Irradiation induced optical and electrical modification of Lexan films

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Low energy Argon ions have been irradiated on to the surface of Lexan polycarbonate (PC) films using an electron cyclotron resonance ion source (ECRIS). Different energy of Argon ions have been used for the study by limiting the value of fluence to 1.04×10<sup>16</sup> ions/cm<sup>2</sup>. The ion irradiation has brought changes in electrical, optical and chemical properties of Lexan films. The results obtained from the study show an increase in the surface conductivity after irradiation, shift in optical absorption edge with decrease in optical energy gap and decrease in the intensity of peaks related to C=O, C-C, C-O groups. The irradiated films can find its application in antireflection materials, microelectronics devices and other surface coating applications.

Keywords: Irradiation, Lexan, Surface conductivity, Optical energy gap

1 Introduction

Lexan polycarbonate is a type of thermoplastic polymer having plenty of applications in the field of nuclear<sup>1</sup>, optical<sup>2</sup>, biomedical<sup>3</sup>, electronics<sup>4</sup> and other industrial applications<sup>5</sup>. Due to the excellent toughness, high impact strength, transparency, low inflammability and many other advantageous properties, Lexan has become one of the most promising materials. By modifying the different properties of Lexan films in a controlled way using different techniques, the application of the material can be extended significantly for fulfilling its increasing demand in each and every domains of the need. Ion beam irradiation is one of the approaches to alter the material property by controlled means. Interaction of ions with polymer would bring changes in material by cross linking, chain scission, creating free radicals and functional groups, etc. These changes are closely related to the species of ions, energy and fluence of ions with beam current and other corresponding radiation parameters<sup>6-9</sup>. All these changes result in the modification of physical, chemical, morphological and other corresponding properties of the polymer. The present work is focused on the modification of optical and electrical behaviors of Lexan polymer films using ion beam irradiation technique, so that it can be utilized in different optical, electrical and surface coating applications.

2 Materials and Methods

200 µm thick Lexan sheet was cut into 1 cm×1 cm sized films and then exposed to low energy Argon ions using an ECR ion source available at the Variable Energy Cyclotron Centre (VECC), Kolkata. ECR ion source is a typical ion accelerator, which produces multiply charged positive ions in keV range. The higher possible ion fluence was maintained at 1.04×10<sup>16</sup> ions/cm<sup>2</sup> to get the maximum possible damage and the energy of Argon ions was varied from 100 keV to 198 keV.

3 Results and Discussion

The ion polymer interaction involves in the breaking of different molecular bonds, scissioning or/cross linking of polymer chains, creation of free radicals and functional groups, etc. These changes have lead to the behavioural changes of polymer in terms of its physico-chemical, morphological, mechanical and other associated properties.

3.1 Electrical characterization

The current-voltage (I-V) characteristics of pristine and irradiated Lexan films were studied using a Keithley Source Measure Unit (Keithley - 236 SMU) in the voltage range of 0 to 100 V at room temperature using a two probe method. Using I-V characteristics, the resistance over the surface of both pristine and irradiated Lexan films was calculated.

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Figure 1 explains the $I-V$ characteristics of both pristine and irradiated Lexan films. Here, the current reaches its maximum value after irradiation. This is due to the ion induced increment in the number of mobile charge carriers and carbon clusters in the polymer. The surface conductivity ($\sigma_{\text{DC}}$) of the Lexan films was calculated using the relation given below:\(^{10}\):\(^{10}\)

$$\sigma_{\text{DC}} = \frac{\cosh^{-1}\left(\frac{d}{2r}\right)}{\pi R}$$

... (1)

Where, $d$ is the separation between the tip of electrodes, $r$ is the radius of the circular electrode and $R$ is the resistance measured on the surface of the film.

Table 1 gives values of $\sigma_{\text{DC}}$ for all energy of Argon ions. The measured value of surface conductivity of Lexan films before irradiation was $3.66 \times 10^{-11}$ S/cm and it was found to be increased up to $1.37 \times 10^{-9}$ S/cm after irradiating to higher energy (198 keV) of Argon ions. This change attributes the ion beam induced creation of free radicals and formation of carbonaceous networks in the polymer surface which has led to an enhancement of surface conductivity. The amount of enhancement in the surface conductivity is sufficient for the surface of the polymer to act as conductive surface. In this regard, the polymer with its enhanced surface conductivity could find applications in surface coatings applications, sensitive measuring units and other possible microelectronics applications. It is suggested that, the coordination of energy and fluence of ions with different species and different radiation parameters would bring required changes on the polymer surface according to the need and necessity of the application\(^{11}\).

### 3.2 UV–visible spectroscopy

The examination of optically influenced transition gives the information about the optical energy gap of the material. The UV-visible absorption spectra of Lexan films were obtained from Shimadzu UV-1800 Spectrophotometer by keeping air as reference. Figure 2 represents the UV-visible absorption spectra of pristine and irradiated Lexan films. The absorption edge in the spectrum of pristine Lexan film was found to be around 295 nm corresponding to n-$\pi^*$ electronic transition. But, after irradiation, a shift in the absorption edge of the spectra of Lexan films was observed towards the higher wavelength region.

This attributes the transitions of electrons which will lead to form carbonaceous networks of conjugated unsaturated bonds. Hence, the optical transparency of irradiated films has also decreased\(^{12-14}\). After irradiation, the transparent Lexan films turned into dark brown in color due to the formation of amorphous hydrogenous carbon clusters. The photographic image of color change in Lexan films is shown in Fig. 3. The color change in Lexan films after irradiation is the indication of some kinds of alteration is taking place in terms of its physico-chemical properties. In addition to this, the shifts in the optical absorption were found to be dependent on the energy of impinging ions. This is also

![Fig. 1 — I-V characteristics of Lexan films.](image1)

![Table 1 — Optical and electrical parameters of Lexan films before and after irradiation.](image2)

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>$E_g$ (eV)</th>
<th>$M$</th>
<th>$\sigma_{\text{DC}}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.02</td>
<td>129</td>
<td>$3.66 \times 10^{-11}$</td>
</tr>
<tr>
<td>100</td>
<td>2.37</td>
<td>209</td>
<td>$8.26 \times 10^{-10}$</td>
</tr>
<tr>
<td>144</td>
<td>2.36</td>
<td>211</td>
<td>$1.25 \times 10^{-9}$</td>
</tr>
<tr>
<td>198</td>
<td>2.34</td>
<td>215</td>
<td>$1.37 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

![Fig. 2 — UV-Visible absorption spectra of pristine and irradiated Lexan films.](image3)
related to the values of the optical energy gap of the material. The graph obtained by plotting $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) as shown in Fig. 4 gives a linear behavior and the extrapolation of the linear portion gives the values of optical energy gap ($E_g$).

The optical energy gap of unirradiated Lexan film was 3.02 eV and it was found to be decreased after irradiation. For the higher energy of Argon ions it was decreased up to 1.51 eV as shown in Fig. 5. The decrement in optical energy gap attributed to the formation of free charge carriers and these free charge carriers with increased mobility with increase in the energy are responsible for the decrease in the optical energy gap. Irradiation has also intensified the number of carbon atoms in carbonaceous clusters ($M$), which are calculated using Robertson’s equation as given in Eq. (2).

$$M = \left( \frac{34.3}{E_g} \right)^{3/2}$$  \hspace{1cm} \ldots (2)

Where, $E_g$ is the optical energy gap.

This result is well supported by electrical characterization of the polymer. The decrease in the optical energy gap is corroborated by increase in the electrical conductivity. Table 1 gives the values of optical energy gap, number of carbon atoms in carbonaceous clusters and the surface conductivity of Lexan films before and after irradiation.

### 3.3 FTIR-ATR studies

Identification of molar constituents is carried out by assigning the experimentally observed bands to corresponding functional groups and stretching/bending vibrations of bonds.

Figure 6 shows the Fourier transform infrared (FTIR) spectra of pristine and irradiated Lexan films taken in Attenuated Total Reflectance (ATR) mode using IR Prestige-21 Shimadzu FTIR Spectrophotometer. The spectrum of pristine film shows characteristic absorption band at wave number 1770 cm$^{-1}$ corresponding to carbonyl stretching (C=O) and another absorption band at 1502 cm$^{-1}$ due to C-C stretching of aromatic groups. The absorption bands observed in the wave number region 1300-1150 cm$^{-1}$ are attributed to C-H wagging. The absorption band...
observed at 1075 cm⁻¹ is due to C-O stretching. The absorption bands were also observed between the region of 1000 cm⁻¹ to 650 cm⁻¹ due to =C-H bending of alkenes. But the spectrum of irradiated sample shows decrement in their absorption bands. This result attributes irradiation induced breakage of C-H bonds and cleavage in carbonate networks and as a byproduct of this process release of volatile gases such as carbon monoxide/dioxide¹⁵-¹⁷. Therefore, it can be concluded that, the irradiation has influenced the carbonate networks of polymer and broke a few molecular bonds. This has resulted in the modification of the polymer properties.

4 Conclusions

The electrical, optical and chemical properties of Lexan films were studied before and after irradiation. Electrical characterization has revealed an increase in the surface conductivity from 3.66×10⁻¹¹ S/cm to 1.37×10⁻⁹ S/cm. UV-Visible studies have shown that the optical absorbance of irradiated films has increased and optical energy gap has decreased from 3.02 eV to 1.51 eV. Lexan films have shown change in color after irradiation. FTIR spectra have shown that there is a decrease in intensity of absorption bands in irradiated Lexan films. Altogether, it can be concluded that, even the low energy range of Argon ions have modified the properties of polymer and the enhancement of optical and electrical properties of Lexan polycarbonate can be useful in microelectronics and other associated applications with the proper tuning of energy, fluence and other radiation parameters.

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References