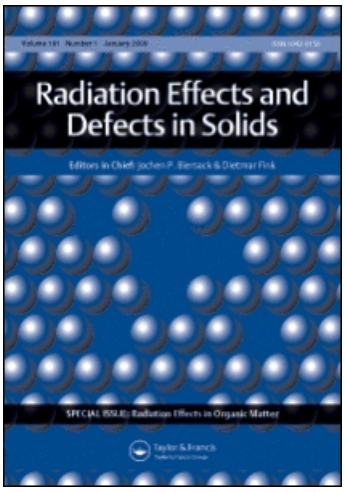

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Electron induced modification in poly(ethylene terephthalate)

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ELECTRON INDUCED MODIFICATION IN POLY(ETHYLENE TEREPHTHALATE)

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The effect of 100 kGy dose of 2 MeV electron irradiation on Poly(ethylene terepthalate) (PET) has been studied by different characterisation techniques such as the Fourier transformed IR spectroscopy, electron spin resonance spectroscopy, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction analysis. Oxidative degradation leading to amorphisation of the polymer has been observed from spectral analysis. The thermal stability of the polymer was found to decrease due to electron irradiation. The thermal decomposition temperature as well as the melting temperature in case of irradiated PET was found to be decreased due to electron bombardment. A decrease in crystallinity of the polymer has also been observed after irradiation.

Keywords: Poly(ethylene terephthalate); Electron irradiation; Degradation; Amorphisation; Thermal stability; Crystallinity; Melting temperature

1. INTRODUCTION

Radiation damage is a consequence of deposition of energy of the primary particle in the target, which results in changes in physical

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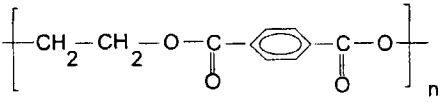
properties which are stable for a time scale essentially longer than the time of slowing down of the primary particle. The bombardment of polymers by energetic ions produces dramatic changes due to disruption of the original chemical bonding. This disruption occurs as chain scission, cross linking and carbonisation causing gas evolution and ejection of polymer fragments with a wide distribution of molecular weights. The physical and chemical changes in the polymer due to irradiation depend both on the total amount of deposited radiation energy density and on the rate at which this energy is transferred. They determine both the number of reactive transient intermediates and their local concentration along the particle tracks.

Poly(ethylene terephthalate) (PET) is a polyester popularly known as Terylene having the structure:



It is semicrystalline in nature. The crystalline lamellae surrounded by the amorphous region make the whole structure mechanically intact. It has a very good mechanical strength up to 175°C. It has a glass transition temperature of 73°C to 80°C and a high melting point of 245–265°C due to the presence of the aromatic ring. It is resistant to heat and moisture. It is virtually unattacked by chemicals. It is extensively used to make textile fibres.

Electrons are low LET (linear energy transfer) projectiles which affect the physical and chemical properties of the polymeric films. The distribution of ionisation products along the electron tracks is more uniform than in case of heavier charged particles. A literature survey indicates that electron irradiation on PET results in chain scissioning, crosslinking, molecular emission, and formation of double bonds thus leading to the formation of olefines, carboxylic acids, alcohols and carbon dioxide [1]. 2 MeV electron irradiation does not affect the optical band-gap of PET because of the presence of aromatic groups in the repeating units of the polymer which accounts for its radiation stability [2]. On the contrary, heavy ion irradiation of PET leads to hydrogen loss [3, 4], decrease of the optical band-gap [5] and breaking of C—H bonds [6].

The aim of our study was to describe electron induced modifications in PET by using Fourier transformed infrared (FTIR) spectroscopy, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction analysis.

2. EXPERIMENTAL DETAILS

2.1. Preparation of the Targets

Ten pieces of PET (composition: $C_{10}H_8O_4$, density: $1.41\,g\cdot cm^{-3}$) of sizes $(2 \times 2)\,cm^2$ were cut from commercially available sheets. The thickness of the polymer foils was measured by a Heidenhain device and was found to be 13 μm. The samples were washed thoroughly with soap solution and deionised water, and thereafter dried inside a vacuum desiccator. A stack of ten PET foils was prepared, and covered at both ends by radiation sensitive Poly vinyl acetate (PVA) to check the uniformity of the impinging beam. This target assembly was then taken for electron irradiation.

2.2. Irradiation

The irradiation of the target stack was done by a 2 MeV electron beam from the electron generator at the Hahn–Meitner Institute, Berlin. The electron beam was allowed to pass through a collimator and then to fall onto the target stack placed perpendicularly, at a distance of 2 metres from the collimator. The dose of the 2 MeV electron beam was 100 kGy. The beam size was bigger than $(2 \times 2)\,cm^2$, and therefore covered the whole target area.

2.3. Polymer Characterisation

After irradiation, the samples were characterised by the techniques described below.

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the first foil of the irradiated stack along with a pristine foil for comparison were recorded in transmission mode using

the FTIR instrument NICOLET, IMPACT 410 with air as reference. All the measurements were done in the 4000 cm^{-1} to 500 cm^{-1} wave number range.

2.3.2. Electron Spin Resonance Spectroscopy (ESR)

The ESR measurements were performed with a Varian (E-109, X-band) spectrometer with 100 kHz field modulation. The samples were cut to pieces of $0.5 \times 0.5\,cm^2$ size, placed in a quartz tube, and then the spectra were recorded at room temperature. The spectrometer works at 9.6 GHz frequency with the following setup: Field set: 3382 Gauss, Scan range: 1000 Gauss, Time constant: 0.25 sec, Scan time: 4 minutes, Modulation amplitude: 0.5×1, Receiver gain: 6.3×104, Microwave power: 2 mW.

2.3.3. X-ray Diffraction (XRD)

XRD patterns were recorded using the Cu–Kα ($\lambda = 1.54$ Å) radiation with 8.04 keV energy from the Rigaku $\theta-2\theta$ X-ray spectrometer at Inter University Consortium, Indore, India. A rotating anode source and a Sodium Iodide scintillation detector have been used. The dimension of the entrance slit was 0.2 mm and the step size was 0.04 mm. The samples were cut to sizes of 1 cm $\times$ 1 cm, mounted onto the sample holder and placed into the XRD chamber. The value of 2θ ranged from 3° to 90°.

2.3.4. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis of both the irradiated and the pristine PET was done by using a Perkin Elmer Delta series Thermal Analysis system. The samples were cut into very small pieces, crimped in small aluminium pans and weighed with a micro balance. The samples were then heated from 30°C to 600°C at a rate of 20°C/min. The error in recording the TGA thermogram is $\pm$ 2°C.

2.3.5. Differential Scanning Calorimetry (DSC)

In the same way as above, the irradiated and pristine PET samples were crimped in aluminium pans and weighed in a thermobalance.

DSC measurements were done using a Perkin Elmer Delta-series Thermal analysis system. Nitrogen is used as flushing gas for the measurements. Aluminium was taken as the reference material. The heat power was adjusted so as to maintain a constant temperature in the sample and the reference. The temperature was scanned from 50°C to 520°C at a rate of 20°C/min. The error in recording the DSC thermogram is ± 2°C.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectral Analysis

The vibrational modes of the chemical bonds in the polymer are characterised by the absorption bands in the FTIR spectra. The spectra obtained by the spectrophotometer for the irradiated as well as the pristine samples are shown in Figures 1(a) and (b). The absorbances corresponding to certain wave numbers for both the pristine and the irradiated PET and the interpretation of these peaks are compiled in Table I. PET is a condensed polymer of terephthalic acid and ethylene glycol. The IR peaks belong to C=C double bonds of the phenyl ring, C—H bonding of phenyl ring and the CH_2 group. Irradiation induces stretching of all functional units of the polymer, plus a deformation of the phenyl ring as a whole and its C—H bonding. The fact that the positions of all IR lines change slightly, without any emergence of new peaks, indicates that the irradiation affected regions are distributed randomly all over the polymer molecules and that there do not exist special radiation sensitive functional groups in the polymer. The following informations are derived from the spectral analysis:

(a) Amorphisation of PET under electron irradiation was monitored by specific bands of *trans* configuration of the ethylene glycol residue at 1471 cm^{-1} due to CH_2 bending, 850 cm^{-1} due to CH_2 rocking and 972 cm^{-1} due to the C—O stretching vibration of the *trans* configuration of the ethylene glycol residue [7, 8]. Amorphisation of the crystalline fraction of the polymer is evident from the band at 1471 cm^{-1}. The increase in absorbance of this band indicates some loss of crystallinity

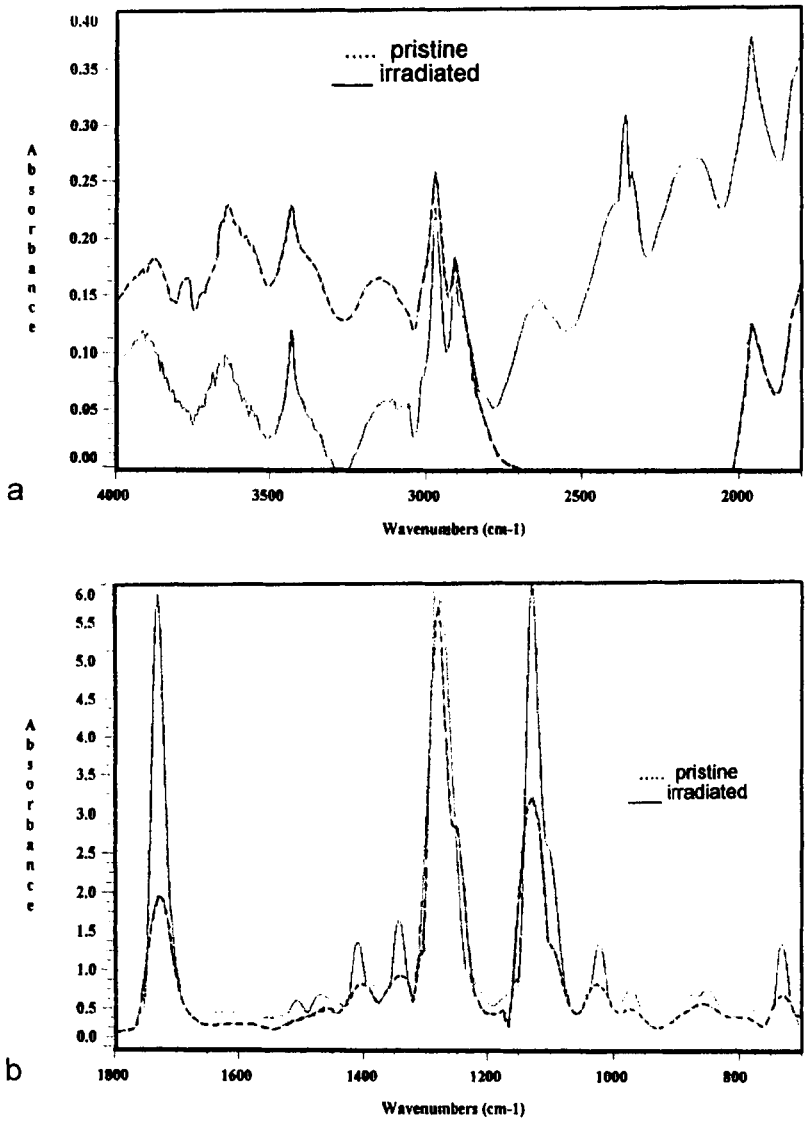


FIGURE 1

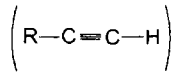
of the polymer. The increase in absorbance of the band at $873\,cm^{-1}$ again implies amorphisation of the polymer due to irradiation.

TABLE I Interpretation of IR absorption peaks for pristine and irradiated PET along with their absorbances

Pristine PET		*Irradiated PET*		
Wave no. (cm^{-1})	*Absorbance*	*Wave no.* (cm^{-1})	*Absorbance*	*Interpretation*
2969.6	0.2	2969.3	0.2	CH stretching of CH_2 groups [10]
		2361.9	0.3	CO_2 from air [10]
1729.4	2.3	1726.0	6.0	C=O stretching vibration
1614.9	0.4	1614.6	0.4	C—C stretching of phenyl ring [10] Vibration band of *para*-substituted benzene rings [1]
1466.1	0.6	1471.3	0.8	CH_2 bending [1]
1409.1	1.0	1409.7	1.7	Vibration band of *para*-substituted benzene rings [1]
1133.1	5.7	1124.3	6.0	Vibration band of *para*-substituted benzene rings [1]
1021.1	0.6	1021.0	1.8	C—O—C stretching of ester [1]
972.5	0.7	971.9	0.9	C—O stretching vibration of *trans* configuration of ethylene glycol residue [1]
871.2	0.6	873.8	0.8	Vibration band of *para*-substituted benzene rings [1]
849.8	0.7	849.2	0.9	CH_2 rocking [1] CH deformation of phenyl ring [10]
730.6	1.0	729.4	1.8	Ring deformation of phenyl ring [10] Bending vibration of CH_2 group of crystal phase [1]

(b) The increase of the absorbance lines characteristic for vibration bands of *para*-substituted benzene rings illustrates the stability of the benzene ring. So, even under electron irradiation, the aromatic systems are stable owing to delocalisation of the excitation energy [9]. Earlier it has also been found that bond breaking at the aliphatic parts of the main chain occurs more likely than the destruction of the benzene ring [1].

(c) No signal at all has been found at the wave number 3294 cm^{-1} which usually is assigned to the characteristic C—H stretching mode of the alkyne end group [1];



so that we can not reconfirm the claim of radiation induced alkyne formation as made in Ref. [1] in case of electron irradiation. The overall increase in absorbance as evidenced from Figure 1(a) and

(b), indicates some (oxidative?) degradation of the polymer during irradiation.

3.2. ESR Spectral Analysis

The ESR spectral analysis of our samples shows the absence of any free radical in the irradiated PET at the time of analysis. As, due to technical reasons, our samples were kept at room temperature for a few months between irradiation and measurement, the originally present free radicals formed apparently have already recombined during that time.

3.3. Thermogravimetric Analysis

The TGA thermograms of both the irradiated and the pristine PET are shown in Figure 2. The thermograms indicate that the polymer always remains stable up to a certain temperature and then undergoes a two

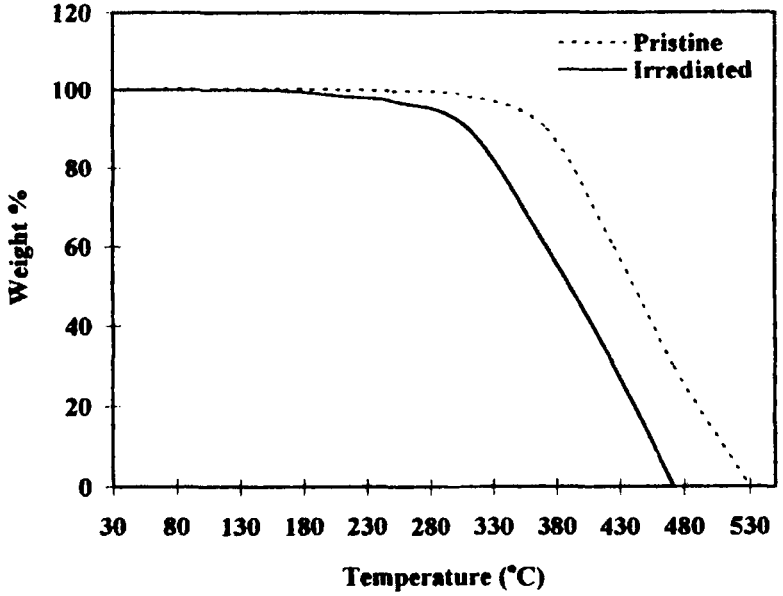


FIGURE 2

step decomposition, first at a slow rate and thereafter at a fast one till complete decomposition. The weight loss being a complex function of chemical reactions, decomposition, solvent and water evolution, oxidation *etc.*, it is hardly possible to conclude more. The overall results are compiled in Table II. The pristine sample remains completely stable from 30°C to 165°C, with no weight loss at all. This stable zone is followed by a very slow rate of decomposition from 165°C to 371°C, with 10% weight loss, after which decomposition occurs at a fast ratetill 530°C, where the pristine PET is completely decomposed. The irradiated sample remains stable up to a relatively low temperature of only 97°C, after which slow decomposition starts up to 359°C, with 12% weight loss. There is a subsequent fast rate of decomposition up to 100% weight loss at 472°C of the sample when the sample is further heated above 359°C. Hence the TGA thermograms indicate a decrease in thermal stability of the irradiated polymer.

3.4. Differential Scanning Calorimetry

The DSC thermogram of the pristine sample shown in Figure 3 indicates an exothermal peak of crystallisation at 208°C involving a heat of 3083 J/gram. It shows that the melting transformation occurs in the temperature range 229°C–443°C. For contrast, the exothermal peak of crystallisation of the irradiated sample at 208°C involves a heat of only 575 J/gram. The irradiated PET shows that melting

TABLE II Thermal analysis data derived from the TGA thermograms for pristine and electron irradiated PET

Sample weight (mg)	*Zone*	*Temperature range (°C)*	*Weight loss % in zone*	*Total weight loss %*	*Interpretation*
PET (pristine)					
0.8	I	30 ± 2 - 165 ± 2	0.0	0.0	Stable zone
	II	165 ± 2 - 371 ± 2	10.0	10.0	Slow decomposition
	III	371 ± 2 - 530 ± 2	90.0	100.0	Fast decomposition
PET (irradiated)					
0.4	I	30 ± 2 - 97 ± 2	0.0	0.0	Stable zone
	II	97 ± 2 - 359 ± 2	12.0	12.0	Slow decomposition
	III	359 ± 2 - 472 ± 2	88.0	100.0	Fast decomposition

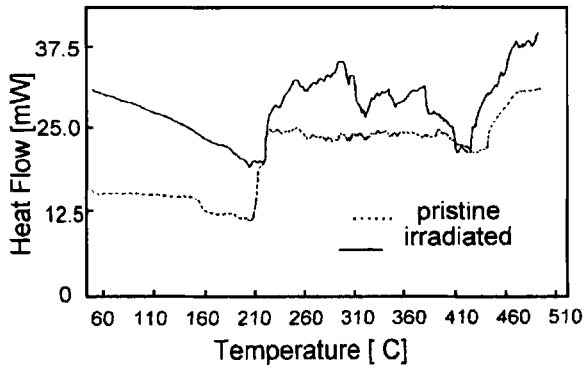


FIGURE 3

TABLE III Thermal analysis data derived from the DSC thermograms for pristine and electron irradiated PET

Peak	*Temperature(°C)*	*Specification*	*Explanation*
PET pristine			
A	208 ± 2	Exothermal	Crystallisation
B	229 ± 2–443 ± 2	Exothermal	Melting
PET irradiated			
A	208 ± 2	Exothermal	Crystallisation
B	222 ± 2–428 ± 2	Endothermal	Melting

transformations occur at slightly lower temperatures of 222°C–428°C. The data derived from the thermograms of the pristine and the irradiated PET are compiled in Table III.

3.5. X-ray Diffraction Analysis

The XRD spectra for the pristine and irradiated PET are shown in Figure 4 and are tabulated in the Table IV. The spectra of the pristine sample exhibit a sharp peak at 2θ of 26.26° which points at the crystalline nature of that polymer. This peak is shifted to $2\theta = 26.38°$ for the irradiated sample. Moreover this peak also shows a slight decrease in intensity. Both the shift and the decrease indicate some destruction of the crystal structure, which are attributed to essentially the chain scissioning after electron irradiation.

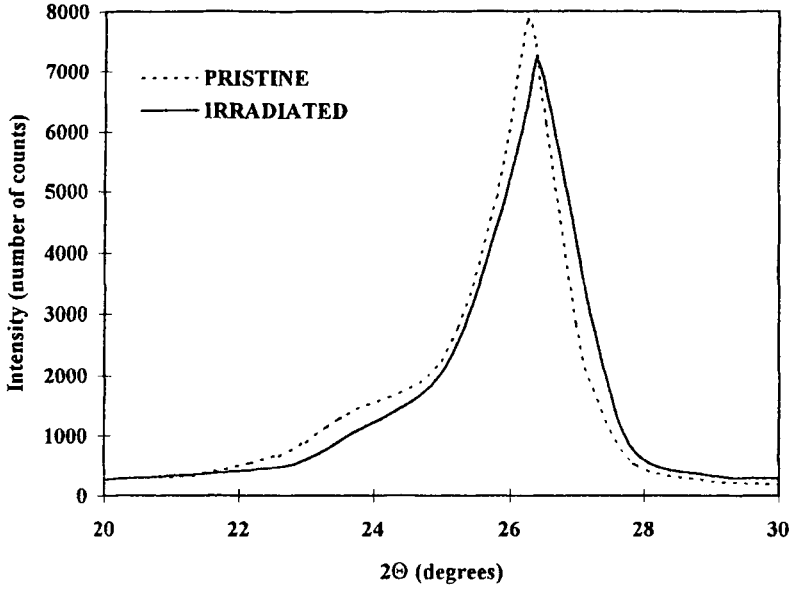


FIGURE 4

TABLE IV Position, Intensity and full width half maximum of the main peak in the pristine and irradiated PET obtained from XRD spectra

Sample	*2θ (degrees)*	*I(Rel)*	*I(CPS)*	*FWHM*
pristine	26.26	100.0	7825.0	0.7
irradiated	26.38	100.0	7204.0	0.9

4. CONCLUSION

The characterisation of PET irradiated by 2 MeV electrons at 100 kGy by different experimental techniques leads to the following conclusions:

- Amorphisation of the crystalline fraction of the polymer is evident from the FTIR spectra. An increase in absorbance indicates some loss of crystallinity of the polymer. The amorphisation process is strongly enhanced because the polymer has been irradiated in oxygen atmosphere, but the presence of aromatic groups in the polymer structure accounts for some remaining stability of the

polymer. The amorphisation of the polymer is thought to be a consequence of chain scissioning by the electron bombardment. Electron irradiation has not been able to induce alkyne formation in PET, as was observed occasionally earlier after heavy ion irradiation.

- A decrease in thermal stability and of the temperature at which complete decomposition of the polymer takes place has been observed after electron irradiation. Chain-scissioning leads to decrease in the strength of the polymer thus decreasing its ability to withstand high temperatures. Though the melting characteristics of both the pristine and the irradiated PET remains almost the same, yet the destruction of crystal structure is quite evident.
- The decrease in the X-ray diffraction intensity indicates some destruction of crystallinity due to electron irradiation.

Further work is in progress to study the effect of electron irradiation on track registration properties of PET.

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