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APPLICATION OF BLOCH ANALYSIS TO EVALUATE ACTIVATION ENERGY FROM TEMPERATURE DEPENDENT ESR SPECTRA OF IRRADIATED PET

K. RAJENDRA PRASAD*, D. E. KALPANA RANI[a], E. VENKATESWAR RAO[b], CH. SRINIVAS[c], S. KALAHASTI[b] and B. SANJEEVA RAO[d]

Department of Physics, Kakatiya Institute of Technology & Science, WARANGAL (A.P.) INDIA
[a]Department of Physics, JNTUH, KARIMNAGAR (A.P.) INDIA
[b]Department of Physics, Kakatiya University, WARANGAL (A.P.) INDIA
[c]Department of Physics, SR Degree & PG College, Hanamkonda, WARANGAL (A.P.) INDIA
[d]Department of Physics, Kakatiya Govt UG & PG College, Hanamkonda, WARANGAL (A.P.) INDIA

ABSTRACT

Gamma irradiation of poly (ethylene terepthalate) (PET) results in formation of different types of free radicals. Identification of free radicals has been done by recording ESR spectra of irradiated PET. Effect of temperature on the decay of free radicals has been investigated. The free radicals produced in irradiated PET are found to decay around 410 K. Activation energy corresponding to free radical decay has been evaluated using Bloch analysis. Using this method, a plot has been drawn 1/T values and log τ. The slope of the curve gives activation energy. The value of activation energy obtained by this method is very high suggesting the thermal stability of free radicals produced in PET.

Key words: ESR spectra, PET, Activation energy, Bloch analysis.

INTRODUCTION

Gamma irradiation of polymers leads to various processes like excitation, ionization and generation of free radicals[1]. These processes cause degradation of polymers, resulting in loss of mechanical properties. In order to measure mechanical properties, degradation characteristics of polymers have to be ascertained. Since free radicals initiate degradation in polymers, a study of free radicals play an important role.

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*Author for correspondence;

Formation of free radicals in an irradiated polymer depends on various aspects like temperature, pressure and nature of monomer. In order to investigate the free radicals, electron spin resonance (ESR) is an important tool.

Free radicals generated in polymers, decay in a complex manner. The free radical decay is associated with an activation energy, which characterizes physical state of radical neighbourhood[2]. In this article, the authors have used Bloch analysis, which is applied to polymers by Ohinishi et al.[3] in case of irradiated polyethylene.

Solving Bloch equation for line widths is -

$$(\Delta\nu/\Delta\nu_0) = \{[1\text{-}2\,\pi^2\tau^2(\Delta\nu_0)^2]^{-1}\}^{-1/2} \qquad \ldots(1)$$

Where, $\Delta\nu$, $\Delta\nu_0$ - separation of peaks at intermediate and slow rate of exchange, and

τ – Relaxation time

τ is related to the life times at sites A and B by following equation -

$$\tau_A = \tau_B = 2\,\tau \qquad \ldots(2)$$

These equations have been used by Ohinishi et al.[3] to explain temperature dependent changes in ESR spectra of irradiated polyethylene.

Ohinishi expressed ($\Delta\nu$) in terms of B, coupling constants by the following relation -

$$\Delta\nu = g\,\beta/h\,(A_{\beta 1}\text{-}\,A_{\beta 2}) \qquad \ldots(3)$$

Where $\Delta\nu$ = The peak separation/line width

g = g- Value of free electron

β = Electron Bohr magneton

h = Planck constant and

$A_{\beta 1}$, $A_{\beta 2}$ = Coupling constants.

Using these equations, a plot has been drawn by taking 1/T on X-axis and log ($1/\tau$) on Y- axis. The slope of the curve directly gives activation energy corresponding to free radical decay.

EXPERIMENTAL

Poly (ethylene terepthalate) (PET) in the form of granules has been used in the present studies. PET is exposed to gamma rays to a total radiation dose of around 3 M. Rad. ESR spectra of irradiated PET are recorded on Varian E -112 spectrometer and it is fitted with necessary accessories to record variable temperature ESR spectra.

RESULTS AND DISCUSSION

ESR spectra of PET irradiated to 3 M.rad radiation dose at different temperatures are shown in Fig. 1. Curve 1, 2, 3, 4, 5, 6 and 7 indicate the ESR spectra recorded for irradiated PET at 300 K, 310 K, 350 K, 370 K, 390 K and 410 K, respectively. The spectra at lower temperature possess some hyperfine pattern, while the hf pattern gradually decreased with increase of temperature. The spectra observed at 400 K is a singlet with decreased intensity. Beyond 400 K, the singlet also decayed and finally no signal was observed around 410 K. The values of magnetic parameters employed to simulate the ESR spectra at different temperatures as given in Table 1.

Table1: Magnetic parameters of irradiated PET at different temperatures

Temp. (K)	Relative intensity $Y_{max\ i}$	Line width a_i (G)	Centre of spectrum X_{oi}(G)	Hyperfine splittings (G)		n_i	m_i	S_e^2
				A_i	B_i			
300	1	5	3237	7	0	2	1	
	3	15	3241	11	6	2	3	0.086
310	1	5	3236	7	0	2	1	
	3	14	3240	11	6	2	3	0.1442
330	1	5	3236	7	0	2	1	
	3	13	3240	11	6	2	3	0.31102
350	1	5	3236	7	0	2	1	
	3	10	3240	11	6	2	3	0.1857
370	1	3	3237	7	0	2	1	0.2544

Cont…

Temp. (K)	Relative intensity $Y_{max\ i}$	Line width a_i (G)	Centre of spectrum X_{oi}(G)	Hyperfine splittings (G)		n_i	m_i	S_e^2
				A_i	B_i			
390	1	1.5	3237	7	0	2	1	0.1823
410	1	0.5	3238	7	0	2	1	0.1724

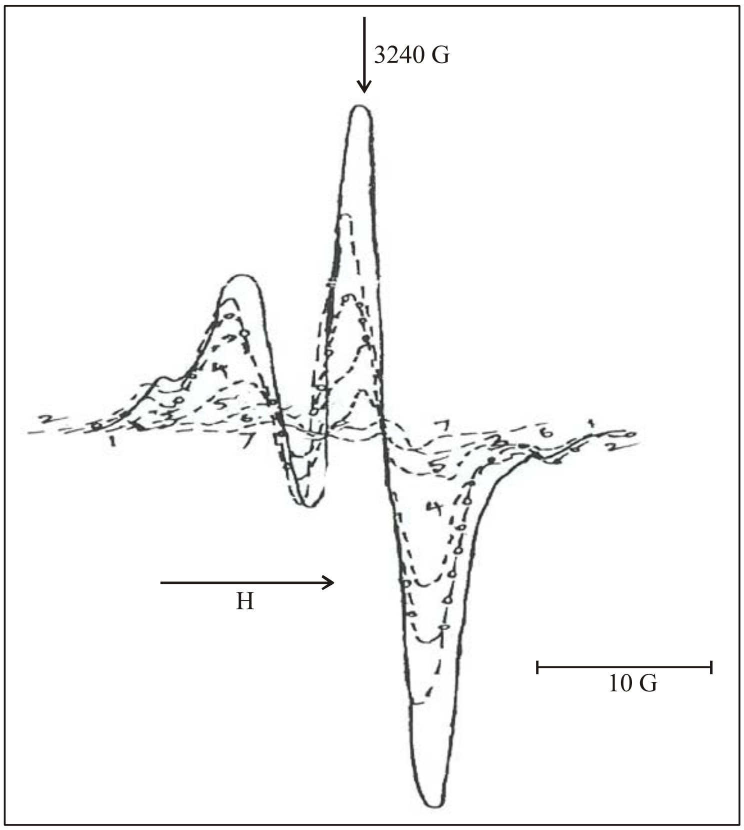

Fig. 1: ESR spectra of PET irradiated to a radiation dose of 3 M. rad and spectra recorded at various temperatures

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

The spectra are simulated to be a superposition of component spectra arising due to macroradicals. It gives components multiplet and doublet which is assigned due to ~ CHO ~ radical[4,5].

To calculate the value of activation energy, the values of line widths are used, to simulate the ESR spectra are employed and the value of Δν and Δτ are calculated using eq. 3. These values are listed in Table 2.

Table 2: $1/T \times 10^3$ and $1/\tau$ values at different temperatures

Temperature (K)	$1/T \times 10^3$	Δν	1/τ	log (1/τ)
300	3.33	15	-	-
310	3.23	14	23.932	1.379
330	3.03	13	33.257	1.522
350	2.86	10	49.088	1.696
370	2.70	3	63.36	1.815
390	2.56	1.5	66.305	1.82
410	2.44	0.5	66.625	1.824

A plot of $1/T \times 10^3$ vs. log (1/τ) is shown in Fig. 2. The figure is a straight line,

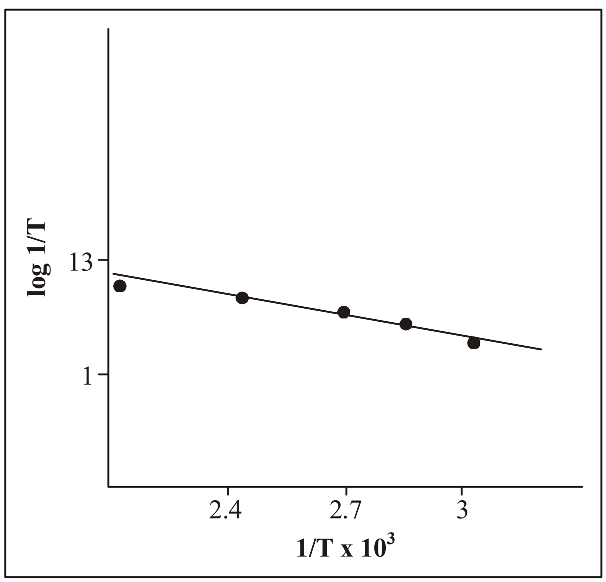

Fig. 2: Plot of 1/T vs log 1/τ of irradiated PET

whose slope gives the value of activation energy. This value is very high and it is anticipated in case of PET. Since PET is an aromatic polyester, it contain aromatic groups in main chain. Therefore, mobility of these radicals is very low, and it required more energy for recombination.

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