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# Effect of gamma irradiation on the optical properties of CR-39 polymer

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**Abstract** The UV-Visible absorption spectra of virgin and gamma irradiated (20–800 kGy) CR-39 polymer have been deduced by using Shimadzu Double beam Double Monochromator UV-Visible Spectrophotometer (UV-2550). The existence of the peaks, their shifting and broadening as a result of gamma irradiation has been discussed. Finally the indirect and direct band gap in virgin and gamma irradiated CR-39 has been determined. The values of indirect band gap have been found to be lower than the corresponding values of direct band gap.

## Introduction

Demand for polymers having improved surface and bulk properties is continuously on the rise due to their use for various scientific and technological applications [1–2]. Irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly [3–16].

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Irradiation in polymers destroys [17] the initial structure by way of cross linking, free radical formation, irreversible bond cleavages etc. that results in the fragmentation of molecules and formation of saturated and unsaturated groups [12]. All these processes introduce the so called defects inside the material that are responsible [3] for change in the optical, electrical, mechanical and chemical properties of the material.

Importance of optical properties of polymers in fabrication of optical sensors, LEDs, antireflective coatings etc. justify the need for studying the effects of irradiation on the optical properties of polymers such as absorption and band gap [18–20].

In the present work, we have studied the effect of gamma irradiation on the absorption and band gap of CR-39 polymer by using UV-VIS spectrophotometery. The monomer structure of CR-39 polymer [21] is as shown in Fig. 1.

Similar studies have been carried out by several other authors [13–16] however in a different context. Saad et al. [13] have indicated qualitatively the decrease in the band gap with increasing gamma dose with maximum up to 400 kGy. El-Shahawy [14] has reported the slight decrease in direct band gap with increase in gamma dose up to a maximum of 100 kGy. El.Ghandoor et al. [15] have studied the effect of gamma irradiation on the refractive index of CR-39 polymer. Singh and Prasher [16] have quoted decrease in band gap with increase in gamma dose without mentioning whether the band gap was direct or indirect.

In this paper, we present the quantitative measurements of band gap of CR-39 polymer with increase in gamma dose (maximum up to 800 kGy). The simultaneous existence of indirect and direct band gap in

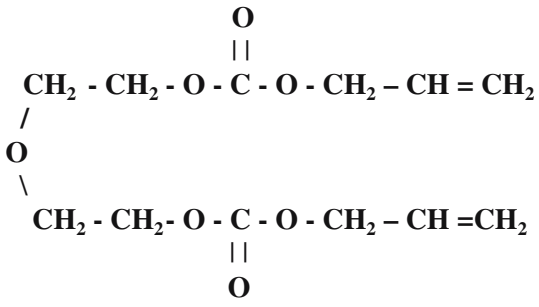

**Fig. 1** Monomer composition of CR-39 polymer

CR-39 polymer is also reported, perhaps for the first time to the best of our knowledge.

## Experimental details

Samples of CR-39 polymer (TASTRAK, Bristol, England) were cut from flat polished sheets. These samples were placed in polyethylene sachets and the irradiation was carried out with $^{60}$Co gamma source in air at a dose rate of 2.76 kGy/h using the irradiation facility at Bhabha Atomic Research Centre, Mumbai (India). The samples were irradiated for various times and the total gamma doses obtained were 20, 50, 117, 199, 500 and 800 kGy respectively.

The virgin and gamma irradiated CR-39 polymer samples were subjected to spectral studies in the Ultraviolet and Visible region. These studies were carried out by using Shimadzu Double beam Double monochromator UV-Visible Spectrophotometer (UV-2550) in the wavelength range of 190–900 nm having resolution of 0.1 nm. All the spectra were recorded by mounting the samples in the Integrating Sphere Assembly ISR-240A attached with the Spectrophotometer, keeping air as the reference.

## Results and discussion

The UV-Visible absorption spectra of virgin and gamma irradiated (with 20, 117, 199, 500 and 800 dose) CR-39 samples in the wavelength range 190–600 nm have been presented in Fig. 2. Above 600 nm, no absorption was detected. These spectra have been analyzed to explain the existence of the peaks; their shifts and broadening as a result of gamma irradiation and finally to determine the optical band gap.

The UV-Visible spectrum of virgin CR-39 sample (Fig. 2 curve 'a') clearly indicates two peaks at 208 and 240 nm. These peaks may be attributed to the transitions

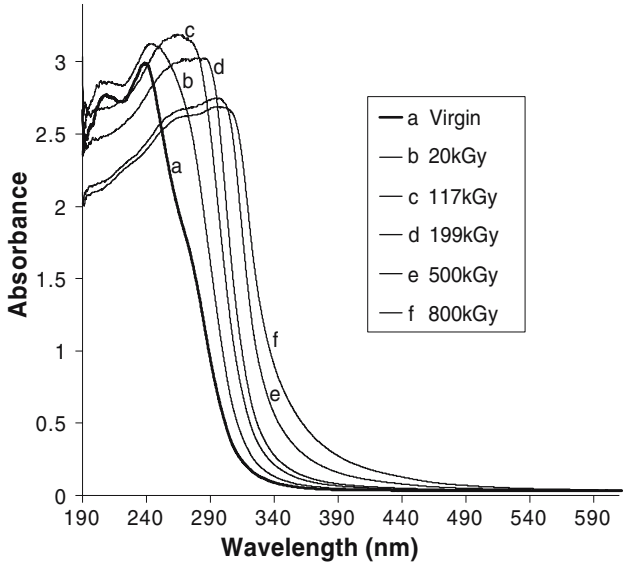


**Fig. 2** UV-Visible absorption spectra of virgin and gamma irradiated (with 20, 117, 199, 500 and 800 kGy dose) CR-39 polymer

from n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ orbitals, occurring as a result of double bond between carbon and oxygen with lone pair of electrons present on oxygen [22].

The effect of gamma irradiation on CR-39 polymer results in shifting and broadening of peaks as shown in Fig. 2 (curves 'b' to 'f'). It appears that there is a continuous red shift accompanied by peak broadening as we increase the gamma dose from 0 to 800 kGy and two peaks observed at 208 and 240 nm in virgin sample shift to 262 and 297 nm at a maximum dose of 800 kGy. Such a red shift can be ascribed to a number of possibilities. It is well known that [3, 12, 17] various processes during irradiation of polymers such as ionization and excitation lead to breaking of original bonds, chain scission, radical formation, cross linking, etc. This in turn results in the formation of radicals, cations, anions, double bonds, triple bonds, aromatic species etc. However destruction of the virgin polymer structure upon irradiation caused by high doses of gamma quanta leading to the formation of multiple (double or triple) bonds or aromatic species seems to be more likely process responsible for red shift in the peaks. Other possibility for red shift can be the increase in conjugation with increasing gamma dose resulting in a decreased HOMO-LUMO gap forcing the position of n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions towards lower energy [22]. Such a shift of peak positions from UV towards Visible under irradiation has also been reported previously by other workers [5, 13, 16]. The broadening of the peaks can also be attributed to the production of radiation induced defects such as anions,

cations, radicals, organic species or centers etc. [3]. Such defects may result in the formation of new energy levels leading to the broadening of peaks.

## Determination of band gap

From the UV-Visible spectra, the indirect and direct optical band gap of virgin and gamma irradiated CR-39 polymer have been determined.

For the determination of indirect and direct band gap, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ were plotted as a function of photon energy ($h\nu$) respectively [18, 23–28], taking into account the linear portion of the fundamental absorption edge of the UV-Visible spectra (curves 'a' to 'f' in Fig. 2). Such plots have been presented in Fig. 3; 4 respectively. From the intercept of the best fit lines (Fig. 3; 4) on $h\nu$ axis, indirect and direct band gaps along with their standard errors have been determined for virgin and gamma irradiated (different doses) CR-39 polymer and the results are presented in Table 1. The magnitude of standard errors is maximum up to ~ 3%. The regression coefficient 'R' has been found to be greater than 0.95 for the fitted lines (Fig. 3; 4) for the determination of indirect as well as direct band gap. This, in turn, clearly indicates the simultaneous existence of indirect and direct band gap in CR-39 polymer with decreasing tendency at higher gamma dose. Furthermore, the values of indirect band gap have been found to be lower than the corresponding values for the direct band gap. To the best of our knowledge simultaneous existence of indirect as well as direct band gap in CR-39 polymer has not yet been reported although such a coexistence of direct and indirect band gap have been observed in some other materials [18, 24, 29–31].

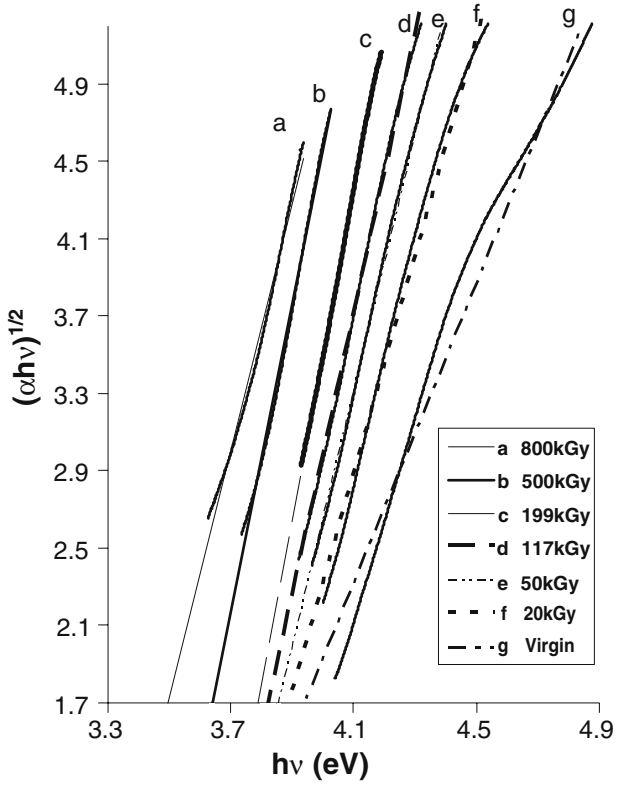


**Fig. 3** Plots for Indirect Bandgap (eV) in virgin and gamma irradiated (with 20, 50, 117, 199, 500 and 800 kGy dose) CR-39 polymer

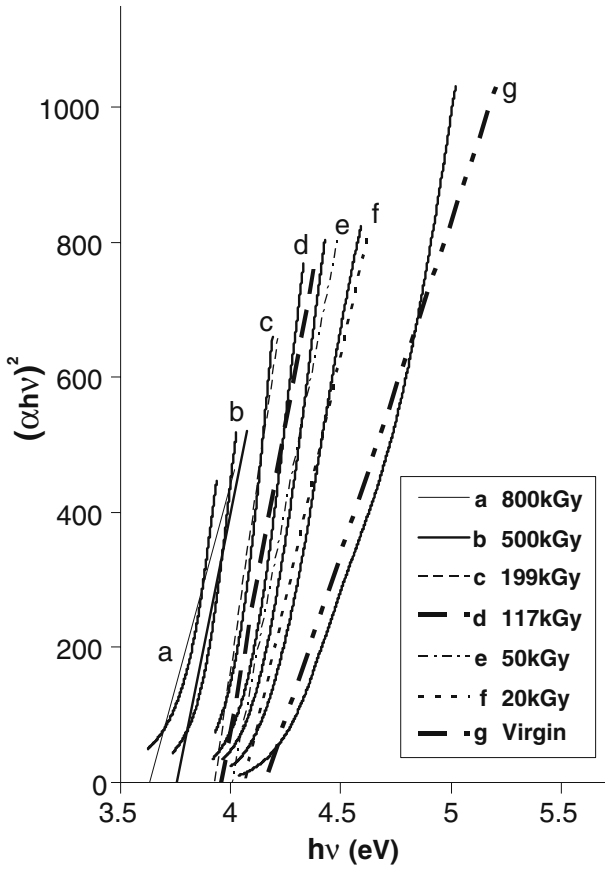


**Fig. 4** Plots for Direct Bandgap (eV) in virgin and gamma irradiated (with 20, 50, 117, 199, 500 and 800 kGy dose) CR-39 polymer

## Conclusion

UV-VIS Spectrophotometric studies of virgin and gamma irradiated CR-39 polymer reveals the coexistence of indirect and direct band gap; an observation which is being reported for the first time to the best of our knowledge. The values of indirect band gap are lower than the corresponding values of direct band gap in virgin and gamma irradiated CR-39 polymer.

**Table 1** Indirect and direct band gap values for virgin and gamma irradiated CR-39 polymer

| S. No. | Gamma Dose | Indirect Band Gap (eV) | Regression Coefficient 'R' | Direct Band Gap (eV) | Regression Coefficient 'R' |
|---|---|---|---|---|---|
| 1 | Virgin | 3.50 ± 0.03 | 0.99 | 4.16 ± 0.05 | 0.97 |
| 2 | 20 kGy | 3.59 ± 0.03 | 0.99 | 4.06 ± 0.05 | 0.98 |
| 3 | 50 kGy | 3.60 ± 0.02 | 0.99 | 4.01 ± 0.07 | 0.97 |
| 4 | 117 kGy | 3.59 ± 0.01 | 0.99 | 3.96 ± 0.08 | 0.97 |
| 5 | 199 kGy | 3.59 ± 0.01 | 0.99 | 3.93 ± 0.08 | 0.98 |
| 6 | 500 kGy | 3.43 ± 0.02 | 0.99 | 3.75 ± 0.09 | 0.96 |
| 7 | 800 kGy | 3.23 ± 0.03 | 0.99 | 3.63 ± 0.09 | 0.95 |

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