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DEGRADATION STUDIES OF GAMMA IRRADIATED POLY (VINYL ALCOHOL)

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ABSTRACT

Degradation of poly (vinyl alcohol) (PVAL) by gamma rays has been studied by electron spin resonance (ESR) technique. ESR spectra of irradiated PVAL are recorded in the temperature range of RT. (300 K) – 410 K. The spectrum is basically a triplet with intensity distribution of 1 : 3 : 1 and hyperfine splitting of 35G. The spectrum is assigned to the free radical of the type ~ CH_2-C-(OH)-CH_2 ~ formed by the cleavage of hydrogen from PVAL on gamma irradiation. The hyperfine pattern gradually increases up to 360 K beyond which the ESR signal gradually decrease with temperature and finally disappeared around 410 K. Free radical concentration at different temperature have been calculated and compared.

Key words: Degradation, PVAL, ESR, Free radicals, Gamma irradiation, Poly (vinyl alcohol).

INTRODUCTION

Poly (vinyl alcohol) is an industrially important polymer due to its superior strength, adhesive nature and film forming ability[1]. During these applications, the polymer is likely to be exposed to different types of irradiation. Hence, degradation of PVAL has been attempted by various authors[2-7]. Thermal degradation of PVAL has led to the formation of several volatile products and evolution of gases[2,3].

Photodegradation of PVAL has resulted in the formation of C = O based products[4,5]. Gamma irradiation of PVAL is accompanied with the formation of various types of free radicals[6-8].

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Degradation of PVA solutions by gamma rays was reported by Zhang and Yu[9]. It is observed that degradation was influenced by parameters like concentration, dose rate, pH and other factors.

Poly (vinyl alcohol) is blended with chitosan and corresponding hydrogels are reported to be formed on electron beam irradiation[9], UV irradiation of PVA lased polymer leads to cell adhesion according to Keith et al.[10]

The authors have attempted degradation of PVAL by gamma rays in the present studies. Since high energy radiation induce cleavages in polymeric chains, formation of free radicals takes place. They could be detected by the ESR technique. The authors attempt to investigate nature of free radicals formed on gamma irradiation of PVAL and their behavior at different temperatures.

EXPERIMENTAL

Poly (vinyl alcohol) (PVAL) in the form of powder has been used in the present studies. The polymer is supplied by CDH Laboratories in New Delhi. Gamma irradiation was carried by cobalt – 60 gamma source with a dose rate of 15 KG ray / hour. ESR spectra of irradiated polymer have been recorded on Varian E-112 spectrometer at X-band frequencies and 100 KHz modulation.

RESULTS AND DISCUSSION

ESR spectra of gamma irradiated PVAL at different temperature are as shown in Fig. 1.

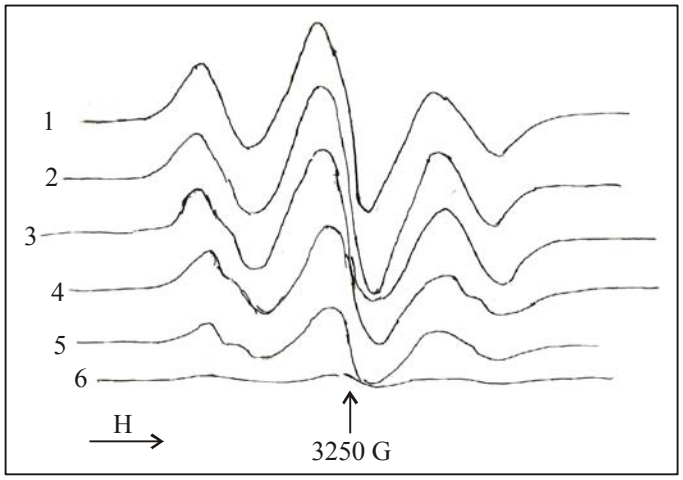

Fig. 1: ESR Spectra of irradiated PVAL of different temperatures

Curves 1, 2, 3, 4, 5 and 6 represent ESR Spectra recorded at 310 K, 330 K, 350 K, 370 K, 400 K and 410 K, respectively. The spectral parameters are listed in Table 1.

Table 1: Spectral parameters of PVAL

Temp. (K)	Number of hyperfine lines	Line position (G)					Hyperfine splittings (G)	Description in Fig. 1.
		1	2	3	4	5		
300	3	3210	--	3245	--	3280	35	Curve 1
310	3	3210	--	3245	--	3280	35	Curve 2
330	3	3210	--	3245	--	3280	35	Curve 3
350	3 + 1	3210	3215	3245	--	3280	30-35 & 5	Curve 4
370	3 + 2	3210	3215	3245	3275	3280	30-35 & 5	Curve 5
400	3	3210	--	3245	--	3280	35	Curve 6

Since the total area of ESR spectrum represents the total number of free radicals, area under the ESR spectra have been calculated by double integration methods. The values of intensities at different temperatures are listed in Table 2.

Table 2: Integrated intensities of ESR spectra

Temperature (K)	Integrated intensity (Arbitrary units)	Spread (G)
300	150	120
310	145	120
330	142	120
350	81	130
370	94.5	135
400	30	100
410	24	50

A plot of ESR intensity and spread against temperature are shown in Fig. 2 and Fig. 3, respectively.

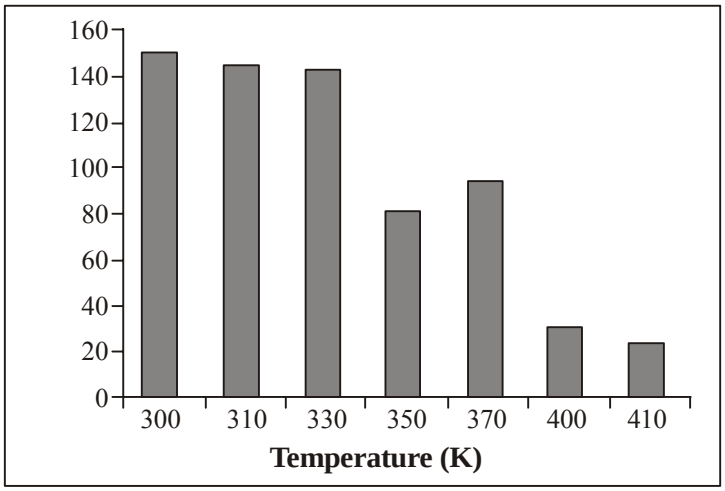

Fig. 2: Temperature variation of intensity against temperature

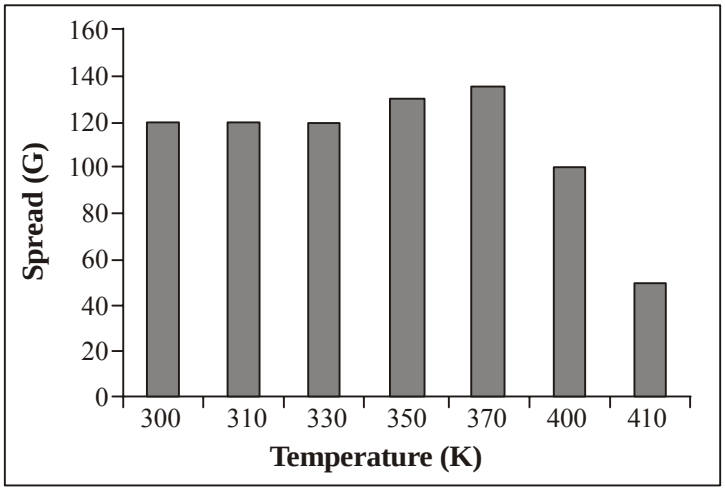

Fig. 3: Temperature variation of spread against temperature

Chemical formula of PVAL is shown in Fig. 4.

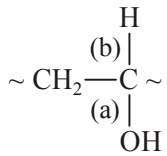

Fig. 4: Chemical formula of PVAL

Upon exposure to radiation, the PVAL is reported to possess two types of free radical[2-8]. They are

(i) Free radical of the type ~ CH_2-$\dot{C}H$-CH_2 ~ (I), which is assumed to be formed by cleavage of OH groups shown at position 'a'.

(ii) Free radical of the types ~ CH_2-$\dot{C}$(OH)-CH_2 ~ (II) formed by cleavage of proton shown at position 'b'.

The hyperfine splitting of radical (II) is reported to be in the range of A_α = 23-20 G and A_β = 20-30 G. However, the hyperfine splitting observed in the present studies are in the range of 35 G, which are very large and highly improbable to suggest the presence of radical (II). Ogawa[6] has proposed that β – hyperfine interaction in ~ CH_2-$\dot{C}$(OH)-CH_2 – radical will contribute to a hyperfine splitting of 35 G. Therefore, presence of radical (I) is more appropriate in irradiated PVAL. This result suggest that irradiation of PVAL with gamma rays might have generated radical (II), with the cleavage of proton shown at position 'a' in Fig. 4.

The free radical at RT (300 K) will give a triplet spectrum with hyperfine splitting of 35G. On increasing the temperature to 350 K, the hyperfine lines together with spread have increased. Beyond 350 K, the hyperfine lines together with spread have further increased. Beyond 370 K, a decrease in the splittings and spread was observed.

Plots of ESR intensity and spread against temperature were drawn (Fig. 2 and Fig. 3), respectively. It was found that the ESR intensity gradually decreased with temperature and finally signal decayed above 410 K. In contrast, the spread decreased upto 350 K, then increased upto 370 K and suffered a decrease beyond this temperature.

Since the glass transaction temperature (T_g) of PVAL is around 360 K, the on set of molecular motions at T_g facilitate more hyperfine interaction, increasing the spread of the spectrum. After crossing the T_g, the molecular motion begins to retard, causing a decrease in hyperfine interaction, consequently, a reduction in spread beyond the 'T_g'. Therefore, changes in hyperfine pattern with temperature is assigned to molecular motion in PVAL about the 'T_g'.

CONCLUSION

In conclusion, irradiation of PVAL with gamma rays result in formation of radical (II), assuming the cleavage of protons. The radical (II) at RT gives an ESR triplet spectrum.

At the glass transition temperature, the hyperfine interactions and spread increase are due to molecular motions.

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