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EVALUTION OF INTEGRATED INTENSITIES OF ESR SPECTRA OBSERVED FOR IRRADIATED POLYMER – POLYETHYLENE TEREPHTHALATE (PET)

B. SANJEEVA RAO[*], J. SAPTAGIRI PRASAD[a], G. RAMA RAO[b], N. SREENIVASA RAO[c], A. RAJU[d] and V. SRIDHAR[e]

Dept. of Physics, Kakatiya Govt. College, HANAMKONDA (A.P.) INDIA
[a]Dept. of Physics, Malla Reddy Institute of Technology & Science, SECUNDERABAD (A.P.) INDIA
[b]Govt. Jr. College, BANIGANDLAPADU (A.P.) Dist.: Khammam, INDIA
[c]Govt. Jr. College, KHAMMAM (A.P.) INDIA
[d]Dept. of Physics, Chaitanya P.G. College (Autonomous), Hanamkonda, WARANGAL (A.P.) INDIA
[e]Dept. of Chemistry, A.V.V. Jr. College, WARANGAL (A.P.) INDIA

ABSTRACT

Electron spin resonance (ESR) spectra of irradiated poly (ethylene terephalate) (PET) have been recorded to study radiation induced changes. The ESR spectra have shown complicated structure caused by formation of various types of free radical species formed on radiation of polymer. Free radical concentration under different conditions has been evaluated by theoretical methods. Plots have been drawn for free radical concentration against temperature. The graph indicates complex decay of free radical kinetics.

Key words: PET, Free radicals, ESR Spectroscopy, Computer simulation, Free radical concentration.

INTRODUCTION

Poly (ethylene terepthalate) (PET) is an industrially important polymer. The polymer is reported to exhibit good wear resistances and radiation resistances. As a result, it is utilized as door handles, cases, textile equipment, magnetic tape and soft drink bottles[1].

During the course of these applications, the polymer may degrade. Degradation is a process by which a change in chemical and physical properties occurs. To study, degradation processes, various experimental techniques are used in literature. Mar Cotte et al.[2] and Jabrin et al.[3] have used UV absorption and tensile measurements to study degradation of PET.

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[*]Author for correspondence;

Radioactive degradation of PET has been reported by Bartos and Klimova[4] and Sanjeeva Rao et al.[5] Then authors have also used ESR and FTIR techniques to study degradation of PET.

In the present study, the authors have attempted to study the effect of temperature on ESR spectra of irradiated PET. As the intensity of ESR spectrum is related to free radical concentration, attempts have been made to evaluate accurate value of free radical concentration. For this purpose, the authors have used computer simulation techniques.

EXPERIMENTAL

Poly (ethylene terepthalate) (PET) is in the form of small granules and it has been used in the present studies (commercial origin). ESR Spectra of irradiated PET have been recorded on Varian E line spectrometers operating at X-band frequencies and 100 kHz modulation. The spectrometer is fitted with necessary accessories to record spectra in the temperature range 300-420 K. Gamma irradiation have been carried out by cobalt 60 gamma source with dose rate of 0.15 KGy/hr. Computer simulation has been carried out on a personal computer with necessary software.

RESULTS AND DISCUSSION

ESR spectra of un-irradiated PET do not possess any hyperfine pattern indicating the absence of any free radical species. As the polymer was irradiated with gamma rays, cleavage of chains / bonds occur leading to the formation of free radical species, which could be detected by ESR technique. The ESR spectra observed for irradiated PET at 300, 310, 330, 350, 370, 390 and 410 K are shown as curves 1, 2, 3, 4, 5, 6, and 7 in Fig. 1. The spectral parameters are as listed in Table.1.

Table 1: Spectral parameters of irradiated PET at different temperatures

Temp. (K)	Line positions/Line intensities					Spread (G)
300	3225 (34)	3234 (-13)	3240 (70)	3246 (-77)	3265	60
310	3226 (28)	3235 (-13)	3240 (50)	3250 (-54)	--	50
330	3225 (25)	3233 (-15)	3240 (26)	3246 (-47)	--	57

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Temp. (K)	Line positions/Line intensities					Spread (G)
350	3224 (18)	3233 (-5)	3240 (16)	3246 (-34)	--	50
370	3227 (17)	3232 (-6)	3240 (14)	3245 (-30)	--	45
390	3228 (15)	3238 (-4)	3242 (3)	3245 (-10)	--	40
410	3230 (4)	3240 (-2)	3243 (1)	3246 (-3)	--	34

Since total area under ESR spectrum represents free radical concentration, attempts have been made to evaluate intensity by double integration method. Three methods are used for this purpose. They are:

(i) Trapezoidal method

(ii) Simpson method

(iii) Graphical mehtod

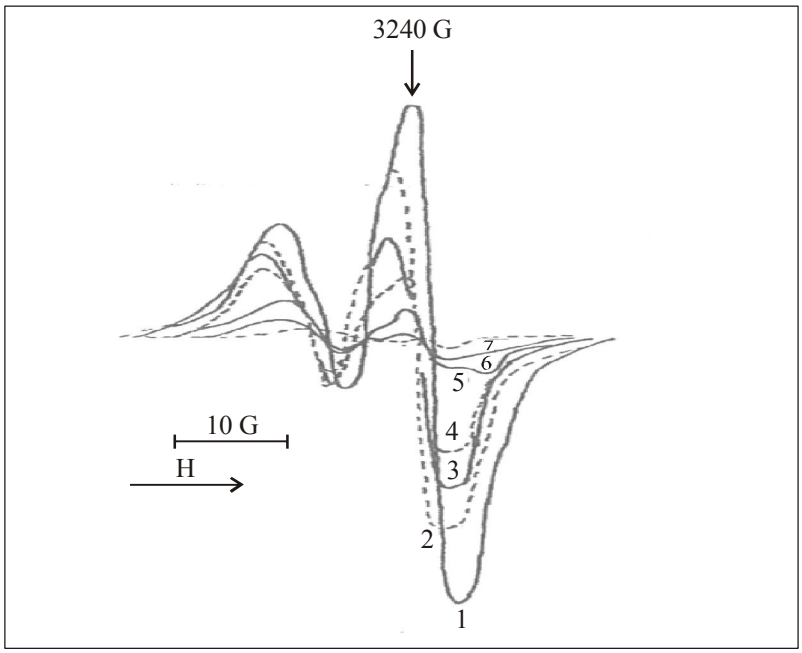
The integrated intensities at different temperatures are as listed in Table 2.

Table 2: Integrated intensities of irradiated PET at different temperatures

Temp. (Kelvin)	Methods		
	Trapezoidal	Simpson rule	Graphical
300	602	589	598
310	422	413	418
330	321	312	318
350	250	249	250
370	180	178	180
390	90	89	88
410	40	40	40

ESR spectrum of irradiated PET at room temperature is shown as Curve 1 (Fig. 1). The spectrum is a quartet with additional hyperfine structures. The spectral parameters

indicate that neither the intensity pattern nor the hyperfine spacing is compatible with the expected values. Therefore, presence of more than one free radical species is expected. Sanjeeva Rao et al.[5] have simulated the spectrum to be a superposition of component spectra arising due to macro radicals and free radicals of the type ~CH~. The component spectra arising due to this radical together with component spectra yield the observed spectrum at 300 K.



Curve 1: 300 K Curve 2: 310 K Curve 3: 330 K Curve 4: 350 K
Curve 5: 370 K Curve 6: 390 K Curve 7: 410 K

Fig. 1: ESR spectra of irradiated PET of different temperature

In the present studies, the authors have calculated integrated intensities of ESR spectra observed for irradiated PET at different temperatures. Double integration methods have been employed for this purpose. The intensities obtained by different methods are compared and correlated. Assuming the curve to be x-y plot, the values of intensities are tabulated for different magnetic fields. Using the standard formulae, the values of integrated intensities are obtained. As the total area under each curve represents the free radical concentration, measurements are performed at different temperatures. Plots of intensities at different temperatures by the three methods are plotted as shown in Figs. 2, 3 and 4. These figures indicate that the intensities obtained by three methods are almost equal. A plot of

integrated intensity against temperature is shown in Fig. 5, which indicate a gradual decrease in intensity against temperature. Therefore with the increase of temperature, the free radical concentration decreases, indicating the recombination of free radicals.

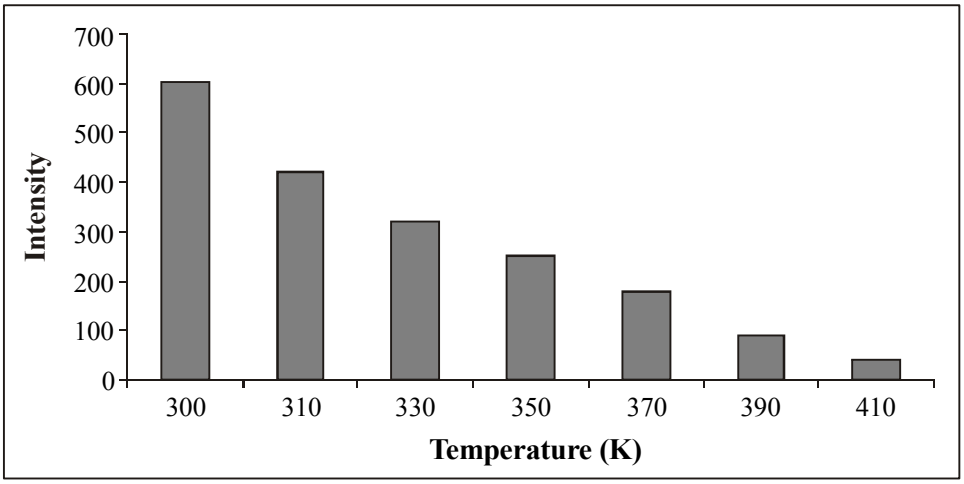


Fig. 2: Histogram depicting ESR intensity against temperature by trapezoidal method

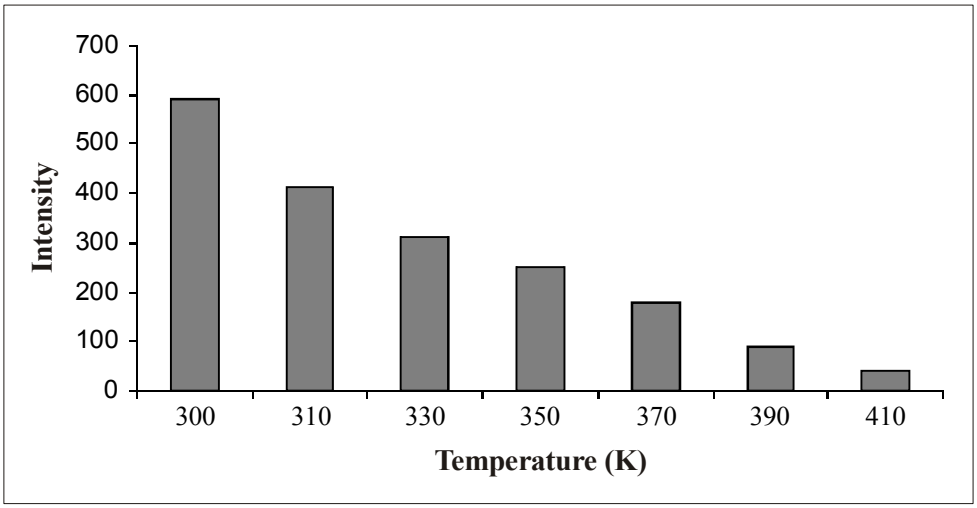


Fig. 3: Histogram depicting ESR intensity against temperature by Simpson method

With the increase of temperature, the molecular chains of polymers begins to relax, facilitating the migration of free radicals. Therefore the free radical, may either recombine themselves or with other radicals, causing a reduction in the concentration[6].

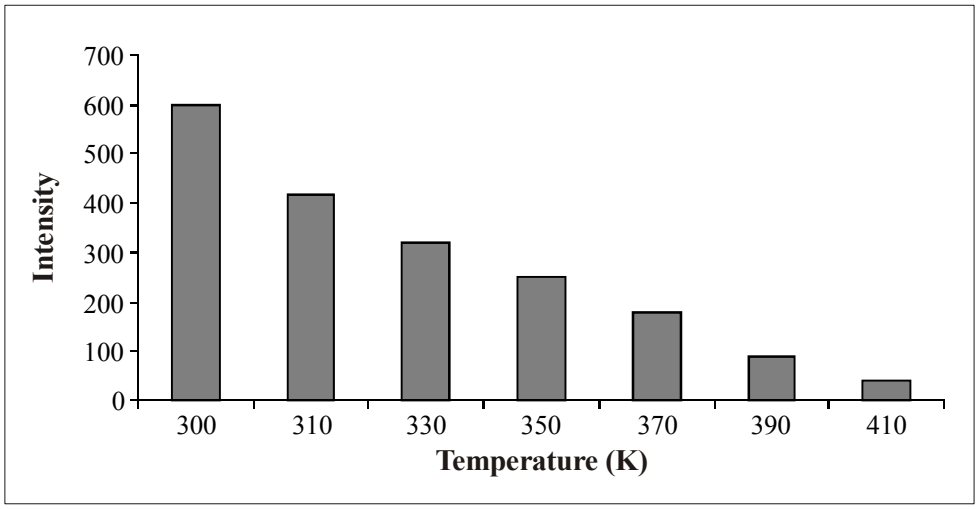


Fig. 4: Histogram depicting ESR intensity against temperature by graphical method

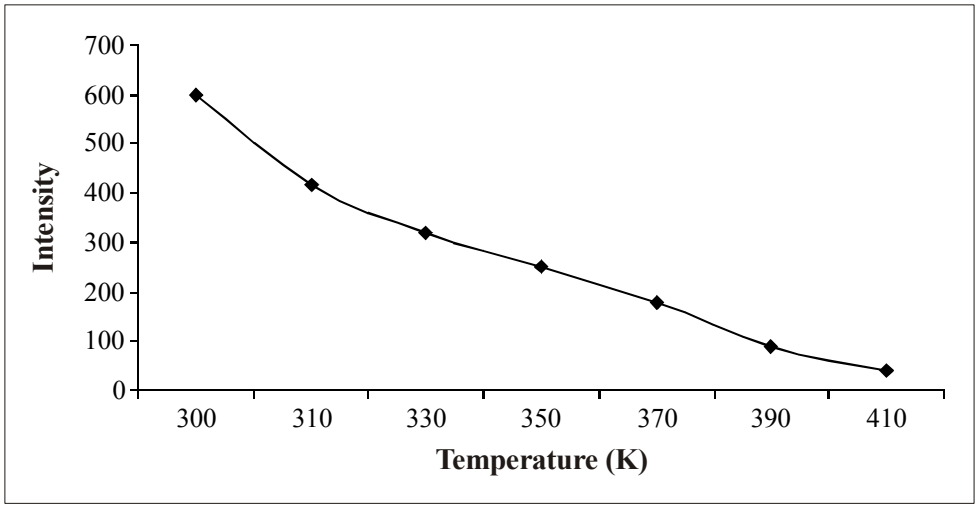


Fig. 5: Variation of ESR intensity against temperature

REFERENCES

1. Mc Cormick, Polym. Eng. Sci., **16**, 292 (1986)
2. S. A. Jabarin and E. A. Lofgren, Polym. Eng. Sci., **24**, 1056 (1984)
3. J. B. Morcotte, D. Campbell, J. A. Cleaveland and P. T. Turner J. Polym. Sci., **A5**, 481 (1967)

4. J. B. Bartos and V. Klimova, J. Polym. Sci., **A24**, 1741 (1996)

5. B. Sanjeeva Rao and V. Sridhar, S. Indira and G. Punnaiah, Red. Eff. Def. Solids, **160**, 145 (2006).

6. T. C. Chiang and J. P. Sibilia, J. Polym. Sci., **B10**, 2240 (1972).

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