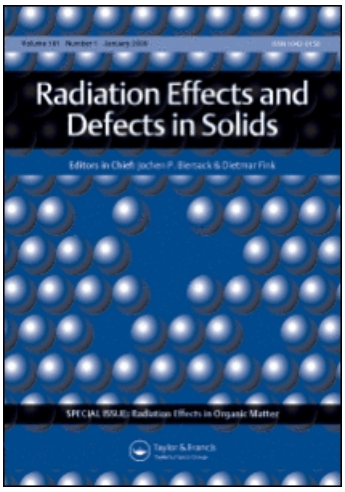

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Structural modifications and track registration response of some gamma irradiated polycarbonate detectors

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STRUCTURAL MODIFICATIONS AND TRACK REGISTRATION RESPONSE OF SOME GAMMA IRRADIATED POLYCARBONATE DETECTORS

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Makrofol-E, Lexan and Polycarbonate detectors exposed to gamma irradiation in the dose range of 10^1-10^6 Gy have been characterized by track methods and UV–Vis, IR and ESR spectroscopy. The track registration response is studied through variation of etching characteristics and the activation energy for bulk-etching at different doses of gamma rays was determined. Thermal stability studies were also carried out for understanding the effects of gamma irradiation on the thermal resistance of these irradiated polymers. The experimental results show that up to 10^6 Gy gamma exposure the examined materials are rather gamma insensitive radiation hard detectors.

Keywords: Bulk-etch rate; Track length; Makrofol-E; Lexan; Polycarbonate; ^{60}Co; ^{252}Cf; Gamma dose; Activation energy

1. INTRODUCTION

Solid state nuclear track detectors (SSNTDs) have been widely used in recent years in many fields of nuclear sciences [1,2]. These plastic track detectors consist of long-chain organic molecules and have different thresholds for charged particle detection [1]. Exposure of organic polymers to gamma radiation may lead to either scission of bonds or cross-linking. Both these processes change the etching characteristics of

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the plastic detector [3–12]. It is also known that radiation some times changes the optical properties [13], morphology [5] and structures [9,12,14–16]. This feature allows these materials to be used as possible gamma dosimeters. In this study, the detectors Makrofol-E, Lexan and Polycarbonate have been chosen as track detectors. Since these detectors are used in a number of nuclear experiments, it is worthwhile to study the effects of gamma irradiation on these solids. This work may also be helpful in terms of understanding the track registration response as well as in studying the quantitative effects of gamma dose on these detectors. It is an established fact that molecules with long side chains are known to be especially radiation sensitive. On the other hand, the backbone structure is frequently preserved. Further, aromatic groups are known to reduce the polymer irradiation sensitivity due to delocalization of the excitation energy [16]. Since all three detectors chosen here are bisphenol-A polycarbonates, having two benzene rings in the monomer unit, it will be interesting to investigate these samples under different doses of gamma rays.

2. EXPERIMENTAL PROCEDURE

Three types of detectors Makrofol-E and Polycarbonate (manufactured by Bayer AG, Leverkusen, Germany), and Lexan (manufactured by GEC, USA) were used. Several pieces (size $3 \times 3\,\text{cm}^2$) were cut from thin (200–500 μm) commercially available sheets. They were then washed thoroughly with soap solution and rinsed with deionised water. The cleaned samples were then dried and used for irradiation.

Two sets of seven samples each, of sizes $3 \times 3\,\text{cm}^2$ were prepared. One set was first irradiated by normal incidence to a ^{252}Cf fission fragment source which has a fission activity of 1360 fissions per second. The average energy of a medium heavy fragment is 80.1 MeV ($Z = 55.5$, $A = 142.0$) and that of the medium light fragment is 108 MeV ($Z = 42.5$, $A = 108.5$) so that a crude estimate of the overall average energy yields 95 MeV. The detectors were exposed in vacuum for 10 min, and then, together with the unirradiated (second) set, were exposed to ^{60}Co gamma rays at a dose rate of 3.0 kGy/h at room temperature up to various gamma doses ranging from 10^1–10^6 Gy. Two samples of the pre-gamma-irradiated set (10^3 and 10^6 Gy) along with a pristine sample

were cut into small pieces ($0.5 \times 0.5\,cm^2$) and then irradiated in vacuum by fission fragments at an angle of 45°. After irradiation the detectors were etched with 6 N NaOH solution, at four different temperatures viz., 55°C, 60°C, 65°C, 70°C. The etching was done in successive steps. The times indicated in the graph do not refer to the real times of one-step etching and therefore are denoted as the effective times. These times are the sum of incubation times and the real etching times and therefore include n incubation times after n etching steps. In contrast, one-step etching for the same etching time incorporates only one incubation time. The accuracy in the maintenance of temperature was ± 1°C. After every etching, the samples were thoroughly washed with distilled water and dried. Then the diameters of the fission fragment tracks were measured using a Leitz Microscope fitted with a special objective magnification of 100 × (water immersion). The bulk-etch rate (V_G) was determined by plotting diameter versus etching time. The detectors which were exposed at 45°, were etched at 60°C for different time periods and the corresponding track-lengths were measured under an objective with 40 times magnification. The error involved in the measurement of track diameters was $\pm 0.87\,\mu m$, and for track length measurements the uncertainty was $\pm 1.12\,\mu m$.

Samples were cut into small pieces. For each set of detectors there were seven samples including the unexposed one. UV–Vis spectra of the pristine and irradiated samples were taken for these materials by a Beckman DU-650 spectrophotometer. The samples were then put vertically inside a quartz-shell and the absorption spectra were recorded in the range 200–800 nm, keeping air as the reference. The scan speed was 1200 nm/min. For IR study, the irradiated samples were cut into small pieces. The spectra were recorded by a NICOLET (IMPACT 410), Fourier-transforming (FT) instrument keeping air as the reference. The samples were put vertically on a sample holder and the spectra were taken in the range 4000–500 cm^{-1}. First derivative ESR measurements were done using a Varion (E-109, X-band) spectrometer with 100 kHz field modulation. For these studies small samples were put inside a quartz tube and the spectra were recorded at room temperature. A 9.6 GHz microwave frequency was used for this instrument. The instrumental set-up for ESR studies is as follows: field set 3380 ± 800 Hz, time constant 0.250 s, scan time 8 min, amplitude 0.5 G, receiver gain 1.25×10^5, microwave power 5 mW. Thermogravimetric

studies were performed using a PERKIN-ELMER instrument. Here the samples were cut into very small pieces and were kept on a thermobalance. The samples were then heated up to a temperature of around 600°C for Makrofol-E, around 680–700°C for Lexan and up to a temperature of around 700°C in the case of Polycarbonate. The heating rate was 20°C/min for all the cases. The heating resulted in weight loss, which was recorded as a function of temperature in the TGA thermogram.

3. RESULTS AND DISCUSSION

It was observed that up to a dose of 10^5 Gy, there were no visible changes in these detectors. But at 10^6 Gy of gamma dose the colourless films of these materials became light yellow. The bulk-etch rates (V_G) at different etching temperatures for both pre- and post-gamma-irradiation of these detectors exposed to different doses (no dose, 10^3 and 10^6 Gy) can be derived from Tables I and II for Makrofol-E and Lexan, respectively. The results show that there is no appreciable change in V_G. The bulk-etch rate remains invariant until a dose of

TABLE I Track-length in μm for Makrofol-E at different etching times

Etching time (h)	*No dose*	10^3 Gy	10^6 Gy
0.50	5.71 ± 1.1	5.65 ± 1.1	7.30 ± 1.1
0.75	8.44 ± 1.1	8.68 ± 1.1	11.22 ± 1.1
1.00	11.87 ± 1.1	10.80 ± 1.1	14.06 ± 1.1
1.25	14.88 ± 1.1	14.96 ± 1.1	16.93 ± 1.1
1.50	14.85 ± 1.1	14.89 ± 1.1	17.29 ± 1.1
1.75	14.73 ± 1.1	14.96 ± 1.1	16.14 ± 1.1
2.00	12.70 ± 1.1	12.77 ± 1.1	14.06 ± 1.1

TABLE II Track-length in μm for Lexan at different etching times

Etching time (h)	*No dose*	10^3 Gy	10^6 Gy
0.50	5.50 ± 1.1	5.80 ± 1.1	5.85 ± 1.1
0.75	8.50 ± 1.1	8.90 ± 1.1	9.03 ± 1.1
1.00	10.94 ± 1.1	11.15 ± 1.1	12.99 ± 1.1
1.25	13.93 ± 1.1	13.73 ± 1.1	15.99 ± 1.1
1.50	13.86 ± 1.1	13.93 ± 1.1	15.84 ± 1.1
1.75	13.74 ± 1.1	13.69 ± 1.1	15.71 ± 1.1
2.00	11.66 ± 1.1	11.59 ± 1.1	13.35 ± 1.1

10^6 Gy is reached, due to the fact that only negligible cross-linking and scission of the polymeric chains has taken place both of which influence the dissolution rate of the material. Frank and Benton [3] also found for Lexan track detectors up to a gamma dose of 1.0×10^6 Gy, that there were no significant changes in V_G.

For better understanding of radiation damage along the tracks, we also studied the track length of fission fragments in these detectors which had been pre-exposed at different doses of gamma rays, see Tables I and II. The maximum etchable track length as well as the complete etching time for fission fragments were determined. Figure 1 shows the track lengths measured for different etching times for the Lexan detector. From the results it is evident that track length is not altered by gamma radiation of different doses below 10^6 Gy. At the dose of 10^6 Gy, only a slight increase in track length was observed. The maximum etchable track length for Makrofol-E ranges between 14 and 15 μm. At 10^6 Gy it becomes 17.3 μm. The complete etching time is approximately 85 min for the three doses for Makrofol-E detector. For Polycarbonate, we see that the complete etching time is about 105 min and the maximum etchable track length ranges between 8 and 9.5 μm. Lexan also behaves in a similar way. Here the complete

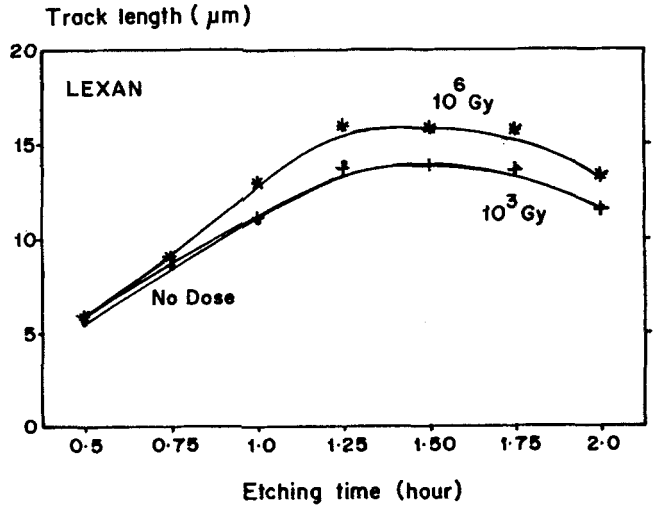

FIGURE 1 Variation of average track-length with etching time for Lexan detector at different gamma doses.

etching time is about 78 min and the maximum etchable track length ranges between 13.9 and 5.9 μm. The plot shows a decrease in the maximum etchable track lengths with prolonged etching times. This may be due to the fact that after the track is completely etched further etching only succeeds in removing the bulk material leading to a consequent shortening of the track length.

The activation energies for bulk-etching of these detectors were determined. The change in the activation energy with gamma exposure is insignificant. Since the bulk-etch rate has not altered to an appreciable extent by the gamma dose exposure, obviously significant changes in the activation energies were not expected.

The UV–Vis spectra of Makrofol-E are shown in Fig. 2. The transmittance spectra of Makrofol-E exposed to doses below 10^4 Gy are identical with the spectrum at the dose of 10^4 Gy. No significant changes were observed beyond 500 nm. Though the UV–Vis study does not give any information about bond cleavage or bond formation, it is evident from these results that above the dose of 10^4 Gy, transmittance decreases with increasing gamma dose. The decrease is significant in the region 280–500 nm.

The UV–Vis study of Lexan also shows a similar trend. From Fig. 3, one can understand that up to a dose of 10^4 Gy, there are no changes in the absorption pattern. Only from 10^5 Gy dose onwards the changes

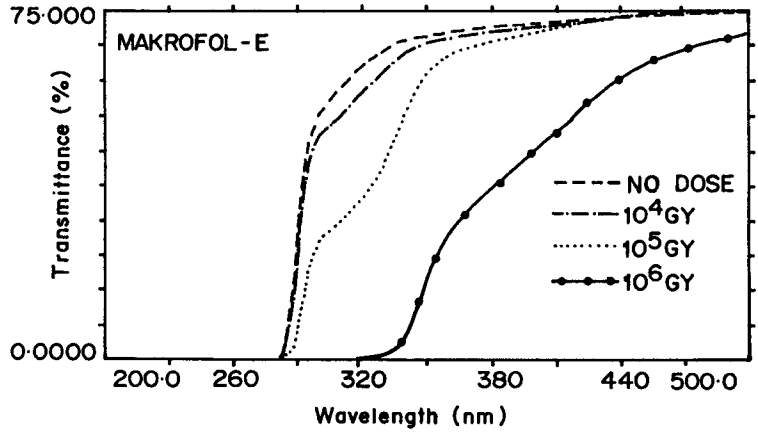

FIGURE 2 UV–Vis transmittance spectra of Makrofol-E detector exposed to different gamma doses.

become apparent. Though no absorption peaks are observed, it has been noted that the absorption shifts towards higher wavelength because of gamma exposure. The change is significant in the region 300–500 nm. For dosimetric applications lower gamma doses ($< 10^4$ Gy) may not be as useful as higher doses. Figure 4 shows the dose dependent transmission at different wavelengths. There is no

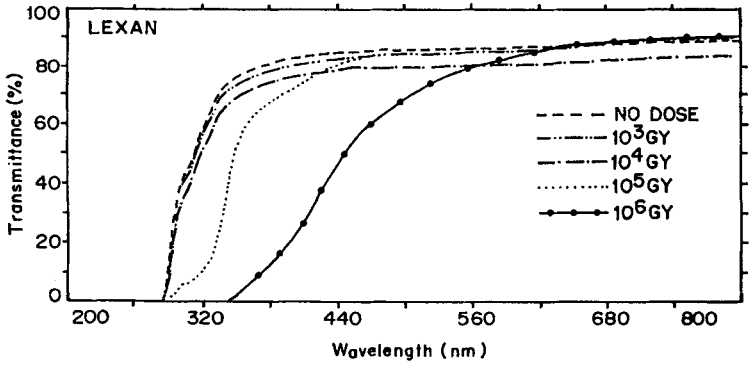

FIGURE 3 UV–Vis transmittance spectra of Lexan detector exposed to different gamma doses.

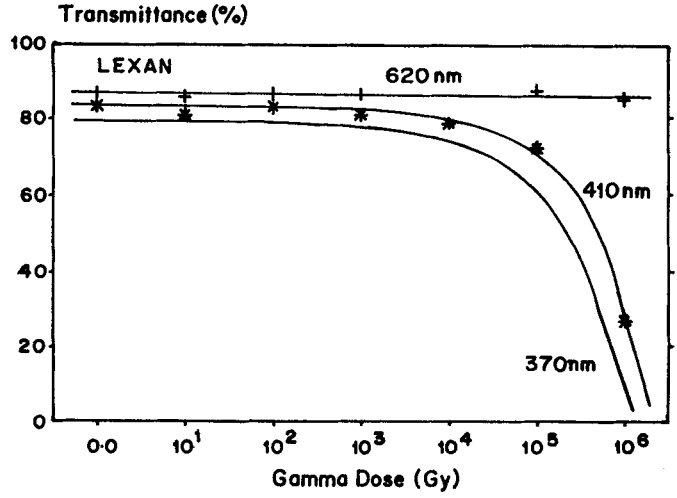

FIGURE 4 Variation of transmittance with gamma doses for Lexan detector at different wavelengths.

observable influence on transmittance at 620 nm for different gamma doses. However, at lower wavelengths (370 and 410 nm) the transmittance decreases rapidly for gamma doses of 10^5–10^6 Gy, as these wavelengths comprise the fingerprint region for the formation of double bonds, quinones and carbonaceous clusters.

The transmittance spectra of Polycarbonate detectors exposed to different gamma doses are shown in Fig. 5. Again it can be seen that there is no remarkable decrease in the transmittance up to doses of 10^4 Gy but beyond. This decrease can be observed only above 390 nm. The largest changes in transmittance are found at 420 nm. It may be concluded that the transmittance at 420 nm can be best used in gamma ray dosimetric measurements.

The IR study of these gamma irradiated polymers is not very informative. It was observed in all the cases that the concentration of some of the existing groups or bonds decreased at high dose of gamma irradiation. Neither total cleavage of bonds nor any new bonds were observed.

However, the ESR study of these detectors revealed some interesting information about the chemical modifications. For all three polymers, no radical formation was observed below the dose of 10^5 Gy. But at the dose of 10^6 Gy, one could get clear signals for the radical formation as shown in Fig. 6. It is quite significant to observe that in all three cases the radical does not show any hyperfine splitting. Moreover, the radical signals give the same g-value. This clearly signifies the presence of a

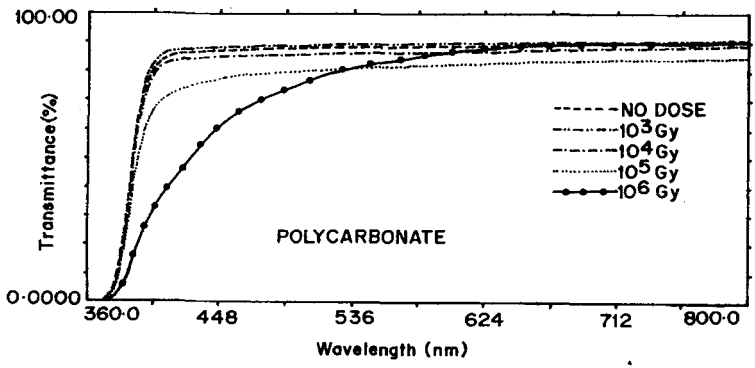

FIGURE 5 UV–Vis transmittance spectra of Polycarbonate detector exposed to different gamma doses.

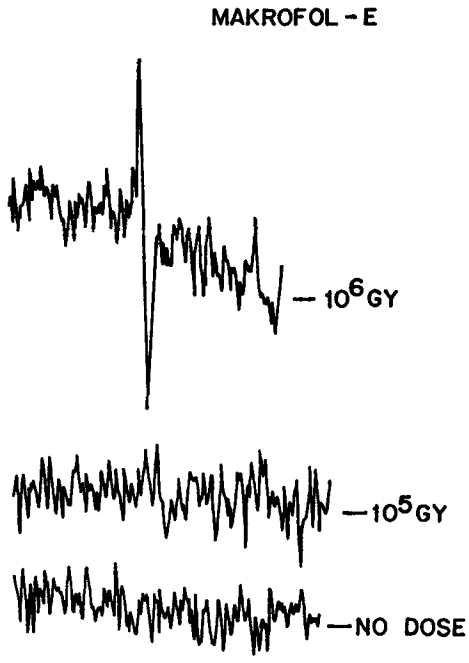

FIGURE 6 ESR spectra of gamma irradiated Makrofol-E detector shows the radical signal at the dose of 10^6 Gy.

similar type of radicals in these polymeric films. A similar ESR signal was also observed by Chambaudet *et al.* [17] in Makrofol. Edmonds and Durrani [18] also observed the same type of radical for gamma irradiated Lexan. They ascribed this signal vaguely to the presence of "carbon like" radicals, where the unpaired electron is delocalized over a number of carbon cycles or conjugated linear chains.

Since all the detectors discussed here have the same chemical structure and since the radical signals were also identical, we can assume that similar chemical changes might have taken place. The radical which is observed may be due to the scission of a C–H bond of the phenyl ring. After scission the unpaired electron of the carbon atom delocalizes over the benzene ring system. The hydrogen radical that is formed due to bond cleavage probably combines with some other hydrogen radical and forms a hydrogen molecule. That is why only the radical signal for carbon is observed. Also the colour changes of the samples at the dose

of 10^6 Gy point at the presence of such radicals in the polymeric film matrix.

Thermogravimetric analysis of Makrofol-E shows decomposition in a single step. In all cases, no decomposition was observed till 430°C. Strong weight loss starts at around 430°C, and ends at around 580°C, where around 75% of the total weight is lost. Thereafter no more decomposition is observed. Also Lexan decomposes in a single step. In all cases these detectors are stable up to about 440°C, and show some weight loss between 440°C and 580°C and only at a dose of 10^6 Gy. At around 580°C, and for a dose up to 10^5 Gy, 70% weight loss was observed. At higher doses (10^6 Gy) this weight loss amounted to 75%. Hence gamma radiation at high dose (10^6 Gy) decreases the thermal stability of Lexan at high temperature (580–680°C).

The decomposition pattern of polycarbonate with temperature is quite striking. As shown in Fig. 7, it is a single step decomposition up to the dose of 10^5 Gy. But when the dose becomes 10^6 Gy, a two-step decomposition is observed. In all cases, the decomposition starts around 480°C and ends around 570°C. Above 570°C, no weight loss

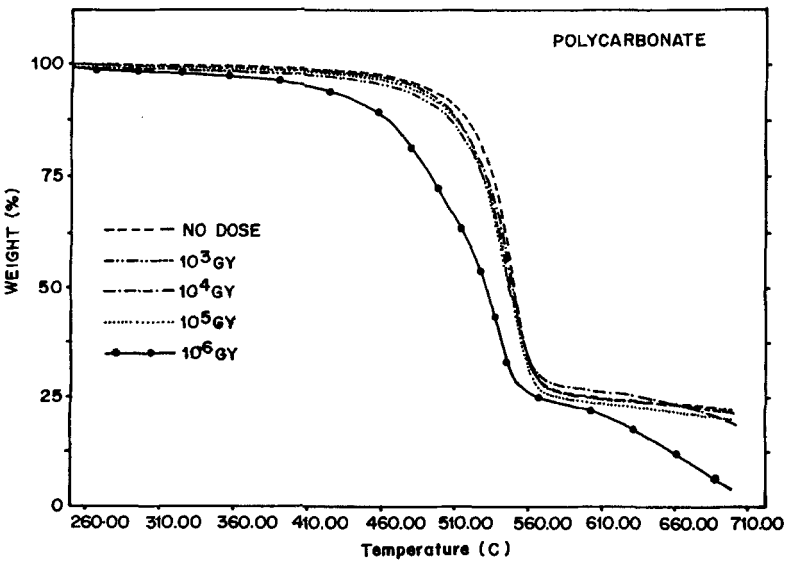

FIGURE 7 Thermogram of gamma irradiated Polycarbonate detector.

was observed at doses up to 10^5 Gy. The total weight loss in the range between 480°C and 570°C amounts to some 70%. But in the case of 10^6 Gy exposure, the weight loss starts already at around 420°C and ends at around 570°C. Again the second step of weight loss starts at 570°C and continues up to 700°C. At 700°C, 7% of the total weight remains.

4. CONCLUSION

All polymers discussed here are bisphenol-A polycarbonates, having two benzene rings in the monomer unit. These aromatic groups are known as radiation stabilizers, which reduce the polymer irradiation sensitivity due to delocalization of the excitation energy. Probably the presence of aromatic group in these polymeric films makes them radiation insensitive and hence the back-bone structure remains intact. Due to this fact no significant change in the bulk-etch rate of these detectors is observed even after exposure to gamma radiation as high as 10^6 Gy. From the UV–Vis studies one may conclude that these detectors are suitable for dosimetric applications at gamma doses of 10^4 Gy and above. Also the thermal resistance of these detectors has not been modified by the different doses of gamma radiation. In both Makrofol-E and Lexan, weight loss starts at around 430–440°C, and ends at around 570°C. Polycarbonate also shows the same behaviour up to the dose of 10^5 Gy. In this case a major weight loss is registered between 480°C and 570°C but at higher doses (10^6 Gy), the weight loss starts at lower temperature (i.e. at 420°C) and continues up to 700°C. ESR studies give information about the cleavage of C–H bond of the benzene rings. The radical which is formed from the carbon atoms delocalizes in the ring system. The hydrogen radical formed probably combines with other hydrogen radicals to form hydrogen molecules.

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