Structural Modifications of PMMA and PMMA/CNT Matrix by Swift Heavy Ions Irradiation

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Abstract: The effects of multi walled carbon nanotube (MWCNT) as well as swift heavy ion (SHI) irradiation on the optical and electrical properties of polymethyl methacrylate (PMMA) have been investigated. The self-sustaining films of non-conducting PMMA and PMMA/MWCNT nanocomposites were irradiated under vacuum with 50 MeV Lithium (Li³⁺) and 80 MeV Carbon (C⁵⁺) at 1×10¹⁴ ion fluence. One peak photoluminescence (PL) band was found in Raman spectra. All these results were explained on the basis of charge transfer complex (CTC).

Keywords: Hydrogenated amorphous carbon (HAC), Multiwalled carbon nanotubes (MWCNT), Polymethyl meth acrylate (PMMA), and Swift heavy ion (SHI).

1. INTRODUCTION

The electrical and optical properties of insulating polymers can be changed by the presence of nanoparticles such as carbon nanotubes (CNTs)[1]. After the discovery of CNTs by Iijima in 1991[2], lot of interest was shown in the preparation of CNT/polymer matrix. Addition of CNT to a simple polymeric material show drastic changes to their properties like good electrical conductivity, good mechanical strength, etc.[3],[4]. Ajayan et al. firstly incorporated CNT in an epoxy matrix[5], until now, CNT have been used as fillers in the insulating polymer matrix to enhance the optical and electrical properties[6]. Amongst the insulating polymers, PMMA was selected as the matrix polymer for this study due to its amorphous character; good tensile strength; hardness; high rigidity; transparency; good insulation properties; good impact strength, higher than glass; easy to structure[7]; its suitability for a wide range of production, etc.

We synthesized PMMA and 0.2 wt % CNT/PMMA matrix by using casting method. 0.2CNT/PMMA composites are used in many application such as electromagnetic interference (EMI) shielding materials[8], transparent conducting films[9], gas sensors[10]. Beside addition of CNT we have irradiated our samples with SHI because in recent years the interest in ion beam treatment of polymers has increased as it induces modification in the polymer and causes irreversible modification to the mechanical, structural, optical, chemical and electrical properties through depositing the energy in the matter (electronic energy loss, Sₑ).

Our aim in the present study is to enhance the optical and electrical properties through the induction of insulating PMMA to semiconducting by insertion of MWCNT and to analyses the changes produced by
50 MeV Li$^{3+}$ and 80 MeV C$^{5+}$ ions and modifications in the optical, chemical, structural and surface behavior of PMMA and 0.2CNT/PMMA film as a function of ion beam fluence.

2. EXPERIMENTAL DETAILS

PMMA [powdered PMMA was purchased from Sigma-Aldrich AR Grade, CAS No. 9011-14-7], Carbon nanotube, multi-walled [powdered CNT was purchased from Sigma-Aldrich AR Grade, CAS No. 755117] and chlorobenzene [purchased from Sigma-Aldrich, CAS No. 108-90-7 anhydrous, 99.8%] as solvent.

2.1 Irradiation facilities

The irradiation experiments were performed at Inter University Accelerator Centre (IUAC), New Delhi, India. Prepared samples were irradiated by 50 MeV Li$^{3+}$ and 80 MeV C$^{5+}$ ion at $1 \times 10^{13}$ ions cm$^{-2}$. To suppress the thermal decomposition the beam current was kept 1 pnA (below 5 pnA). The range of the incident ion was estimated by a simulated program SRIM[11] which is always higher than the thickness of the polymer film.

2.2 Sample Characterization

UV-Visible absorption studies are performed using a U-3300 Spectrophotometer. Powdered XRD was carried out by a Bruker D 8 Advance X-Ray diffractometer with Cu-Kα radiation (1.54 Å). The Thermo Scientific In-Situ spectroscopy FTIR system modal no. Nicolet 6700 was used for (FTIR). Structural and chemical changes mainly PL as result of exposure to SHI (Li$^{3+}$ and C$^{5+}$) irradiation were analysed by utilizing RENISHAW Raman spectrometer taken at an excitation wavelength of 514.5 nm.

3. RESULTS AND DISCUSSION

3.1 Optical response

3.1.1. UV-Vis absorption spectroscopy

The optical absorption spectra of pristine PMMA and 0.2CNT/PMMA with 50 MeV Li$^{3+}$ and 80 MeV C$^{5+}$ (at $1 \times 10^{13}$ ions cm$^{-2}$) are shown in Fig. 1. (A and B). It is clear from the Fig. 1. that a band near 228 nm is observed for pristine PMMA which may be attributed to the n-π* transition of the carbonyl group.
in the polymeric macromolecule. Pristine and irradiated PMMA and 0.2CNT/PMMA films spectra shows two peak centered at about 265 (peak I) nm 281 (peak II) nm are due to π-π* and n-π transition[12].

3.1.2. Energy band gap

The relation between the optical absorption coefficient (α) for a direct transition and the photon energy ($h\nu$) was given by Fahrenbruch and Bude,

\[ \alpha = A \left( h\nu - E_g \right)^{1/2} \] \hspace{1cm} (1)

For the determination of direct optical band gap, α$^2$ was plotted as a function of photon energy ($h\nu$). The direct optical band gap before and after irradiation can be determined from the plot of (α$^2$) as a function of photon energy ($h\nu$) are shown in Fig. 2.(A and B). It was clear from Fig. 2. that at 1×10$^{13}$ ions cm$^{-2}$ the value of $E_g$ decreases from 4.08 eV for pristine sample to 2.98 eV for Li$^{+3}$ and 4.08 eV for pristine sample to 2.70 eV for C$^{+5}$ dose respectively. And for 0.2CNT/PMMA the $E_g$ of pristine is 4.05 eV decreases to 2.85 for Li$^{+3}$ and 4.05 eV decreases to 2.55 for C$^{+5}$ dose respectively.

The increase in the numbers of conjugation at 1×10$^{13}$ ions cm$^{-2}$ shifted the absorption bands regarding longer wavelength for all irradiated samples[13]. This shift specify a lowering in the $E_g$ and successively, an increase in the electrical conductivity of the irradiated polymer [14]. As a result of which the color of the pristine sample changes from milky white to light brown for Li$^{+3}$ and milky white to yellowish for C$^{+5}$ at 1×10$^{13}$ ions cm$^{-2}$[15].

3.1.3. Carbonaceous clusters

The atomic number of carbon per conjugation length (N) is determined according to Fink el al.[16].

\[ N = \frac{2\beta\pi}{E_g N} \] \hspace{1cm} (2)

where $2\beta$ gives the energy of the band structure of pair of adjacent π sites. The value of $\beta$ is considered to be 2.9 eV. Variation of $E_g$ and N with ion doses and CNT doping are shown in Fig. 2.(A and B).

3.1.4. Activation energy

The activation energy values were resolved using Urbach rule[17]

\[ \alpha = B \exp \left( \frac{h\nu}{E_a} \right) \] \hspace{1cm} (3)

where B is a constant and $E_a$ is the activation energy. Fig. 3.(A and B) shows the variation in the log of the absorption coefficient as a function of the photon energy for pristine and irradiated PMMA and 0.2CNT/PMMA. It can be seen that $E_a$ gradually decrease at 1×10$^{13}$ ions cm$^{-2}$ may be attributed to the improvement of the disorderness in PMMA and 0.2/PMMA polymer observed from Fig. 3.(A and B).

| Ion   | Fluence (ions cm$^{-2}$) | Direct band gap ($E_g$) in (eV) | Activation Energy ($E_a$) | No. of Carbon atoms per conjugated length (N) |
|-------|-------------------------|---------------------------------|---------------------------|---------------------------------------------|
| Li$^{+3}$ | 1×10$^{13}$ | 4.05                           | 4.18                       | 4.45                                        |
| C$^{+5}$ | 1×10$^{13}$ | 2.85                           | 2.65                       | 6.30                                        |

The relation between the optical absorption coefficient (α) for a direct transition and the photon energy ($h\nu$) was given by Fahrenbruch and Bude,
This indicates that heavier C$^{+5}$ ions caused more impact in the properties for both the samples as compare to the lighter Li$^{+3}$ ions. All these moderation in the UV-Vis spectra are tabulated in Table 1 indicates the interaction between PMMA and CNT, which promote to the formation of CTC within the polymer matrix.

3.2. Structural response

The XRD spectrum of pristine and irradiated sample of PMMA and 0.2CNT/PMMA at glancing angle 0.2º at

![XRD spectra](image)

Table 2. Variation in crystallite size, crystallinity percentage and interchain separation of pristine PMMA and 0.2CNT/PMMA irradiated by Li$^{+3}$ and C$^{+5}$ ion beams at 1×10$^{13}$ ion cm$^2$.

| Ion     | Fluences (ions cm$^{-2}$) | 2θ (degree) | FWHM (in degree) | Crystallite size (Å) | Crystallinity % | Interchain separation (Å) |
|---------|--------------------------|-------------|------------------|---------------------|-----------------|----------------------------|
| Li      | 0 × 10$^{13}$            | 13.76       | 7.36             | 10.87               | 29              | 1.17                       |
| C       | 0 × 10$^{13}$            | 13.92       | 15.46            | 5.17                | 25              | 1.55                       |
| PMMA    | Pristine 0.2PMMA         | 13.96       | 16.84            | 4.75                | 23              | 1.50                       |
| Li      | 0 × 10$^{13}$            | 14.91       | 26.28            | 3.04                | 20              | 1.04                       |
| C       | 0 × 10$^{13}$            | 15.29       | 29.71            | 2.69                | 15              | 0.99                       |

The average crystallite size $D$ for the pristine and irradiated sample has been calculated by using followinglequation[18]:

$$D = \frac{\frac{\lambda}{b \cos(\theta)}}{K} \quad (4)$$

where $K$ is shape factor and is 0.9, $\lambda$ is known as the wavelength of the Cu-K$_{\alpha}$ X-ray radiation used to record GXRD spectra and is 0.154 nm, $b$ is known as the FWHM of the diffraction peak, and $\theta$ is known as the diffraction angle or Bragg angle (used in radians).

The percentage of crystallinity ($X$) can becalculated using equation[19],

$$X = \frac{A_c}{A_c + A_a} \times 100(5)$$

where $A_c$ and $A_a$are the area of crystalline and amorphous halos respectively. It has been noticed from Table 3 that both the crystallite size, percentage of crystallinity and interchain separation were decreases after irradiation and CNT doping due to destruction of polymeric bonds and release of some volatile gases, which may confirm the disordered state in polymeric film[20]. A lowering of ~7% in the PMMA and ~2% in the 0.2CNT/PMMA for irradiated samples clearly indicates that there are formations of defects in the irradiated layers of the polymer.

The average interchain separation can be estimated from the maxima using relation:

$$R = \frac{d}{\theta} \left( \frac{1}{\sin \theta} \right) \quad (6)$$

1×10$^{13}$ ions cm$^2$ is shown in Fig. 4.(A and B). The diffraction pattern indicates that the pristine PMMA and 0.2CNT/PMMA is semi-crystalline in nature with main peak at 13.76 for PMMA and 13.96 for 0.2CNT/PMMA dominating amorphous content in it due to scission of polymer chains. For irradiated samples, identical peaks were obtained but they slightly shift towards higher angle i.e. 13.76 to 13.92 for Li$^{+3}$ and 13.76 to 14.84 for C$^{+5}$ ion of PMMA and 13.96 to 14.91 for Li$^{+3}$ and 13.69 to 15.29 for C$^{+5}$ ion of 0.2CNT/PMMA, indicating decrease in lattice spacing tabulated in Table 2.
where $\lambda$ is the X-ray wavelength of Cu-K$_\alpha$ and $\theta$ is the diffraction angle at the maximum intensity of the peaks. It reveals that the heavier mass C$^{+5}$ ion caused more amorphization of material than that of lighter Li$^{+3}$ ions. All these moderation in the XRD spectra indicates the possible interaction between PMMA and CNT, which promotes the development of CTC within the polymer matrix.

3.3. Chemical response

FTIR spectra of pristine and irradiated PMMA and 0.2CNT/PMMA films are shown in Fig 6.(A andB).

![FTIR spectra of pristine and irradiated PMMA and 0.2CNT/PMMA films](image)

Fig. 5. FTIR spectra (A) pristine PMMA irradiated at 50 MeV Li$^{+3}$ and 80 MeV C$^{+5}$ at the highest fluence i.e. $1 \times 10^{13}$ ion cm$^{-2}$ (B) pristine 0.2CNT/PMMA irradiated at 50 MeV Li$^{+3}$ and 80 MeV C$^{+5}$ at the highest fluence i.e. $1 \times 10^{13}$ ion cm$^{-2}$.

Table 3. FTIR peak assignments for pristine PMMA and 0.2CNT/PMMA irradiated by Li$^{+3}$ and C$^{+5}$ ion beams at $1 \times 10^{13}$ ion cm$^{-2}$.

| Wavenumber (cm$^{-1}$) | Peak Assignment | Li$^{+3}$ irradiated PMMA and 0.2PMMA wavenumber (cm$^{-1}$) | C$^{+5}$ irradiated PMMA and 0.2PMMA wavenumber (cm$^{-1}$) |
|----------------------|-----------------|------------------------------------------------|------------------------------------------------|
| 2852                 | CH$_2$ stretching vibrations | 2860 & 2836 | 2856 & 2832 |
| 1748                 | C=O stretching vibrations | 1735 & 1734 | 1731 & 1729 |
| 1578                 | C-H bending vibrations | 1578 | 1578 |
| 1462                 | CH$_3$ symmetric bending of CH$_3$ deformation | 1462 | 1462 |
| 1381                 | CH$_2$ asymmetric bending | 1381 | 1381 |
| 1252                 | C-O stretching vibration or C-O$_2$ stretching and deformation | 1252 | 1252 |
| 1163                 | C=O asymmetric stretching or C-O$-$ stretching and deformation | 1163 | 1163 |
| 973                  | C-C$-$CH$-$ rocking or C-H bending vibration | 973 | 973 |
| 844                  | CH$_3$ bending –rock or C-H bending vibration | 844 | 844 |
| 749                  | Attributed to vibration of polym chain | 749 | 749 |

The corresponding peak assignments are tabulated in Table 3. Fig. 5 shows the general decrease in the intensity of the peaks of irradiated and CNT doping samples as compared to the pristine sample. C=H stretching vibrations show a maximum absorption (0 % transmittance) in the range 2800-3000 cm$^{-1}$. The band around 749 cm$^{-1}$ is attributed to vibration of polymer chain[21]. It is confirmed from these data that the PMMA and 0.2CNT/PMMA has successfully polymerized.

It is clear from Fig. 5. that after irradiation and CNT doping there is no significant shifting of vibration mode and no appearance of new mode of vibration in the polymer film. This means that the overall polymeric structure remains same which is more significant for C$^{+5}$ ion compared to Li$^{+3}$ ion. All these
moderation in the FTIR spectra tabulate in Table 3, indicates the possible interaction between PMMA and CNT, which leads to the development of charge transfer complex (CTC) within the polymer matrix.

### 3.4. Raman spectra and Photoluminescence (PL)

Fig. 6.(A and B) shows green-light-excited ($\lambda_{ex} = 514.5$ nm) Raman spectra of the pristine and irradiated PMMA and 0.2CNT/PMMA samples in the range of 520–610 nm. Actually, the well-defined Raman responses of HAC structures in Li$^{+3}$ and C$^{+5}$ irradiated PMMA and 0.2CNT/PMMA[22] or other pristine materials[23],[24] have been already reported. It is observed that, Li$^{+3}$ and C$^{+5}$ irradiation cause integral quenching and red shift of broad PL band. Table 4 shows the parameters of the photoluminescence emission spectra of pristine PMMA and 0.2CNT/PMMA irradiated by Li$^{+3}$ and C$^{+5}$ ion beams at $1 \times 10^{13}$ ion cm$^{-2}$.

The measured values of the peak position and bandwidth of the PL intensity are tabulated in Table 4. It is clear from It is clear from Fig. 6. that the decrease in peak intensity is more significant for C$^{+5}$ (0.37E5) ion as compared to Li$^{+3}$ (0.58E5) ion at the highest fluence. This proves that the C$^{+5}$ ion caused considerably more damage than Li$^{+3}$ ions. All these moderation in the Raman spectra indicates the possible interaction between PMMA and CNT, which promotes the development of charge transfer complex (CTC) within the polymer matrix.

![Fig. 6. PL spectra of pristine PMMA (I) shows the instrumental peaks (A) irradiated at 50 MeV Li$^{+3}$ and 80 MeV C$^{+5}$ in the fluence range $1 \times 10^{13}$ ion cm$^{-2}$ and pristine 0.2CNT/PMMA (II) shows the instrumental peaks (A) irradiated at 50 MeV Li$^{+3}$ and 80 MeV C$^{+5}$ in the fluence range $1 \times 10^{13}$ ion cm$^{-2}$.

| Ion     | Fluence (ions cm$^{-2}$) | Peak Intensity | PL Peak Position (nm) | PL Bandwidth (nm) |
|---------|--------------------------|----------------|-----------------------|-------------------|
| PMMA    | 0.39E5                   | 571.94         | 21.36                 |
| Li      | 1E13                     | 560.26         | 22.6                  |
| C       | 1E13                     | 560.26         | 22.6                  |
| 0.2PMMA | 0.24E5                   | 2072.53        | 796.86                |
| Li      | 1E13                     | 2099.61        | 962.96                |
| C       | 1E13                     | 2097.40        | 108.82                |

### 4. CONCLUSION

UV-Vis spectroscopic analysis of pristine and irradiated PMMA and 0.2CNT/PMMA sample reveals that the optical band gap ($E_g$) and the optical activation energy ($E_a$) decreases and cluster size (N) increases at $1 \times 10^{13}$ ion cm$^{-2}$ of Li$^{+3}$ and C$^{+5}$ ions which lead to an increase in electrical conductivity of the irradiated sample. The irradiation creates some changes in the structure of PMMA and 0.2CNT/PMMA because of formation of carbon clusters, defects and unsaturation due to cleavage of the polymer chain. This means that the SHI and CNT doping increase the surface conductivity of the PMMA film, while bulk properties remains unchanged. These changes in the structural properties enhance the optical and electrical properties of PMMA and 0.2CNT/PMMA irradiated sample. XRD and FTIR analyses of irradiated PMMA and 0.2CNT/PMMA samples reveals that the crystallite size, crystallinity percentage and interchain separation decrease which may lead to an increase in the amorphization at $1 \times 10^{13}$ ion cm$^{-2}$. This is because of the degradation of both the sample structure after
irradiation by SHI. Based on the changes of Raman spectra, the evolution of PL intensity clearly reveals variation of hydrogen content HAC structures. It is also observed that heavier C$^{+5}$ ions caused more impact in the properties for both the samples than the lighter Li$^{+3}$ ions. The presented results have proven that ion irradiation and CNT doping in a controlled way is an efficient and reliable tool to tailor properties of polymeric materials. All these variations in the polymer and doping were grasping by inducing the existence of defect levels within the CNT doped PMMA films due to the development of charge transfer complex and are used in many applications such as electromagnetic interference (EMI) shielding materials, transparent conducting films and gas sensors etc.

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