CONDENSED MATTER

Electron-Beam-Induced Modifications in High-Density Polyethylene

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Abstract Post-irradiation studies have been carried out
to elucidate the effects of electron beam irradiation on
the structural, optical, dielectric, and thermal proper-
ties of high-density polyethylene (HDPE) films. The
experimental results showed that both the optical band
gap and activation energy of HDPE films decreases
with an increase in the doses of electron radiation. The
electrical measurements showed that dielectric con-
stant and the ac conductivity of HDPE increases with
an increase in the dose of electron radiation. The ther-
mal analysis carried out using DSC and TGA revealed
that the melting temperature, degree of crystallinity,
and thermal stability of the HDPE films increased, ob-
viously, due to the predominant cross-linking reaction
following high doses of electron irradiation.

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1 Introduction

Polymers, due to their high strength to weight ratio,
easy processability and excellent physical properties,
have been used in many applications such as in packag-
ing, electric cable insulations, microelectronics, dosime-
ter, and medical applications [1–3]. Furthermore, in
recent years there has been extensive utilization of
polymers in safety systems of nuclear power plants,
insulation of superconducting magnets used in fusion
reactors and in space applications [4]. In these appli-
cations polymers are often exposed to various kinds
of ionizing radiation, which results in the modifica-
tions in their physical properties. Therefore the studies
on ionizing radiation induced modifications in polymer
properties is gaining interest in recent years. Many
experimental investigations revealed that the interac-
tion of ionizing radiations with polymers lead to the
excitation and ionization of the atoms and molecules,
which cause subsequent rupture of the chemical bonds
resulting in the formation of polymer chain fragments
and free radicals. These transformations are responsi-
ble for most of the physical and/or chemical changes
observed in the polymers [5–18].

Among the thermoplastic polymers, the hydro-
genated polymers, such as polyethylene are of partic-
ular interests that are being employed in many com-
mercial and scientific applications. Polyethylene when
irradiated with the electron beam, gamma-rays, and

other forms of ionizing radiation predominately undergoes cross-linking [19]. Furthermore, it is observed that the irradiation of polyethylene leads to the creation of polar groups on the polymer surface. Therefore, it is important to study the effect of these dipoles on the intensity of the optical transitions and dielectric properties of polymers.

In the present work, we made an effort to study the post irradiation effects on the structural, optical, dielectric, and thermal properties of electron-irradiated high-density polyethylene (HDPE) films over a dose range of 0–360 kGy. The modifications in the optical parameters viz., the optical band gap, activation energy, transition dipole moment, and oscillator strength were investigated from the UV-Vis absorption spectral analysis. Furthermore, the changes in the dielectric and thermal properties of HDPE films irradiated at different doses of electron radiation were respectively studied using impedance analyzer, differential scanning calorimeter (DSC) and thermo-gravimetric analyzer (TGA).

2 Experimental

The HDPE samples in the form of granules was compression molded into films of thicknesses 50 and 120 μm using polymer press equipment (Technosearch, India, PF-15). The compression molding was carried out by placing the polymer granules between the stainless steel dies at a temperature of 150°C under a pressure of 10 MPa for 10 min and was then cooled under pressure by circulating water through the mold platens. The samples were taken out when the platen temperature reached 40°C. The films were stored in polyethylene zipper packet and subjected to electron irradiation using electron accelerator (ILU-6) at the Board of Research in Isotope Technology (BRIT), Bhabha Atomic Research Centre, Mumbai, India. The electron beam of energy 1.2 MeV from the linear accelerator was employed at 1.0 mA beam current to give a dose rate of 10 kGy s^{-1}, and the films were irradiated separately over the doses of 90, 180, 270 and 360 kGy. The temperature of the samples during the irradiation was maintained constant at about 25°C by breezing air onto the samples.

The FTIR spectra of the pristine as well as the irradiated HDPE films were recorded using an FTIR spectrometer (Perkin–Elmer) over the wavenumber range of 4,000–400 cm^{-1} with a resolution of 4 cm^{-1}.

The polymer samples of a thickness of 50 μm were cut into a 1.0×4.0 cm^2 dimension and inserted into a quartz cell for recording the optical absorption spectra using a UV–Vis spectrophotometer (Perkin–Elmer, Lamda- 35). The absorption spectra were recorded using an identical empty quartz cell as a reference over the wavelength range of 190–500 nm.

The HDPE films of thickness 120 μm were cut into dimension 1.0×1.0 cm^2 and a thin coating of air drying type silver paste was provided on both sides of the films to achieve good electrical contact for dielectric measurements. As the silver particles of the paste have diameter of typically 1 μm, they stick to the sample surface only and hence do not influence the conductivity by interacting with the polymer. The samples were held between two nominally spring loaded copper plates and were subjected to dielectric measurements using the LCR Hitester (HIOKI-3532-50) over the frequency range of 100 Hz–1 MHz at the ambient temperature of 28°C. The values of the dielectric constant (ε') and ac conductivity (σ_{ac}) were estimated from the measured values of the capacitance (C_p) and loss tangent (tanδ) at the different frequencies using the following relations

$$\varepsilon' = C_p/C_0; \, \sigma_{ac} = 2\pi f C_p Dt/A(\text{ohm}^{-1} \text{ cm}^{-1}) \quad (1)$$

where C_0 is the geometrical capacitance of vacuum of the same dimensions as that of the sample; $\mathbf{D} = \tan\delta$, where δ being the phase angle; t, the thickness and A is the cross-sectional area of the HDPE films. The DSC measurements of both the pristine and the irradiated HDPE samples were made using a Mettler Toledo thermal analysis system. The samples weighing about 6.0 mg were scanned in the temperature range of 50–600°C under nitrogen atmosphere at a heating rate of 10°C min^{-1}. The degree of crystallinity was calculated using the following relation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (2)$$

where Xc is the degree of crystallinity, ΔH_m is the specific enthalpy of melting and $\Delta H_m^\circ (= 288$ J g^{-1}) is the specific melting enthalpy for 100% crystalline HDPE [20].

The weight loss (%) was recorded as a function of temperature for the pristine and the electron-beam-irradiated HDPE samples using thermo gravimetric analyzer (Mettler TA). The samples were cut into very small pieces, crimped in small aluminum pans and weighed in a microbalance with a precision up to 10 ppm. The samples were scanned in the temperature range of 50–600°C with a heating rate of 20°C min^{-1}. The resulting weight loss was recorded as a function of temperature in terms of TGA thermograms.

3 Results and Discussions

3.1 Structural Analysis

We have given in Fig. 1 the FTIR transmission spectra of the pristine and the electron irradiated HDPE films over the wave number range 4,000–400 cm^{-1}. The FTIR spectrum of the pristine HDPE films showed the appearance of the strong bands in the wave number region 2,830–2,950 cm^{-1} due to the C−H stretching vibration of −CH$_2$ group; the bands near ∼724 cm^{-1} due to the rocking deformation of long chain −CH$_2$ group; the bands around at ∼1,463 cm^{-1} due to the bending of −CH$_2$ group; and the bands at ∼1,375 cm^{-1} due to the symmetrical bending of −CH$_3$ group. The FTIR spectra of irradiated HDPE films showed that the intensity of most of the bands slightly increased with the increase in dose of electron radiation. Furthermore, the occurrence of weak and strong bands around 3,440 cm^{-1} and 1,715 cm^{-1} indicated respectively the formation of oxidation hydroxyl (OH) and carbonyl (C=O) groups as the electron irradiation of the polymer was carried out in air. The co-existence of C=O and OH groups suggested that the oxygen during the irradiation resulted in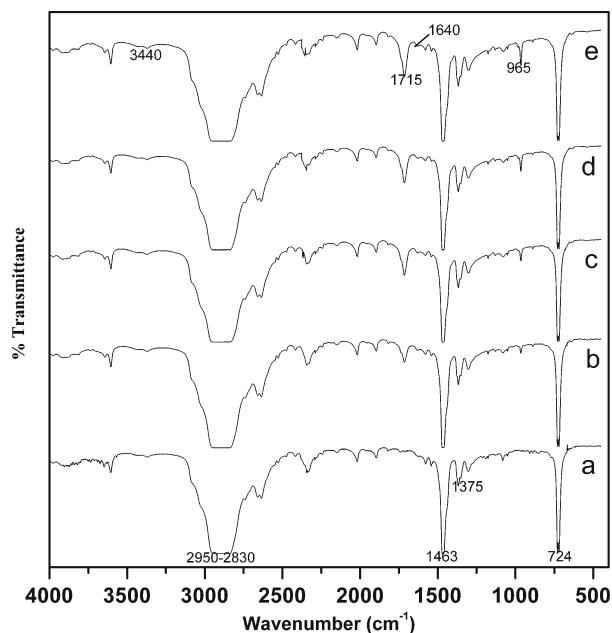 the formation of peroxide radicals on the polymer back bone. The increase in the intensity of the band at 965 cm^{-1} corresponding to =C−H indicated the creation of trans-vinylene group in the irradiated samples. Further occurrence of the band at ∼1,640 cm^{-1} in the irradiated samples is due to the formation of C=C bonds. Thus the appearance of new absorption bands in the irradiated HDPE films indicates certainly the radiation induced structural modifications in the polymer due to the breaking of molecular chains leading to the increment of trans-vinylene unsaturation, formation of carbonyl groups, and conjugated double bonds.

3.2 Changes in Optical Properties

The UV-Vis absorption spectrum for the pristine as well as the electron-beam-irradiated HDPE films over the wavelength range 190–500 nm are given in Fig. 2. The pristine HDPE has an absorption peak at ∼195 nm. It is noticed that the height of the absorption peak increases gradually and shifts slightly towards the longer wavelength region upon electron irradiation. Furthermore, in increasing the dose of electron radiation, broadening of the absorption peak was noticed. The shift in the absorption edge towards the longer wavelength region and broadening of peak for irradiated polymers is generally attributed to the formation of radicals, unsaturated bonds and possible formation of carbon clusters.
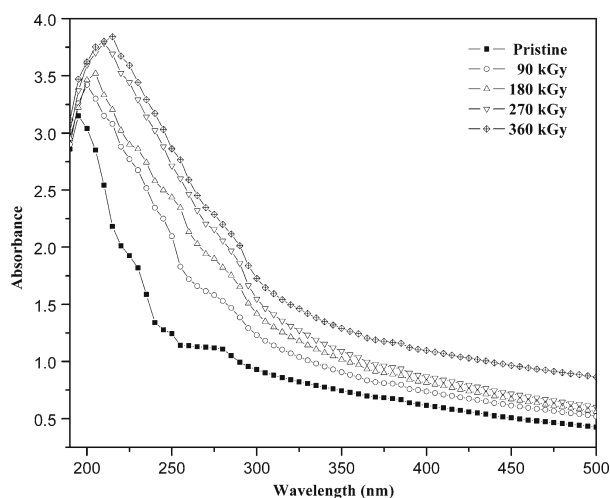

Fig. 1 FTIR spectra for the pristine as well as the irradiated HDPE films at different doses of electron radiation: **a** Pristine, **b** 90 kGy, **c** 180 kGy, **d** 270 kGy, and **e** 360 kGy

Fig. 2 UV–Vis absorption spectrum for the pristine as well as the irradiated HDPE films at different doses of electron radiation

In the high absorption region the absorption coefficient (α) as a function of photon energy ($h\nu$) can be expressed as [21]

$$\alpha h\nu = B(h\nu - E_g)^r \tag{3}$$

where ($h\nu$) is the incident photon energy, E_g the optical band gap energy, B is a constant and r is an exponent which can take values 1/2, 3/2, 2, and 3 depending on the nature of the electronic transition responsible for the optical absorption. The best fit value of r can be determined from the slope of the linear part of $(\alpha h\nu)^{1/r}$ versus $h\nu$. We obtained a best straight line fit to our spectral data for $r = 1/2$, which indicated that a direct transition is allowed. We estimated the values of the band gap energy from the extrapolation of the linear fit of straight line part of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the zero absorption as shown in Fig. 3 and the estimated values of the **E_g** are given in Table 1. We observe that the optical band gap of pristine HDPE film decreased from 5.44 to 4.36 eV with increase in the electron radiation dose. The decrease in the optical band gap of HDPE films with increasing dose of electron radiation could be attributed to the formation of chromophore groups (C=O) and extended systems of conjugated bonds, e.g., carbon clusters as shown in FTIR analysis. The number of carbon hexagon rings (M) in the cluster can be estimated from the Robertson relation given by [22]

$$E_g = 2\,|\beta|\,M^{-0.5} \tag{4}$$

where 2β is the band structure energy of a pair of adjacent π sites and $\beta = -2.9$ eV for six-membered carbon ring, C_6. But Fink et al. [23] have shown that

Table 1 The estimated values of the optical band gap energy (E_g), activation energy (E_u), oscillator strength (f), transition dipole moment (μ) and number of carbon atom per cluster size (N) for the pristine as well as the electron-beam-irradiated HDPE films at different radiation doses

Dose (kGy)	E_g (eV)	E_u (eV)	f	μ (Debye)	N
0	5.44	2.459	1.04	6.5	~39
90	4.69	1.9053	1.10	6.9	~53
180	4.63	1.872	1.18	7.1	~55
270	4.42	1.849	1.65	8.5	~60
360	4.36	1.831	1.85	9.1	~62

the Robertson equation underestimates the cluster size and hence they assumed the structure of the clusters to be like that of Buckminsterfullerene, C_{60}, instead of C_6, and arrived at the following relation given by

$$E_g \approx 34.3/\sqrt{N} \tag{5}$$

where N is the number of carbon atoms per cluster. We used this relation to obtain the number of carbon atoms per cluster in the irradiated HDPE films, given in Table 1. Furthermore, in Fig. 2 one can observe that the absorption spectra showed an extending tail for lower photon energies below the band edge which can be described by Urbach's formula given by [24]

$$\alpha = A \exp(h\nu/E_u) \tag{6}$$

where E_u is the activation energy which is a measure of energy width of the tail of localized states in the band gap. Figure 4 shows a plot of $(\ln \alpha)$ versus $h\nu$ at different electron radiation doses for the HDPE films. The activation energy **E_u** was estimated from the reciprocal of the slope of the linear portion of the behavior
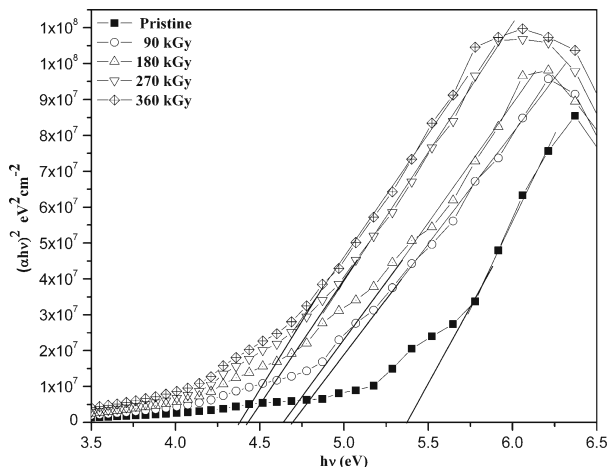

Fig. 3 Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the pristine as well as the irradiated HDPE films at different doses of electron radiation
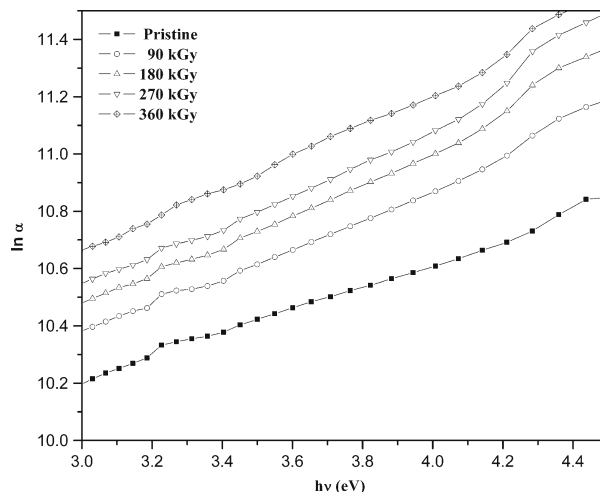

Fig. 4 Plot of $(\ln \alpha)$ versus $h\nu$ for the pristine as well as the irradiated HDPE films at different doses of electron radiation

of $(\ln \alpha)$ with $h\nu$. The estimated values $\mathbf{E_u}$ are given the Table 1.

Furthermore, the oscillator strength (f), which express relative strength of the electronic transition within the molecular system and is related to the integrated molar absorption coefficient (ε) by the following relation [25]

$$f = 4.315 \times 10^{-9} \int \varepsilon \, \mathrm{d}\nu \qquad (7)$$

where the molar absorption coefficient (ε) is equivalent to (α/C) and C represents the molar concentration of the material. Furthermore, the oscillator strength (f) is related to the dipole strength (D) of the transition by the following expression [26]

$$f = \left(\frac{4\pi m_e \nu}{3e^2 \hbar} \right) D \qquad (8)$$

where e is the electron charge, $\mathbf{m_e}$, the electron mass and ν, the frequency of transition. From the dipole strength, one may then calculate the magnitude of the transition dipole moment from valence band to conduction band using the following expression [26]

$$\mu = D^{1/2} \qquad (9)$$

We have estimated the values of the oscillator strength (f) and the transition dipole moment (μ) for the pristine as well as the irradiated HDPE films using (7) and (9), respectively, whose values are presented in Table 1. The plot of both the oscillator strength and
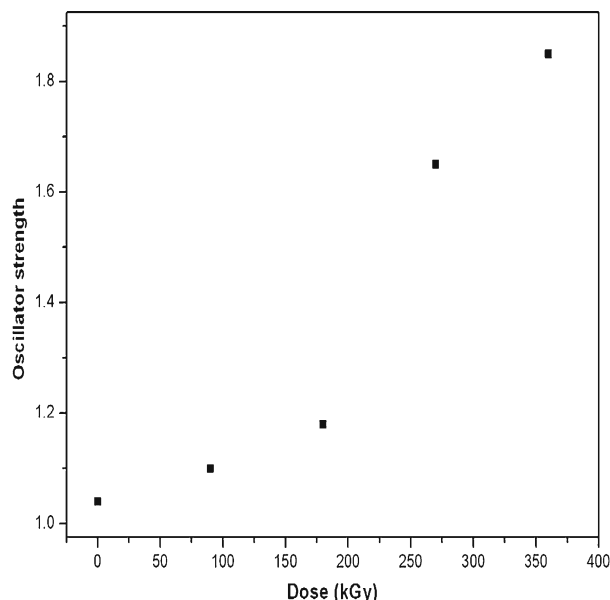
Fig. 5 Variation of oscillator strength (**f**) for HDPE films irradiated at different dose of electron radiation
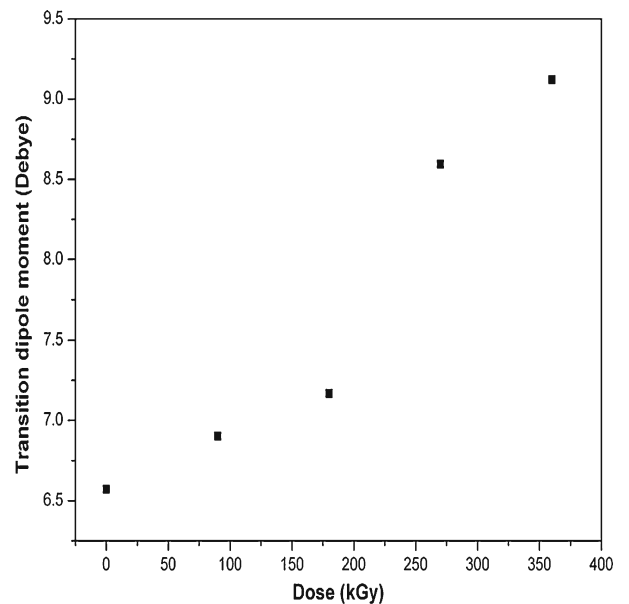
Fig. 6 Variation of transition dipole moment (μ) for HDPE films irradiated at different dose of electron radiation

the transition dipole moment as a function of electron radiation dose are given in Figs. 5 and 6. It was observed that both the oscillator strength and the transition dipole moment of HDPE increases with increase in the dose of electron radiation. The value of f, in fact, is found to increase from ~1.04 for the pristine to ~1.85 for the irradiated films and μ, from ~6.5 Debye for the pristine to ~9.1 Debye for the irradiated HDPE films at 360 kGy of electron radiation. The increase in the oscillator strength confirms an increase in the intensity of optical transitions in HDPE films upon electron irradiation. The increase in both f and μ with increasing electron dose could be attributed either to the creation of new molecular dipoles as a result of formation of point defects in the band gap of the polymer or reorientation of the existing dipoles [27].

3.3 Modifications in Dielectric Properties

The variation of the dielectric constant (ε') with log frequency (**log f**) for the pristine and the electron-beam-irradiated HDPE films is given in Fig. 7. It can be observed that the ε' measured at 1 kHz increases from 2.16 for the pristine to 2.91 for the irradiated HDPE films at 360 kGy. The increase in dielectric constant of HDPE films with the increase in electron radiation doses might be attributed to scissoring of the polymer molecular chains, which leads to the formation of defect sites in the band gap of the polymer. These defects could result in traps of charge carriers that
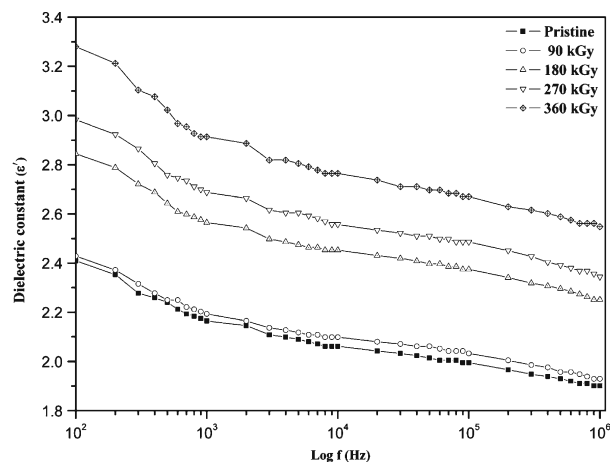
Fig. 7 Plot of dielectric constant (ε') versus $\log f$ for HDPE films irradiated at different doses of electron radiation

increase the ability of the polymer to store charges and hence cause an increase in the dielectric constant of the samples. The experimental results further showed that the dielectric constant for the pristine as well as the electron-beam-irradiated HDPE films decreases with the increase in frequency. It might be observed that as the frequency increases, the charge carriers migrate through the dielectric and get trapped against a defect site and induce an opposite charge in its vicinity and thus the polarization of the trapped and the bound charges cannot take place resulting in a decrease in the dielectric constant at these frequencies.

Figure 8 depicts the dependence of the ac conductivity (σ_{ac}) on log frequency (**log** f) at the ambient
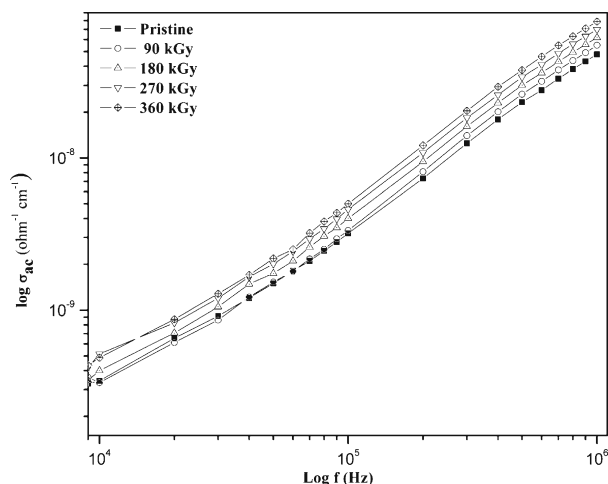
temperature for both the pristine and the electron-beam-irradiated HDPE samples. It is observed that σ_{ac} of the HDPE films increases slightly with increase in the electron radiation dose and, in fact, a sharp increase in the conductivity is observed above 105 Hz for all the irradiated films. The increase in conductivity could be due to the scissoring of polymer chains upon irradiation which results in the formation of free radicals, unsaturated bonds etc. This leads to an increase in the free-charge carrier density in the polymer, which obviously contributes to an enhancement in the ac conductivity of the films at higher doses.

3.4 Modifications in Thermal Properties

The DSC thermograms for the pristine and the irradiated HDPE samples at an electron radiation dose of 180 and 360 kGy are given in Fig. 9. The thermograms showed changes in melting temperature and specific enthalpy of melting of HDPE samples upon electron irradiation. For the pristine samples the melting peak is observed at 128.85°C and the degree of crystallinity estimated using (2) is about 63%. However upon electron irradiation the melting temperature and specific heat of enthalpy of HDPE found to increase with increase in the dose of electron radiation. It is found that for HDPE films irradiated at 360 kGy the melting temperature increases to 133.42°C and degree of crystallinity was also found to enhance to 67%. We have given
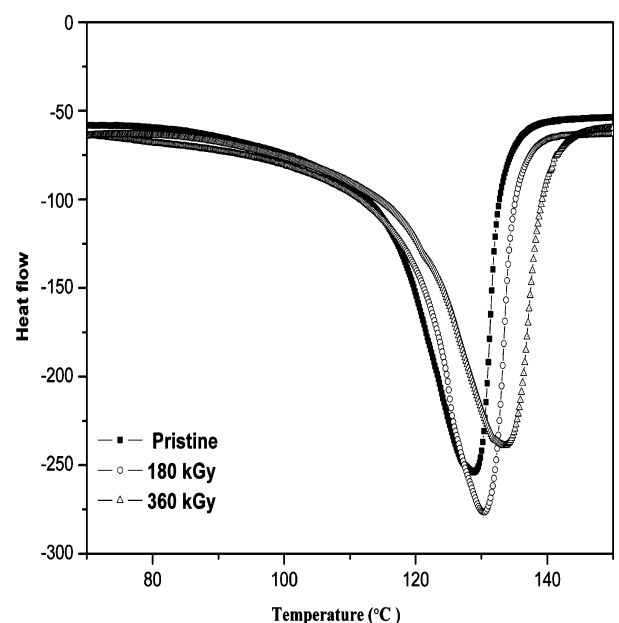

Fig. 8 Plot of ac conductivity (σ_{ac}) versus $\log f$ for HDPE films irradiated at different doses of electron radiation

Fig. 9 DSC thermogram for the pristine and the irradiated HDPE at 180 and 360 kGy dose of electron radiation

Table 2 DSC characterization of HDPE irradiated to different dose of electron radiation

Dose (kGy)	Melting peak (°C)	Heat of enthalpy (J g^{-1})	Degree of crystallinity (%)
0	128.85	183.83	~63
180	130.37	187.57	~65
360	133.43	192.56	~67

in Table 2 the melting temperatures as well as the degree of crystallinity of HDPE samples irradiated at different doses of electron radiation. The increase in melting temperature in irradiated HDPE samples thus indicates a predominant cross-linking of polymer chain upon electron irradiation.

Furthermore, the increase in thermal stability in irradiated HDPE samples was confirmed by TGA. We have given the TGA thermograms for both the pristine and the electron-irradiated HDPE samples at 180 and 360 kGy in Fig. 10. It is seen that for the pristine sample, a slow decomposition zone is observed up to 300°C where there is a weight loss of about 4%. A faster rate of decomposition starts from 300°C till the polymer is completely decomposed at 416°C where there is a weight loss of about 86%. Similarly for the electron irradiated HDPE at 360 kGy, a slower rate of decomposition is noticed up to 415°C where the sample loses about 11% of its initial weight. This is followed by a fast decomposition over the range 415–484°C at which the weight loss is about 89%. Thus, it is observed that the thermal stability of HDPE increases due to the electron beam irradiation. The reason for the increase in the

thermal behavior of the irradiated HDPE might be due to the predominant cross-linking upon electron-beam-irradiation which increases the molecular weight and compactness of the polymer, imparting more strength to withstand the thermal strain.

4 Conclusions

We conclude from the present studies that the electron-beam irradiation modified the structural, optical, dielectric and thermal properties of HDPE films. The FTIR spectra showed the creation of trans-vinylene unsaturation, carbonyl group and conjugated double bonds in the electron-beam-irradiated of HDPE films. The UV-Vis spectroscopic studies showed a decrease in the optical band gap and activation energy of HDPE films with increase in the dose of electron radiation. Furthermore, an increase in the transition dipole moment and oscillator strength was observed in the irradiated HDPE films due to the creation of new molecular dipoles. The dielectric measurements further revealed that the electron-beam irradiation resulted in a slight increase in the dielectric constant and ac conductivity of HDPE films upon electron irradiation which could be attributed to the enhanced free electron density in the irradiated samples as a consequence of molecular chain scission, formation of free radicals and unsaturated bonds. Furthermore, the DSC analysis showed the increase in specific enthalpy of melting and degree of crystallinity in irradiated HDPE and TGA analysis indicated the occurrence of predominant cross-linking in HDPE upon electron irradiation which increased the thermal stability of irradiated samples.

Fig. 10 TGA thermogram for the pristine and the irradiated HDPE at dose of 180 and 360 kGy electron radiation

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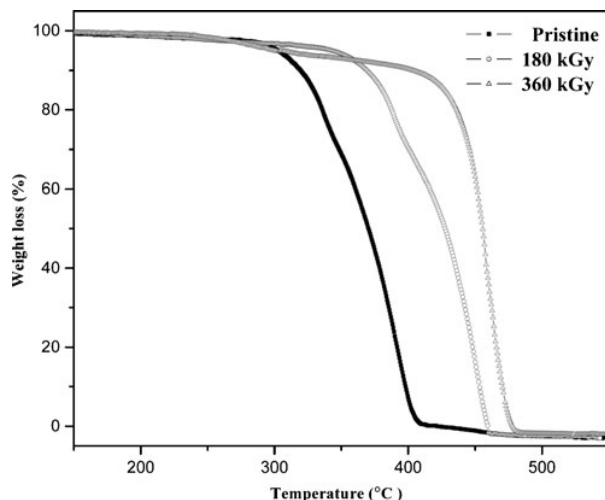7. S. Dalai, C. Wenxiu, J. Appl. Polym. Sci. **186**, 1296 (2002)

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