalline regions in the polymer film which show the crystalline behavior of the polymers with SHI. The degree of crystallinity for the polymers calculated by following formula

$$C = \frac{A}{A'} X100\%$$

Where A is the total area of the peaks (area of crystalline and amorphous peaks) and A' is the total area under the diffractogram [17]. The % crystallinity calculated by above relation is shown in Table 1.

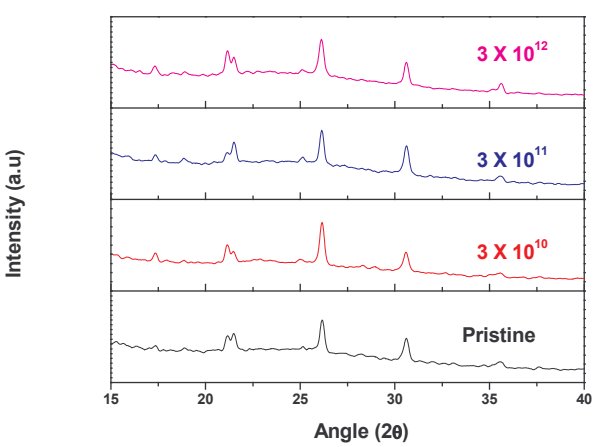


Fig1. XRD of Poypyrrole irradiated with $O^{+7}$ beam.

| $O^{+7}$ ion fluences (Ions/cm$^2$) | % K of Ppy | Gamma rays dose (gray) | % K of Ppy |
|---|---|---|---|
| Pristine | 23.02 | pristine | 23.02 |
| $3X10^{10}$ | 26.91 | 6.8 | 23.45 |
| $3X10^{11}$ | 30.39 | 12 | 23.90 |
| $1X10^{12}$ | -- | 30 | 25.69 |
| $3X10^{12}$ | 32.21 | 68 | 26.60 |

Table 1 : Calculated %crystallinity in Polypyrrole.

The crystallinity of the polymers arises due to the formation of single or multiple helices along their length [18]. [16] Also studied the Polypyrrole irradiated with Ni $+^{12}$ ion and found that the crystallinity of PPY increases after irradiation.

### 3.2.1 UV-VISIBLE SPECTROSCOPY

The electronic structure and the carrier type in the polymers can be visualized by UV-visible spectra. The UV-visible spectra recorded for the $O^{+7}$ ion beam irradiated polypyrrole Fig 2 & Fig 3. The absorption peak around 450 nm is polaron absorption peak of the conducting polypyrrole [19]. A shift in the absorption peak towards higher wavelength was found indicating a decrease in the energy bandgap of the polymer after SHI irradiation which gives rise increase in the dc conductivity of polymers.

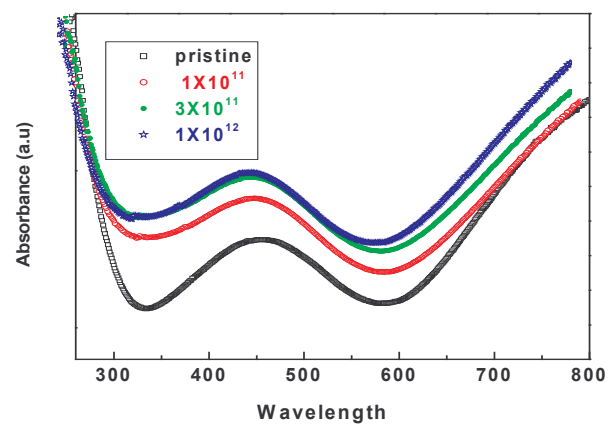


Fig. 2: Absorbance of Ppy irradiated by $O^{+7}$ ion beam

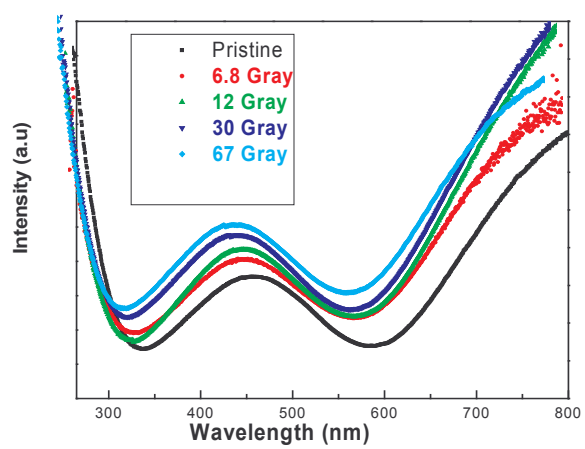


Fig. 3: Absorbance of Ppy irradiated by gamma rays

This shift in the absorption may be produced in creation of free radicals or ions and thus have a capability of increasing the conductivity of the polymers [20]. From the absorption the direct band gap of the polymers was calculated by linear part of the Tauc's plot [21]. The band gap was found 3.4 eV for the pristine PPY, which decrease upto 3.0 eV after irradiation, by oxygen beam.

It may be higher rate of electronic energy loss of oxygen ions, which affect the optical properties of polymers to greater extent. The calculated values of band gap are shown in Table 2.

| $O^{+7}$ ion fluences (Ions/cm$^2$) | band gap (eV) | Gamma rays dose (gray) | band gap (eV) |
|---|---|---|---|
| Pristine | 3.4 | pristine | 3.4 |
| $3X10^{10}$ | ---- | 6.8 | 3.4 |
| $1x10^{11}$ | 3.3 | 12 | 3.4 |
| $3X10^{11}$ | 3.2 | 30 | 3.3 |
| $1X10^{12}$ | 3.0 | 67 | 3.3 |

Table 2: Band gap calculation in Polypyrrole.

## 3. SCANNING ELECTRON MICROSCOPY

The dopant and the solvent used during the synthesis affect the morphology of the polymer and also their physical, chemical and the electrochemical properties [22].

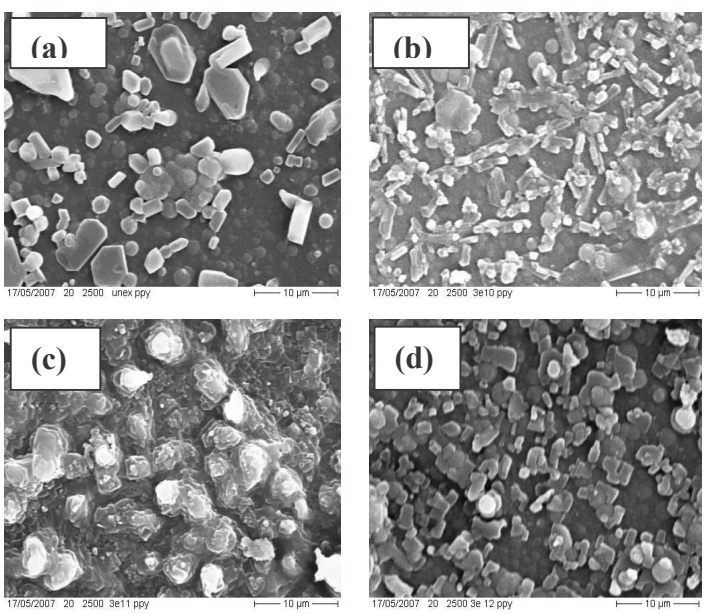


Fig 4. SEM of Poypyrrole irradiated with $O^{+7}$ beam (a) unexposed, (b) $1x10^{11}$ ions/cm$^2$ , (c) $3x10^{11}$ ions/cm$^2$ and (d) $3x10^{12}$ ions/cm$^2$. Scales in the images are 10 µm.

Some other workers stated that Ppy prepared by using different dopants shows different morphological structures [23]. The SEM images recorded for the $O^{+7}$ ion beam irradiated polypyrrole is shown in Fig 4. Grain like structure was observed in the unexposed polypyrrole thin film. After irradiation with SHI microcrystalline structure can be seen at a fluence of $3X\ 10^{10}$ ions cm$^{-2}$. But higher fluence of $3x10^{11}$ ions cm$^{-2}$ & $3x10^{12}$ ions cm$^{-2}$ exhibit growth of Grain like structure after irradiation. The Grain like structure growth upon SHI irradiation may be due to huge energy deposition by heavy ions by the process of electronic energy loss.

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