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8 MeV Electron Induced Changes in Structural and Thermal Properties of Lexan Polycarbonate

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ABSTRACT

Lexan polycarbonate films were irradiated by 8 *MeV electron beam at different fluences and characterized using X-ray Diffractogram* (*XRD*), *UV-Visible spectroscopy*, *Fourier Transform Infrared* (*FTIR*) *spectroscopy*, *Differential Scanning Calorimetry* (*DSC*) *and Thermogravimetric Analysis* (*TGA*). *The structural parameters such as degree of crystallinity and crystallite size were found to decrease after irradiation due to chain-scission. The UV-Visible spectroscopic study show the formation of chromophore groups upon irradiation and was reduced at larger wavelength. FTIR Study shows the carbonate linkage was found to be the radiation-sensitive linkage and benzene ring does not undergo any changes after irradiation. The DSC studies showed a decrease in glass transition temperature and heat of fusion after irradiation due to chain-scission which indicates polymer was moving towards more disordered state. Thermal decomposition temperature of Lexan polycarbonate increases upon irradiation.*

Keywords: *Lexan Polycarbonate*, *Irradiation*, *Structural*, *Thermal Properties*

1. Introduction

In the recent few years, studies related to irradiation effects on polymers have emerged as an important area of basic as well as applied research [1]. The irradiation of polymers can modify their structure and properties due to chain-scission and cross-linking. Therefore, some of the irradiation-based polymer processing methods have emerged such as radiation assisted diffusion, growth of polymer nano-composites, polymer blends, polymer grafting etc. [2,3]. Systematic investigations on effects of a wide range of radiations on various polymers are thus important for providing useful information for radiation processing of polymers. The radiation induced changes in the properties are very specific to type of polymer, radiation and its environment [4]. Amongst the range of low to high energy radiations, electron beam are of special interest. The polymers, which are difficult to process by chemical methods, can be easily modified using electron irradiation [5,6]. This leads to significant changes in structural [7-11] and thermal [12] properties due to radiochemical alterations such as unsaturation, evolution of gases [13], formation of carbon clusters, change in free volume [6], creation of defects and amorphization [6,14] etc. As a result, electron beam irradiation of polymers has shown great potential for the fields such as microelectronics, biomedical, device technology, nano-materials and materials science [15-17].

Lexan polycarbonate (Lexan) is the most promising polymer utilized in all fields of science and technology, especially in optical, medical [18] and electronic applications due to its low cost, easy processability and low weight. Literature survey indicates that the effects of radiation on Lexan are being extensively studied. Exposure to gamma [13,18,19] and RF plasma [20] shows significant optical, chemical and surface modifications. However, to modify the polymer, energy loss of ion beam is very important and specific to its nature, energy and environment. The effects of such parameters of electron beam on structural and thermal properties of Lexan have not been paid much attention. Therefore, in this paper, the effects of 8 MeV electron on structural and thermal properties of Lexan have been studied in detail.

2. Experimental

Lexan films of thickness 200 µm were irradiated at different fluences sealed in polyethylene bags. The irradiation was carried out at Microtron Centre, Mangalore University, India using 8 MeV electron beam. The details of the Microtron accelerator were reported elsewhere [21]. The electron fluence delivered to the samples was measured using current integrator calibrated against appropriate radiation dosimeters. XRD diffractogram were recorded in the 2θ range (4˚ - 60˚) with a scanning speed and step size of 1˚/min and 0.01˚ respectively using a Advance X-ray diffractometer (Bruker AXS D8) with CuK_α radiation of wavelength $\lambda = 1.5406$ Å. UV-Visible spectra of the pristine and electron irradiated Lexan samples were analysed using, UV-Visible spectrophotometer (UV-1800, Shimadzu, JAPAN) in the wavelength range 190 - 1100 nm with reference to air. FTIR spectra of all samples were recorded using spectrophotometer (NICOLET 5700, FTIR, USA) in the wave number range 400 - 4000 cm^{-1} having a resolution of 4 cm^{-1}. The thermograms *i.e.* plot of heat flow as a function of temperature for pristine and electron irradiated Lexan samples weighing 1.3 - 2.3 mg were obtained using DSC (Q20 TA Instruments, USA) in the temperature range of 27˚C - 200˚C at a constant predetermined heating rate of 10˚C /min under nitrogen atmosphere. The most reliable technique for obtaining thermal degradation parameters for polymer is the Thermogravimetric analysis. The apparatus consists of a microbalance within a furnace, allowing the weight of the sample to be continuously monitored while the temperature is controlled. So, the weight (%) of the sample is recorded as a function of temperature. In this work, the thermograms of the decomposing polymers were recorded using SDT (Q600 TA Instruments, USA) heated at a rate of 10˚C/min under Nitrogen atmosphere.

3. Results and Discussions

The schematic representation of the mechanism of electron irradiation induced reaction of Lexan is as shown in **Figure 1**.

3.1. X-Ray Diffraction Study

XRD technique has been utilized to detect changes in crystalline and amorphous regions along with the degree of crystallinity. It is used to measure crystallite size, percentage of crystallinity, microstrain and dislocation density of materials through interaction of X-ray beams with samples. The XRD spectra of pristine and electron irradiated Lexan films is as shown in **Figure 2**. The diffracttion pattern clearly indicates that the Lexan is semicrystalline in nature with main peak at 17.56˚. For irradiated samples also identical peaks were obtained but they slightly shift towards higher angel indicating decrease in lattice spacing. As compared to pristine sample, the diffraction pattern of irradiated films show the broadening of main peak indicating the decrease in crystallite size [22,23]. The crystallite size (D) was calculated using following equation [24],

$$D = \frac{K\lambda}{b\cos(\theta)} \tag{1}$$

where K is shape factor and is 0.9, λ is wavelength of X-ray beam and is 1.5406 Å, b is full width at half maximum, θ is diffraction angle or Bragg angle. The calculated values of crystallite size are listed in **Table 1**.

The percentage of crystallinity (X) can be calculated using equation [25],

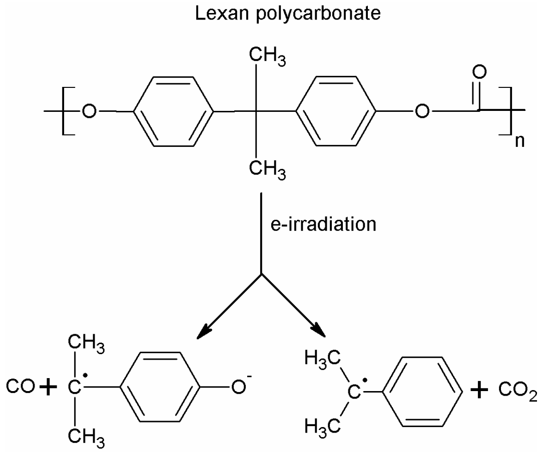

Figure 1. Schematic representation of chemical reaction induced in Lexan after electron irradiation.

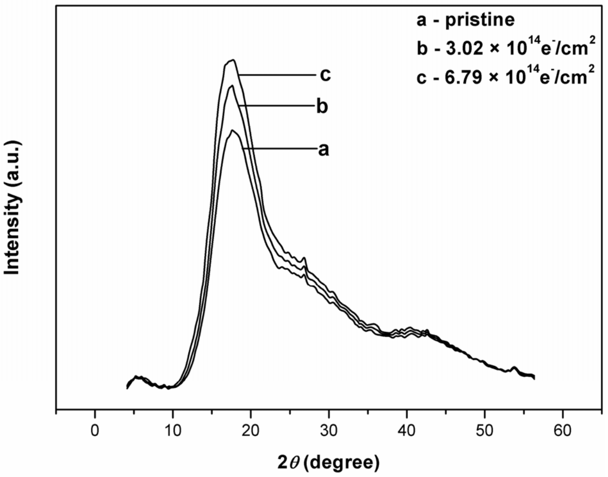

Figure 2. XRD pattern for pristine and electron irradiated Lexan.

Table 1. Crystallite size (*D*) and percentage of crystallinity (*X*) of pristine and electron irradiated Lexan.

Fluence (electrons/cm^2)	2θ (degree)	D (Å)	X (%)
0	17.56	15.98	43
3.02×10^{14}	17.68	14.15	33
6.79×10^{14}	17.95	13.79	27

$$X = \frac{A_c}{A_c + A_a} \times 100 \quad (2)$$

where A_c and A_a are the area of crystalline and amorphous halos respectively. The percentage of crystallinity for all the samples is listed in **Table 1**. It has been observed from **Table 1** that both crystallite size and percentage of crystallinity were decreases after irradiation due to breakage of polymeric bonds and emission of some volatile gases, which may form the disordered state in the polymeric film. The decrease in crystallinity can be further confirmed from DSC studies.

3.2. UV-Visible Spectroscopic Study

The optical absorption spectra of pristine and electron irradiated Lexan samples are shown in **Figure 3**. After electron irradiation, the polymer surface showed a visible colour change from transparent to yellow and the intensity of the colour increases with increase in electron fluence. This is also confirmed with UV-Visible absorbance spectra where the absorption edge shifts progressively towards longer wavelength. This may be attributed to the formation of chromophore groups (conjugated double bonds) as a consequence of the beam induced bond breaking and reconstruction. If there are enough chromophore groups in the conjugation within the sample, absorption edge is expected to move towards the visible region [25,26]. But in the present study, the absorption edge was in the UV region indicating less formation of chromophore groups.

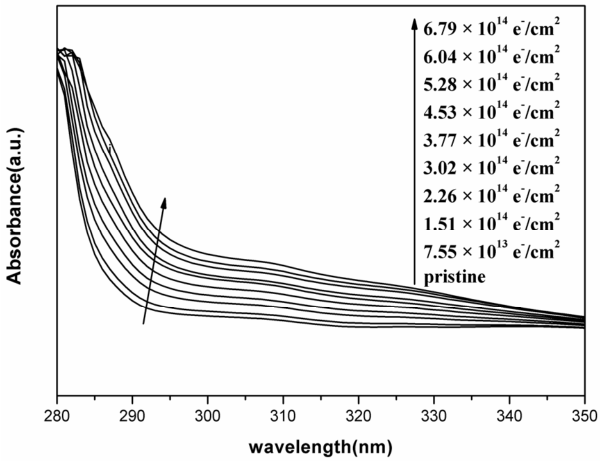

Figure 3. Absorbance spectra for pristine and electron irradiated Lexan.

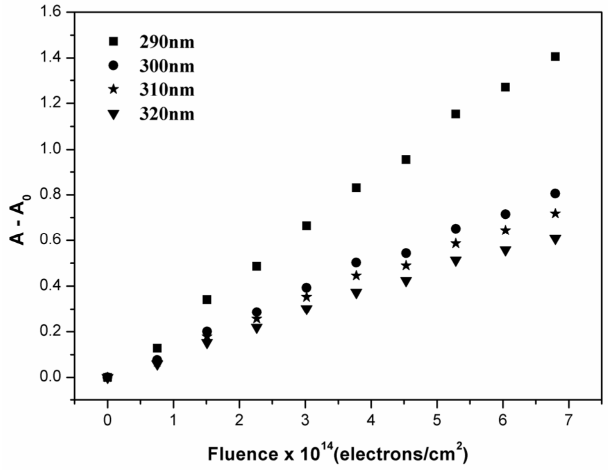

Figure 4. Plot of absorbance difference (A-A$_0$) versus electron fluence for Lexan samples.

The absorbance difference (A-A_0) versus electron fluence was plotted in **Figure 4** at wavelengths 290 nm, 300 nm, 310 nm and 320 nm. The linear dependence of absorbance with the electron fluence was observed. The solid lines in **Figure 4** fit the experimental data using the relation [25],

$$A_\lambda \approx k_\lambda n\sigma\phi + A_0 \quad (3)$$

where $A_\lambda(\phi)$ is the absorbance at a wavelength λ and at a fluence ϕ; k_λ is absorption coefficient of the chromophores produced (cm^{-2}); n is the number of chromophores which absorb at a particular λ created per incident primary ion and per unit area, and σ is the cross-sectional area of a cylinder within which n chromophores are created. Thus $n\sigma$ represent the efficiency of the chromophore groups formation induced by ion beam and there fore, the slope $k_\lambda n\sigma$ of the plot (A-A_0) versus electron fluence (ϕ) represents the efficiency multiplied by k_λ. The value of $k_\lambda n\sigma$ for electron bombardment for λ = 290, 300, 310 and 320 nm are found to be 2.10×10^{-15} cm^2, 1.18×10^{-15} cm^2, 1.05×10^{-15} cm^2 and 0.91×10^{-15} cm^2 respectively. It is observed that the value $k_\lambda n\sigma$ decreases with increase in wavelength. The (A - A_0) value at wavelength 290 nm is significantly more when compared to 300nm. This indicates that the absorption profile of the chromophore groups where different absorption at different wavelengths are due to difference in the absorption coefficients of the chromophore groups, for example, the absorption coefficient (k_λ) at 290 nm is maximum when compared to the absorption coefficient (k_λ) of other wavelengths.

3.3. FT-IR Spectral Analysis

The Vibration modes of chemical bonds are characterized by the absorption bands [27]. **Figure 5** shows the FT-IR spectra for the pristine and electron irradiated Lexan films at different fluences. There is almost no change in the spectra of samples irradiated at the fluence 3.02×10^{14} electrons/cm^2. On irradiation to the fluence of 6.79×10^{14} electrons/cm^2, the intensity of the peak corresponding to 3500 cm^{-1} changed by a small value. Apart

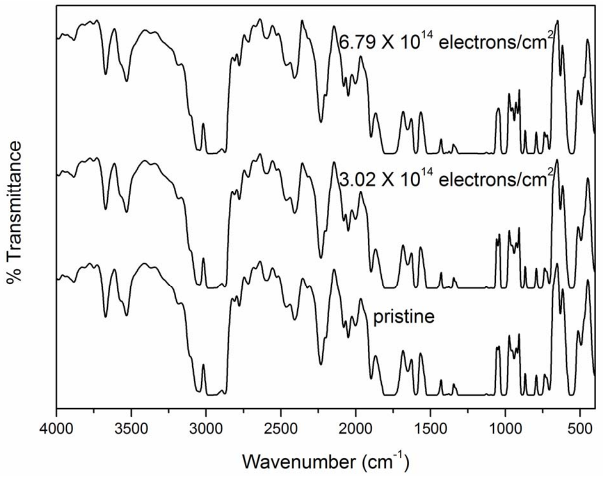

Figure 5. FT-IR spectra of pristine and electron irradiated Lexan.

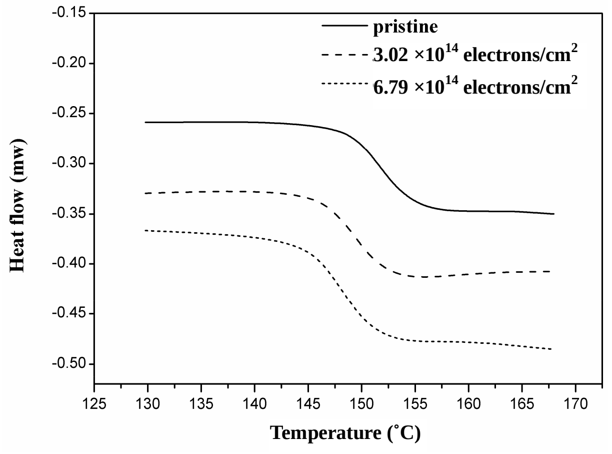

Figure 6. DSC pattern of pristine and electron irradiated Lexan.

from this, the intensity of the peak band corresponding to C=O stretch at 1700 cm^{-1} decreases slightly on irradiation. This may be due to chain-scission at the carbonate site (as shown in **Figure 1**) with the probable elimination of carbon dioxide or carbon monoxide. The corroboration of chain-scission can be deduced from the decrease in the intensity of absorption bands around 1160 cm^{-1} attributed to carbonate stretch. No change in the C-H stress has been observed which indicates that the electron irradiation have not influenced the benzene ring.

3.4. Differential Scanning Calorimetry Study

One of the important parameters of polymer namely glass transition temperature can be determined using DSC data. Glass transition temperature is a temperature where the polymer goes from rigid glassy state to rubbery state as chain becomes more flexible. At the glass transition temperature, the weak secondary bonds that stick the polymer chains are broken and macromolecule starts to move. DSC thermograms of pristine and electron irradiated Lexan samples were measured and are shown in **Figure 6**. The endothermic transformation of the unirradiated Lexan film occurs in a temperature range 145˚C to 154˚C with a glass transition temperature (T_g) of 150˚C and the corresponding heat of fusion was found to be 4.43 J/g. At the electron fluence 3.02 × 10^{14} electrons/cm^2, the DSC curve show a shift of T_g to 146˚C and for 6.79 × 10^{14} electrons/cm^2 T_g was observed at 143˚C, *i.e.* the glass transition temperature decreases with increase in electron fluence. After irradiation, the shift in the T_g to lower temperature reveals that the electron irradiation leads to chain-scission and subsequently reducetion in molecular weight. As a result, the polymeric system was changing towards more disordered state [28] which is also confirmed from XRD studies. It was found that the heat of fusion for unirradiated Lexan was found to be 4.43 J/g. After irradiation, the heat of fusion decreases with increase in electron fluence, *i.e.* for 3.02 × 10^{14} electrons/cm^2 it was found to be 4.34 J/g and for 6.79 × 10^{14} electrons/cm^2 it was found to be 4.15 J/g. This decrease in heat of fusion may be due to bond breaking during electron irradiation.

3.5. Thermogravimetric Analysis Study

The thermal degradation is a very important process which helps to know the influence of the polymer structure on the thermal stability and the temperature at which the polymer can be used. Sinha *et al.* [12] have reported that the thermal stability of the polycarbonate detector decreases at high dose of gamma, and the weight loss starts at around 420˚C and continues up to 700˚C. **Figure 7** shows the thermograms of the pristine and the electron irradiated Lexan samples showing the weight (%) as a function of temperature. From **Figure 7** it was found that the pristine sample thermogram shows a small change in weight loss at 250˚C and sample is thermally stable up to 440˚C. This weight loss was due to water vaporization and was not significant. After 440˚C, the film experienced a great weight loss up to 530˚C because of thermal decomposition, and about 76% of the sample decomposed in to volatiles. After 530˚C, there is a small decrease in weight loss due to emission of volatile gases. The thermal decomposition temperature for pristine Lexan was found to be 495˚C. Lexan sample irradiated at fluence 3.02 × 10^{14} electrons/cm^2 was thermally stable up to 445˚C and then there was a great loss in weight of the sample up to 540˚C. In this region almost 75% of the sample was decomposed in to volatiles. After 540˚C, the weight loss of the sample was slow and corresponding thermal decomposition temperature was found to be

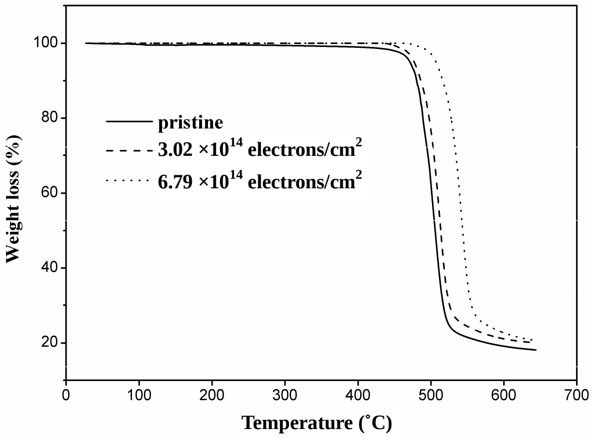

Figure 7. TGA thermogram of pristine and electron irradiated Lexan.

502˚C. The Lexan sample irradiated by electron of fluence 6.79 × 10^{14} electrons/cm^2 was stable up to 480˚C and then sudden decrease in the weight loss was observed up to 570˚C. After 570˚C, the weight loss was less and the corresponding thermal decomposition temperature was found to be 516˚C. From this study it is clear that, the thermal stability of Lexan increases after electron irradiation.

4. Conclusions

The conclusion drawn from the studies of 8 MeV electron irradiation effects on the structural and thermal properties of Lexan are as follows. The XRD results show decrease in crystallite size and percentage of crystallinity upon irradiation indicating that the polymeric system is moving towards more disordered state which is also supported by DSC studies. Using UV-Visible studies, the chromophore group formation were obtained by linear fit and the obtained values for the formation of chromophore groups is decreased at longer wavelength. The carbonate linkage is found to be the radiation-sensitive linkage and benzene ring does not undergo any changes after irradiation as studied from FTIR studies. TGA results reveal that thermal stability of Lexan increases after irradiation.

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