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Electron-beam induced modifications of low 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 properties of low density polyethylene (LDPE) films. The modifications in the optical band gap and activation energy have been investigated as a function of electron radiation dose using UV-Vis absorption spectra of LDPE films. The spectral analysis showed a decrease in both the optical band gap and activation energy Further the dielectric measurements indicated a slight increase in the dielectric constant and the ac conductivity of the LDPE films upon electron irradiation. The thermal analysis carried out by DSC and TGA revealed that the melting temperature, degree of crystallinity and thermal stability of the LDPE films increased, obviously, due to the predominant cross linking following high doses of electron radiation.

KEYWORDS

Low density polyethylene;
Electron-beam irradiation;
UV-Vis Spectroscopy;
Dielectric constant;
Optical band gap and
Activation energy.

INTRODUCTION

Polymers, due to their high strength to weight ratio, easy processability and excellent chemical and physical properties, have been used in many applications such as in packaging, electric cable insulations, microelectronics, dosimeter and medical applications[1-3]. Further polymers have been extensively utilized in safety systems of nuclear power plants, insulation of superconducting magnets used in fusion reactors and in space applications, where they are exposed to different kinds of radiations[4]. Therefore many researchers have shown a special interest on the study of radiation induced modification of polymer properties which is very useful in understanding radiation induced polymer reactions and also helps in the selection of suitable polymeric materials to be used in radiation environments. The modifications of polymer properties are often achieved by different kinds of radiations such as ion beams, accelerated electrons and γ-rays[5-7]. Among them electron-beam irradiation of polymers has several advantages as the free radicals produced during its interaction with target samples is very high and macroscopic modifications of polymers can be achieved at the intermediate doses between that of gamma and ion beam irradiation. The main effects of interaction of ionizing radiations with polymers is to produce excitation and ionization of the atoms and molecules in the polymers, which cause subsequent rupture of the chemical bonds resulting in polymer chain fragments and free radicals. These transformations are responsible for most of the physical and/or chemical changes observed in the polymers[8-11]. The optical and the electrical properties of polymers are the ones which are highly sensitive to the radiations and many experiments aimed to improve the optical and the electrical conductivity of polymers by radiations have been reported and discussed[12-18].

Among the thermoplastic polymers, the hydrogenated polymers, such as polyethylene are of particular interests that are being employed in many commercial and scientific applications. LDPE is one of the popular thermoplastic polymers which is produced under high pressure (82-276MPa) and high temperature (405-605K) with a free radical initiator such as peroxides and oxygen and contains some long chain branches which could be as long as chain backbones, and short chain branches[19]. LDPE when irradiated with electron-beam, gamma-ray and other forms of high energy radiation predominately undergoes cross-linking[20]. Cross-linked polyethylene has become widely adapted for a number of industrial applications, which require withstanding high temperature environments such as wire and cable insulation, heat shrinkable material, hot water tubing and steam resistant food packaging. 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 LDPE films. The modifications in the optical parameters *viz.,* the optical band gap, activation energy was studied from the UV-Vis absorption spectra of the pristine and the irradiated LDPE films at different electron doses in the range 0-360 kGy. Further, the variations in the dielectric and thermal properties of the pristine as well as the irradiated LDPE films were studied at different doses of electron radiation using impedance analyzer, Differential scanning calorimeter (DSC) and thermo gravimetric analyzer (TGA).

EXPERIMENTAL

The low density polyethylene (LDPE) samples in the form of granules was compression molded into films of thickness 50 μm 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^{0}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^{0}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 (BARC), 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 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 25^0 C by breezing air onto the samples.

For structural analysis, the FTIR spectra of both the pristine as well as the irradiated LDPE films were recorded using a FTIR spectrometer (Perkin-Elmer) over the wave number range of 4000 - 400 cm^{-1} with a resolution of 4.0 cm^{-1}.

The polymer samples of thickness 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 of both the pristine as well as the electron irradiated LDPE films using 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 LDPE 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 1μm, 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 28^0 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 ($tan\delta$) at the different frequencies using the following relations

$$\varepsilon' = C_p/C_0;\ \sigma_{ac} = 2\pi f C_p D t / A\ (\mathrm{ohm}^{-1}\mathrm{cm}^{-1}) \qquad (1)$$

where, C_0 is the geometrical capacitance of vacuum of the same dimensions as that of the sample; D= tan δ, where δ being the phase angle; *t*, the thickness and *A* is the cross-sectional area of the LDPE films.

The melting temperature, melting enthalpy and the degree of polymer crystallinity for both the pristine as well as the electron-beam irradiated LDPE samples were made using the differential scanning calorimeter (Mettler DSC). The samples weighing about 6.0 mg were scanned in the temperature range of 50-600^{0}C under nitrogen atmosphere at a heating rate of 20 ^{0}C/min. The degree of crystallinity was calculated using the following relation:

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

where X_c -is the degree of crystallinity, ΔH_m-the specific enthalpy of melting and ΔH_m° (=288 J/g) is the specific melting enthalpy for 100% crystalline LDPE[21].

The weight loss (%) was recorded as a function of temperature for both the pristine and the electron-beam irradiated LDPE 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^{0}C with a heating rate of 20 ^{0}C/ min. The resulting weight loss was recorded as a function of temperature in terms of TGA thermograms.

RESULTS AND DISCUSSIONS

Structural analysis

We have given in Figure 1 the FTIR transmission spectra over the wave number range 4000- 400 cm^{-1} for both the pristine and the electron irradiated LDPE films. The strong bands in the wave number region 2830 - 2950 cm^{-1} correspond to C–H stretching vibration of –CH_2 group; the bands near ~724 cm^{-1} indicate the rocking deformation of long chain –CH_2 group; the bands around ~1463 cm^{-1} correspond to bending of –CH_2 group; and the bands at ~1375 cm^{-1} correspond to symmetrical bending of –CH_3 group in both the pristine and the irradiated samples. The occurrence of weak and strong bands around 3440 cm^{-1} and 1716 cm^{-1} indicate 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 suggests that the presence of oxygen induces 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 indicates the creation of trans-vinylene group in the irradiated samples. The appearance of C – C characteristic bands at ~1620 cm^{-1} in the irradiated samples might be due to the irradiation induced cross-linking effects. Thus the appearance of new transmission bands in the irradiated LDPE 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 group, cross-linking and conjugated double bonds.

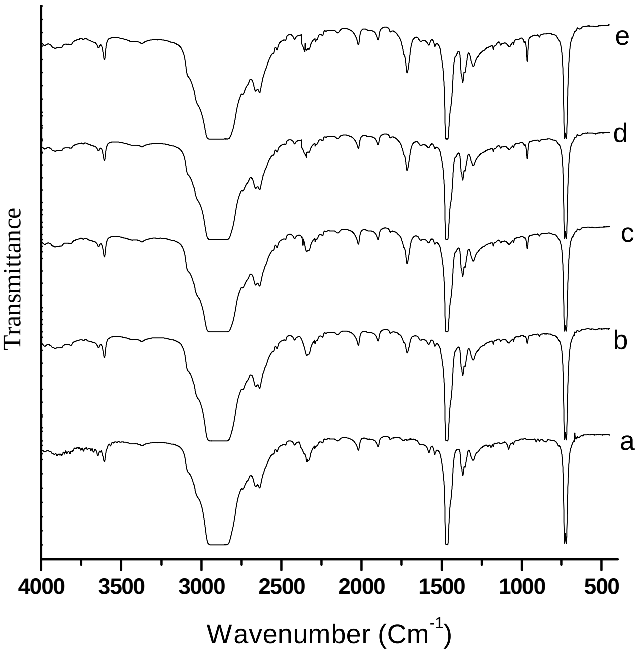

Figure 1 : FTIR spectra for the pristine as well as the irradiated LDPE films at different doses of electron radiation (a) Pristine (b) 90 kGy (c) 180 kGy (d) 270 kGy (e) 360 kGy

Changes in optical properties

The UV-Vis absorption spectra of both the pristine as well as the electron-beam irradiated LDPE films over the wavelength range 190-500 nm are given in Figure 2. The absorption spectrum of the pristine LDPE show absorption peaks at ~195 nm. The height of the absorption peak of LDPE films increases gradually and shifts slightly towards the longer wavelength region upon electron irradiation. Further on increase in the dose of electron radiation a small broadening of the absorption peak was noticed in the irradiated samples. The shift in the absorption edge towards the longer wavelength region for irradiated is generally interpreted as caused by the formation of chromophore groups or extended system of conjugated bonds, i.e. possible formation of carbon clusters in the irradiated polymers.

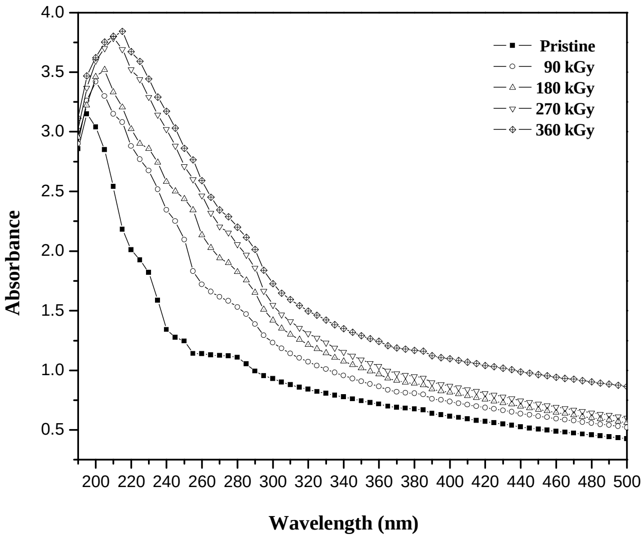

Figure 2 : UV-Vis absorption spectrum for the as well as the irradiated LDPE films at different doses of electron radiation

In the high absorption region the absorption coefficient (α) as a function of photon energy ($h\nu$) in the high absorption region can be expressed as[22]

$$\alpha(\nu)h\nu = B(h\nu - E_g)^r \qquad (3)$$

where ($h\nu$) is the incident photon energy, E_g, the optical band gap energy and B is a constant (= $4\pi\sigma_0 / nc\Delta E$) where c, speed of light, σ_0, extrapolated dc conductivity at T=∞ , D*E*, measure of the extent of band tailing, *n*, refractive index and *r* is an exponent which can take values ½, 3/2 2 & 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 $(\alpha h\upsilon)^{1/r}$ versus $h\upsilon$. We obtained a best straight line fit to our spectral data for *r* = ½, which indicate that the transition is allowed direct. We estimated the values of the band gap energy from the extrapolation of the straight line part of the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ to the zero photon energy as shown in Figure 3 and the estimated values of the E_g are given in TABLE 1. We observe that the optical band gap of pristine LDPE film decrease from 5.30 eV to 4.33 eV with increase in the electron radiation dose. A similar decrease in the value of E_g of gamma irradiated polyvinylchloride (PVC), polypropylene (PP) and polyallyl diglycol carbonate (CR-39) films have been reported by others[23-25]. Abdel-Fattah *et al*[23] reported that irradiation of the unpalsticized PVC films by 25 MeV proton beams over a fluency range of 0 - 1 $\times 10^{15}$ ions/cm^2 decreases its optical band gap from 4.35 to 2.04 eV. Sinha *et al*[24,25] showed that gamma irradiation of PVC and PP films over the dose range of 0 - 10^6 Gy decreases respectively their optical band gap energy from 2.68 to 1.43eV and 4.59 to 2.07 eV. The decrease in the optical band gap of LDPE films with increasing dose of electron radiation could be attributed to the formation of extended systems of conjugated bonds, *e.g.* carbon clusters. The number of carbon hexagon rings (*M*) in the cluster can be estimated from the Robertson relation given by[26]

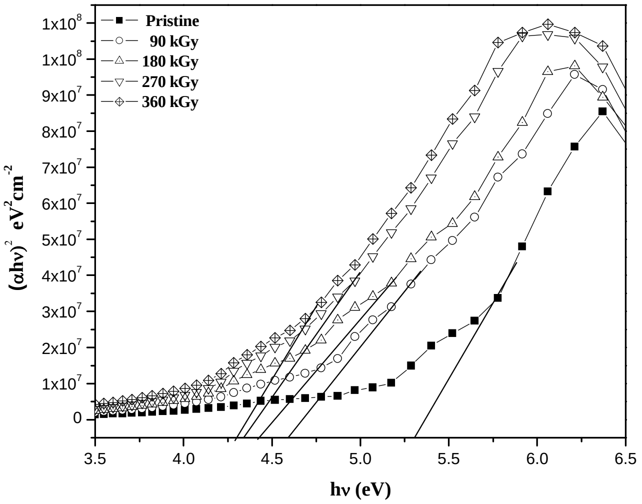

Figure 3 : Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the pristine as well as the irradiated LDPE films at different doses of electron radiation

TABLE 1 : The estimated values of the optical band gap energy (E_g), activation energy (E_u) and number of carbon atom per cluster size (*N*) for the pristine as well as the electron-beam irradiated LDPE films at different radiation doses

Dose (kGy)	E_g	E_u	*N*
0	5.30	2.459	~ 42
90	4.58	1.9053	~ 56
180	4.42	1.872	~ 60
270	4.32	1.849	~ 63
360	4.29	1.831	~ 64

$$E_g = 2|\beta|M^{-0.5} \quad (5)$$

where 2β is the band structure energy of a pair of adjacent π sites and β = - 2.9 eV for six-membered carbon ring, C_6. But Fink *et al*[27] have shown that 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

$$E_g \approx 34.3/\sqrt{N} \quad (6)$$

where N is the number of carbon atoms per cluster. We obtained using this relation the number of carbon atoms per cluster in the irradiated LDPE films and are given in TABLE 1. Further from Figure 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[28]

$$\alpha = A\exp(h\nu / E_u) \quad (4)$$

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 LDPE films. The activation energy E_u was estimated from the reciprocal of the slope of the linear portion of the behavior of $(\ln\alpha)$ with $h\nu$. The estimated values E_u are given the TABLE 1. It is estimated that pristine LDPE films have activation energy of 2.45 eV. Upon electron irradiation it is decreases to 1.83 at a dose of 360 kGy.

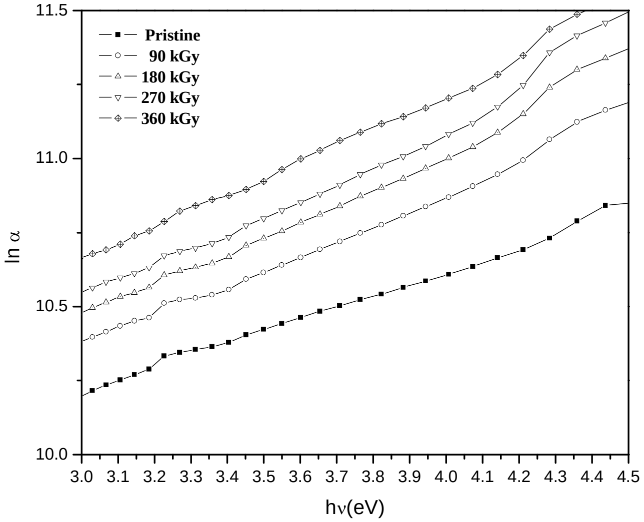

Figure 4 : Plot of (ln α) versus $h\nu$ for the pristine as well as the irradiated LDPE films at different doses of electron radiation

Modifications in dielectric properties

The variation of the dielectric constant (ε') with log frequency (*log f*) for the pristine and the electron-beam irradiated LDPE films is given in Figure 5. It can be observed that the ε' of pristine LDPE films measured at 1 kHz increases from 2.16 to 2.91 for the irradiated LDPE films at 360 kGy. The increase in dielectric constant of LDPE 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 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 LDPE 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.

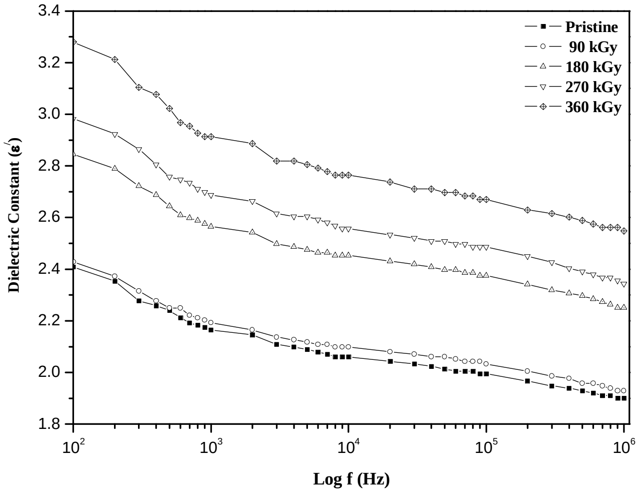

Figure 5 : Plot of dielectric constant (ε') versus *log f* for LDPE films irradiated at different doses of electron radiation

Figure 6 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 LDPE samples. It is observed that σ_{ac} of the LDPE films increases slightly with increase in the electron radiation dose and, in fact, a sharp increase in the conductivity is observed above 10^5 Hz for all the irradiated films. The increase in conductivity could be understood in terms of the free electron model. The scissoring of polymer chains upon irradiation results in an increase of free radicals, unsaturated bonds etc leading to an increase in the free-electron density in the polymer, which obviously contributes to an enhancement in the ac conductivity of the films at higher frequencies.

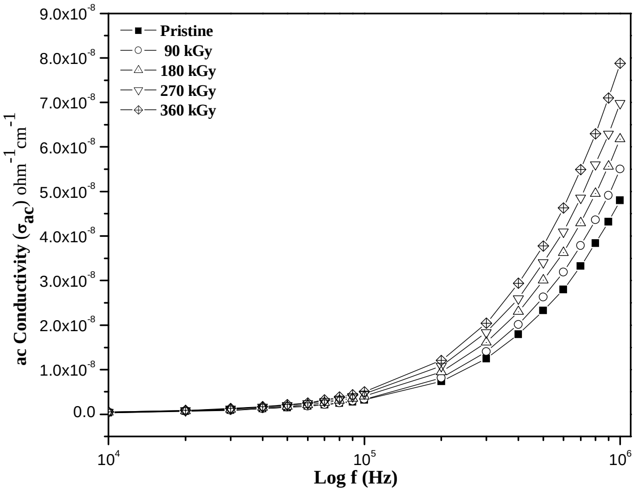

Figure 6 : Plot of ac conductivity (σ_{ac}) versus *log f* for LDPE films irradiated at different doses of electron radiation

Modifications in thermal properties

The DSC thermograms for the pristine and the irradiated LDPE samples at an electron radiation dose of 180 and 360 kGy are given in Figure 7. The thermograms show changes in melting temperature and degree of crystallinity of LDPE samples upon electron irradiation. The melting peak is observed at 132.35 ^{0}C and the degree of crystallinity estimated using Equation (2) is about 58% for the pristine samples. However, for the electron irradiated LDPE at 360 kGy the melting temperature increases to 140.42 ^{0}C and degree of crystallinity was also found to enhance to 62.5%. We have given in TABLE 2 the melting temperatures as well as the degree of crystallinity of LDPE samples at different doses of electron radiation. The increase in melting temperature in irradiated LDPE samples thus indicates a predominant cross-linking of polymer chain upon electron irradiation.

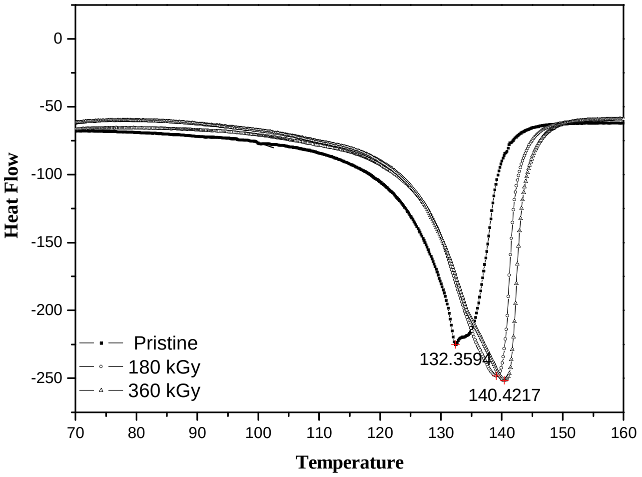

Figure 7 : DSC thermogram for the pristine and the irradiated LDPE at 180 kGy and 360 kGy electron radiation

TABLE 1 : The estimated values of the optical band gap energy (E_g), activation energy (E_u) and number of carbon atom per cluster size (N) for the pristine as well as the electron-beam irradiated LDPE films at different radiation doses

Dose (kGy)	E_g	E_u	N
0	5.30	2.459	~ 42
90	4.58	1.9053	~ 56
180	4.42	1.872	~ 60
270	4.32	1.849	~ 63
360	4.29	1.831	~ 64

Further the increase in thermal stability in irradiated LDPE samples was confirmed by TGA. We have given the TGA thermograms for both the pristine and the electron irradiated LDPE samples at 180 kGy and 360 kGy in Figure 8. It is seen that for the pristine sample a slow decomposition zone is observed up to 300 ^{0}C where there is a weight loss of about 4%. A faster rate of decomposition starts from 300 ^{0}C till the polymer is completely decomposed at 416 ^{0}C where there is a weight loss of about 86 %. Similarly for the electron irradiated LDPE at 360 kGy, a slower rate of decomposition is noticed up to 415 ^{0}C where the sample loses about 11% of its initial weight. This is followed by a fast decomposition over the range 415-484 ^{0}C at which the weight loss is about 89%. Thus it is observed that the thermal stability of LDPE increases due to the electron beam irradiation. The reason for the increase in the thermal behavior of the irradiated LDPE 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.

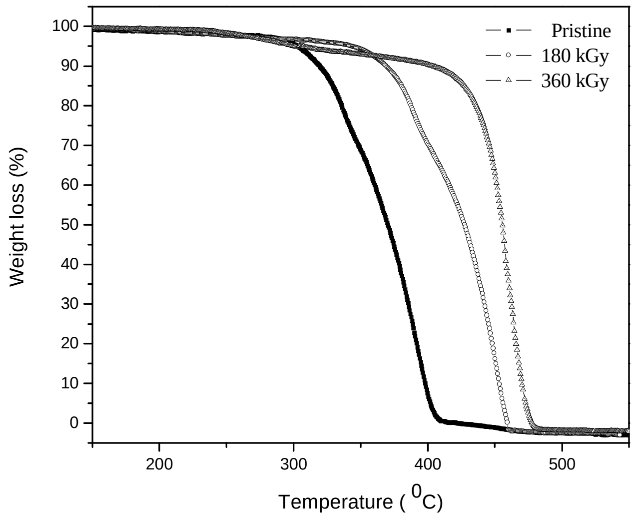

Figure 8 : TGA thermogram for the pristine and the irradiated LDPE at 180 kGy and 360 kGy electron radiation

CONCLUSION

We conclude from the present studies that the electron-beam irradiation certainly modified the structural, optical, dielectric and thermal properties of LDPE films. The FTIR spectra showed the creation of trans-vinylene unsaturation, formation of carbonyl group, cross-linking and conjugated double bonds upon electron irradiation of LDPE films. The UV-Vis spectroscopic studies showed a decrease in the optical band gap and activation energy of LDPE films with increase in the dose of electron radiation. The dielectric measurements further revealed that the electron-beam irradiation resulted in a slight increase in the dielectric constant and ac conductivity of LDPE 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. Further, the DSC and TGA analysis indicated the occurrence of predominant cross-linking in LDPE upon electron irradiation which increased the thermal stability of irradiated samples.

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