Swift heavy ions induced modifications in structural and electrical properties of polyaniline

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The ion fluences range from $5 \times 10^9$ to $1 \times 10^{12}$ ions/cm$^2$ irradiation effects of 50 MeV Li$^{3+}$ and 90 MeV C$^{6+}$ ion beams on free-standing polyaniline (PANI) films have been investigated. The X-ray diffraction study shows an increase in crystalline nature of the PANI film with increasing fluence, followed by a decrease beyond the critical ion fluence. I–V characteristics reveal increased conductivity in the irradiated films. Scanning electron microscopy shows the formation of clusters and craters at higher fluences.

Keywords: Electrical properties, polyaniline, scanning electron microscopy, swift heavy ions, X-ray diffraction.

Conjugated polymers, having delocalized $\pi$ electrons, constitute an important class of materials due to their properties such as high electrical conductivity and large nonlinear optical responses. One of these polymers, particularly polyaniline (PANI) has been the centre of considerable scientific interest in recent years. PANI is a favourable polymer to work with because of its chemical stability\textsuperscript{5}, ease of synthesis\textsuperscript{2, 23} and variability of its conductivity through doping\textsuperscript{4}. PANI displays a wide spectrum of applications such as conductive surface\textsuperscript{4}, electrochromic devices\textsuperscript{5}, piezoelectric devices\textsuperscript{2}, photoconductive\textsuperscript{5} and microactuators\textsuperscript{2}. The flexibility of PANI coupled with the high conductivity of doped PANI has made it a good material for electromagnetic shielding. PANI has been modified by number of methods like plasma processing, laser ablation\textsuperscript{10}, scanning probe microscopy\textsuperscript{11} and ion beam treatment\textsuperscript{12} resulting in molecular arrangement, crystallinity, cross-linking and scission of polymer chains\textsuperscript{13}, hardness changes\textsuperscript{14, 15}, improved wear resistance\textsuperscript{16}, increased electrical conductivity\textsuperscript{17} and change of optical properties.

Irradiation of materials by swift heavy ions (SHI) has attracted much attention as it induces large property variations. Ion beams have induced significant changes in structural, electrical and optical properties of conjugated polymers\textsuperscript{18–21} and was shown to form electrically conducting nanowires along the ion track\textsuperscript{22, 23}. During irradiation of polymers by high-energy ions, their energy is transferred into the target material by electronic energy loss. This energy transfer leads to the formation of reactive species like radicals, gases and defects in the form of unsaturation, scissoring and cross-linking of the polymers. Recently a transition from insulating to carbonized conducting state was observed in PANI by high energy C$^{2+}$, F$^{2+}$ and Cl$^{2+}$ ions\textsuperscript{23}. The I–V characteristics of PANI irradiated with Ar ions from a dense plasma focus (DPF) showed a diode-like behaviour\textsuperscript{24}. Polymer dissolution and selective depletion of volatile species by ion bombardment may lead to new useful composites\textsuperscript{25}. Changes of crystallinity of polymers by ion irradiation have been reported in the literature\textsuperscript{27–34}. However, changes in crystallinity under high-energy ion irradiation in conjugated polymers have not been studied in detail till now. Our interest is to quantify changes induced by SHI on conductivity and crystallinity. In this communication, the effects of 50 MeV Li$^{3+}$ and 90 MeV C$^{6+}$ ions on structural, electrical and morphological properties of the free-standing PANI films are reported.

PANI films of thickness ~100 $\mu$m were synthesized by a standard procedure\textsuperscript{35}. For the polymerization of PANI, the aniline monomer (0.1 M) was dissolved in HCl (1 M) at ice temperature and stirred for 30 min or till the droplets of the monomer disappear. The ammonium persulphate (0.2 M) was then added dropwise to the solution at the same temperature for about 90 min. The resulting solution was filtered and washed with double distilled water and alcohol. This solution was again filtered and treated with the Soxhlet assembly for the removal of oligomers or any impurity present in the solution. The solution was then dried and washed with ammonia for undoping; then again it was filtered and dried at 40°C. The resulting brown powder was dissolved in N-methyl-2-pyrrolidone (NMP) and stirred for 24 h. The solution was again filtered and the filtrate was kept in a tray at 60°C. A smooth film was obtained, which was doped by HCl.

The free standing films of 1 sq. cm were irradiated with 50 MeV Li$^{3+}$ and 90 MeV C$^{6+}$ ion beams under high vacuum in a 15 UD Pelletron accelerator. The ion beam fluence varied from $5 \times 10^{10}$ to $3 \times 10^{12}$ ions/cm$^2$ with a beam current of 3 pnA for Li$^{3+}$ and 1.5 pnA for C$^{6+}$ ions. The ion ranges exceeded the film thickness. To expose the whole area, the beam was scanned by an electromagnet scanner. The irradiated PANI films were characterized by X-ray diffraction (XRD) in Bragg-Brentano geometry (Philips X-ray Diffractometer) with Cu-K$\alpha$ radiation (=1.5918 Å). Electrical properties were measured using a conventional four probe method at room temperature. The current was varied using a Keithley meter and the voltage was measured using a low-voltage power

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Table 1. The SRIM 2003 calculated $S_x$, $S_y$ and range for Li$^{+}$ and C$^{6+}$ ions in polyaniline films

<table>
<thead>
<tr>
<th>Target</th>
<th>Ion beam</th>
<th>Energy (MeV)</th>
<th>$S_x$ (eV/A)</th>
<th>$S_y$ (eV/A)</th>
<th>Range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline</td>
<td>Lithium</td>
<td>50</td>
<td>5.836E+00</td>
<td>3.288E-03</td>
<td>485.23</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>90</td>
<td>2.229E+01</td>
<td>1.191E-02</td>
<td>240.18</td>
</tr>
</tbody>
</table>

The stopping power of PANI film as calculated by the stopping range of ions in matter (SRIM) programme is 5.84 eV/A for Li$^{+}$ and 22.3 eV/A for C$^{6+}$ ions. The range of ions in the PANI film was calculated by the SRIM programme. The projected ranges for the Li$^{+}$ and C$^{6+}$ ions in PANI films are 485 μm and 240 μm respectively. The projected range is much higher than the thickness of the polymer film and thus allows ions to pass through the film. The SRIM calculations for both of the ions are given in Table 1.

The XRD of PANI films before and after the irradiation by 50 MeV Li$^{+}$ and 90 MeV C$^{6+}$ ions is presented in Figures 1 and 2 respectively. The pristine PANI film shows semicrystalline behaviour. A significant increase in the degree of crystallinity (DOC) was observed after irradiation.

The DOC is determined by integrating over the XRD peak. The normalized integral intensity gives volume fraction crystallinity ($\Phi_x$). The determination of DOC implies using the two-phase model. Determination of $\Phi_x$ from the XRD pattern under the two-phase assumption, involves separation of diffraction pattern into three parts: (i) crystalline, (ii) amorphous and (iii) Compton background (incoherent scattering). The diffracted intensity is proportional to the sum of these contributions. The $\Phi_x$ is given by the ratio of the integral of crystalline diffraction intensity over the total coherent scattering, after subtracting the incoherent scattering. Table 2 shows the DOC for lithium and carbon irradiated films. The DOC was found to increase proportionally with fluence up to a dose of $1 \times 10^{12}$ ions/cm$^2$ beyond which it decreases. The increase in DOC of polymer films by SHI irradiation could be attributed to reorganization of molecular bonds, related to multiple excitation and ionization events on an extremely short space and time scale. In SHI irradiation, the density of the polymer increases making the polymer more compact, which may have produced closely packed regions by chain folding, cross-linking of polymer chains or by the formation of single or multiple helices, which produces more crystalline regions in the polymer films resulting in an increase in DOC. The density of these modified zones, having crystalline structures, increases with the increase in ion fluence. However, the polymer is carbonized at higher fluence due to overlapping of damaged zones, resulting in the decrease in DOC. The broadening of peaks in Figures 1 and 2 with increase in fluence suggests a change in the crystallite size on irradiation. The values of crystallite size, calculated using Sherrer’s equation, are given in Table 3. The crystallite size of...
Figure 3. The I–V characteristic of polyaniline films: (a) Normal and (b) Log–log plot of I–V characteristics of polyaniline films for pristine and irradiated with 50 MeV Li⁺ ions having fluences of $5 \times 10^{10}$, $1 \times 10^{11}$, $3 \times 10^{11}$ and $1 \times 10^{12}$ ions/cm².

Table 2. Degree of crystallinity of polyaniline films irradiated with 50 MeV Li⁺ and 90 MeV C⁶⁺ ions

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>50 MeV Li⁺</th>
<th>90 MeV C⁶⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>30.2</td>
<td>30.2</td>
</tr>
<tr>
<td>$5 \times 10^{11}$</td>
<td>32.8</td>
<td>–</td>
</tr>
<tr>
<td>$1 \times 10^{11}$</td>
<td>43.7</td>
<td>37.4</td>
</tr>
<tr>
<td>$3 \times 10^{11}$</td>
<td>43.7</td>
<td>39.4</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>52.7</td>
<td>46.3</td>
</tr>
<tr>
<td>$3 \times 10^{12}$</td>
<td>–</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Table 3. Crystallite sizes of Li⁺ and C⁶⁺ irradiated polyaniline films

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>50 MeV Li⁺</th>
<th>90 MeV C⁶⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>14.2</td>
<td>14.3</td>
</tr>
<tr>
<td>$5 \times 10^{11}$</td>
<td>12.6</td>
<td>–</td>
</tr>
<tr>
<td>$1 \times 10^{11}$</td>
<td>10.9</td>
<td>15.2</td>
</tr>
<tr>
<td>$3 \times 10^{11}$</td>
<td>9.8</td>
<td>13.1</td>
</tr>
<tr>
<td>$1 \times 10^{12}$</td>
<td>8.7</td>
<td>11.3</td>
</tr>
<tr>
<td>$3 \times 10^{12}$</td>
<td>–</td>
<td>10.4</td>
</tr>
</tbody>
</table>

The I–V characteristics of Li⁺ and C⁶⁺ ion beams irradiated PANI films are shown in Figures 3 and 4 respectively. A nonlinear behaviour was observed. It is clear from log plots (Figures 3 b and 4 b) that the characteristics follow two power-law regions with different exponents. The power-law relationship can be expressed as $J = kI^n$, where $k$ is a constant and $n$ the exponent determined by slope of the curve. At low voltages, the current is proportional to the electric field. This corresponds to an Ohmic regime (exponent $n \approx 1$), which extends almost up to 1 volt (Figures 3 b and 4 b). With increasing bias voltage, the curve tends towards space charge limited conduction (SCLC) with $n > 2$, which is highly influenced by the presence of traps. The power $n$ depends upon the type of trap distribution, viz. single level traps, exponential distribution or Gaussian distribution, etc. in the energy space. It is observed that the transition voltage from the Ohmic regime to the space charge limited regime ($V$) increases slightly with increasing fluence. This implies that the background free charge carrier density increases slightly with increasing ion fluence. This trend is observed in both cases; carbon and lithium irradiation. An exception is observed in the film irradiated with carbon at a fluence of $3 \times 10^{12}$ ions/cm², where $V$ was reduced. The reduction in $V$ is due to lower number of free charge carrier density for highest fluence, which can be explained by the degree of order induced in the film by irradiation.

The XRD studies of PANI films show that they consist of nm sized (8–17 nm) crystallite zones surrounded by amorphous material. The charge transport takes place via
two contributions: (i) metallic conduction through a crystallite core and (ii) thermally activated tunneling (hopping) through an amorphous barrier. The macroscopic conductivity of the film can be determined by measuring charge transport through amorphous barrier. An amorphous phase of PANI can exist in various conformations like ‘coil’, ‘expanded coil’ or ‘rod-like’ entities. The re-crystallization induced by irradiation leads to chain alignment and increases the degree of order in the film. Thus conductivity can be looked upon as metallic conduction interrupted by small barriers. Conduction electrons are three dimensionally delocalized in the ‘crystalline’ ordered regions and diffuse along the electronically isolated chains through disordered regions, where electrons are localized. The higher the crystallite ordered regions in the material, higher the conductivity expected. With the increasing fluence, the DOC increases (Table 2) and hence the density of free charge carriers increases in
the form of defects, polarons and bipolarons. Thus a slight increase in transition voltage ($V$) with increasing fluence is observed (except for highest fluence, where DOC decreases due to overlapping of damaged zones).

The surface morphology of pristine and irradiated films was analysed by SEM. Figure 5 shows SEM images of PANI films before and after irradiation with Li$^{+}$ ions. The film irradiated with a fluence of $5 \times 10^{10}$ ions/cm$^2$ shows formation of random shape clusters having dimensions of 0.1–3 μm (Figure 5b). On increasing the fluence to $1 \times 10^{11}$ ions/cm$^2$, cylindrical shape structures with longer and shorter axis of 500 nm microtact and 100 nm respectively are observed (Figure 5c). No such structures were observed for samples, irradiated with a fluence of $1 \times 10^{12}$ ions/cm$^2$, though craters (~15 μm) were observed in some places (Figure 5d). The formation of clusters may be due to large amount of electronic energy deposited in the films by Li ions. The SEM images of PANI film irradiated with 90 MeV carbon ions are shown in Figure 6. The formation of clusters of granular structures at low fluence ($5 \times 10^{10}$ ions/cm$^2$) can be attributed to energy loss-induced collision cascades, which take place near the surface and are responsible for the displaced atoms forming clusters (Figure 6a). As the fluence increases ($1 \times 10^{11}$ ions/cm$^2$), electronic energy loss induced sputtering effects remove the surface layers and subsequent reduction in cluster size is observed (Figure 6b). At higher fluence ($3 \times 10^{11}$ ions/cm$^2$), the higher sputtering rate contributes to formation of craters.

The crystalline nature of free-standing PANI films was found to increase with increasing ion fluence, followed by a decrease beyond the critical fluence. With increasing ion fluence, the DOC increases, whereas the crystallite size decreases. After irradiation, a slight variation was also observed in the resistivity of the film, which is due to the formation of polaron and bipolaron. SEM study shows that the ion beam irradiation leads to formation of clusters and craters in PANI films.


RESEARCH COMMUNICATIONS


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Formulation design of cyhalothrin pesticide microemulsion

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Microemulsion is regarded as the most promising pesticide formulation. However, the formulation of pesticidal microemulsion is not easy and an efficient, scientific and inexpensive formulation design still remains elusive. Here, we present our formulation method based on the pseudo-ternary phase diagram and orthogonal design. In addition, the preparation of cyhalothrin microemulsion has been described and an explanation of the use of our approach is included.

Keywords: Cyhalothrin microemulsion, formulation design, orthogonal design, pesticide formulations, pseudo-ternary phase diagram.

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