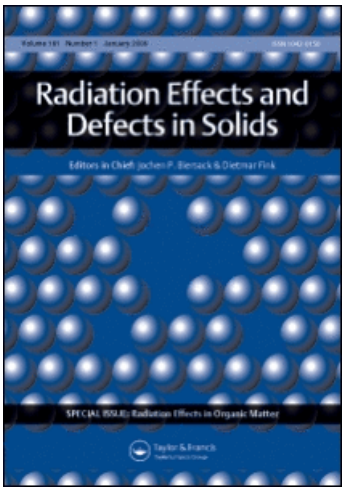

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PROTON INDUCED MODIFICATION IN POLY(ETHYLENE TEREPHTHALATE)

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A systematic investigation of 62 MeV proton irradiated Poly(ethylene terephthalate) (PET) has been carried out using Fourier Transformed Infrared Spectroscopy, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction spectroscopy. The experiments revealed a restoration of the crystalline matrix and simultaneous decrease in thermal stability in the irradiated polymer as a function of dose, indicating that PET underwent both degradation and cross-linking by proton irradiation.

Keywords: Poly(ethylene terephthalate); Proton irradiation; Degradation; Crystallinity; Thermal stability

1 INTRODUCTION

Polyethylene terephthalate (PET) is a polyester, having a high melting point and very good mechanical strength due to presence of the aromatic ring in the polymeric structure. It is resistant to heat and moisture and virtually unattacked by many chemicals. In addition to chain scissioning, cross-linking, molecular emission and formation of double bonds, which occur by low LET irradiations in PET, formation of an alkyne group is an additional effect in PET by swift heavy ions [1].

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Both cross-linking and degradation take place during proton irradiation and are closely related to irradiation dose. At certain doses, cross-linking becomes predominant and mechanical properties are improved [2]. Another study by 62 MeV proton irradiation on Polypropylene and Polytetrafluoro ethylene showed a decrease in their optical band-gap, whereas no effect on the optical properties was observed in Polyethylene terephthalate and Polyimide [3]. 62 MeV proton irradiation was also found to modify the track registration properties of Polyallyl diglycol carbonate (PADC) by fullerene destruction [4] as well as by the use of thin metal foils in contact with its surface [5]. On the contrary, electron irradiation on PET resulted in amorphisation of the polymer thereby decreasing the thermal stability [6], whereas production of hydroxyterephthalates and dihydroxyterephthalates in the polymer backbone as radiolysis products and molecular orientation in the ion tracks was observed by heavy ion irradiation on PET [7]. Also, the dose dependent modification in PADC by 62 MeV proton irradiation has been studied and it was found that the crystallinity and thermal stability of the polymer decreased as a function of dose, whereas there was no change in the optical band-gap of the polymer [8].

As a continuation of the work, this paper presents our systematic investigation of the post-proton irradiation effect on PET as a function of dose. Modifications induced in the structural and thermal behaviour of PET were analysed by spectroscopic and thermal techniques.

2 EXPERIMENTAL DETAILS

2.1 Target Preparation and Proton Irradiation

Forty pieces of PET (composition: $C_{10}H_8O_4$, density: $1.41\,g\cdot cm^{-3}$, thickness: $13\pm0.1\,\mu m$) of sizes (1×1) cm^2 were taken and four stacks were prepared containing 10 pieces each. Each stack was covered by radiation sensitive Polyvinyl acetate (PVA) at both ends to check the uniformity of the impinging beam by its colour change. These were separately irradiated in presence of air to four different doses, viz. 10 kGy, 30 kGy, 60 kGy and 80 kGy by a scanned 62 MeV proton beam in the Ion Beam Laboratory "ISL" of Hahn Meitner Institute (HMI), Berlin. The collimated proton beam of dimension $(0.3\times1)\,cm^2$ passed perpendicularly through each stack. Then, the pristine and the irradiated samples were characterised by the following techniques.

2.2 Characterisation of Irradiated Polymers

2.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of all the samples were recorded in the wave number range of 4000 to 500 cm^{-1} using the Fourier transforming instrument (NICOLET, IMPACT 410) to study the structural changes including the alteration in position and intensity of the characteristic bands with an accuracy better than $\pm 1\%$ to $\pm 3\%$.

2.2.2 X-ray Diffraction Spectroscopy (XRD)

X-ray diffraction studies were carried out by using the Cu–Kα ($\lambda = 1.54$ Å) radiation with 8.04 keV energy from a Rigaku θ-2θ X-ray spectrometer at Inter University Consortium, Indore, India. A rotating anode source and a Sodium Iodide scintillation detector have been used. The value of 2θ ranged from 3° to 90° with step size 0.04 mm.

2.2.3 Thermogravimetric Analysis (TGA)

The TGA thermograms were recorded by using the Perkin Elmer Delta series Thermal Analysis system. The samples were crimped in small aluminium pans and were heated from 30°C to 600°C, at a predetermined rate of 20°C/min with N_2 as the flushing gas. The error associated with TGA analysis is ± 2°C.

2.2.4 Differential Scanning Calorimetry (DSC)

In the same way as above, the samples were crimped in small aluminium pans and the thermal analysis of the hermetically sealed samples was done by the Perkin Elmer Delta series Thermal Analysis system. The temperature was scanned from 50°C to 450°C, at a predetermined rate of 20°C/min with N_2 as the flushing gas. A plot of heat flow (Y-axis) as a function of temperature (X-axis) for DSC was obtained within the instrumental error of ± 2°C.

3. RESULTS AND DISCUSSION

3.1 FT-IR Spectral Analysis

The spectra of the pristine and irradiated PET (80 kGy) are shown in Figure 1. Here, the change in most of the characteristic peak positions

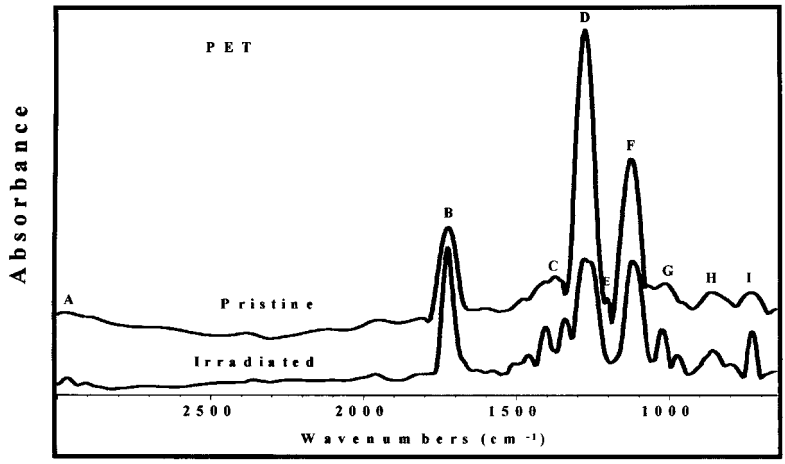

FIGURE 1 FT-IR spectra of the pristine and the proton irradiated PET (80 kGy) in the range of 3000–650 cm^{-1}.

denotes the deformation of the polymer structure. The simultaneous change of all IR lines indicate that the irradiation-affected regions are distributed randomly all over the polymer molecules. The absorption bands obtained from the spectra are interpreted in Table I.

- No new band was observed at 3294 cm^{-1}, which is usually assigned to C-H stretching vibrations of the alkyne group. This is in contrast

TABLE I The identification of the absorption bands in PET corresponding to their wave numbers ($1/\lambda$)

Peak	*$1/\lambda$ (cm^{-1})*	*Identification [1, 9]*
A	2975	CH stretching of CH_2 group
B	1723	C=O stretching vibration
C	1373	C–C stretching of phenyl ring, Vibration band of para substituted benzene rings
D	1273	
E	1203	
F	1123	C–O–C stretching of ester
G	1013	
H	873	CH deformation of phenyl ring, Vibration band of para substituted benzene rings
I	730	Ring deformation of phenyl ring, Bending vibration of CH_2 group

with the result obtained by Steckenreiter *et al.* [1] regarding the alkyne group formation after heavy ion irradiation.

- For the PET irradiated to the highest dose (80 kGy), the increase in absorbance at 730 cm^{-1} (I) implied the possible recrystallisation after proton irradiation but the simultaneous increase in absorbance at 873 cm^{-1} (H) points at some amorphisation of the newly formed crystals. This kind of simultaneous behaviour is possible when the pristine polymer is partly crystalline.
- An increase in absorbance of para-substituted benzene ring bands (H) at the highest dose indicated the stability of the aromatic unit. Similarly, there are instances when the polymer underwent degradation without aecting the whole structure of the polymer.

3.2 XRD analysis

The XRD spectra of the pristine and proton irradiated PET (80 kGy) are shown in Figure 2 and the parameters assigned with the peaks are given in Table II. The result shows that:

- The intensity of the main peak (C) at $2\theta = 26.26^\circ$ for the pristine material increased and shifted to $2\theta = 25.92^\circ$ after irradiation with the highest proton dose (80 kGy). This change can be attributed to the differences in density of the pristine and irradiated zones arising out of the restoration of the crystal structure due to the increasing strain on the irradiated PET.
- Three new peaks (A, B, D) emerged at $2\theta = 9.46^\circ$, 13.18° and 28.63° after irradiation, which might be due to the newly formed fine polymer crystallites in the amorphous zone of PET.
- Since the diraction pattern depends upon the internal structure of the polymer, the observed changes in the X-ray diraction spectra represent the growth in order of the original lamella (crystalline) structure of PET, thus, leading to a considerable increase in its crystallinity after proton irradiation at the dose of 80 kGy.

3.3 TGA analysis

The decomposition behaviour of the pristine and the irradiated polymers were studied by this technique. The thermograms are shown in Figure 3

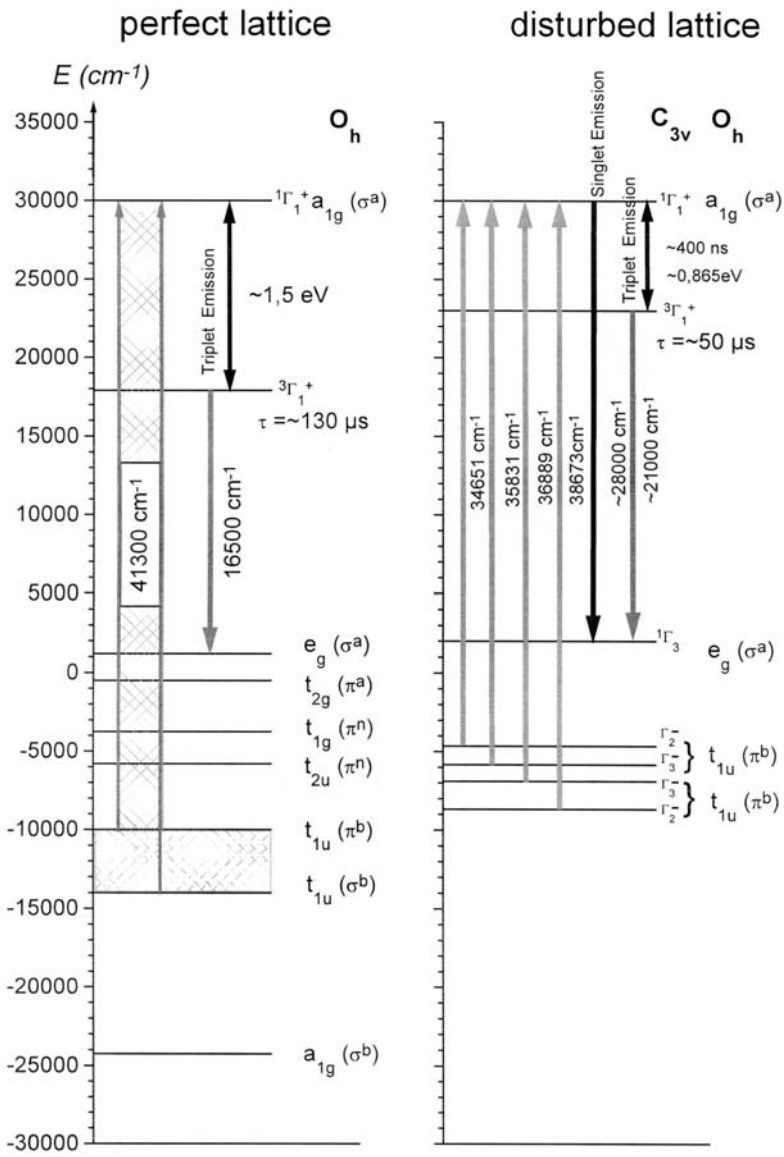

FIGURE 2 XRD spectra of the pristine and the proton irradiated PET (80 kGy).

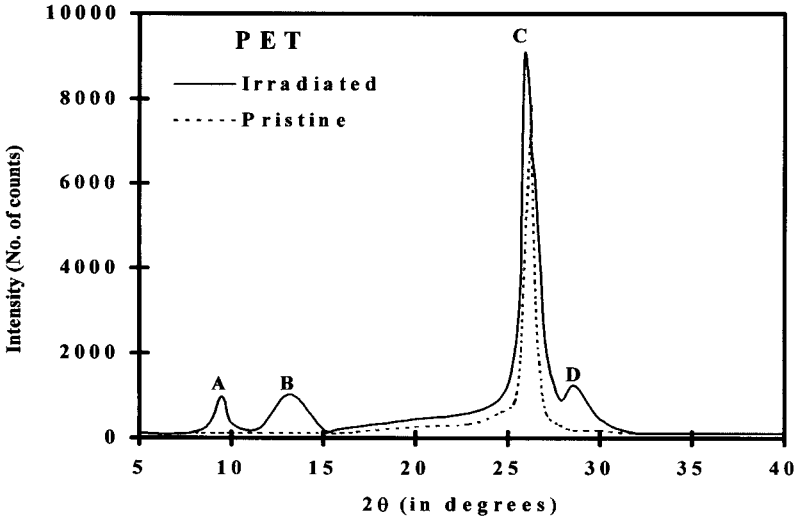

FIGURE 2 Continued.

and the temperatures along with the respective weight-loss (%) for different zones are given in Table III.

- As depicted from the figure, the stable zone disappeared for the rradiated polymers, which ranged up to 165°C for the pristine PET. The irradiation made the polymer to undergo a slow decomposition from the moment of application of heat.

TABLE II Position (2θ) Intensity (I) and full width half maximum (FWHM) of the XRD peaks of the pristine (P) and proton irradiated PET (80 kGy)

	2θ (degree)		*I_{rel}*		*I(CPS)*		*FWHM (degrees)*	
Peak	*P*	*80 kGy*	*P*	*80 kGy*	*P*	*80 kGy*	*P*	*80 kGy*
*A	–	9.46	–	11	–	967	–	0.13
*B	–	13.18	–	18	–	909	–	3.40
C	26.26	25.92	100	100	7825	7303	0.50	0.70
*D	–	28.63	–	14	–	1247	–	1.20

*New peaks formed after irradiation.

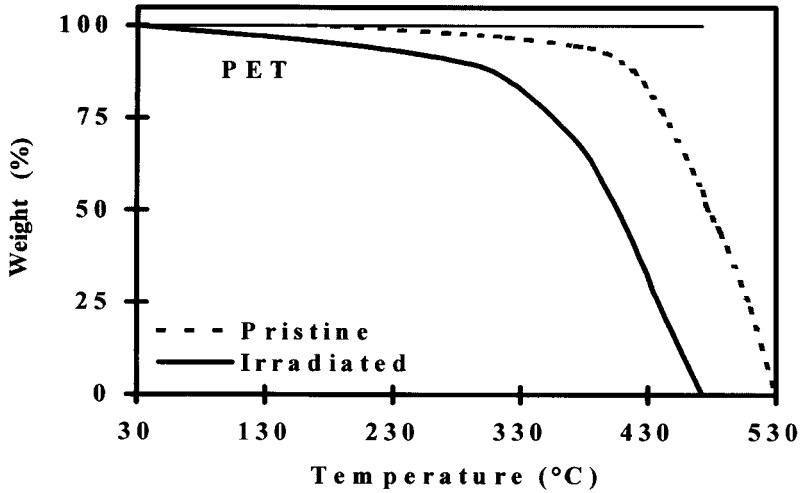

FIGURE 3 TGA thermograms of the pristine and the proton irradiated PET (80 kGy).

- This slow decomposition zone continued up to 165°C involving only about 10% of weight loss for the pristine PET, whereas a weight of about 20–25% was lost in case of the irradiated samples at a lower temperature (346–390°C).
- Similarly, the fast decomposition zone went up to 530°C involving a weight loss of about 90% for the pristine and up to 460–475°C for the irradiated polymers associated with a weight loss of about 75–80%.

From the data, it is observed that the thermal decomposition of the polymer depends upon the dose of the proton beam irradiation, *i.e.*, the more the dose, the less the thermal stability. This denotes a degradation of the polymer matrix under proton beam irradiation making it to decompose earlier than the pristine PET.

3.4 DSC Analysis

The DSC thermograms of the pristine and the proton irradiated PET are shown in Figure 4. It was observed that the exotherms denoting the temperature of crystallisation (T_c) appeared at around 208°C (A_0 in pristine, A_1 in irradiated) in all the cases. But the endotherms denoting the melting

TABLE III Thermal decomposition temperatures at different zones for the pristine PET and the PET samples irradiated to different doses (10, 30, 60, 80 kGy) of 62 MeV proton

Dose (kGy)	*Zone*	*Temperature range (°C)*	*Weight loss % in the zone*	*Interpretation*
0	I	30–165	0	Stable zone
	II	165–410	10	Slow decomposition
	III	410–530	90	Fast decomposition
10	I	–	0	Stable zone
	II	30–390	20	Slow decomposition
	III	390–475	80	Fast decomposition
30	I	–	0	Stable zone
	II	30–390	20	Slow decomposition
	III	390–475	80	Fast decomposition
60	I	–	0	Stable zone
	II	30–377	23	Slow decomposition
	III	377–465	77	Fast decomposition
80	I	–	0	Stable zone
	II	30–346	25	Slow decomposition
	III	346–460	75	Fast decomposition

temperatures (T_m) underwent a change after proton irradiation. The endotherm is sharp for the pristine PET appearing at about 229°C (B_0), but continuous endothermal distortions were found in all the irradiated PET samples, spreading over a temperature range up to 450°C, the starting

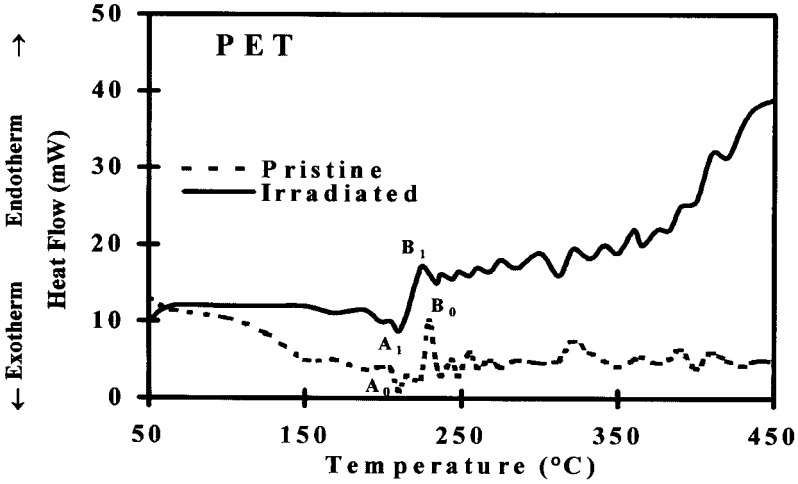

FIGURE 4 DSC thermograms of the pristine and the proton irradiated PET (80 kGy).

point of which was around 224°C (B_1). This can be attributed to the fact that some of the degraded molecules are cross-linked which are not decomposing simultaneously at the same temperature. However, the thermal analysis supports the fact that, the polymer has undergone a degradation due to proton irradiation and thus, makes it decompose earlier than the pristine PET.

4. CONCLUSION

Basically, two types of phenomena are observed in PET by proton irradiation: degradation and cross-linking. The emergence of new crystallisation peaks and increase in main peak intensity denoted the growth of crystallinity in the irradiated PET. From FT-IR spectral analysis, recrystallisation in the amorphous zone and simultaneous amorphisation as a function of degradation and cross-linking of the irradiated PET (80 kGy) are evidenced, which is further supported by the disappearance of sharp melting peak in DSC thermogram. However, chain-scission by proton irradiation seems to be the dominant process as seen from the thermal analysis.

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References

[1] Steckenreiter, T., Balanzat, E., Fuess, H. and Trautmann, C. (1997). *Nucl. Instr. Meth.*, **B131**, 413.
[2] Wang, G. H., Pan, G. Q., Dou, L., Yu, R. X., Zhang, T., Jiang, S. G. and Dai, Q. L. (1987). *Nucl. Instr. Meth.*, **B27**, 410.

[3] Mishra, R., Tripathy, S. P., Sinha, D., Khathing, D. T., Dwivedi, K. K., Ghosh, S., Müller, M., Fink, D. and Chung, W. H. (2000). *Nucl. Instr. Meth.*, **B168**, 59.
[4] Dwivedi, K. K., Ghosh, S., Fink, D., Mishra, R., Tripathy, S. P., Kulshreshtha, A. and Khathing, D. T. (1999). *Radiat. Meas.*, **31**, 127.
[5] Tripathy, S. P., Mishra, R., Kulshreshtha, A., Dwivedi, K. K., Khathing, D. T., Srivastava, A., Ghosh, S. and Fink, D. (2001). *Radiat. Meas.*, **33**, 171.
[6] Mishra, R., Tripathy, S. P., Dwivedi, K. K., Khathing, D. T., Ghosh, S., Muller, M. and Fink, D. (2001). *Radiation Effects and Defects in Solids*. In Press.
[7] Eßer, M. and Fuhrmann, J. (1999). *Nucl. Instr. Meth.*, **B151**, 118.
[8] Tripathy, S. P., Mishra, R., Dwivedi, K. K., Khathing, D. T., Ghosh, S. and Fink, D. (2001). *Radiat. Meas.*, In Press.
[9] Fink, D., Hosoi, F., Omichi, H., Sasuga, T. and Amaral, L. (1994). *Radiation Effects and Defects in Solids*, **132**, 313.