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Thermo Gravimetric Analysis of Electron-Beam Irradiated Ultra High Molecular Weight Polyethylene (UHMWPE)

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Abstract

Thermogravimetric analysis (TGA) of electron-beam irradiated ultrahigh molecular weight polyethylene (UHMWPE) has been studied. The modification in thermal properties of UHMWPE is investigated by measuring the onset temperature of thermal decomposition, the temperature corresponding to maximum mass loss and activation energy using TGA thermogram. The activation energy of thermal degradation of polymer samples was evaluated by different kinetics of thermal degradation viz., Anderson-Freeman, Sharp-Wentworth, Horowitz-Metzger and Friedman method. The onset temperature of thermal decomposition, the temperature corresponding to maximum mass loss and activation energy of thermal degradation of UHMWPE, is found to increases with the increase in the dose of electron radiation. The result thus indicates that the thermal stability of irradiated UHMWPE is more than that of unirradiated UHMWPE. Further, the FTIR spectral investigation reveals that the new functional group such as the conjugate C = C bond and carbonyl (C=O) group are formed in the irradiated UHMWPE polymers.

***Keywords**: - Ultra-high molecular weight polyethylene, Electron-beam, Fourier transform infrared spectroscopy, Thermogravimetric analysis, Activation energy.*

INTRODUCTION

Thermoplastic polymers are not only extensively used in domestic applications but also in scientific, engineering and biomedical applications. The increase in the use of thermoplastic polymers is due to their easy processability, low price, low viscosity, better UV, abrasion and high chemical resistance. Ultrahigh molecular weight polyethylene (UHMWPE) is one such well-known important high-performance thermoplastic plastic that is used in biomedical applications and as an insulating material for electronics, wire and cable. However, UHMWPE polymer, which is an organic substance, is thermally sensitive due to the limited strength of covalent bonds that make up their structure. Therefore the structure of UHMWPE has to be modified to improve its physical properties to benefit a particular application with long-term thermal stability. Ionizing radiation is one of the methods used to modify the structure of polymers with specific physical properties [1-6]. The irradiation leads to the formation of reactive species known as free radicals in the polymers, which in the large scale of lattice defects in the polymer structure. The free radicals permanently modify the chemical structure of polymers by several possible reactions such as macromolecular chain destruction, crosslinking, carbonization and oxidation. These radiations induced chemical reaction 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 [7-9].

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 thermal stability. TGA is also is used to predict the lifetime of polymers under actual service conditions. TGA requires only a small quantity of sample, and it offers precise control overheating conditions such as accurate heating rate and variable temperature range. Further, using TGA, one can measure the decomposition of polymers at various temperatures and also evaluate the kinetic parameter of thermal degradation *viz.*, the activation energy of decomposition, order of reaction and pre-exponential factor [10-11]. 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 the thermal stability of polymers.

Several researchers studied the effects of ionizing radiation viz., ions, electron-beam and gamma radiation effects on the structural, optical, mechanical and electrical properties of UHMWPE polymers [12-15]. However, to the best of our knowledge, no detailed studies have been done to investigate the modifications of thermal properties of electron-beam irradiated UHMWPE. The in the present study, we irradiated UHMWPE by electron-beam radiation of energy 1.2 MeV over a dose range of 0 – 1000 kGy. The modifications in thermal properties of pristine and irradiated UHMWPE polymers are investigated by a Thermogravimetric analyzer. In order to understand the modifications in thermal stability of UHMWPE polymers irradiated at various doses, we evaluated the activation energy of thermal decomposition by different methods, viz., Anderson-Freeman [16], Sharp-Wentworth [17], Horowitz-Metzger [18] and Friedman methods [19].

EXPERIMENTAL DETAILS

The UHMWPE powder was procured from DSM engineering plastics, UK. The UHMWPE films are prepared by compression molding techniques, and details of which are already reported elsewhere [15]. In the present study, UHMWPE films of thickness 120 µm are used for irradiation. The electron-beam irradiation of prepared UHMWPE polymer films was carried out using an ILU-6 electron accelerator at the BRIT, BARC, Mumbai, India. The electron-beam of the energy of 1.2 MeV, at a beam current of 1.0 mA and at a dose rate 10 kGy per pass, is employed to obtain the required dose during the irradiation. The polymer films were irradiated to different doses *viz.,* 200, 400, 600, 800 and 1000 kGy.

The FTIR spectra of both the pristine as well as the irradiated UHMWPE films were recorded in the transmission mode using FTIR spectrometer (perkin-Elmer, Lamda-35) having a spectral resolution of 0.5 cm^{-1}. The FTIR spectra of all the polymer films were recorded over the wavenumber range 4000-400 cm^{-1} keeping the air as reference. TGA thermograms were recorded, for pristine as well as irradiated UHMWPE samples, as a function of temperature using a thermogravimetric analyzer (Mettler TA). The polymers weighing about 10-11 mg were cut into very small pieces, crimped in small aluminum pans and weighed in a microbalance with a precision of up to 10 ppm. The polymers were scanned over a temperature range of 50-600^{0}C under a nitrogen atmosphere with a heating rate of

10^0C/min. The resulting weight loss was recorded as a function of temperature in terms of TGA thermograms. From the thermogram, the activation energy of thermal decomposition was determined by Anderson-Freeman, Sharp-Wentworth, Horowitz-Metzger and Friedman methods.

RESULT AND DISCUSSION

FTIR Spectroscopic Analysis

The FTIR transmission spectra of the pristine, as well as the UHMWPE irradiated at different doses of electron radiation, are given in Figure 1. The transmission bands observed in the FTIR spectra of the pristine UHMWPE are identified as follows.

The bands over the wavenumber range 2830-2950 cm^{-1} correspond to the C–H stretching vibration of $–CH_2$ group and that over the wavenumber range 1050-550 cm^{-1}, to the bending vibrations of the C-H bonds; at ~1463 cm^{-1}, to the bending of $–CH_2$ group; at ~1375 cm^{-1}, to the symmetrical bending of $–CH_3$ group; and the bands at 720 and 730 cm^{-1} correspond to the bending and rocking vibration of the methylene group. However new bands are found to appear around, 1720 cm^{-1}, 969 cm^{-1}, 1620 $cm^{-1}$and 984 cm^{-1} which correspond respectively to the formation of carbonyl (C=O), trans-vinylene unsaturation (-CH=CH-) and trans-trans conjugated dienes (-CH = CH - CH = CH-) groups in the irradiated UHMWPE (Ravinder *et al.*, 2008; Dole, 1958; Patel, 1975). The formation of the C=O functional group in the irradiated UHMWPE samples was attributed to the reaction of atmospheric oxygen with the polymer during the irradiation.

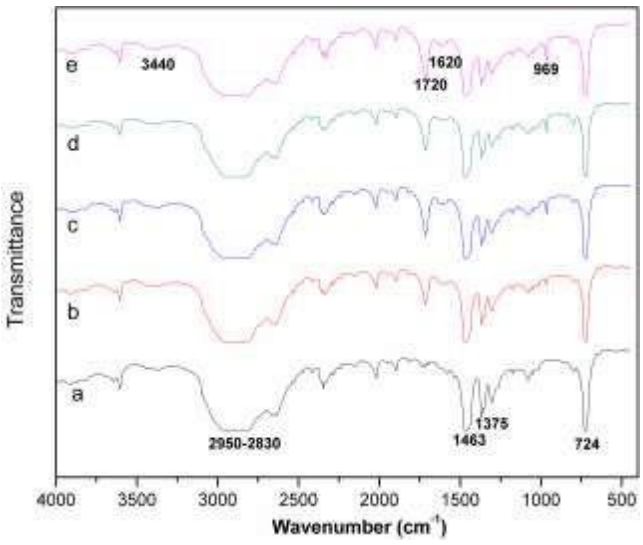

Figure 1: FTIR spectra of UHMWPE polymer films irradiated at different doses of electron radiation. (a) 0 kGy (b) 400 kGy (c) 600 kGy (d) 800 kGy (e) 1000 kGy.

Thermo Gravimetric Analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the pristine, as well as the irradiated UHMWPE polymer, are respectively given in **Figures 2** and **3**. The TG and DTG curve shows that both pristine and irradiated UHMWPE undergoes single-stage decomposition due to heating.

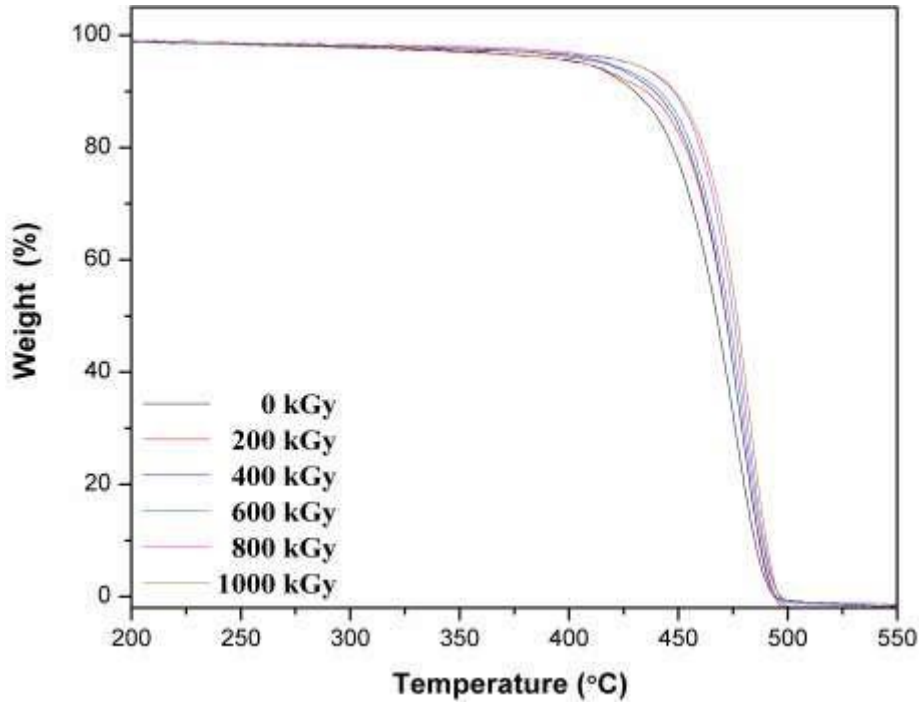

Figure 2: TGA thermogram of UHMWPE polymers irradiated at different doses of electron radiation

Table 1: The measure values of Onset of thermal decomposition temperature (T_o) (°C) Temperature corresponding to maximum mass loss (T_m) (°C) for UHMWPE polymer samples irradiated at different doses of electron radiation

Radiation dose (kGy)	T_o (°C)	T_m (°C)
0	391	475
200	392	477
400	396	478
600	402	480
800	408	482
1000	412	484

The temperature corresponding to the starting point of decomposition, i.e., the onset temperature of thermal decomposition (T_0) for both pristine and irradiated UHMWPE, was obtained DTG curve. Further, the temperature corresponds to maximum mass loss (T_m) for both pristine and irradiated UHMWPE was measured from a maximum of the DTG curve. The measured values of onset temperature of thermal decomposition (T_0) and temperature correspond to a 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_0 and T_m for irradiated UHMWPE are higher than the pristine samples. This indicates that the irradiated UHMWPE is thermally more stable than the pristine UHMWPE.

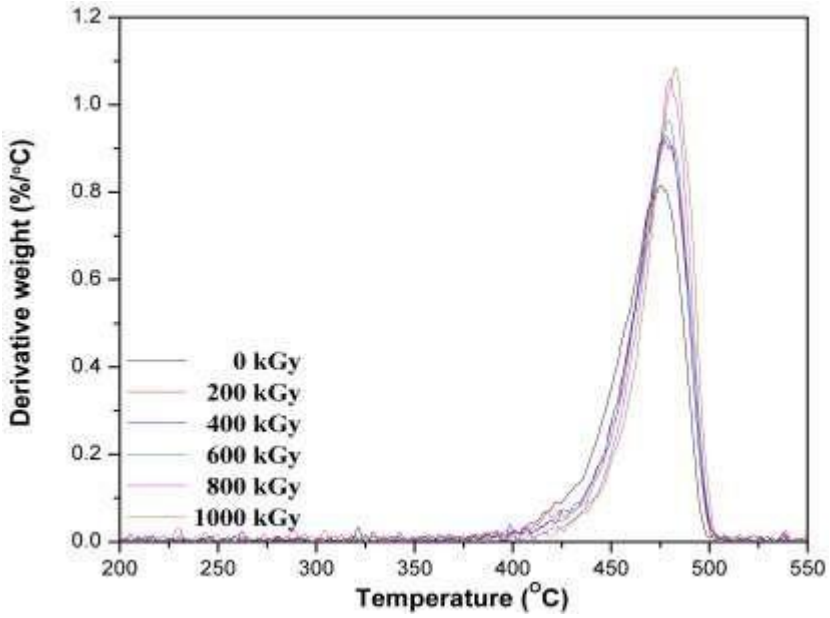

Figure 3: DTG curve of UHMWPE polymers irradiated at different doses of electron radiation

Horowitz – Metzger method

The relation derived by Horowitz – Metzger to determine a kinetic parameter of thermal degradation is given as

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

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 $\frac{E_a}{RT_e^2}$ from which E_a can be calculated.

Friedman Method

Friedman provides the following expression for thermal degradation.

$$\ln\frac{d\alpha}{dt} = \ln z + n\ln(1-\alpha) - \frac{E_a}{RT} \qquad (8)$$

Where α = conversion at time t, R = gas constant (8.314 J/mol/K) and T is the absolute temperature. The plot of ln $(d\alpha/dt)$ vs. $1/T$ gives a straight line with the slope equal to E_a/R, from which E_a can be obtained.

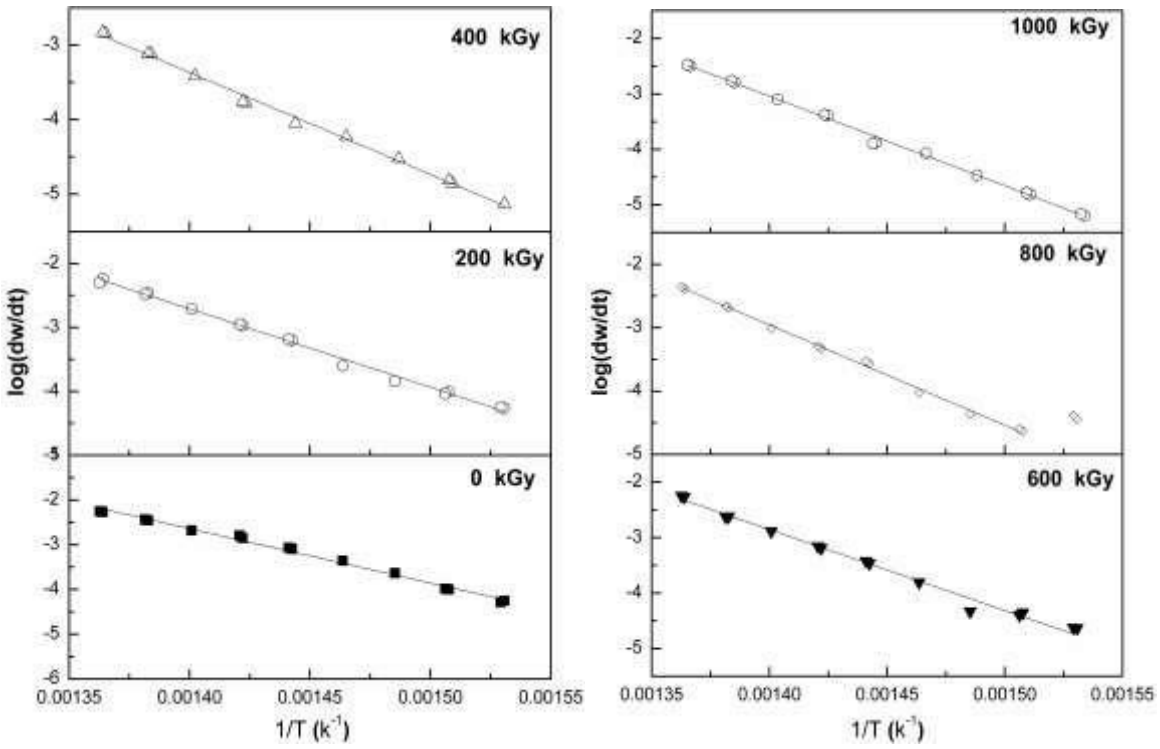

Figure 4: Anderson- Freeman plots to determine the activation energy of thermal degradation of UHMWPE polymers irradiated at different doses of electron radiation

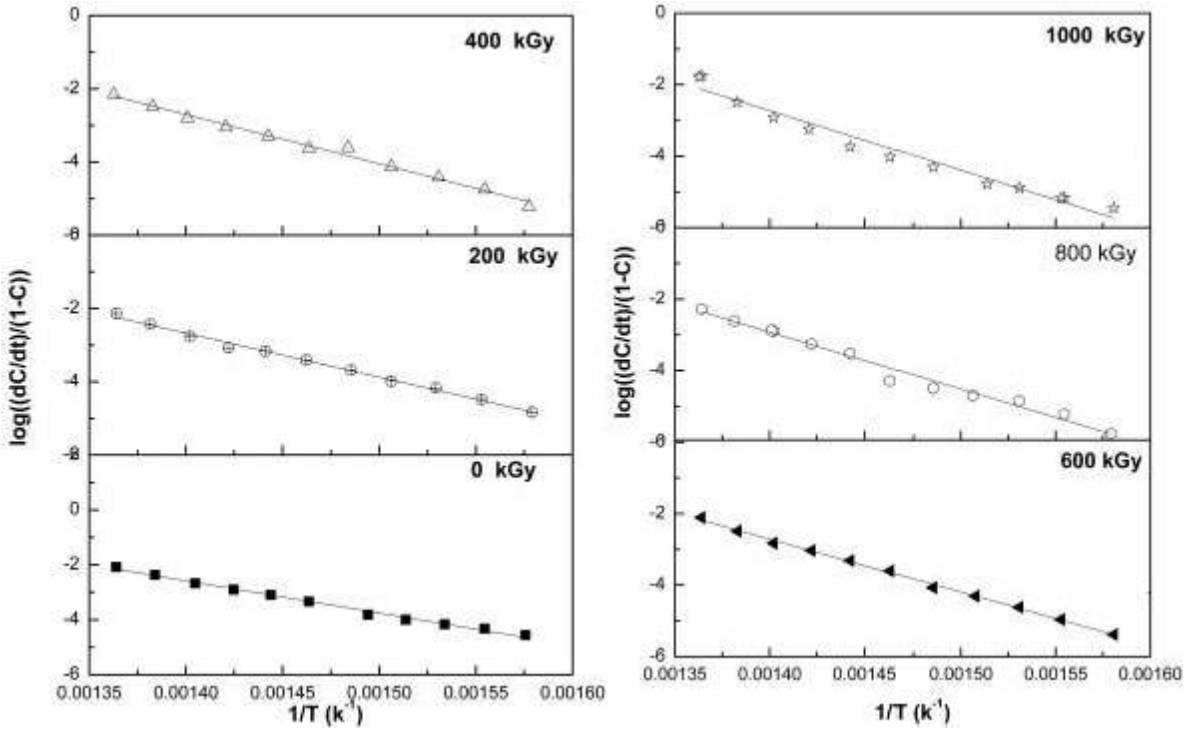

Figure 5: Sharp-Wentworth plots to determine the activation energy of thermal degradation of HMWPE polymers irradiated at different doses of electron radiation

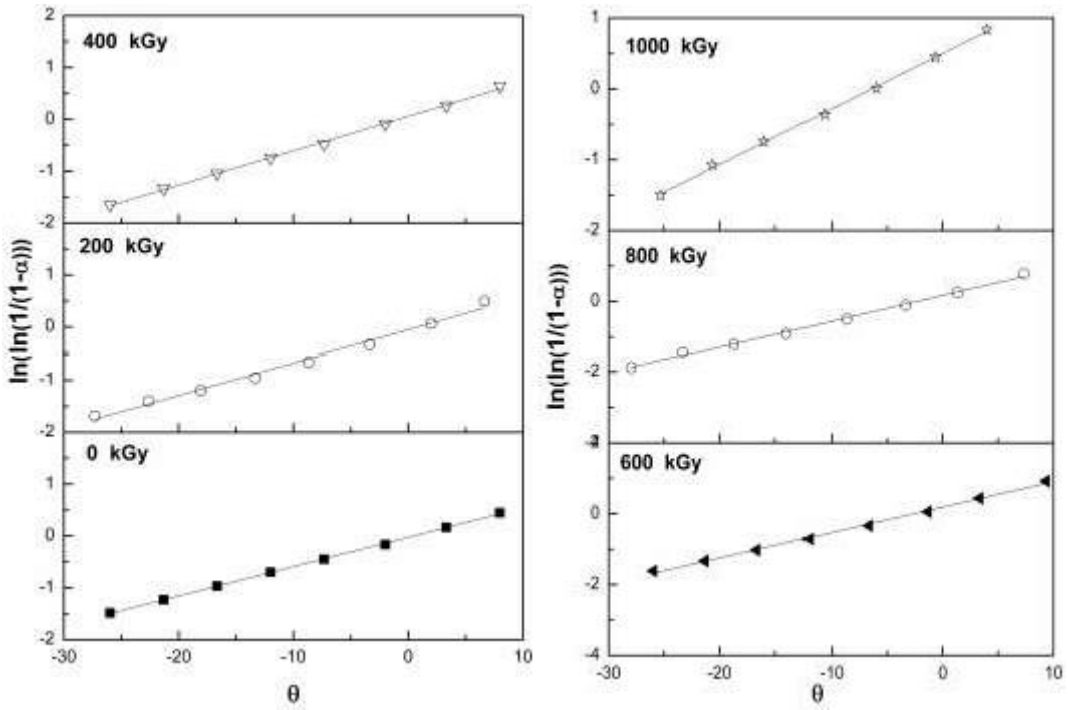

Figure 6: Horowitz – Metzger plots to determine the activation energy of thermal degradation of UHMWPE polymers irradiated at different doses of electron radiation

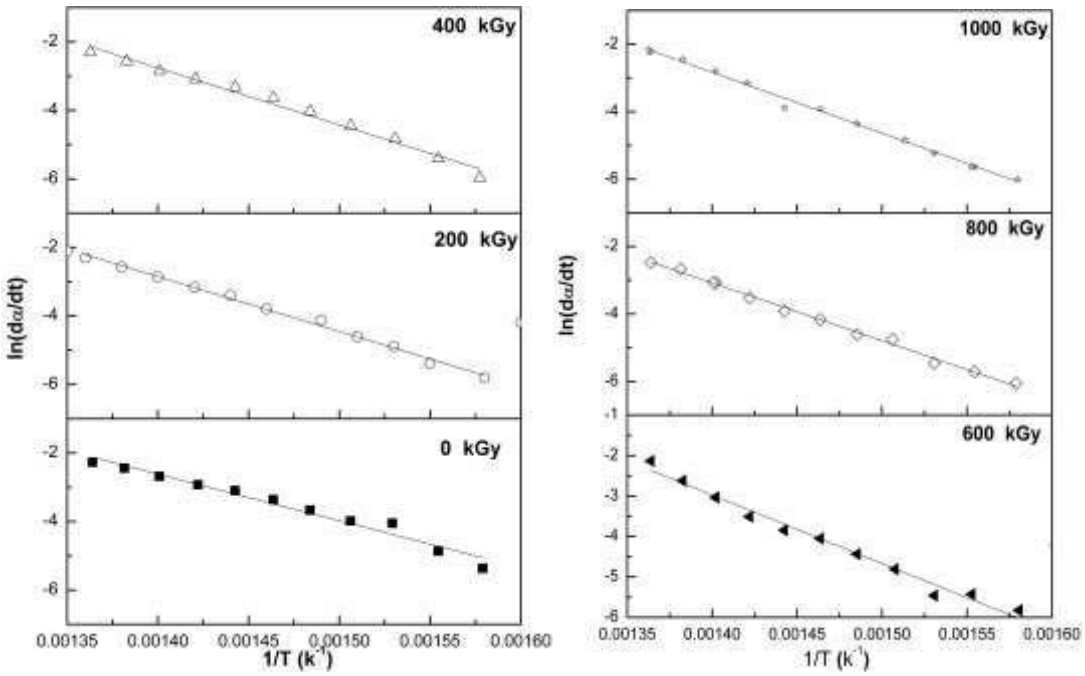

Figure 7: Friedman plots to determine the activation energy of thermal degradation of UHMWPE polymers irradiated at different doses of electron radiation

Table 2: The estimated values of activation energy of thermal decomposition (E_a) for UHMWPE 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***	***Friedman method***
0	232.90	224.46	244.83	260.60
200	238.80	229.71	259.77	306.62
400	255.52	257.04	274.21	318.26
600	279.50	282.93	286.09	323.60
800	302.93	304.59	301.87	328.06
1000	308.96	318.30	308.50	345.21

The activation energy of thermal decomposition for pristine as well as electron-beam irradiated UHMWPE films are determined by using above mentioned methods. The plots of the above mentioned methods that are used to evaluate the

activation energy of thermal decomposition are shown in Figures. 4 – 7. Figure 4 shows the Anderson-Freeman plot, Figure 5 shows the Sharp-Wentworth plot, Figure 6 shows the Horowitz-Metzger plot and Figure 7 show the Friedman plot.

The values of activation energy of thermal decomposition as evaluated by the above four methods for UHMWPE polymers irradiated at different doses of electron radiation are given in Table 2. We found that the values of activation energy evaluated by all four methods viz., Anderson-Freeman, Sharp-Wentworth, Horowitz-Metzger and Friedman methods are comparable. Further, it was found that the activation energy of thermal decomposition of UHMWPE increases with an increase in the dose of electron radiation. This indicates that the thermal stability of UHMWPE increases upon electron irradiation. This may be due to the formation of a new functional group such as the conjugated double bond (C = C) and carbonyl (- C = 0) group in the irradiated sample, as confirmed by FTIR spectral studies. These bonds require higher dissociation energy and hence the thermal stability of irradiated UHMWPE is more than the pristine UHMWPE.

CONCLUSION

Thus the present research work shows that the modifications in the structural and thermal properties of UHMWPE induced by electron-beam radiation. The modifications in the thermal stability of UHMWPE polymers irradiated at different doses of electron radiation are investigated using TGA. The values activation energy (E_a) of thermal decomposition evaluated by four different kinetic methods *viz.*, Anderson-Freeman, Sharp-Wentworth, Horowitz-Metzger and Friedman method are found to be comparable. Further, the values of E_a, the onset temperature of decomposition (T_o) and temperature corresponding to a maximum rate of mass loss (T_m) of UHMWPE are found to increase with the increase in the dose of electron radiation, which confirms the increase in the thermal stability of UHMWPE polymer upon electron-beam irradiation. This increase in the thermal stability of irradiated UHMWPE may be attributed to the formation of a new functional group in the irradiated samples, as confirmed by FTIR spectral analysis.

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