

Thermogravimetric analysis of electron-beam irradiated high density polyethylene

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Abstract— High density polyethylene (HDPE) polymer films are irradiated with 1.2 MeV electron-beam over a dose range of 0-600 kGy. The modifications in structural and thermal properties HDPE polymers irradiated at different doses of electron radiation are investigated using FTIR and thermogravimetric (TG) analysis. The FTIR spectral studies indicates the formation of carbonyl (C=O) group and conjugate C = C bonds in the irradiated polymer samples. From the TG curve we measured onset temperature of thermal decomposition and temperature corresponding to maximum rate of mass loss. Further we evaluated the activation energy of thermal degradation by various kinetics of thermal degradation methods viz., Anderson-Freeman, Sharp-Wentworth and Horowitz-Metzger method, to study the modification in the thermal properties of HDPE exposed to electron radiation. It was found that onset temperature of thermal decomposition, temperature corresponding to maximum rate of mass loss and activation energy of thermal degradation of HDPE increases with the increase in the dose of electron radiation. Thus the electron-beam irradiated HDPE polymer films are found to be more thermally stable than unirradiated sample.

Keywords: High density polyethylene; Electron-beam irradiation; Fourier transform infrared spectroscopy; Thermogravimetric analysis; Thermal decomposition; Activation energy.

1 INTRODUCTION

High density polyethylene (HDPE) is a well-known engineering thermoplastic polymer which has been used in varieties of commercial and scientific applications viz., packaging, nuclear technology, as insulating material in electronics, wire and cable etc. However HDPE polymer is an organic substance which is thermally sensitive due to limited strength of covalent bonds that make up its structure. Therefore the structure of HDPE has to be modified to improve its thermal properties to benefit for particular application with long-term thermal stability. Several methods such as blending, incorporation of filler particles etc are used to increase the physical properties of polymers. The ionizing radiation is another method used to modify the structure of polymers with specific physical properties. The radiation induced modifications of polymer properties has been discussed in detail by many researchers [1-7]. The interaction of radiation with polymers results in formation of reactive species known as free radicals that permanently changes the chemical structure and produces large scale of lattice defects along their path in the polymer. These free radicals are responsible for observed radiation induced reaction such as macromolecular chain destruction, crosslinking, carbonization and oxidation. The degree to which damages that occurs in polymer depends on the chemical structure, morphology, irradiation conditions and dose. The radiation induced reaction mentioned above in turn influence the thermal, mechanical,

electrical and optical properties of polymers that open the way to design a variety of devices with required parameters [8-10].

Among the different studies on polymeric materials, thermogravimetric analysis (TGA) is one of the most useful and commonly used techniques which help in understanding the degradation mechanism and also to know the influence of the polymer structure on the thermal stability. TGA is also used to predict the lifetime of polymers under actual service conditions. TGA requires only a small quantity of sample and it offers precise control over heating condition such as accurate heating rate and variable temperature range. Further using TGA one can measure the decomposition of polymers at various temperatures and also can evaluate the kinetic parameter of thermal degradation viz., activation energy of decomposition, order of reaction and pre-exponential factor [11-12]. The activation energy is the minimum energy needed to activate the molecules to undergo a phase transition. The activation energy is thus viewed as an energetic threshold for fruitful reaction and hence it must be measured for better understanding of thermal stability of polymers.

The present study deals with study of modifications in the structural and thermal properties of HDPE polymers irradiated at various doses of electron-beam radiation of energy 1.2 MeV. In this paper we the thermal decomposition of HDPE polymers irradiated at various doses are measured using TGA. Further we have calculated the activation energy of thermal decomposition using three different methods viz., Anderson-Freeman[13], Sharp-Wentworth[14] and Horowitz-Metzger [15] method.

2. Experimental details:

The HDPE polymer granules were procured from Reliance India Ltd. These granules are compression molded

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into a film of thickness 120 μm by applying pressure of 10 MPa at 150 $^{\circ}\text{C}$ using Polymer press equipment (Technosearch-PF-15, India). The electron-beam irradiation of prepared HDPE polymer films are carried out using ILU-6 electron accelerator at the BRIT, BARC, Mumbai, India. The electron-beam of energy 1.2 MeV, at a beam current 1.0 mA and at dose rate 10 kGy per pass is employed to obtain required dose during the irradiation. The polymer films are irradiated to different doses *viz.*, 200, 400, 600 kGy.

The FTIR spectra of the both the pristine as well as the irradiated HDPE films are recorded in the transmission mode using FTIR spectrometer (Perkin-Elmer) having a spectral resolution of 0.5 cm^{-1} . The FTIR spectra of all the polymer films are recorded over the wavenumber range 4000-400 cm^{-1} keeping air as reference.

TGA thermograms for pristine as well as irradiated HDPE samples are recorded using thermogravimetric analyzer (Mettler TA). The HDPE samples weighing about 10-11 mg were cut into very small pieces, crimped in small aluminum pans and weighed in a microbalance with a precision up to 10 ppm. The polymers are scanned over a temperature range of 50-600 $^{\circ}\text{C}$ under nitrogen atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The resulting weight loss is recorded as a function of temperature in terms of TGA thermograms. From the thermograms the activation energy of thermal decomposition is determined by Anderson-Freeman, Sharp-Wentworth and Horowitz-Metzger method.

3. Result and discussion

3.1. FTIR spectroscopic analysis

The FTIR transmission spectra HDPE irradiated at different doses of electron radiation over the range 0-600 kGy are given in Fig. 1. The transmission bands observed in the FTIR spectra of the pristine HDPE are identified as follows. The strong bands over the wave number range 2830-2950 cm^{-1} correspond to the aliphatic C-H stretching vibration of $-\text{CH}_2$ group; that at $\sim 1463 \text{ cm}^{-1}$, to the bending absorption of $-\text{CH}_2$ group; at $\sim 1375 \text{ cm}^{-1}$, to the symmetrical bending of $-\text{CH}_3$ group; and the bands at 720 and 730 cm^{-1} are respectively correspond to the bending and rocking vibration of the methylene groups.

However in the irradiated HDPE films new bands are found to appear around 3440 cm^{-1} , 1715 cm^{-1} and 965 cm^{-1} which correspond respectively to hydroxyl ($-\text{OH}$), carbonyl ($\text{C}=\text{O}$) and trans-vinylene ($=\text{C}-\text{H}$) groups. The formation of these functional groups in the irradiated HDPE samples is attributed to the reaction of atmospheric oxygen with polymer upon irradiation. The increase in the intensity of these peaks in HDPE polymer with the increase in the dose of electron radiation confirm that the concentration of $\text{C}=\text{O}$ and $=\text{C}-\text{H}$ groups increases in irradiated samples.

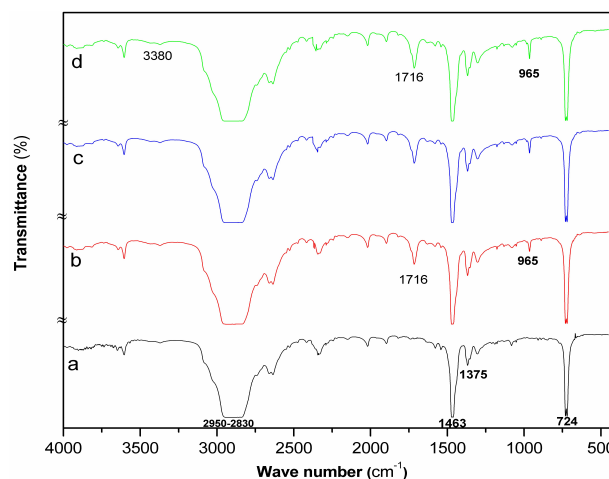


Fig. 1. FTIR spectra of HDPE polymer films irradiated at different doses of electron radiation. (a) 0 kGy (b) 200 kGy (c) 400 kGy (d) 600 kGy.

3.2. Thermal decomposition behavior

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the pristine as well as the irradiated HDPE polymers are respectively given in Fig 2 and 3. The TG and DTG curve shows that both pristine and irradiated HDPE polymers undergo single stage decomposition due to heating. The temperature corresponding to the starting point of decomposition i.e. the onset temperature of thermal decomposition (T_o) for both pristine and irradiated HDPE samples are obtained DTG curve. Further the temperature corresponds to maximum rate of mass loss (T_m) for both pristine and irradiated HDPE samples are measured from maximum of the DTG curve. The measured values of onset temperature of thermal decomposition (T_o) and temperature corresponds to maximum rate of mass loss (T_m) are given in Table 1. From the table it can be found that both the values of T_o and T_m for irradiated HDPE are higher than the pristine sample. This indicates that the irradiated HDPE are thermally more stable than the pristine HDPE.

Table 1. The measure values of Onset of thermal decomposition temperature (T_o) ($^{\circ}\text{C}$) Temperature corresponding to maximum mass loss (T_m) ($^{\circ}\text{C}$) of HDPE polymer samples irradiated at different doses of electron radiation

Radiation Dose (kGy)	T_o ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
0	285	390
200	332	448
400	396	449
600	412	477

3.3. Kinetic analysis

The thermogravimetric (TG) and DTG curves are not only helpful to find the onset temperature of thermal decomposition (T_o) and temperature of maximum mass loss rate (T_m), but also it allows determine the kinetics parameter of thermal decomposition such as activation energy of thermal

decomposition (E_a).

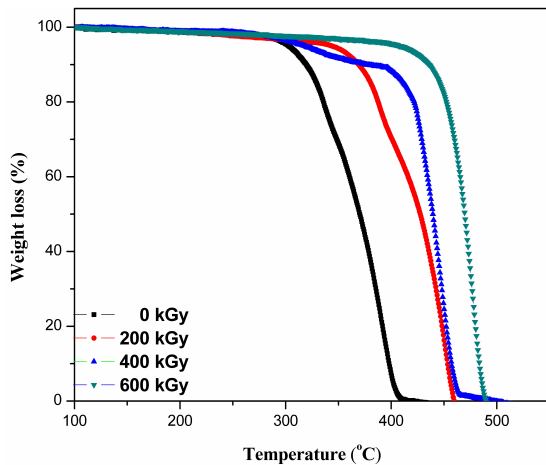


Fig. 2. TGA thermograms of HDPE polymers irradiated at different doses of electron radiation

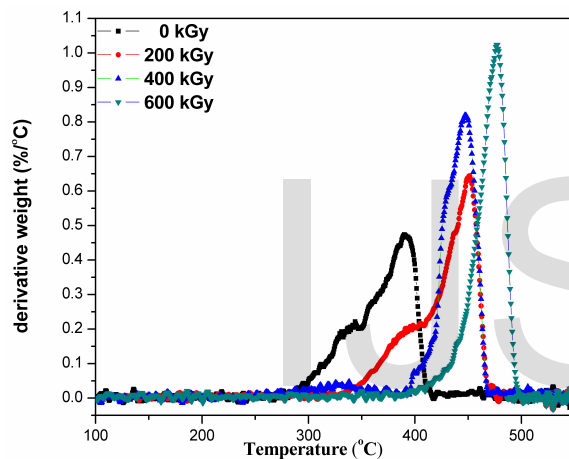


Fig. 3. DTG curve of HDPE polymers irradiated at different doses of electron radiation

The polymer decompositions are generally considered as heterogeneous reactions since the sample is solid and the products are gases. The equation which relates rate of polymer degradation (da/dt) with the extent of conversion or fraction reacted (α) is given by

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (1)$$

where the degree of conversion, α , for non- isothermal TGA is defined as the ratio of the actual weight loss to the total weight loss. i.e. $\alpha = \frac{m_0 - m}{m_0 - m_\infty}$; where m is the actual mass at time t (or at temperature T), m_0 – initial weight, and m_∞ – weight at the end of the isothermal or non-isothermal experiments; $f(\alpha) = (1-\alpha)^n$ and $k(T)$ is the rate constant which may be expressed in terms of in terms of Arrhenius equation

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

Where A - frequency factor which gives the frequency of the occurrence of a condition that may lead to reaction; E_a - activation energy of thermal decomposition; R the gas constant and T the thermodynamic (Kelvin) temperature.

By substituting the values of $f(\alpha)$ and $k(T)$ in Eq. 1 we can write Eq. 1 as

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (1-\alpha)^n \quad (3)$$

By considering a constant rate of temperature changes,

$$\beta = \frac{dT}{dt}, \text{ Eq. 3 can be transformed as follow}$$

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) (1-\alpha)^n \quad (4)$$

Using equations (3) and (4) and applying appropriate approximations, several methods based on either rate of conversion[16] or heating rate [17-18] are proposed to determine kinetic parameter thermal degradation. Among them few methods viz., Anderson - Freeman, Sharp-Wentworth and Horowitz-Metzger methods are quite popular which can use single heating rate for the discussion of thermal degradation and are discussed below.

3.3.1. Anderson-Freeman method

The expression derived by Anderson – Freeman to study the kinetics of thermal degradation is given as

$$\Delta \log(dw/dt) = n \log W - \frac{E_a}{2.303R} \left(\Delta \frac{1}{T} \right) \quad (5)$$

Where dw/dt - the rate of thermal decomposition which represent the change in weight loss per minute; W – weight of reactant; R gas constant; E_a – activation energy.

The plot of $\Delta \log(dw/dt)$ versus $\Delta \frac{1}{T}$ gives a straight line

whose slope gives the value of $\frac{E_a}{2.303R}$ from which E_a was calculated.

3.3.2. Sharp – Wentworth method

The relation derived by Sharp – Wentworth to determine the kinetics of thermal degradation is given as

$$\log\left(\frac{dC/dT}{1-C}\right) = \log \frac{A}{\beta} - \frac{E_a}{2.303R} \left(\frac{1}{T} \right) \quad (6)$$

Where dC/dT - the rate of change of fraction of weight with the change in temperature, $\beta = dT/dt$ - the linear heating rate.

The plot of $\log\left(\frac{dC/dT}{1-C}\right)$ versus $\frac{1}{T}$ gives a straight line

whose slope gives the activation energy and intercept gives frequency factor A .

3.3.3. Horowitz – Metzger method

The relation derived by Horowitz – Metzger to

determine kinetic parameter of thermal degradation is given as

$$\ln \left[\ln \left(\frac{W_0 - W_f}{W - W_f} \right) \right] = \frac{E_a \theta}{R T_e^2} \quad (7)$$

where W_0 – initial weight of the sample; W_f – final weight of the sample; W – weight remaining at a given temperature, T ; E_a – activation energy; $\theta = T - T_e$, where T – temperature at time t and T_e – DTG peak temperature. The plot of $\ln \left[\ln \left(\frac{W_0 - W_f}{W - W_f} \right) \right]$ versus θ gives a straight line whose

slope gives the value of $\frac{E_a}{R T_e^2}$ from which E_a can be calculated.

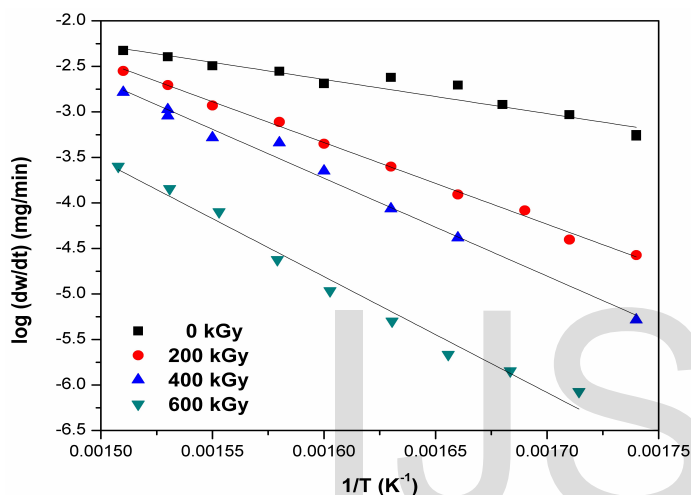


Fig. 4. Anderson- Freeman plots to determine the activation energy of thermal degradation of HDPE polymers irradiated at different doses of electron radiation

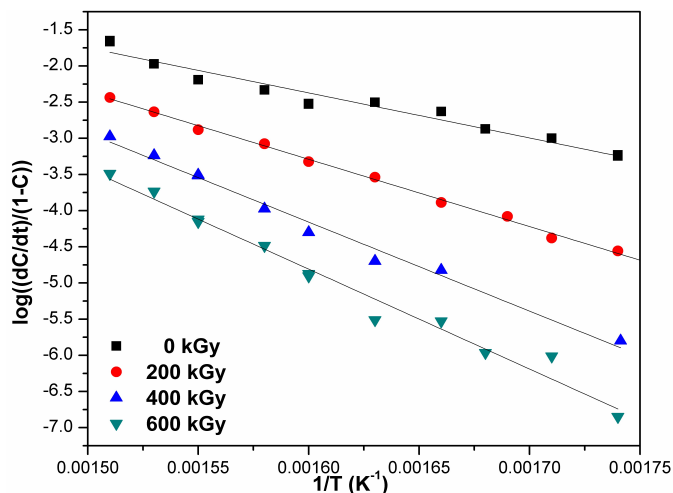


Fig. 5. Sharp-Wentworth plots to determine the activation energy of thermal degradation of HDPE polymers irradiated at different doses of electron radiation

The activation energy of thermal decomposition is determined for pristine as well as electron-beam irradiated

HDPE films by using above mentioned methods. The plots of classical laws of kinetics those used to evaluate the activation energy of thermal decomposition are shown in Fig. 4 – 6. Fig 4 shows Anderson-Freeman plot, Fig. 5 shows Sharp-Wentworth plot and Fig. 6 shows Horowitz-Metzger plot.

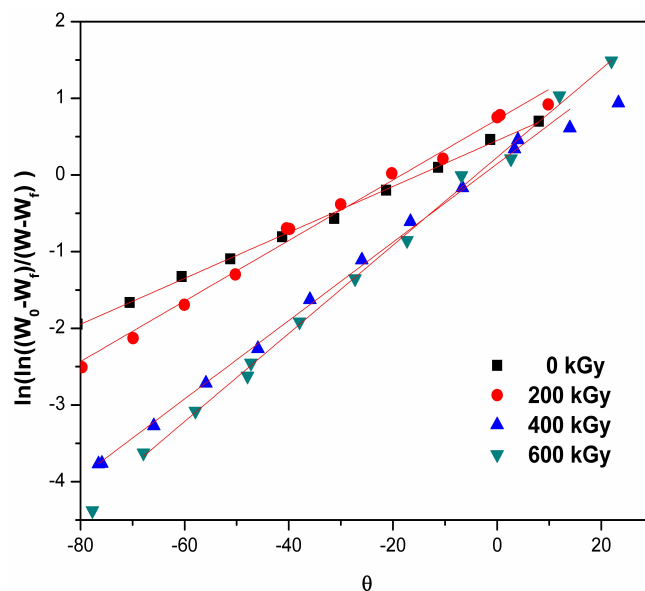


Fig. 6. Horowitz – Metzger plots to determine the activation energy of thermal degradation of HDPE polymers irradiated at different doses of electron radiation

The calculated values of activation energy of thermal decomposition for HDPE polymers irradiated at different doses of electron radiation determined by abovementioned methods are given in Table 2.

The activation energy evaluated by all three methods *viz.*, Anderson-Freeman Sharp-Wentworth and Horowitz-Metzger are found to be comparable. Further it was found that the activation energy of thermal decomposition of HDPE increases with increase in the dose of electron radiation.

Table 2. The estimated values of activation energy of thermal decomposition (E_a) of HDPE polymer samples irradiation at different doses of electron radiation

Radiation dose (kGy)	activation energy of thermal decomposition (E_a) (kJ/mol)		
	Anderson-Freeman Method	Sharp-Wentworth method	Horowitz-Metzger Method
0	81.02	119.63	108.12
200	167.03	174.25	168.47
400	203.81	225.98	220.92
600	244.50	267.27	268.30

This indicates that the thermal stability of HDPE increases upon electron irradiation. This may be due to the formation of new functional group such as conjugated double bond ($C = C$)

and carbonyl ($C=O$) group in the irradiated sample as confirmed by FTIR spectral studies. These bonds require higher dissociation energy and hence the thermal stability of irradiated HDPE is more than the pristine HDPE.

4. Conclusion

In the present work thermogravimetric analysis (TGA) is carried out to understand the thermal stability and degradation kinetics of HDPE polymers irradiated at different doses electron-beam radiation. The structural modifications in the irradiated HDPE samples are also discussed. The values activation energy (E_a) of thermal decomposition evaluated by three degradation kinetics methods, viz., Anderson-Freeman, Sharp-Wentworth and Horowitz-Metzger, are found to be comparable. Further the values of E_a of HDPE increases with the increase in the dose of electron radiation which confirms the increase in the thermal stability of HDPE polymer upon electron-beam irradiation. The increase in the thermal stability of irradiated HDPE may be attributed to the formation of new functional group in the irradiated HDPE samples which is confirmed by FTIR spectral analysis.

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