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# Optical and Structural Modifications of $\gamma$ irradiated Cr-39 Polymers

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**Abstract** The UV-Visible absorption spectra of CR-39 polymer, unirradiated and irradiated to gamma radiation up to 500 kGy dose were studied. The development of new peaks, shifting of absorption bands and their broadening as a result of gamma irradiation were observed and analyzed. The values of optical constant like direct and indirect band gaps have been determined. The values of indirect band gap have been found to have lower values then the corresponding values of direct band gap. The increase in carbon conjugation length and size of carbon clusters has also been pointed out from the results of UV-Visible spectroscopy.

## 1. INTRODUCTION

CR-39 is a polymer formed from diallyl monomer made by polymerization of diethyleneglycol bis allylcarbonate (ADC) in presence of diisopropyl peroxydicarbonate (IPP) initiater. The presence of the allyl groups allows the polymer to form cross- links; therefore, it is a thermoset resin. CR-39 is transparent in the visible spectrum and is almost completely opaque in the UV range. It has high abrasion /scratch resistance and has weight about half of the glass. It is an advantageous material for making eyeglasses and sunglasses. CR-39 is also resistant to most solvents and other chemicals, and to material fatigue. It is also used in a number of industrial and medical applications. The most recent studies with CR-39 involve neutron gamma and high energy ion irradiation induced changes in its structure and properties.

The ion irradiation of polymers with X-rays/ $\gamma$-rays or swift heavy ions deposit high amount of energy in the polymers along the track of their passage creating the formation of free radicals, ion tracks, cross linking, evolution of

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volatile species (1–3). Chong et al. (4) has been made a study on the UV-VIS and FTIR spectra of CR-39 plastics irradiated with 50 kVp tube X-rays in the dose range 0 and 45 MR. The optical transmittance over the wavelength region of 200–1000 nm was found to decrease with the X-ray exposure, much greater decrease being observed in the UV region. The IR absorption spectra of the irradiated samples show the presence of two new strong absorption bands at the frequencies 655 and 2340 $cm^{-1}$ i.e. an indicative of the gas $CO_2$ produced inside the plastic. The absorbance of these bands increases linearly with the X-ray dose. Fink et al. made an attempt of FTIR studies on low energy Ar ion irradiated Polycarbonate [5] using nuclear magnetic resonance spectroscopy. Malek et al. studied the X-ray and $\gamma$- ray induced degradation of Cr-39. They studied the diffusion of $CO_2$ with time. Navarro et al (7) showed that PC irradiation is accompanied with the preferential release of carbon monoxide followed by minor production of hydrogen, carbon dioxide and methane.

The effects of 320 keV Ar and 130 keV He ions at fluences ranging from $1 \times 10^{13}$ to $2 \times 10^{16}$ ions/$cm^2$ ion-beam bombardment on the physical and chemical properties of poly CR-39 have been investigated by Abdul-Kader et al. (8). UV–VIS spectra of bombarded samples reveal that the optical band gap decreases with increasing ion fluence for both Ar and He ions. In the FTIR spectra, changes in the intensity of the bands on irradiation relative to pristine samples occurred with the appearance of new bands. XRD analyses showed that the degree of ordering of the CR-39 polymer is dependent on the ion fluence. Changes of surface layer composition and an increase in the number of carbonaceous clusters produced important change in the energy gap and the surface wettability. The surface hardness increased from 10.54 MPa for pristine samples to 28.98 and 23.35 MPa for samples bombarded with Ar and He ions at the highest fluence, respectively. The physical and chemical properties of polymer electrolyte (PEO-$CdCl_2$) films irradiated with $\gamma$- rays were investigated by Raghu et al. (9). The degradation of the irradiated films was observed mainly due to chain scission/cross linking. The thermal stability and crystallinity were also found to decrease significantly. As a result of $\gamma$- ray irradiation a destruction of the polymer polypropylene lead to the formation of ketonic and alcoholic groups(10). In the polymer polyacetate, elimination of carbon dioxide was observed due to damage of the ester group. In polycarbonate, at the dose $10^6$Gy, formation of phenolic group was observed due to cleavage of ester bonds. In PVC, The FTIR spectral studies indicated the formation of C=C bond with the simultaneous reduction in the concentration of C-Cl bond when irradiated to $\gamma$- radiation (10).

In the present work we investigated physical and chemical response of $\gamma$-radiation on CR-39 polymer, specially the modification in the optical, chemical and structural properties through UV/Vis spectrometry.

## 2. EXPERIMENTAL

The samples of about 30×30 mm size of CR-39 were cut from flat sheets of thickness 250 micron. These samples were put in polyethylene sachets and irradiated with $\gamma$- radiation from a $^{60}$Co $\gamma$- source in air at room temperature at a dose rate 2.76 kGy/h at Bhabha Atomic Research Center, Mumbai (India). The samples were irradiated for various time periods to obtain the total accumulated $\gamma$- radiation doses as 1, 2, 5, 10, 20, 50, 117, 199 and 500 kGy respectively.

The optical absorption spectra were recorded at room temperature in the wavelength range 190 to 900 nm with the help of Shimadzu Double Beam Double Monochromator UV- Visible spectrophotometer (UV-2550) with a resolution of 0.05 nm. The samples were placed in the integrating sphere assembly ISR-240A attached with the spectrophotometer. The air was taken as reference. From these data the optical constants such as optical band gap (both direct and indirect) were determined.

## 3. RESULTS AND DISCUSSIONS

The unirradiated CR-39 samples are colorless. The visual observations of irradiated films indicate that the CR-39 samples above 50 kGy turn yellow with the increase of $\gamma$ radiation dose and ultimately turn to dark brown at 500 KGy $\gamma$ absorbed radiation dose. The CR-39 films also become brittle with increasing dose of $\gamma$ radiation.

The UV- Visible absorption spectra of unirradiated and $\gamma$ irradiated CR-39 films with a dose of 20, 50, 117, 199, and 500 KGy in the wavelength range 190 to 350 nm in terms of absorbance ($\alpha$) Vs $\gamma$-radiation dose are shown in Figure 1. Since at lower doses (1, 2, 5 and 10 kGy) there was no significant difference in the spectra of irradiated CR-39 samples, therefore for simplicity their spectra are not shown.

It is clear from the Figure 1 that above 350 nm, no significant absorption occurs and a flat plateau region is observed for all radiation doses. Above 20 KGy dose of $\gamma$ radiation the absorption bands within 250-350 nm range of all irradiated samples become broad and the tail of the absorption spectra shifts towards visible region from UV. An increase in absorbance at wavelength about 275 nm (hyper chromic shift) with the development of a new peak is also observed. All the above observations can be attributed to the formation of new

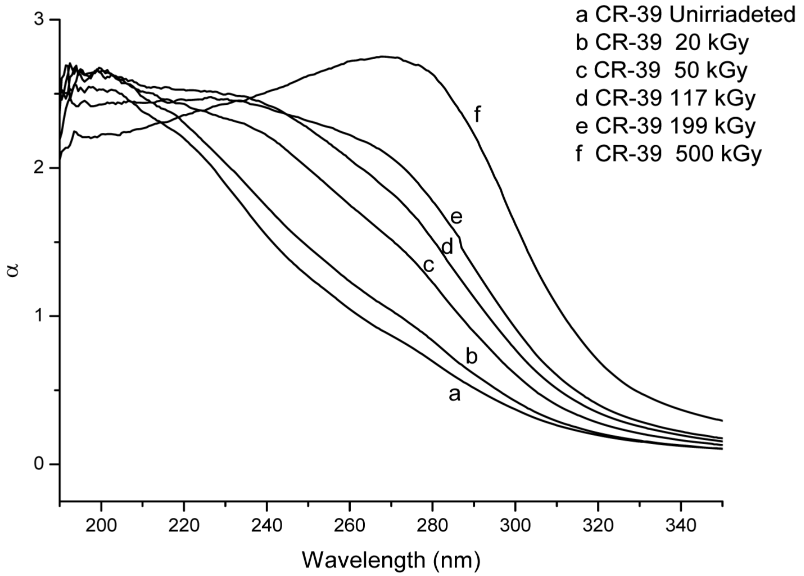

**Figure 1:** UV-Vis absorption spectra of unirradiated and irradiated CR-39 films.

chemical species as a result of energy deposition from the incident $\gamma$- rays. This energy deposition may lead to the ionization and excitation leading to the breaking of original bonds, chain scission, radical formation, cross linking etc. [2, 7, 8]. This in turn results in the formation of radicals, cations, anions, double/ triple bonds or aromatic species etc. The other possibility for red shift and coloration of CR-39 can be due to the increase in conjugation of double bonds (polyene formation) and formation of carbonaceous clusters with the increase in $\gamma$ absorbed dose as reported earlier by other workers also [8].

### 3.1 Determination of Energy Band Gap

The study of optical absorption gives information about the band structure of solids. The insulators/ semiconductors are generally classified into two types (a) direct band gap materials (b) indirect band gap materials. In direct band gap materials the minimum of conduction band lies directly above the maximum of valance band in momentum space (the momentum of both is same). In indirect band gap materials the momentum of conduction band minimum and the valance band maximum are not the same. In direct band gap material, electrons from the minimum of conduction band can recombine with holes at the maximum of valance band without any exchange in momentum. The energy of the recombination across the band gap will be emitted in the form of a photon of light. This is a radiative transition. In indirect band gap materials the transition across the band gap does not conserve momentum and is forbidden. This recombination occurs with the mediation of a third body, such as a phonon or a crystallographic defect, which allows the conservation of momentum. This recombination often releases band gap energy as phonon instead of photon. Davis and Shilliday (11) showed that near the fundamental band edge, both direct and indirect transitions occur. These can be determined by plotting α1/2 and $\alpha^2$ against frequency where α is called absorbance. According to Thutupalli and Tomlin (12) the direct and indirect band gap ($Eg_d$ and $Eg_i$ respectively), of a semiconductor are related to the absorbance (α) as follows:

$$(n\alpha h\nu) = A\,(h\nu - Eg_d)^{1/2}$$

$$(n\alpha h\nu) = B\,(h\nu - Eg_i)^{2}$$

Where $h\nu$ is the photon energy, n is the refractive index and A and B are constants. These relations have also been found to hold good for polymers also (13).

For the determination of nature and width of direct and indirect band gaps $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ were plotted as a function of photon energy ($h\nu$)

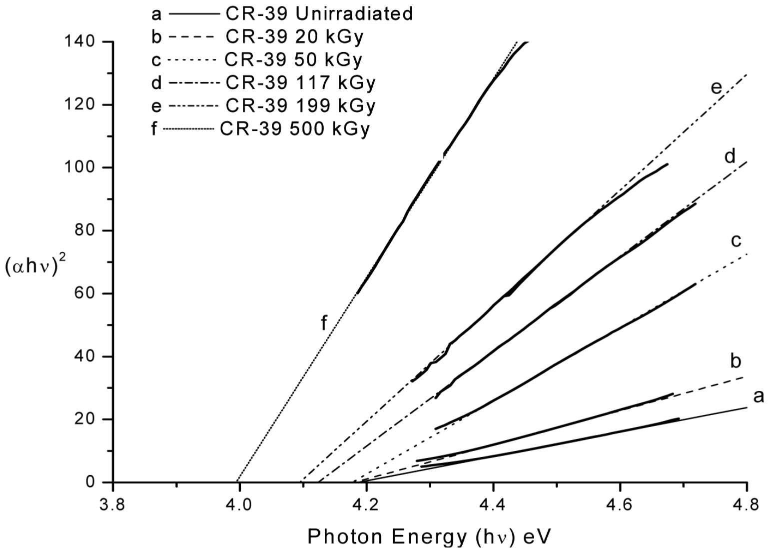

**Figure 2:** $(\alpha h\nu)^2$ versus photon energy (hν) eV curves of unirradiated and irradiated CR-39films.

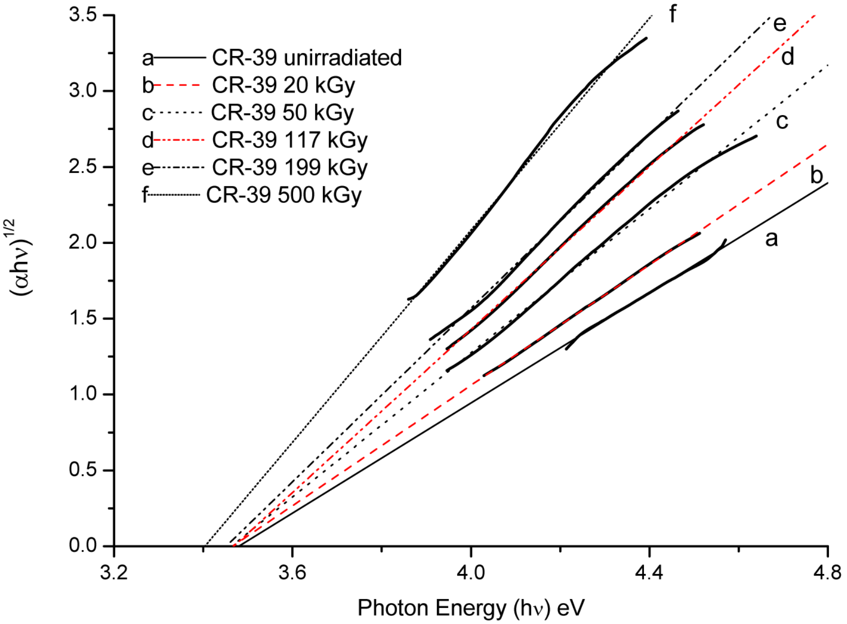

**Figure 3:** $(\alpha h\nu)^{1/2}$ versus photon energy (hν) eV\ curves of unirradiated and irradiated CR-39films.

respectively, taking into account the linear portion of the fundamental absorption tail of the UV- visible spectra as shown in Figures 2-3. The direct band gap energies were determined by extrapolating the linear portions of the $(\alpha h\nu)^2$ vs. hν (photon energy) curves, from the intercepts of the best fit lines on hν axis as shown in Figure 2.

**Table 1:** Direct and indirect optical band gaps of unirradiated and irradiated CR-39films.

| γ- radiation **dose (kGy)** | **Band Gap (eV)** | | **Regression Coefficient 'R'** |
|---|---|---|---|
| | **Direct** | **indirect** | |
| Unirradiated | 4.23 | 3.52 | 0.99 |
| 20 | 4.19 | 3.50 | 0.99 |
| 50 | 4.18 | 3.46 | 0.99 |
| 117 | 4.15 | 3.42 | 0.99 |
| 199 | 4.12 | 3.35 | 0.99 |
| 500 | 3.98 | 3.3 | 0.99 |

The indirect band gaps were obtained from the $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ photon energy curves in the similar manner as shown in Figure 4.

These values along with their slandered errors have been determined for unirradiated and CR-39 samples irradiated to different doses of γ- radiation and the values of direct and indirect band gaps are presented in Table 1.

The magnitude of regression coefficient, have been found to be greater than 0.99 for the fitted lines as shown in Figures [2–3] for the determination of absorption edge, direct band gap and indirect band gaps. This in turn clearly indicates the simultaneous existence of direct and indirect band gap in CR-39 polymer with decreasing tendency with the increasing γ- radiation dose. The values of indirect band gap have been found to be lower than the corresponding values of the direct band gap in the CR-39 polymer subjected to γ- radiation.

### 3.2 Conjugation Length:

From the abscissas of $(\alpha h\nu)^{1/2}$ versus photon energy $(h\nu)$ plots in Figure 3 of irradiated CR-39 the number of carbon atoms per conjugation length has been calculated using Robertson's and O'reilly relation (13, 14) given by equation (1)

$$N = \frac{2\beta\pi}{E_g} \tag{1}$$

Where, N is the number of carbon atoms per conjugation length for a linear chain polymer. $2\beta$ is the band structure energy of a pair of adjacent π site. The value of β is taken to be -2.9 eV as it is associated with $\pi$- $\pi^*$ optical transition in C=C structure. $E_g$ was taken as the lower value of band gap i.e. the indirect

**Table 2:** The number of carbon atoms in conjugation calculated from eq. 1 along with the data number of carbon atoms (M) in cluster.

| γ- radiation dose (kGy) | No. of carbon atoms in conjugation (N) calculated from eq. 1 | Number of carbon atoms (M) in cluster |
|---|---|---|
| 500 | ~6 | 108 |
| 199 | ~5 | 104 |
| 117 | ~5 | 101 |
| 50 | ~5 | 98 |
| 20 | ~5 | 96 |
| Unirradiated | ~5 | 96 |

energy band gap. The number of carbon atoms in conjugation (N) calculated from above equation in the present work at different doses of $\gamma$ -radiation is given in Table 2.

It is evident from Table 2 that the results calculated from eq. 1 show increase in the C=C conjugation length as reported earlier also (2).

### 3.3 Carbon Cluster Size:

It is also understood (Fink et al.) (3) that the Robertson's equation underestimates the cluster size in the irradiated polymers. They have accordingly assumed the structure of the clusters to be buckminsterfullerene, i.e. comprising of $C_{60}$ rings instead of $C_{6,}$ arriving at the relation

$$E_g = \frac{34.3}{\sqrt{M}},$$

Where M is the number of carbon atoms per cluster. The above relation can be used to obtain the number of carbon atoms per cluster in irradiated polycarbonate. Thus,

$$M = \frac{(34.3)^2}{E_g^2} \tag{2}$$

## CONCLUSIONS

The visual inspection of CR-39 films exposed to $\gamma$ radiation show yellowing of the samples with the increase of $\gamma$ absorbed dose. UV-Vis spectrometric studies of virgin and $\gamma$- irradiated CR-39polymer reveals the coexistence of direct and indirect band gaps simultaneously. The indirect band gap values are found lower as compared to the corresponding values of direct band gap in the unirradiated and $\gamma$- irradiated CR-39 polymer. Both types of the optical band gap energies have decreasing tendency with the increasing $\gamma$ radiation dose. The intensity patterns of various bands appearing in the UV-Vis and FTIR spectra of $\gamma$ irradiated CR-39 show the structural modifications that correspond to formation of $\pi$ conjugation sites of various lengths. The number of carbon atoms per conjugation increase with the increase of $\gamma$ absorbed dose. It is also clear that the high value of energy deposition results in reorientation of polymeric molecules leading to the formation of carbon clusters accompanied with increase in size (8) with the increase in $\gamma$ radiation dose.

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