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RADIATION INDUCED CHANGES IN CRYSTALLINITY OF PROPYLENE-ETHYLENE COPOLYMER

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ABSTRACT

Exposure of polymers and copolymers to radiation induce changes in physico-chemical properties. In the article the authors report radiation induced changes in crystallinity and amorphousity, using spectroscopic and thermal techniques. To study the nature of radiation species formed due to irradiation, ESR spectra are recorded in the temperature range of 30-140^{0}C. The ESR signal is observed decay below the crystalline melting temperature of PE copolymer (140^{0}C) suggesting that the free radicals are trapped in amorphous regions of copolymer. Activation energy corresponding to free radical decay has been calculated using Bloch analysis. Change in thermal properties induced by gamma irradiation is measured using Differential Scanning Calorimetry DSC and Thermally Stimulated Luminescence TSL technique. The chemical change occurred in gamma irradiation are identified by Fourier Transform Infrared (FTIR) technique. Among various absorption bands, the 997 cm^{-1} band (associated with the crystalline content) and 1180 cm^{-1} absorption bands (associated with amorphousity of the copolymers.) are used to study the variations in crystallinity and amorphousity of copolymer. Corresponding to these two states the free radical decay is found to follow to different rates, as observed from the Electron Spin Resonance (ESR) studies. Effect of post irradiation time on formation of free radicals has been investigated by recording ESR spectra at different post irradiation times and decay curves are drawn.

KEYWORDS : PE Copolymer, FTIR Absorption Band, Degree of Crystallinity, ESR

The role of ionizing radiations like electron beam gamma irradiation to modify after chemical structure and mechanical and rhetorical properties of plastics or polymer has become a practice over several years (Annc. Abraham et al, 2010). As such treatment of PP with plasma led to surface modification causing miscibility and welt ability (N. Gomati et al, 2009). Further radiation is also used to recycle PP waste.

Therefore changes in chemical and physical properties induced by radiation have become an important tool, when compared to the chemical method. As many of these processes initiated by free radicals, ESR spectroscopy in preferably used. Irradiation of PP led to formation of macro radicals and under oxygenated condition, the peroxy radicals are responsible for auto oxidation process in degradation of PP (D.J.Carlsson et al, 1985). Radiation effects in Poly Propylene (PP) and Propylene-Ethylene (PE) copolymer. A subject of interest over last few years. The PP and PE copolymer is subject to different types of radiations and resultant effects have been reviewed by various authors. (L. Burliniska et al,1996) have reported the presence of Alkyl and peroxy radicals on gamma irradiation of PP. (Adams and Watanabe,1996) have used chemical derivation techniques to estimate the content of various types of peroxide formed on irradiation of PP.

(A.P. Jhadav et al, 2004) have studied the effect of radiation dose and does rate on degradation of PE copolymer using the ESR and FTIR techniques. They have observed ESR spectra at sterilized dose, they have considered to be a super position of component spectra arising due to macro radical, methyl radical, peroxy radical and acyl radicals. It is also reported that the extension degradation in more with decrease of radiation dose. These authors have correlated these data with the FTIR results. Based on the results these authors have proposed mechanism for radiative degradation of PE copolymer. (N.LSingh et al, 2004) have studied the effect of high energy radiation on PP film by FTIR technique and electrical properties. These authors have reported formation alkenes and alkynes and as a result dielectric. Electrical properties of the film were changed.
(B.Sanjeeva Rao et al, 2010) have reported effect of post irradiation time on the ESR spectra of irradiated PE copolymer and found that the ESR signal is stable even up to 1200 hrs. The decay of ESR signal with post irradiation is found to be non-linear. In the present studies, the authors have used FTIR technique to study the effect of radiation oncrystallinity of the PE copolymer. Based on the intensity of certain absorption bands, the ESR technique is also used for their purpose.

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EXPERIMENTAL

Propylene ethylene (PE)copolymer in the for m of powder. The polymer is irradiated with cobalt 60 gamma irradiation source having a dose of 0.15 M.rad/hr. Irradiation of the copolymer is carried out in air at room temperature. The copolymer is made into pellet along with potassium bromide with pellet thickness of around 1-2 mm. ESR spectra of polymer were recorded on Varian E- line spectrometer operating at X-band frequencies and 100 KHz modulation.

DSC thermograms are recorded onTAQ-10 model Calorimeter. About 2-3 mg of complex was sealed in aluminum pan and heated from room temperature (RT) to 250^0 C/minutes. Empty pan is kept as reference and nitrogen gas is flushed throughout the experiment to avoid oxidation of the sample.

TSL glow curves are recorded for the PE copolymer in pellet form having a thickness of 1-2 mm and it is on a mounted in sample holder under which a thermocouple is kept. The sample is heated from room temperature (RT) to high temperature 200°C with a constant heating rate of 10°C/min. the sample holder is kept in front of the window of photomultiplier tube, which is fed to electrometer capable of measuring current up to 10^{-15} Amp.

RESULTS AND DISCUSSION

ESR Studies

ESR spectrum of PE copolymer irradiated to1 M.rad dose radiation at different temperatures are as shown in figure 1.

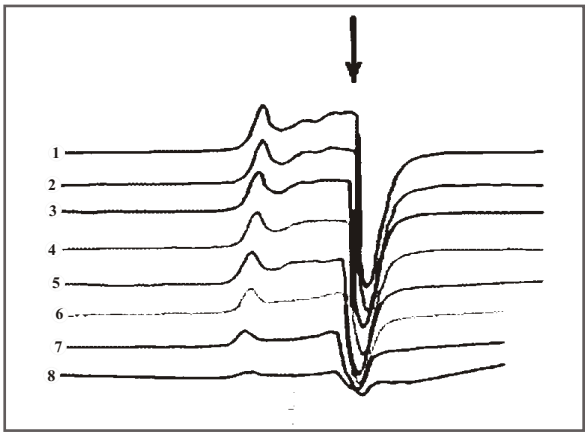


Figure 1: ESR Spectra of gamma irradiated PE coplymer at different temperatures

Curve: 1 30°C Curve: 2 40°C Curve: 3 60°C
Curve: 4 70°C Curve: 5 80°C Curve: 6 90°C
Curve: 7 120°C Curve: 8 140°C

Curves 1,2,3,4,5,6,7 and 8 represent spectra have at 30, 40, 60,70,80,90,100,120 and 140^0C temperature. Spectrum observed at RT (30^0C) has asymmetric line shape but posses some hyperfine structure. On heating the irradiated copolymer to higher temperatures, the hf pattern gradually decreased and a doublet like structure is observed at 120^0C. Finally at 140^0C the doublet structure reduced appeared to a singlet shape. The main event of radiated event of PP is reported to be the cleavage of methine proton,resulting in formation of macroradicals of the type CH_2-Ċ (CH_3)-CH2 (1)~. However presence of other radicals like $\dot{C}H_3$, CH_2-Ċ-CH_2 has also reported. When irradiation is carried in oxygenated conditions, the radical-I interact with the atmospheric oxygen and convert to peroxy radicals (Suryanarayana et al, 1982). Formation of peroxy radical is characterized by asymmetric line shape as observed in the present study R-OȮ (number of hyperfine lines given by the radical-I depend on the surrounding magnetic environment). Variation in temperature dependent hyperfine structure is assigned to be due to the change in magnetic environment of radical-I .Such type of hyperfine interaction in macro radicals has also been observed previously (B.Sanjeeva Rao et al, 1994). The ESR Spectrum finally decayed above 145^0C, designated as radical decay temperature (T_R).

PE copolymer is semi crystalline and its crystalline melting temperature (T_c) is reported to be around 145^0C. Disappearance of ESR signal below 145^0C (T_C) suggest that the free radicals are trapped in amorphous region of copolymer. Such type radical recombination reaction are observed for several semi-crystalline polymers like PGA (N.Rajeshwar Rao, 2015) etc. The radical trapped in amorphous region gain thermal energy and initiate reaction with polymer chain or with same/or other free radical causing their decay. The radical decay temperature (T_R) is found to depend on radical dose. With the increase of radiation dose, the (T_R) is observed to decrease. The decrease of the T_R is thought to be associated with the decrease of crystallinity induced by gamma irradiation. (Anelli et al, 1998) have reported the decrease of degree of

decrease of degree of crystallinity, DSC thermograms are recorded under different condition. ESR intensities are calculated using double integration methods and a plot of ESR intensity against temperature is as shown in figure 2.

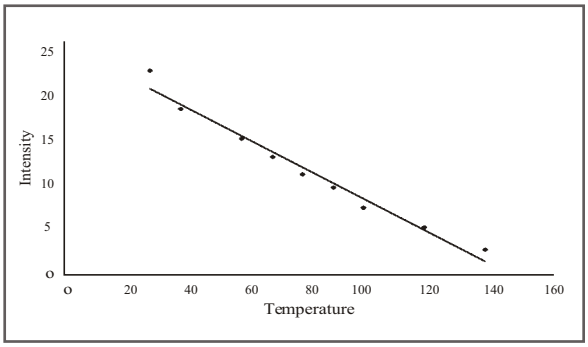


Figure 2 : Variation of ESR Intensities against temperature

In order to calculate activation energy associated with free radical decay, Bloch analysis is applied and line width the values of log (1/τ) and 1/T are calculated as given table1 and a plot is drawn as shown in Figure 3. From the slope of straight line, the value of activation energy is calculated .The value is around 105 K J/ mole.

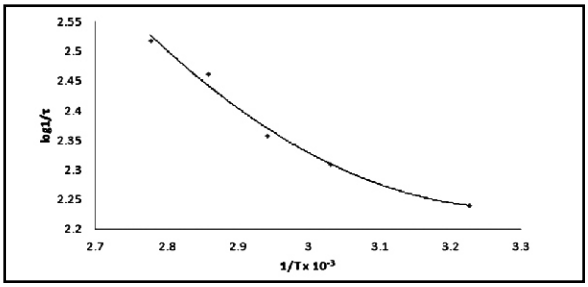


Figure: 3 Variation of ESR Intensities against energy

DSC Studies

DSC thermogram of irradiated PE copolymer under different conditions are recorded as shown in figure 4, 5, 6

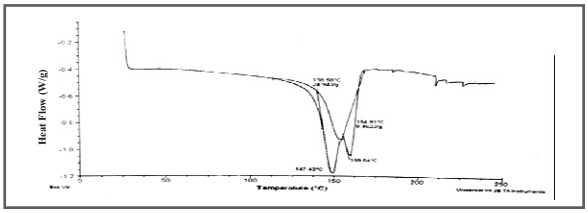


Figure 4: DSC thermogram of PE copolymer irradiated to 10 M. rad dose

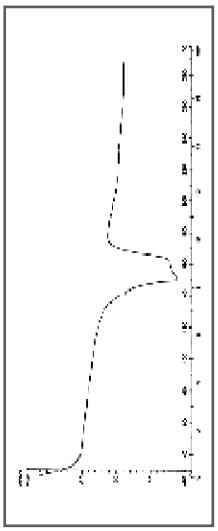


Figure 5 : DSC thermogram of PE copolymer irradiated to 15 M. rad dose

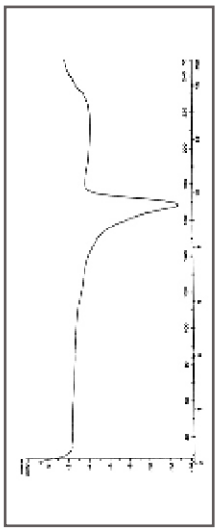


Figure 6 : DSC thermogram of irradiated and annealed copolymer

Fig. 4 and Fig. 5 represent thermogram of copolymer irradiated to 10 and 15 M. rad dose of irradiation. While Fig 6 represents thermogram of irradiated and annealed PP. Thermal properties of are as listed in the table 12.

DSC thermogram of copolymer irradiated 10 M.rad dose consists of two endothermic peaks centered around 147^{0}C, and 159^{0}C. While at higher doses the peaks shifted 145^{0}C and 169^{0}C. For irradiated and annealed copolymer, the peaks merged and a single endothermic peak centered around 169^{0}C is observed shifting of peak temperature with dose suggest radiation induced decrease in degree of the crystallinity. Further, a decrease in HWFH values and depletion of crystallize size distribution on irradiation is observed. Additionally the two endothermic peaks observed at lower dose merged at higher doses suggesting the erosion of the crystalline phases on irradiation. The degree of the crystallinity of copolymer under different conditions is calculated by taking the melting enthalpy of 100%.Cyrstallinity to be 192 J/m. (Sara et al, 2010). The degree of crystallinity is also found to 50% of original value, while for the irradiated and annealed sample the value decrease is found to be only 30%.

TSL Studies

To evaluate thermal properties of unirradiated and irradiated copolymer, TSL glow peaks are recorded as shown in figure 7.

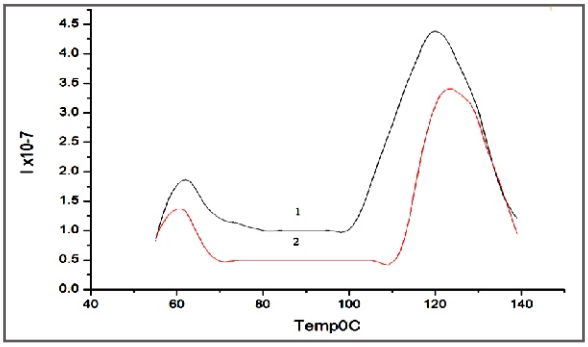
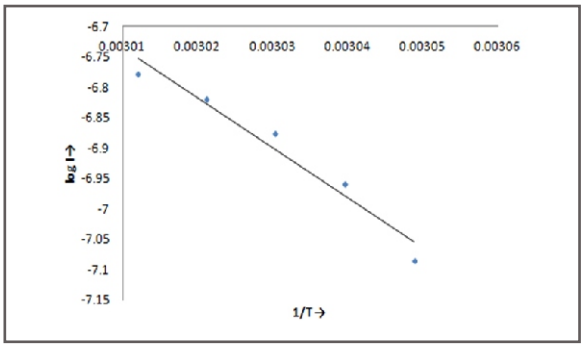
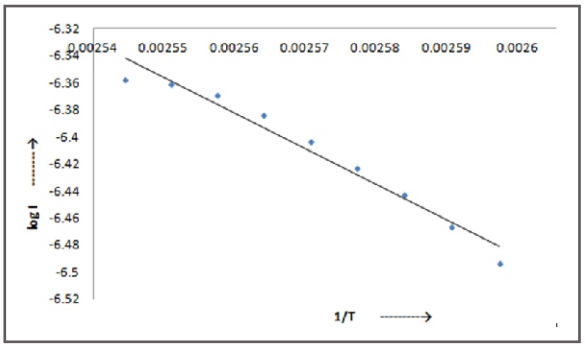


Figure 7 : TSL Glow Curves of PE copolymer Curve1 Unirradiated, Curve2 Irradiated

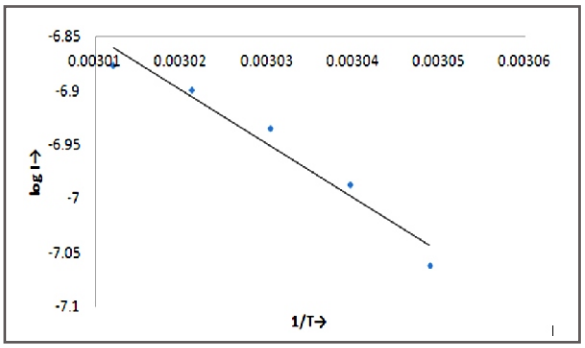


a) Peak P1

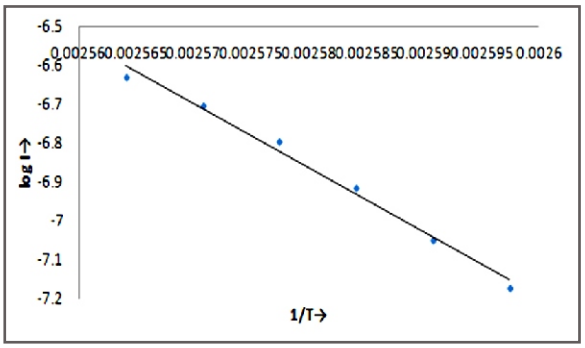


b) Peak P2

Figure 8 : Application of Initial rise method to unirradiated copolymer a) Peak P1 b)Peak P2



a) Peak P1



b) Peak P2

Figure 9 : Application of Initial rise method to Irradiated PE copolymer a) Peak P1 b) Peak P2

TSL glow spectrum of un-irradiated and irradiated PE copolymer are shown curve1 and curve 2 Figure 7.The spectrum consists of two glow peaks centered 65^{0}C and 125^{0}C. On irradiation. The glow been shifted to low temperature side and a decrease in peak intensity is observed. The first peak is thought to be associated with release of luminescent traps facilitated by one set off molecular relaxation occur around the glass transition temperature of PP. The second peak assigned to be release of traps below melting point of PP. The glow peaks observed for PP are analyzed by the three methods described by the authors (Sanjeeva Rao et al, 1993) previously these methods are

Initial rise method

Chen's method

Modified initial rise method

Initial Rise Method

Analysis of glow peak by initial rise method requires plotting of inverse of temperature (1/T) against logarithm of intensity (log I) as shown in figure 8 (unirradiated) and figure 9 (irradiated). The graph is usually a straight line and the slope of straight line gives activation energy. (The values are listed in the table 5)

Chen's Method

For application of Chen's method to analyses glow peak, the value of, ω, τ and δ needs to be needs to be calculated from the experimentally observed spectra. Using these values the activation energy is calculated with the equation given by Chen's for the first and second order kinetics. The values of activation energy by the Chen's method are listed in the Table-3 (Peak P1) and Table-4 (Peak P2).

Modified Initial Rise Method

Modified initialize method is applied to the glow peaks observed for unirradiated and irradiated PP. For the purpose the glow peaks are simulated theoretically using the parameters listed in the table 4. From the simulated values of peak intensities at each temperature, a plot of 1/T against logarithm of intensity (logI) is drawn. Straight line is observed by this method and the slope of straight line gives the values of activation energy and the values listed in the Table 6 and 7. The parameters employed to simulate the glow peaks are as listed in Table 5.

Ftir Studies

Radiation induced changes in crystallinity has also been confirmed by monitoring intensity of 997 cm^{-1} and 1180 cm^{-1} FTIR absorption bands. FTIR spectra of unirradiated and irradiated PP are shown as figure 10 and figure 11. On irradiation absorption bands effected by gamma irradiation are 1720 cm^{-1} due to carboxyl groups (C=O), whose intensity increased with dose of irradiation (K.Allmer et al, 1989).

The 997cm^{-1} absorption band is reported to be associated with crystalline context; while the 1180 cm^{-1} is due to amorphous context of PP (16). A decrease in intensity of 997 cm^{-1} is observed while intensity of 1180 cm^{-1} band with radiation dose is observed. The results suggest that on irradiation amorphousity of the PP increase or decrease of crystallinity is proposed.This is also confirmed from DSC measurements.

Effect of Post Irradiation Time

In order to study the effect of post irradiation time on formation of radicals, ESR spectra are recorded at different post irradiation times, as shown in figure 12.Curves1,2,3,4,5,6,7,8 and 9 represent ESR spectra recorded for irradiated PP at post irradiation times of 0,24,48,72,96,120, 170,225,720 and 1200 hours. It can be observed that spectrum recorded immediately. After irradiation possess some hyperfine structures; while asymmetric peroxy doublets are observed at 96 hrs of post irradiation time. The hf lines of the peroxy dublelet begin to smeared out at 720 hours of the post irradiation. The smearing out of spectral lines is thought to be associated with change in morphology and chemical environment of free radicals. The spectra are assigned to the peroxy radicals formed by the absorption of oxygen by macro radicals (I). As ESR spectra are assigned to peroxy radicals, decay rate

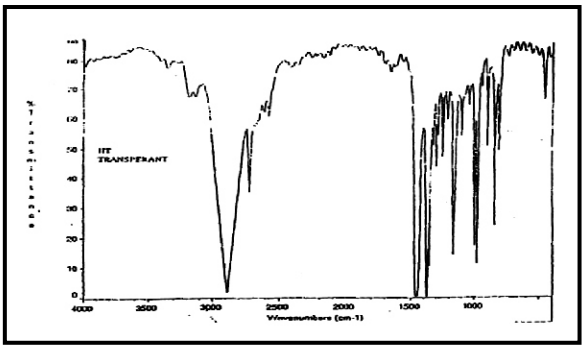


Figure 10: FTIR Spectrum of Unirradited PE Copolymer

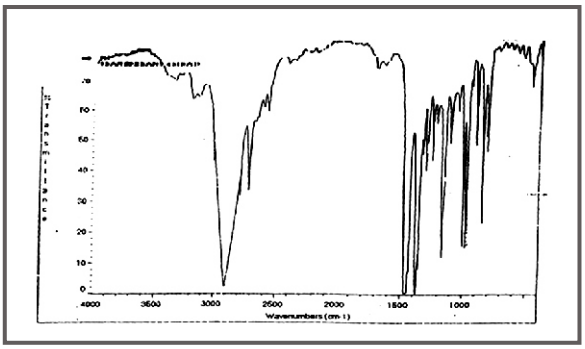


Figure 11: FTIR Spectrum of irradiated PE Copolymer to 4 M.Rad

of II can be ascertained by plotting ESR intensity against post irradiation time as shown curve 1 Figure 13. The curve is non linear indicating that two types of decay regions. Region I corresponding to fast decay; while region II corresponds to slow decay. Effect of post irradiation time on formation of free radicals has also been investigated by recording ESR spectra of PP irradiated to 11 M.rad dose at different post irradiation times. The spectra are shown in Figure 14. The decay curves are as shown in figure15, which two types of regions.

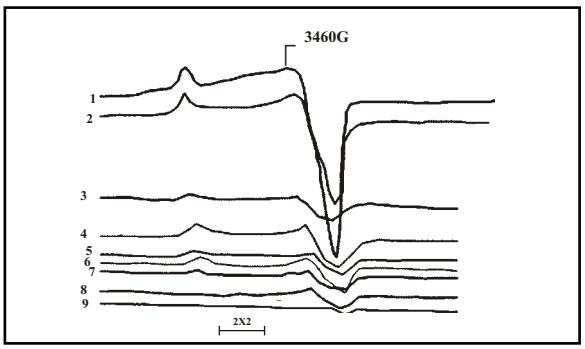


Figure12 : ESR Spectra of PE Copolymer irradiated to sterilized dose at different Post irradiation time

Curve 1	0 hours	Curve 2	48 hours
Curve 3	72 hours	Curve 4	96 hours
Curve 5	120 hours	Curve 6	170 hours
Curve 7	225hours	Curve 8	720 hours
Curve 9	1200 hours		

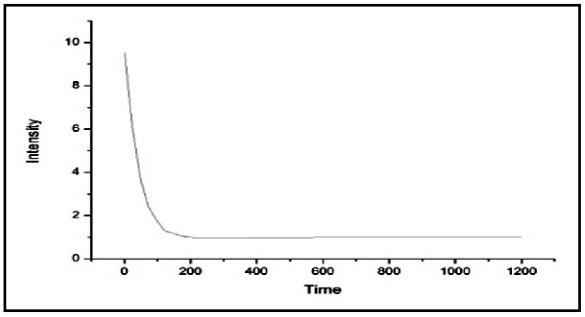


Figure13: ESR Intensity verses post irradiation Time

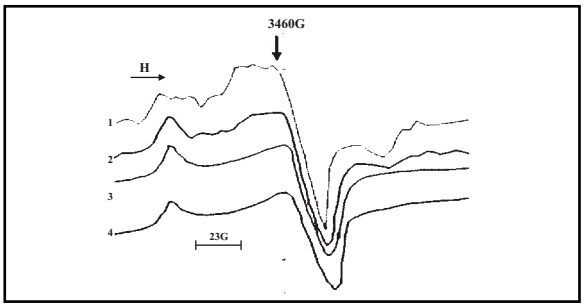


Figure 14: ESR spectra of PE copolymer irradiated to 11 M. Rad radation dose at different time intervals Curve 1:24 Hours, Curve 2: 48 hours, Curve 3: 72 hours, Curve 4: 96 hours

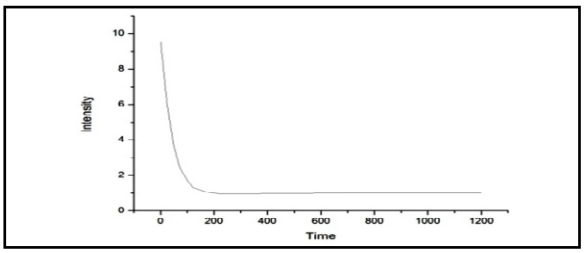


Figure15: ESR Intensity verses post irradiation Time

Table 1 : Bloch Analysis of irradiated PE copolymer

S. No	Temp ^{0}C	1/T x10^{-3}	$\Delta\gamma$	τx10^{-3}	1/τ	log1/τ
1	300	3.333	18	-	-	-
2	310	3.225	16	5.7311	174.48	2.241
3	330	3.030	15	4.896	204.24	2.310
4	340	2.941	14.35	4.367	228.8	2.359
5	350	2.857	14	3.445	290.25	2.462
6	360	2.777	13.75	3.0266	330.39	2.519

Table 2: Thermal Properties of PE copolymer

S,No.	Radiation Doses M.rad.	ΔHJ	$\Delta\beta$	Peak1	Peak2	Xc
1.	10	138.29	21	147	159	66.86
2.	15	65.94	18	145	169	31.87
3.	Irradiated and Annealed	47.85	14		169	30.12

Table 3: Evaluation of Activation Energy by Chen's method Peak 1

S.No	Sample	ω	τ	δ	Tp	First Order Kinetics			Second Order Kinetics		
						Eω	Eτ	Eδ	Eω	Eτ	Eδ
1	Unirradiated	14.4	6.2	8.2	65	1.13	1.20	1.11	1.20	1.21	1.19
2	Irradiated	10.8	7.4	3.4	60	1.15	1.14	1.22	1.23	1.141	1.40

Table 4: Evaluation of Activation Energy by Chen's method Peak 2

S.No	Sample	ω	τ	δ	Tp	First Order Kinetics			Second Order Kinetics		
						Eω	Eτ	Eδ	Eω	Eτ	Eδ
1	Unirradiated	13.6	4.8	3.4	125	1.58	1.99	1.99	1.84	1.19	1.61
2	Irradiated	21.2	8	13.2	130	1.38	1.65	1.27	1.56	1.72	1.99

Table 5: Parameter employed to simulated the glow Peaks

S.No	Sample	YMA		SAI		TOT	
		Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
1	Unirradiated	2.8	6.0	15	18	36	84
2	Irradiated	2.5	5.2	14	17	38	80

Table 6: Parameter employed to simulated the glow Peaks

S.No	Sample	Initial rise method (ev)	Chen's method (ev)						Modified Initial rise method (ev)
			First Order Kinetics			Second Order Kinetics			
			Eω	Eτ	Eδ	Eω	Eτ	Eδ	
1	Unirradiated	1.2	1.13	1.20	1.11	1.20	1.21	1.19	0.91
2	Irradiated	1.3	1.15	1.14	1.22	1.23	1.14	1.40	1.0

Table 7: Evaluation of Activation Energy by different methods Peak 2

S.No	Sample	Initial rise method	Chen's method						Modified Initial rise method
			First Order Kinetics			Second Order Kinetics			
			Eω	Eτ	Eδ	Eω	Eτ	Eδ	
1	Unirradiated	1.1	1.58	1.99	1.99	1.84	1.90	1.61	1.4
2	Irradiated	0.86	1.38	1.65	1.27	1.56	1.72	1.99	1.2

CONCLUSION

Gamma irradiation causes changes inchemical and physical properties of PE copolymer. Chemical changes have been identified by ESR and FTIR technique. Existance of macroradicals and peroxy radicals has been confirmed ESR technique. The free radicals are reported to decay below the crystalline metling point of copolymer suggesting that they are trapped on amorphous region. Changes thermal properties are measure DSC and TSL techniques. Decrease in degree of crystallinity is obserevd. The results are futher confirmed by monitoring changes in intensities of FTIR absorption band and recording ESR spectra at different post irradiation times.

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