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Spectroscopic and Thermal Investigations on Methyl Methacrylate – co – Methacrylic Acid Copolymer

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Gamma irradiation effects on methyl methacrylate (MMA) – methacrylic acid (MAA) copolymer were investigated by spectroscopic (ESR, FTIR) and thermal (DSC) methods. Electron spin resonance (ESR) spectra of the irradiated copolymer are analysed to be caused by different component spectra from the free radicals (~ $CH_2 - CH - CH_2$ ~ and – COOH or – $COOCH_3$) as per computer simulation analysis. The ESR signals could be annealed near the transition temperature of the copolymer, and the free radicals formed irradiation might react to form stable structures at transition temperatures. Fourier transform infrared (FTIR) studies suggested that the 3380 cm^{-1} absorption band (due to COOH groups and or hydrogen bonding) and 1734 cm^{-1} absorption band (due to carbonyl groups) were mostly affected by irradiation. Differential scanning calorimeter (DSC) thermogram indicated that the copolymer is a two-phase system (PMMA and PMAA), and transition temperatures are influenced by gamma irradiation. The dosimetric application of copolymer is tested by the ESR technique, and it was found suitable for dosimetry.

Keywords: Bloch analysis; DSC; ESR; FTIR; Gamma irradiation; MAA; MMA

I. INTRODUCTION

Poly methyl methacrylate (PMMA), commercially known as Perspex, is one of the commercially known industrial polymers used in aerospace and high-altitude applications. PMMA has been used in biomedical (Amer *et al.,* 2014), photocatalytic (Camara *et al.,* 2014), solar cells (Yang *et al.,* 2008), organic memory devices as an organic insulator (Haik *et al.,* 2014) and sensors (Mishra *et al.,* 2014) applications. Similarly, PMAA-based coatings are also used in anti-cancer drugs (Yu *et al.,* 2004; Luo *et al.,* 2014) and insulin-releasing (Victor *et al.,* 2002) applications. Polymethacrylic acid is partially hydrophilic, and PMMA is hydrophobic; a mixture of these two has intermediate and interesting properties, which are needed to be investigated. In this context, the synthesis and characterisation of MMA-MAA copolymer and related compounds were reported by various authors (Girod *et al.,* 2013; Saboktakin *et al.,* 2011; Huang *et al.,* 2003; Sodeifian *et al.,* 2012). The copolymers and their derivatives are reported to have interesting applications. They include coating film for tablets and granules (Paul *et al.,* 1976) in medical areas, microencapsulation (Georgiev *et al.,* 1994), anti-corrosion agents of metals coated on copolymer tablets (Gonsalves *et al.,* 2021), nano gels in biomedical applications (Lee *et al.,* 2001), intelligent material applications (Don *et al.,* 2008) and radiation dosimetry (Alashrah *et al.,* 2021).

With regard to studies on radiation-induced changes, PMMA is extensively investigated (Jebur *et al.,* 2020), and very few attempts are made on PMAA (Yin *et al.,* 2021).

In this paper, we have explained the gamma irradiation effects of copolymer using spectroscopic (ESR and FTIR) and thermal (DSC) techniques. Thermal annealing characteristics and dosimetric aspects of the irradiated copolymer are investigated by ESR techniques. A computer simulation technique is used to analyse ESR spectra.

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II. MATERIALS AND METHOD

In the present work, MMA-MAA copolymer in the powder form supplied by Sigma Aldrich was used.

The ESR spectra of the copolymer were recorded by using a VARIAN E – line spectrometer operated at X – band frequency with 100 k Hz modulation. To study the annealing behaviour of copolymer, the irradiated samples are immediately transferred to sample tubes and sealed throughout the recording of ESR spectra. The FTIR spectrum was recorded by using a PERKIN ELMER spectrometer. The spectra of powder were obtained using KBr pellets. The pressed disk containing 100 – 200 mg of the sample with KBr was scanned at a wave number range of 4000 – 400 cm^{-1}. The DSC thermal analysis was carried out on a TA Q-10 calorimeter with a scan rate of 10 °C/min. Approximately, 10 – 20 mg sample was weighed and sealed in an aluminium pan. To avoid oxidation, sample nitrogen gas was flushed into the chamber throughout the experiment.

A cobalt–60 gamma radiation source was used to irradiate the copolymer sample with a 15 kGy dose rate (0.15 M rad/hr) in the air at room temperature (RT). The radiation dose absorbed by the copolymer is computed to the time of exposure of the sample to the radiation source.

III. RESULTS AND DISCUSSION

A. ESR Studies and Analysis of ESR Spectra

ESR spectra of un-irradiated copolymer do not show any hyperfine (hf) structure, suggesting that free radicals are not present in it. But irradiated copolymer at RT (300 K) exhibited some hyperfine structure (radiation dose 3 M rad) as shown in curve 1, Figure 1. The spectra appear to have a doublet shape with a superposed hyperfine structure. Intensity distribution and line separations are sequenced to the anticipated doublet pattern, suggesting the presence of more resonances.

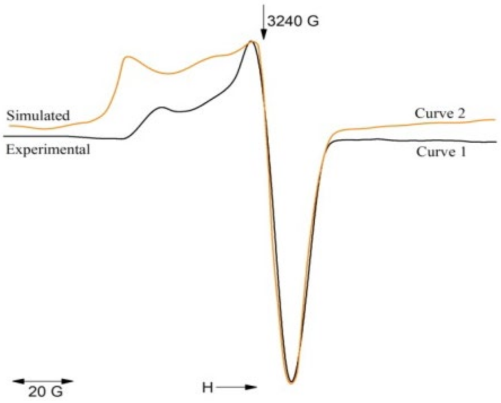

Figure 1. ESR spectra of irradiated copolymer at RT. Curve 1: Experimental; Curve 2: Simulated (superposed)

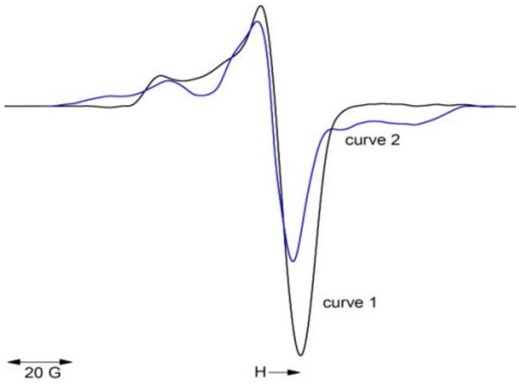

Figure 2. Component spectra of set I. Curve 1: Component multiplet; Curve 2: component triplet.

In order to analyse this type of complex ESR spectra, computer simulation methods are used, which are described previously (Murthy *et al.,* 1990). In brief, various component spectra are generated corresponding to the free radicals expected to be produced on irradiation of copolymer. Some component spectra are selected and superposed, and compared with the experimental spectra every time. Each component spectra specified different values of magnetic parameters. Two sets of parameters are employed in the present studies. Set I correspond to the multiplet–triplet combination, shown in Figure 2, and Set II correspond to the quintet–triplet combination, shown in Figure 3. The magnetic parameters employed in both sets are given in Table 1.

The simulated studies corresponding to Set-I consists of component multiplet (curve 2 Figure 2) and component triplet spectrum (curve 1 Figure 2) with magnetic parameters given in Table 1. Creation of macro radicals (- CH_2 – CH – CH_2 – or CH_2 – C (CH_3) – CH_2 - [I] and component multiplet spectrum from it is expected in poly acrylates like Poly (acrylic acid) [PAA], (Rao *et al.,* 1989) PMMA (Tatar *et al.,* 1997) and PMAA (Hill *et al.,* 1992). Radical I is formed by the cleavage of the pendent group at the alpha position of the copolymer backbone. Free radical-giving component doublet is expected to be formed due to pendent group radicals and any broken/residual chains of the copolymer. In case of non-interaction of adjacent methylene group protons of radical I, doublet may also result. The simulation results of Set–II (magnetic parameters are given in Table 1) correspond to component quintet (arise due to the same radical I with different hyperfine interaction, i.e. with only beta protonic interaction and different values of magnetic parameters) and component triplet (which is expected to be produced on the cleavage of main chains of the copolymer [– CH_2 – (II)]), as shown in Figure 4. Both free radicals are expected to be formed on different parts of the co-monomers on irradiation and reported in the literature (Saraev *et al.,* 2001). The remaining parameters used in the computer simulation of both sets (I & II) are also listed in Table 1. To show the goodness of the fit, the superposed spectrum (resulting from the combination of component spectra) curve 2 Figure 1 and Figure 3, while corresponding experimental spectra curve 1 Figure 1 and Figure 3. The results are in agreement with the reports of Masayuki K *et al.* (1996) on plasma irradiated MMA-MAA copolymer. Four types of radicals are reported to be formed during irradiation of MMA-MAA copolymer. They are: i) macro radicals of the type – CH_2 – C (COOH) – CH_2 -, formed by the breakup of chemical groups present at methine position (pendent groups); ii) monomer-derived free radicals of the type – CH_2(COOH) – CH – CH_2 (COOH) – called as mid-chain alkyl radicals; and iii) monomer derived free radicals (CH_2) – C (COOR) monomer derived radicals. It is observed that 70 % of the radicals formed during radiolysis transform to corresponding peroxy components and show g-anisotropy.

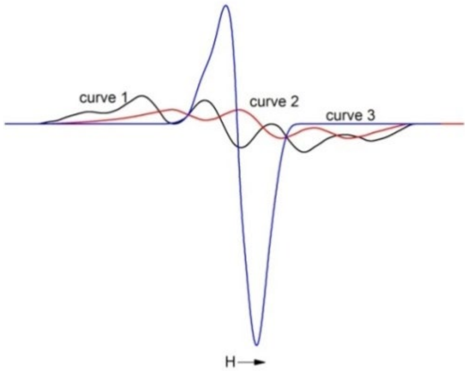

Figure 3. Experimental and simulated (superposed) spectra of irradiated copolymer [Set II]

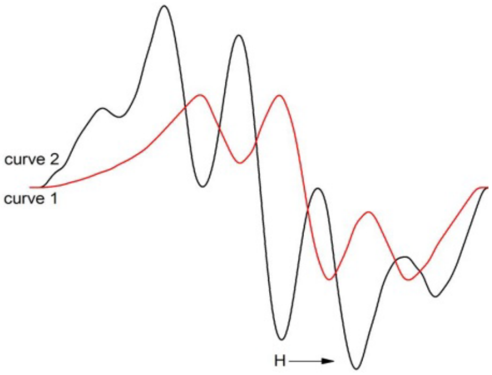

Figure 4. Component Spectra of set II.
Curve 1: Component quintet; Curve 2: Component triplet.

Table 1. Magnetic parameters corresponding to Set I and II

Set	Component	Line width a_i (G)	Relative intensity	Centre of Spectrum X_{oi} (G)	Hyperfine splitting Constants A_i, B_i (G)	n_i, m_i
I	Multiplet	10.5	2.0	3243	23,12	2, 5
	Triplet	8.5	3.0	3242	12, 0	3, 1
II	Quintet	9	12.5	3232	0, 22	1, 5
	Triplet	18	13	3233	24, 0	3, 1
	Singlet	0.5	1.0	3241	0, 0	1, 1

B. Temperature Dependency

ESR spectra of observed for irradiated copolymer at other temperatures of 310, 330, 350, 370 and 390 K (curves 2, 3, 4, 5 and 6) are also shown in Figure 5. The hf structure is stable up to 330 K, and it begins to lose at 350 K and no signal is observed at 390 K.

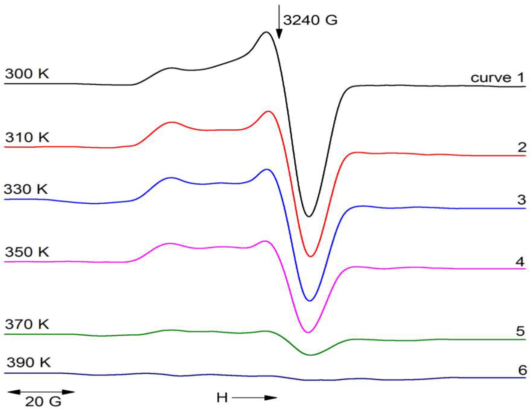

Figure 5. ESR spectra of irradiated MMA-MAA copolymer as a function of temperature.

The result suggests that free radicals produced on irradiation of copolymer may recombine with other/same type of free radicals or unreacted molecular chains to form stable structures. The recombination of free radicals depends on the surrounding physical state of the free radical (Nakka *et al.,* 2015) and is associated with the transition temperature of the molecular system. A change in ESR intensity as a function of temperature is shown in Figure 6. Later the DSC results confirmed that the T_g of the heterogeneous copolymer system is near 400 K.

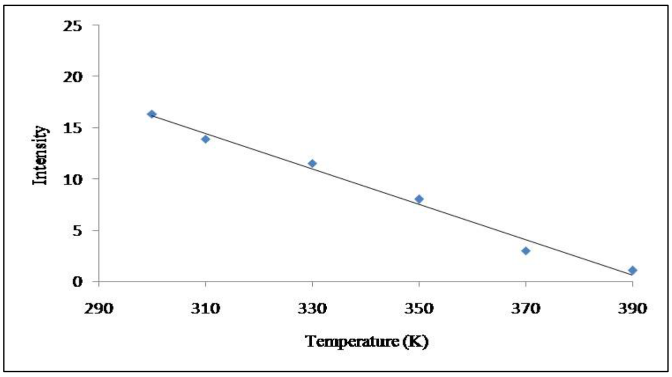

Figure 6. Variation of ESR intensity as a function of temperature.

C. Evaluation of Activation Energy

In order to study the nature of free radical decay and to calculate activation energy connected with radical decay, the Bloch analysis is adapted (Muralidhar *et al.,* 2016). Using the values of line widths at different temperatures, the values of τ are calculated, and a plot of 1 / T against log (1/ τ) is plotted, as shown in Figure 7. The slope of a straight line gives the value of activation energy calculated around 60 K J/mol. The parameters used in the Bloch analysis are specified in Table 2.

Table 2. Parameters used in Bloch analysis of MMA-MAA copolymer.

T (°C)	**T (K)**	**1/T x 10^{-3} (K^{-1})**	**Line width v**	**Relaxation time T**	**1/τ**	**log(1/τ)**
30	300	3.30	12.00	-	-	-
40	310	3.19	11.85	0.0030	338.03	2.53
60	330	3.00	11.75	0.0025	405.84	2.61
80	350	2.83	11.69	0.0020	496.67	2.70
100	370	2.68	11.64	0.0018	561.42	2.75
120	390	2.54	11.60	0.0015	666.51	2.82

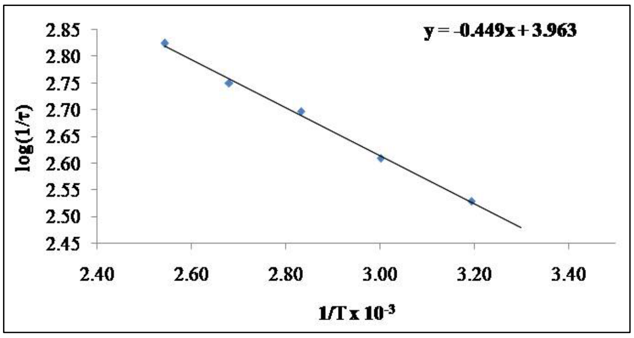

Figure 7. The plot of log (1 /τ) against 1 / T.

D. FTIR Studies

FTIR spectra of un–irradiated MMA–MAA copolymer under different conditions are shown in Figure 8. Band positions (3394.1, 3007.1, 2951.2, 1734.1, 1484.6, 1454, 1392.9, 1265.6, 1199.4, 1163.8, 970.3, 843, 761.5, 527.3 cm^{-1}) and their assignments are given in Table 3, which agree with the results of Al - Khalidi *et al.* (2015) for the un-irradiated copolymer and band positions are compared with the concerned acrylic acid homo polymers as given in Table 4.

On irradiation, the band positions (3282, 2961, 1729, 1485, 1449, 1393, 1270, 1205, 1164, 970, 843, 762 cm^{-1}) and intensities are slightly shifted in congruence with the molecular variations brought out by the radiation. Due to annealing, changes in band positions (band positions are changed to 3420, 3002, 2956, 1734, 1485, 1454, 1393, 1270, 1200, 1164, 970, 843, 756, 527 cm^{-1}) listed in Table 3.

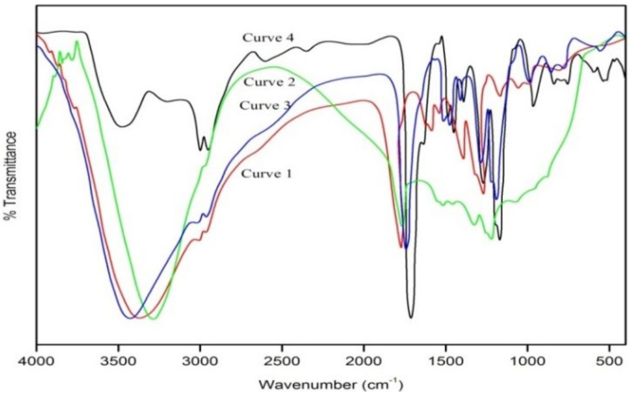

Figure 8. FTIR spectra of P(MMA-co-MAA) copolymer. Curve 1: Un-irradiated, Curve 2: irradiated, Curve 3: irradiated + Annealed Curve 4: Base.

Table 3. Comparison of Band positions and their assignment

S. No	Un-irradiated (cm^{-1})	Irradiated (cm^{-1})	Irradiated + Annealed (cm^{-1})	Assignment
1	3394.1	3282.0	3419.5	- COOH
2	3007.1	2961.2	3002	- CH_2 /CH_3
3	2956.2	-	2956.2	- CH_2 /CH_3
4	1734.1	1729	1734.1	ESTER CARBONYL
5	1484.6	1484.6	1484.6	- CH_3
6	1454	1448.9	1454	- CH_3
7	1392.9	1392.9	1392.9	OH
8	1265.6	1270.7	1270.7	CH_2
9	1199.4	1204.5	1199.4	CH_2/CH
10	1163.8	1163.8	1163.8	CH_2/CH
11	970.3	970.3	970.3	= C - H
12	843.0	843.0	843	C – H
13	761.5	761.5	756.4	C – H
14	527.3	-	527.3	C – H

Table 4. FTIR band positions of acrylic acid homopolymers.

S No	Chemical group	PAA	PMAA
1	Hydroxyl band (OH)	3735	3418
2	C = C band	2316	--
3	C – H band	2980	3000
4	Carbonyl C = O	1693	1700
5	C – O band	1270	1272

The absorption bands examined in the present studies also confirm the above assignments. On irradiation, subsequent variations are examined:

i. The 3380 cm^{-1} absorption band associated with carboxylic acid (COOH) groups/hydrogen/hydroxyl bond suffered a reduction in intensity and band shift, indicating the cleavage of –COOH groups on irradiation of the copolymer. The results are analogous to the FTIR observed by Galocardenas *et al.* (2000) for thermally degraded Poly (acrylic acid) PAA and PMAA. However, on annealing, a shift towards higher wavelengths is observed. The results suggest degradation of the copolymer on irradiation and crosslinking on annealing of the irradiated copolymer.

ii. The 1734 cm^{-1} band, whose intensity considerably decreased, suggests the cleavage of carbonyl groups on irradiation.

With regard to the other functional groups, minor changes have been observed. Therefore, the FTIR data suggest the results of ESR data.

E. DSC Studies

DSC thermograms of MMA–MAA copolymer under different conditions are shown in Figure 9. The thermograms of unirradiated (Curve 1 Figure 9) copolymer contain endothermic-like peaks centred around 100°C, 233°C and 440°C. If the copolymer is a composite system is considered as two immiscible polymers, it consists of two different phases PMAA (T_g = 228 °C) phase and PMMA phase (T_g = 105°C), and distinct DSC peaks of both the homopolymers are to be present. Therefore, the presence of the two DSC peaks at 105°C and 230°C is more appropriate. The results agree with the T_g values reported for homo polymers (Startsev *et al.,* 2018; Goulis *et al.,* 2020) and copolymers (Gatica *et al.,* 2001). Thermal data observed for PMAA and PMMA-PMAA copolymer, while thermal data examined in the present studies are as specified in Table 5. The further appearance of second-order transition near the T_g is attributed to the time-dependent temperature relaxations (Bashir *et al.,* 2001; Madhukar *et al.,* 2013). The following aspect leads to time-dependent temperature relaxations.

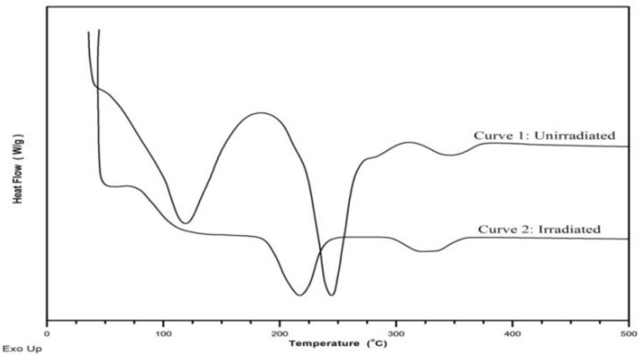

Figure 9. DSC thermogram of the copolymer.
Curve 1: Unirradiated; Curve 2: Irradiated.

The COOH group of PMAA and the $COOCH_3$ (ester) group of PMMA are capable of forming intermolecular hydrogen bonds. Formation of such type of hydrogen bonds is also reported for PA6 (Murthy *et al.,* 2006) and PMMA (Morita *et al.,* 2014). Therefore, the appearance of second-order transition near T_g in MMA – MAA copolymer is fully justified.

On irradiation (Curve 2 Figure 9), a shift together with the reduction in the intensity of the peaks is observed, suggesting that the chains of the copolymer have been dissociated due to gamma irradiation. Due to a decrease in molecular weight, a reduction in transition temperatures is expected.

Table 5. DSC data of homopolymers and copolymers

S. No.	Sample	Peak 1	Peak 2
As per literature			
1	PMMA	105 ± 5 °C	125 ± 5 °C
2	PMAA	228 °C	16 °C
3	P(MMA-co-MAA)	105 °C	152 °C
As per present studies			
4	P(MMA-co-MAA)	119.32	252.98
5	Irradiated copolymer	74.8	216.25

F. Dosimetric Aspects of Copolymer

In order to study the effect of radiation dose on the formation of free radicals and dosimetric aspects of the copolymer, ESR spectra are recorded by exposing the copolymer to different radiation doses, as shown in Figure 10. The spectral features are almost similar, and spectral intensity gradually increased with radiation dose, as shown in Figure 10. A plot of ESR intensity as a function of radiation dose is drawn as showing linear variation with a regression coefficient of 0.995, as shown in Figure 11, reflecting the suitability of the material for dosimetric applications (Prasad *et al.,* 2013). Dosimetric aspects are also studied based on the intensity variation of FTIR absorption bands (3450 cm^{-1} absorption band).

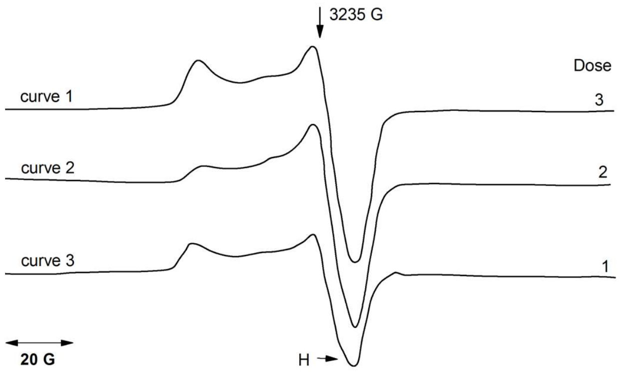

Figure 10. ESR spectra of radiation dose-dependent ESR spectra of the copolymer.

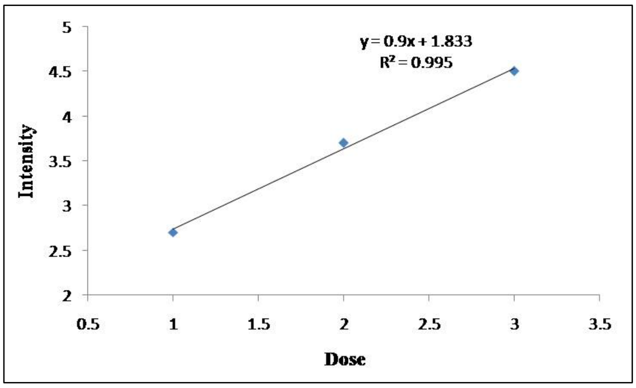

Figure 11. The plot of ESR intensity as a function of radiation dose.

IV. CONCLUSION

In conclusion, irradiation of copolymer causes chain cleavages producing two types of free radicals $\sim CH_2 - CH - CH_2 \sim$ and $- COOH$ or $- COOCH_3$ radicals. The free radicals give ESR spectra component spectra of multiplet, triplet and component singlet, which superpose to give the observed ESR spectrum at RT. Temperature-dependent ESR studies suggest that the free radicals react and form stable structures below the T_g of the copolymer. FTIR data confirm the presence of characteristic functional groups of both the polymers (PMMA and PMAA). On irradiation, cleavage of ester groups and inter-molecular hydrogen bonds is suggested. DSC results indicate that both T_g and T_m decrease mainly due to the cleavage of chemical chains or groups on irradiation.

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