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GAMMA RAY PHOTON-INDUCED MODIFICATIONS IN TRIAFOL-TN AND TRIAFOL-BN POLYMERIC TRACK DETECTORS

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Abstract—Photon induced modifications in Triafol-TN and Triafol-BN polymers have been studied in the dose range of 10^1–10^6 Gy at room temperature using a ^{60}Co source. To monitor the chemical and structural changes induced by gamma rays, UV, IR, and ESR studies were carried out. Thermal studies were also conducted for understanding the effects of gamma irradiations on these polymers. Variation of track etching characteristics and activation energy for bulk etching have been studied at different gamma rays doses. The experimental results are presented and discussed. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Experience shows that the track registration characteristics of polymeric Solid State Nuclear Track Detectors (SSNTDs) are greatly affected when exposed to high doses of gamma rays (Frank and Benton, 1970; Khan *et al*., 1975; Akber *et al*., 1980; Portwood and Henshaw, 1986; Sharma *et al*., 1991; Joseph and Varier, 1995). The modification in characteristics originates from the structural alterations by irradiation of polymers. It may be expected that the interaction of gamma rays with solids causes ionisation (or excitation) of the orbital electrons and possibly atomic displacements (Higazy and Hussein, 1995).

Since polymeric solid state nuclear track detectors consist of long chain molecules, the net effect on the matrix due to irradiations is the production of many broken molecular chains, leading to a reduction in the average molecular weight of the substance. All these modifications caused by gamma rays may influence the track formation mechanism, optical properties (Fink *et al*., 1988) and other structural changes (Calcagno *et al*., 1992) . Some of the important properties like thermal stability (Fukuda, 1979) and morphology (Akber *et al*., 1980) can be altered by gamma irradiation, which again change the track registration characteristics of these track detectors.

Gamma exposures of the dielectric detectors occur in many ways. So far a lot of work has been done on some polymeric detectors (Zamani *et al*., 1986; Singh and Singh, 1988; Schweikani *et al*., 1993; Sinha *et al*., 1997; Abu-Jarad *et al*., 1997). But the work on cellulose triacetate (Triafol-TN) and cellulose acetate butyrate (Triafol-BN) has not been undertaken in a systematic manner. Moreover, these two detectors find use in a number of nuclear experiments, hence 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 formation mechanism as well as in studying the effects of gamma dose on these detectors.

2. EXPERIMENTAL PROCEDURE

Two types of detectors Triafol-TN (cellulose triacetate, thickness $\approx$100 μm, density = 1.30 g/ml) and Triafol-BN (cellulose acetate butyrate, thickness $\approx$200 μm, density = 1.20 g/ml) manufactured by Bayer AG. Leverkusen, FRG were used in this study. Triafol-TN is a fully acetylated product of cellulose. On the other hand Triafol-BN is made by the esterification of cellulose with a mixture of acetic anhydride and butyric anhydride. The Triafol-BN polymer has better impact resistance than Triafol-TN and contains 26–29% acetyl and 17–48% butyl. Two sets each consisting of seven samples of sizes 2×2 cm^2 were prepared. One set was first exposed at normal incidence to fission fragments from a ^{252}Cf source, and then, together

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with the unexposed (second) set was subjected to various doses of gamma rays (10^1–10^6 Gy) at room temperature from a ^{60}Co gamma source having a dose rate of 3.0 kGy/h. The second set was then irradiated with fission products from a ^{252}Cf source. The first and second sets of detectors are generally termed as post-gamma and pre-gamma exposure sets, respectively. After exposure the Triafol-BN detectors were etched in 6N NaOH solution and Triafol-TN detectors in 3N NaOH solution at different temperatures, viz., 55, 60, 65, and 70°C for different time periods. The accuracy in the maintenance of temperature was ±1°C. The diameters of the fission fragments were measured by using a Leitz optical microscope fitted with an objective of 100× (water immersion). About 20–25 track diameters were measured for each detector to find out the most probable track diameter. The error involved in the measurement of track diameters was ±0.87 μm. Then the bulk-etch rate (V_G) was determined by plotting the track diameter versus etching time.

UV and Vis spectra of the pristine and irradiated samples of the detector materials were taken by a Beckman (DU-650) spectrophotometer. The samples were inserted inside a quartz cell and the absorption spectra were recorded in the range of 200–800 nm, keeping air as the reference. The IR spectra were recorded by a Nicolet (Impact 410) Fourier-transforming instrument (FTIR) keeping air as the reference in the range between 4000–500 cm^{-1}. First derivative ESR measurements were done on a Varion (E-109, X-band) spectrometer at room temperature using 100 kHz field modulation. Thermogravimetric studies were performed using a Perkin–Elmer instrument. In order to record the thermogram, the samples were heated up to a temperature of around 610°C for Triafol-TN and around 655°C for Triafol-BN at a heating rate of 20°C/min. The weight loss is recorded as a function of temperature.

3. RESULTS AND DISCUSSION

3.1. *Physically observable changes*

No visible changes were observed in these polymers up to the dose of 10^5 Gy of gamma radiation. But at 10^6 Gy, the Triafol-TN detector became so brittle that it turned into powder after irradiation. Hence no measurements could be performed for Triafol-TN exposed to 10^6 Gy dose. The Triafol-BN detector also became brittle at the same dose, but it did not turn into powder and hence different measurements could be performed.

3.2. *Track study*

The bulk-etch rate (V_G) was determined by the track diameter technique at different etching temperatures (55, 60, 65 and 70°C). The bulk-etch rates for both pre- and post-gamma exposure of the Triafol-TN detector in the temperature range from 55–70°C increased by about 10–15% up to a dose of 10^5 Gy. In the case of Triafol-BN, the bulk-etch rate is practically independent of the gamma dose up to 10^5 Gy. However, at 10^6 Gy a steep increase in V_G is observed which is 30–50 times higher than the average V_G at 10^5 Gy . This marked increase in V_G may be due to the scission of the molecular chains caused by gamma radiation. It was also observed that the etch-rate remains invariant for both pre- and post-irradiated samples. Table 1 lists the bulk-etch rate values for the post gamma set at different doses and at different temperatures.

3.3. *Activation energy (*Q*)*

The activation energies for bulk-etching of these two polymeric solids have been determined by plotting log V_G against the reciprocal etching temperature (in absolute unit) for different doses. The data for Triafol-BN show straight lines which are parallel to each other (Fig. 1) and thus reveal that the activation energy for bulk-etching is not modified under different doses of gamma radiation—even though the etch-rates increase sharply at 10^6 Gy. A similar trend was also found in earlier work on other polymeric detectors like PADC (Homalite), PADC (American Acrylics), Lexan, Polycarbonate and Makrofol-E. The activation energy for bulk-etching was almost independent of gamma doses even though the etch-rate increases at higher dose (Sinha *et al.*, 1997, 1998; Sinha and Dwivedi 1998). The constancy in the values of activation energy (within experimental errors) inspite of an increase in bulk-etch rate is attributed to an increase in the rate constant (A) values derived from the Arrhenius

Table 1. Bulk-etch rate (V_G) in μm/h for Triafol-BN for post-gamma exposure

Etching temperature (°C)	No dose	10^1 Gy	10^2 Gy	10^3 Gy	10^4 Gy	10^5 Gy	10^6 Gy
55	0.38 ± 0.04	0.39 ± 0.04	0.39 ± 0.04	0.39 ± 0.04	0.39 ± 0.04	0.41 ± 0.04	15.60 ± 1.6
60	0.64 ± 0.05	0.63 ± 0.05	0.61 ± 0.05	0.63 ± 0.05	0.65 ± 0.05	0.66 ± 0.05	29.29 ± 2.9
65	0.70 ± 0.06	0.69 ± 0.06	0.69 ± 0.06	0.69 ± 0.06	0.70 ± 0.06	0.72 ± 0.06	39.88 ± 4.2
70	0.82 ± 0.06	0.83 ± 0.06	0.83 ± 0.06	0.84 ± 0.06	0.84 ± 0.06	1.01 ± 0.06	50.49 ± 4.2

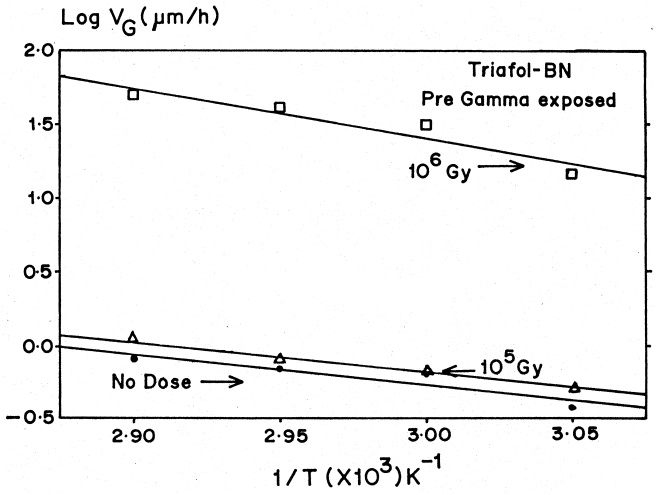

Fig. 1. Plot of log V_G vs $1/T$ for determination of activation energy (Q) of Triafol-BN.

equation. No observable change in activation energy under different doses of gamma radiation suggests that the damage of the bulk material reflects into an initial increase in bulk-etch rate but it follows the similar trend even for a later gamma dose of 10^6 Gy.

3.4. *Spectral study*

Spectral studies were done using three different techniques to identify any structural characteristic changes due to gamma irradiation. Since the track studies of Triafol-BN clearly show some sort of bond scission at 10^6 Gy of gamma dose, we tried to analyse the spectral data in terms of chemical transformations or rearrangements which occurred in this particular detector at different doses. IR, ESR and UV–Vis techniques were used for this analysis.

In all the spectral studies performed on Triafol-TN, there were only minor changes observed up to the gamma dose of 10^5 Gy. This observation supports our results obtained from the track studies and V_G data. UV–Vis study of Triafol-BN shows very significant changes. It can be seen in Fig. 2 that below the dose of 10^5 Gy, there is no change in the absorption pattern, but at the dose of 10^6 Gy the absorption pattern totally changes. The change is significant in the region 200–650 nm. It is to be observed in Fig. 2 that the absorption peak corresponding to 540 nm starts disappearing. This signifies that the purple dye is destroyed and that is why the colour of the detector fades. The shoulder at 310 nm is probably because of the antioxidant present in the film (Mayaki *et al.*, 1996). At 10^6 Gy this shoulder disappears implying that the antioxidant was removed by radiation. That is why the

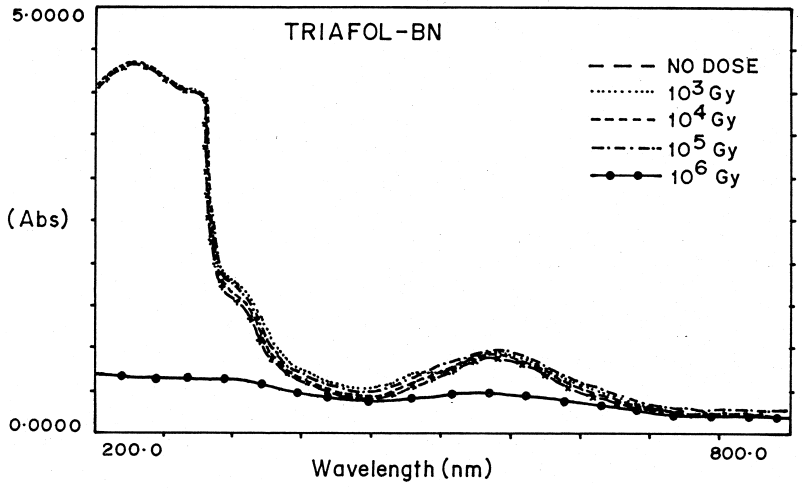

Fig. 2. UV and Vis absorption spectra of gamma irradiated Triafol-BN detector.

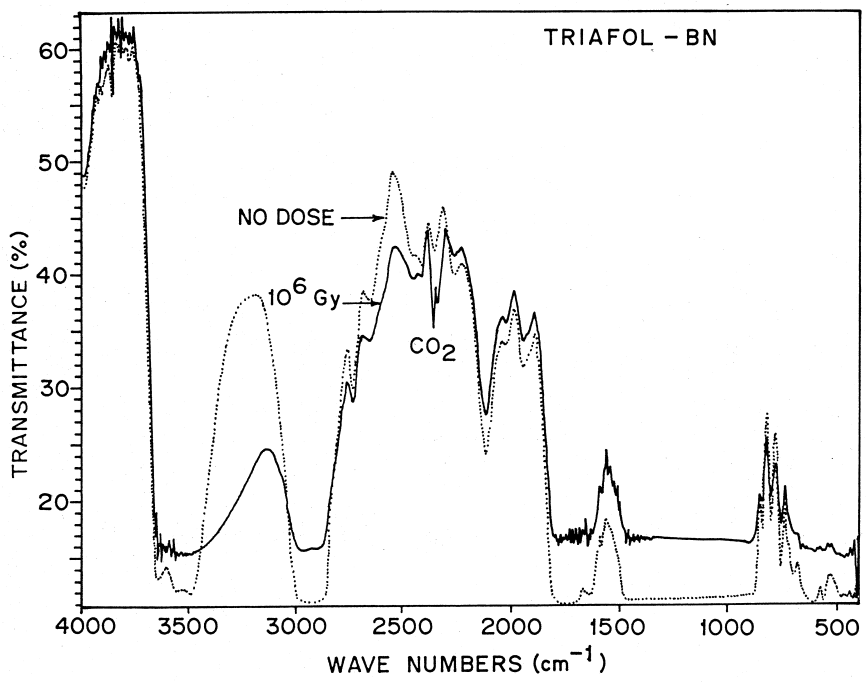

Fig. 3. IR spectra of gamma irradiated Triafol-BN detector.

oxidation was favoured and the detector became brittle.

IR spectra show no significant shift in the peak positions. Only the absorbance or transmittance value of particular functional groups were altered. It can be seen for Triafol-BN that for some of the important regions, like the 1600–1800 cm^{-1} (ester carbonyl region) and the 2850–3000 cm^{-1} (C–H

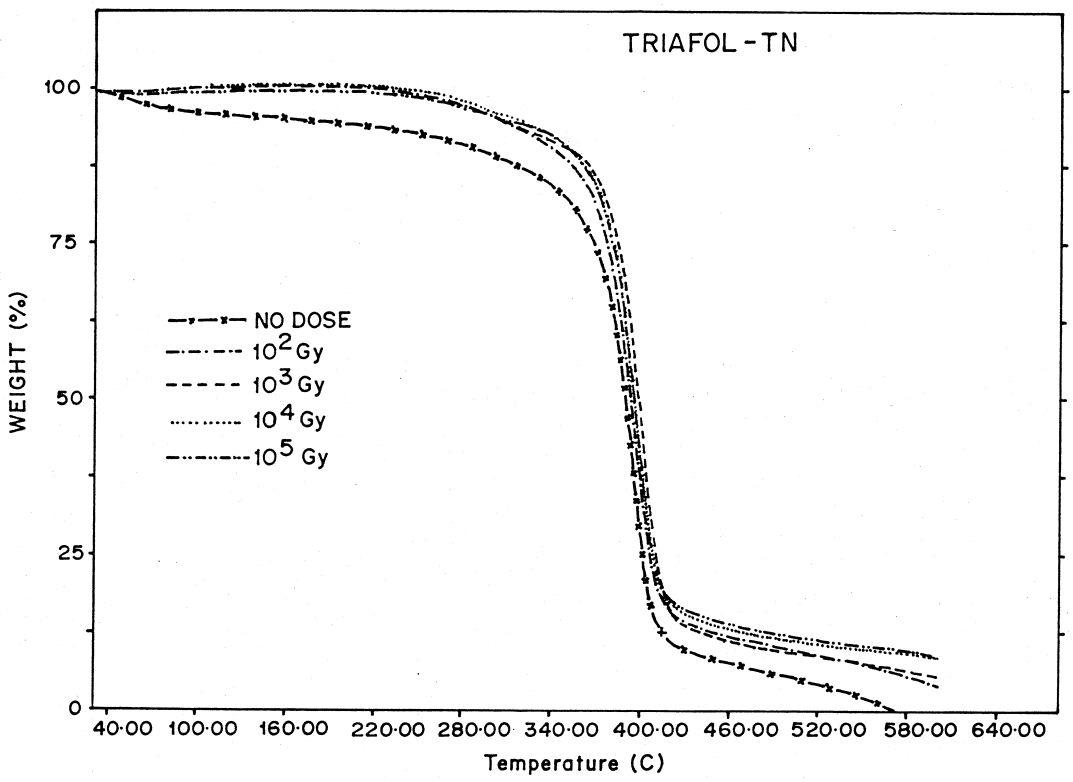

Fig. 4. TGA thermogram of gamma irradiated Triafol-TN.

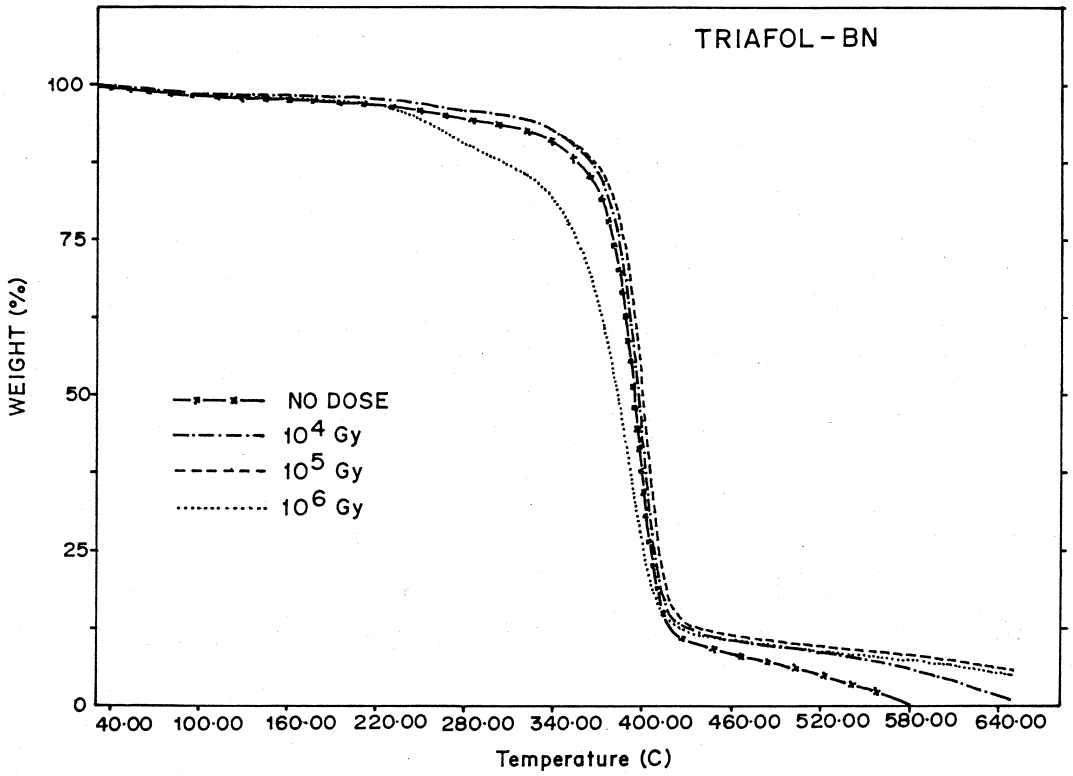

Fig. 5. TGA thermogram of gamma irradiated Triafol-BN.

stretching region), the absorbance decreases at the highest dose as shown in Fig. 3. This is due to the result of decrease in concentration of the pre-existing bonds or groups. It is striking to observe that the peak position at around 2360 cm^{-1}, which is due to the presence of CO_2, also becomes very intense at 10^6 Gy. This is possible if some of the ester and/or ether groups of the detector are destroyed by radiation and produce CO_2 which, in turn, remains trapped in the detector matrix. ESR study does not show any radical signal either in unexposed or in exposed samples, so it could not give any information about the structural transformation.

3.5. *Thermogravimetric analysis*

The thermogram of Triafol-TN (Fig. 4) shows that in all cases (up to 10^5 Gy) a significant weight loss appears at around 330°C and continues till 447°C. The weight loss took place in a single step. It is clear from the TGA response curve (Fig. 4) that Triafol-TN is thermally stable up to 330°C in all cases. Above this temperature it decomposes and looses around 78% of the weight of the polymer. These observations corroborate the conclusions drawn from the track study and spectral studies, that gamma radiations do not produce change in the structure of Triafol-TN. Figure 5 shows the TGA thermogram for Triafol-BN. In the case of pristine material the complete weight loss is observed at around 580°C, but at higher doses (above 10^4 Gy), about 7–9% weight remains at that temperature. The weight loss process begins at a much lower temperature of approx. 220°C in the case of 10^6 Gy. From the present results it can be observed that after high gamma exposure (10^6 Gy) the detector stability decreases and the weight loss process starts at a lower temperature.

4. CONCLUSIONS

The properties of the two polymeric track detectors Triafol-TN and Triafol-BN irradiated to different doses of gamma radiation do not change up to a dose of 10^5 Gy of gamma radiation. But at a dose of 10^6 Gy, the Triafol-TN detector became brittle and turned into powdered form. Triafol-BN also becomes brittle but still maintains some stability. This brittleness of the detector is probably due to oxidation of the film. It is also observed that the dye present in the polymeric film (Triafol-BN) gets destroyed to an appreciable extent by a gamma dose of 10^6 Gy and, therefore, the colour of the Triafol-BN detector fades. The thermal stability for the Triafol-BN decreases at 10^6 Gy of gamma dose and it starts loosing weight at lower temperatures. There are also indications about the ester group

destruction of the Triafol-BN polymeric film at 10^6 Gy gamma dose. This destruction leads to a decrease in the average molecular weight and consequently the bulk-etch rate increases. Though the etch rate increases with gamma dose, the activation energy for bulk-etching remains independent of gamma doses.

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