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## Effect of composition, radiation dose and post irradiation time on radiation behavior of Acrylonitrile-Methacrylate (AM) Copolymer.

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### ABSTRACT

Radiation behaviour of Acrylonitrile – Methacrylate (AM) Copolymer has been investigated by Electron Spin Resonance (ESR), Fourier Transform Infrared (FTIR) Techniques. Effect of composition, radiation dose and post irradiation time on radiation behaviour is studied. ESR spectra at room temperature (RT) and near the glass transition temperature ( $T_g$ ) are recorded for the copolymers of different composition. FTIR spectra of copolymer under different composition have been recorded. The studies suggest that chain cleavage occur either on MA part or AN part depending on the composition of co monomers.

**Keywords:** AM copolymer, gamma radiation, ESR spectrum, FTIR spectrum, free radicals.

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## INTRODUCTION

Radiation resistance of polymer and copolymers is an important aspect because these molecular systems are employed as heat or radiation resistant appliances. Various methods are preferred in literature to improve radiation resistance. Copolymerization is one among them (1). In this context radiation resistance and resultant changes are reported by different authors. They are Styrene based Copolymers (2), Styrene – acrylonitrile – butadiene (SAN) (3), copolymer context the authors have made an attempt to study the gamma irradiation effects in acrylonitrile (AN) and ethyl methacrylate (EMA) (AE) copolymer using spectroscopic and thermal techniques.

Radiation induced changes in Styrene - acrylonitrile (SAN) copolymers have reported in literature authors (4-7). The ESR spectrum observed for irradiated SAN is reported to have contribution from component spectra arising due to both the co-monomers. Degree of cross linking and chain scission is reported to depend on more acrylonitrile content or styrene content. Radiation resistance is reported to improve due to the presence of styrene group, which act as protective agent and dissipate the incoming gamma energy. The protective effect depends on temperature of is less at low temperatures i.e., at liquid nitrogen temperature (LNT). Gamma irradiation effects in methacrylamide (MA)- ethyl methacrylate (EMA) copolymer (MAEMA) have been reported by Sanjeeva Rao et al (8) using ESR and FTIR techniques. The studies indicate that gamma irradiation induces chain cleavages on both MA and EMA parts of the copolymer producing two types of free radicals. They are (1) macro radicals  $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}\sim$  (I) which gives component multiplet spectrum and component singlet spectrum due to  $\dot{\text{C}}\text{ONH}_2$  radicals (II). These authors have recorded FTIR spectra of copolymer under different conditions and identified functional groups affected by gamma irradiation. Gamma irradiation effects in acrylonitrile (AN) ethyl Methacrylate (EMA) (AE) copolymer have been investigated by electron spin resonance (ESR), Fourier transform infrared (FTIR) and differential scanning calorimetric (DSC) techniques. Temperature and radiation dose dependent effects have been investigated by recording ESR spectra under different conditions. Computer simulation techniques are used to analyze ESR spectra to identify of free radical produced on irradiation of copolymer. As such ESR spectrum of irradiated copolymer at RT is simulated to be a super position of component spectra arising due to  $\sim\text{CH}_2-\dot{\text{C}}$  (CN)- $\text{CH}_2$  (I)  $\text{COOC}_2\text{H}_5$  (II) free radicals. The ESR spectrum is found stable up to elevated temperatures of 487K indicating that the free radicals are thermally stable. Intensity of ESR spectrum increased with the increase of radiation dose indicating formation of more number of free radicals. Chemical changes induced by gamma irradiation have been studied by comparing the FTIR spectra of non-irradiated and irradiated copolymer. The results suggest that the ester groups are found to be prone to irradiation; while acrylonitrile groups are unaffected by gamma irradiation. DSC, Thermogram of copolymer consists of a first order transition at 88<sup>o</sup>c corresponding to the  $T_g$  of copolymer, while exothermic peak is observed at 285<sup>o</sup>C. On irradiation both the peaks shifted to lower temperatures (9). Though radiation effects on various copolymers are available, such studies on acrylonitrile – methacrylate copolymer have not previously reported. Therefore the authors have made an attempt with electron spin resonance (ESR), Fourier transform infrared (FTIR) Spectroscopy as experimental techniques.

## EXPERIMENTAL

AE copolymer in the form of powder has been in the present studies. Gamma irradiation of copolymer is carried out using cobalt 60 gamma source with a dose rate of 0.15 M.rad (15KGy) in air at room temperature. The radiation dose absorbed by the copolymer is measured in the terms of time of exposure of the sample. ESR spectra of irradiated copolymer are recorded on GEOL spectrometer operating of X-band frequencies and 100 KHz modulation. The spectrometer is fitted with necessary accessories to be record ESR spectra at high temperatures above RT. FTIR spectra of the copolymer have been recorded in pellet form. Copolymers with three compositions are used in the present studies in given Table 1 (10).

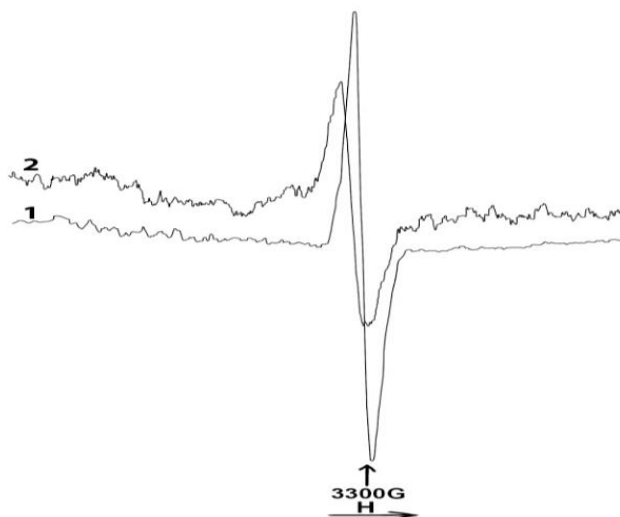
Table 1: AM Copolymers used in the present studies

Designation of Copolymer	Mole fraction of AN	Mole fraction of MA	Glass transition Temperature (°C)	Dielectric Constant (t)
AM <sub>1</sub>	0.50	0.50	70.43	2.45
AM <sub>2</sub>	0.60	0.40	76.96	2.57
AM <sub>3</sub>	0.70	0.30	71.20	2.53

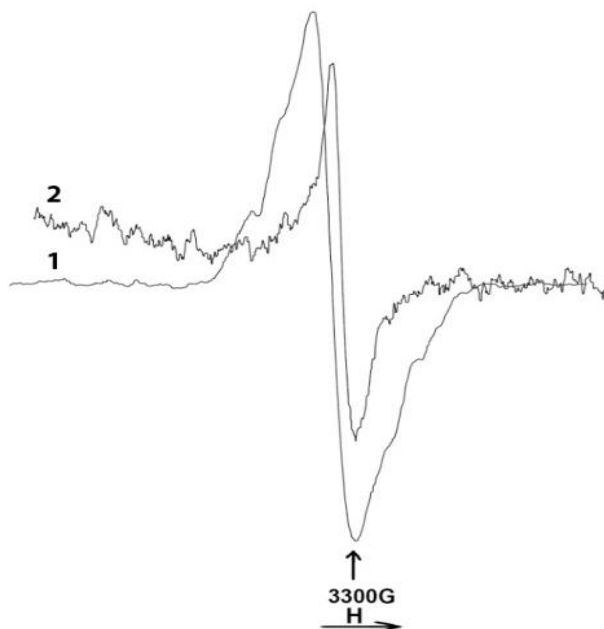
**RESULTS AND DISCUSSION**

ESR spectrum of irradiated AM<sub>1</sub>, AM<sub>2</sub> and AM<sub>3</sub> at RT are shown as Curve 1. Fig 1, Fig 2 and Fig 3 the spectra compose a central singlet together with unresolved hyperfine structure in the wings. Hyperfine structure in is more for the Copolymer with less AN content or more MA content. While curve 2, Fig 1, Fig 2 and Fig 3 represents ESR spectra of AM<sub>1</sub>, AM<sub>2</sub> and AM<sub>3</sub> near glass transition temperature. When compared to the spectra at RT, the spectra of T<sub>g</sub> are resolved. Broadening of the ESR spectra is due to two reasons.

- (i) Change in physical environment around the unpaired electron.
- (ii) Presence of other paramagnetic species.



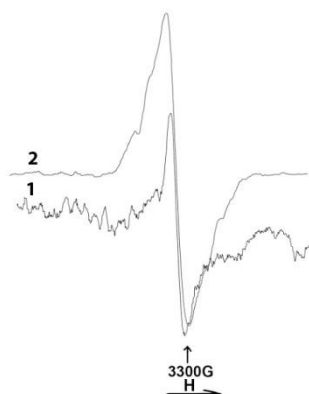
**Figure 1: ESR Spectra of irradiated AM<sub>1</sub> Copolymer**  
 Curve 1: spectra of RT Curve 2: spectra of near T<sub>g</sub>



**Figure 2: ESR Spectra of irradiated AM<sub>2</sub> Copolymer**  
 Curve 1: spectra of RT Curve 2: spectra of near T<sub>g</sub>

Since ESR spectra are recorded under identical conditions, presence of other paramagnetic species is ruled out. Therefore change in physical environment around the unpaired electron is thought to be the reason for broadening of ESR spectra.

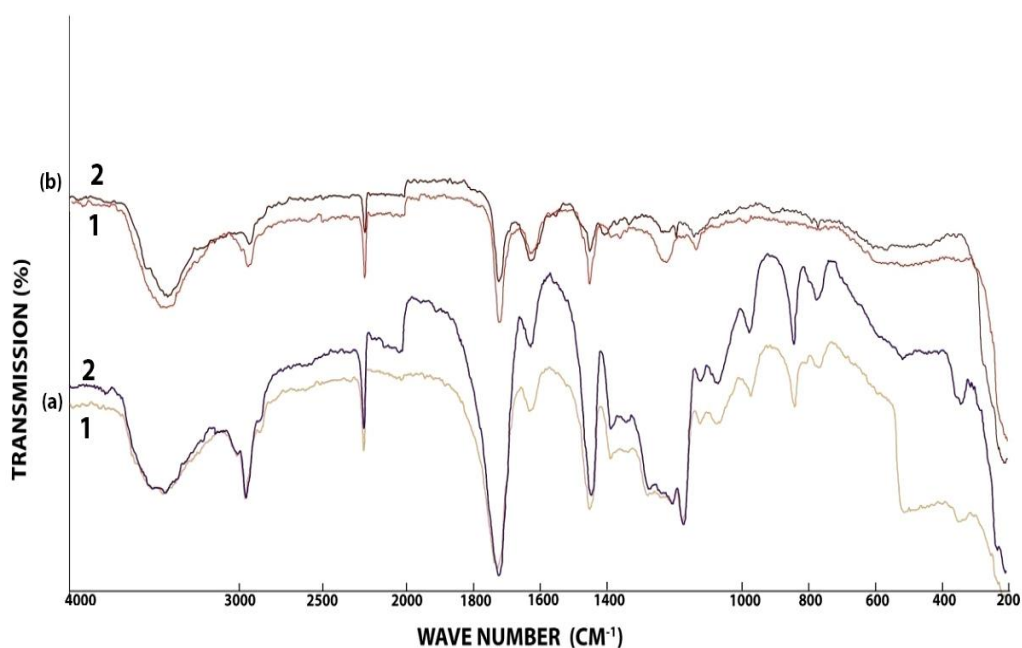
Below glass transition temperature the co polymeric chain are in rigid state, causing less hyperfine interaction so that the ESR spectra are broadens. When the temperature is increased, the chain elasticity increases causing more hyperfine interaction so that the ESR spectra are resolved. Such type of broadening of ESR Spectra is observed previously in irradiated Polyoxymethylene (11) and Poly (methacrylic acid) (12).



**Figure 3: ESR Spectra of AM<sub>3</sub> Copolymer**  
**Curve 1: spectra of RT    Curve 2: spectra of near T<sub>g</sub>**

With regard to the identification of free radicals, cleavages of AN produces free radical giving ESR spectra with similar hyper splittings (10). While cleavage on MA part produce macro radicals in  $\sim \text{CH}_2\text{-}\dot{\text{C}}\text{H-CH}_2$  giving more hyperfine line with splitting constant of 20-23G. Since less hyperfine structure with smaller splittings is observed, presence of macro radicals is ruled out. The free radicals produced on AN part with smaller coupling constants is and more probable. There exist N-H and O-H interaction in macromolecular chains between AN, MA parts of Co polymeric chains (13, 14). Therefore cleavage methane proton C-H (N) is not probable only O-H or N-H bond cleavages are expected, which give component ESR spectra with smaller splittings.

FTIR spectra of unirradiated AM copolymer are shown as Curve 1 Fig 4 and Fig 5. It compose absorption bands corresponding functional groups of both the monomers i.e., 2240 $\text{cm}^{-1}$  absorption band of C  $\equiv$  N groups and 1730  $\text{cm}^{-1}$ , 1620  $\text{cm}^{-1}$  absorption bands of ester chains of acrylate group. Additionally the spectra compose various absorption bands corresponding to the functional groups common to the both monomers. They include 2980  $\text{cm}^{-1}$ , 2960  $\text{cm}^{-1}$  absorption bands corresponding to CH<sub>2</sub>/CH<sub>3</sub> group as linked in Table 2.



**Figure 4: FTIR spectra of unirradiated and irradiated AM Copolymers**  
Curve 1: AM<sub>2</sub> Curve 2: AM<sub>3</sub>

Additionally a 3400-3100 cm<sup>-1</sup> is observed in the FTIR spectra of copolymer.

**Table 2: FTIR absorption bands of AN and MA Copolymers**

Characteristic absorption bands of Acrylonitrile cm <sup>-1</sup>	Characteristic absorption bands of Methacrylate cm <sup>-1</sup>	Absorption bands observed for copolymer cm <sup>-1</sup>	Newly observed Absorption Bands cm <sup>-1</sup>	Assignment cm <sup>-1</sup>
-	-	-	3400-3100	N-H/O-H
-	-	2980-2960	-	CH <sub>2</sub> /CH <sub>3</sub>
2240	-	-	-	C≡N
-	1730	-	-	-C=O
-	1620	1450	-	-
-	1450	1370	-	CH <sub>2</sub> /CH <sub>3</sub>
-	-	1200	-	CH <sub>2</sub> -CH <sub>3</sub>
-	-	1120	-	-
-	-	990	-	-
-	-	840	-	-
-	-	760	-	-

Further upon increase of AN content, intensity of 2240 cm<sup>-1</sup> absorption band, and on increase in MA content, intensity of 1730 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> absorption bands is increased; as expected. Additionally an absorption band on 3400-3100 cm<sup>-1</sup> is observed; which is assigned to N-H/O-H functional groups. These group are not present either in AN or MA. However due to interaction of neighbouring / adjacent side secondary hydrogen bonding may occur; as reported previously by several authors. FTIR spectra of irradiated AM<sub>2</sub> and AM<sub>3</sub> are shown as Curve 2. Fig 4a and Fig 4b only small changed are observed when compared to the spectra of unirradiated copolymer.

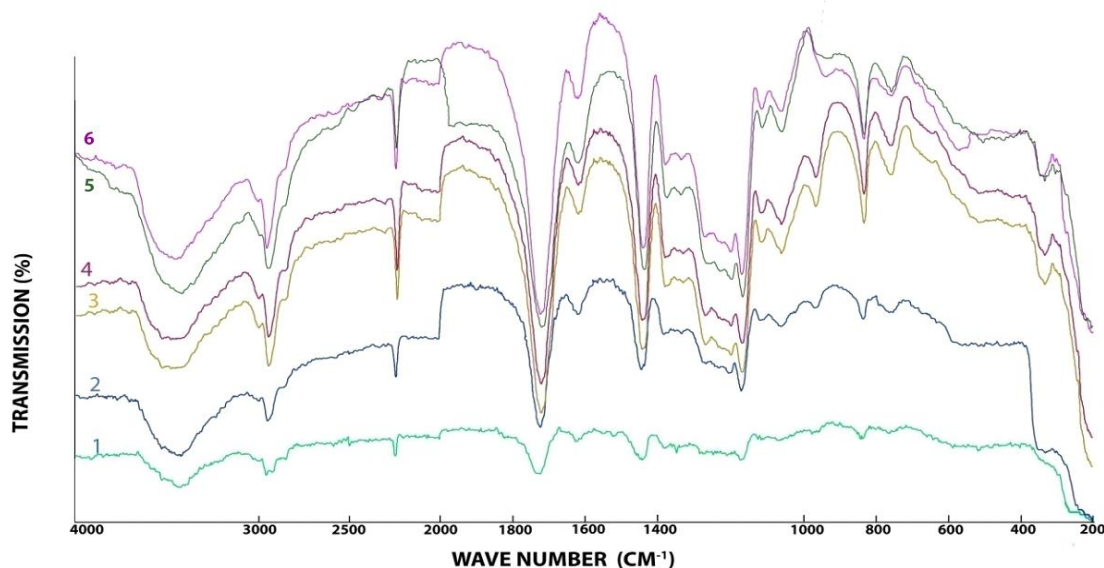


Figure 5: FTIR spectra of unirradiated and irradiated AM<sub>1</sub> Copolymer at different doses.

Curve 1: unirradiated    Curve 2: 7.0 M rad    Curve 3: 14.0 M rad  
 Curve 4: 3.5 M rad    Curve 5: 10.5 M rad    Curve 6: 17.5 M rad

FTIR spectra of unirradiated and irradiated AM<sub>1</sub> are as shown in Fig 5. Curve 1 corresponds to unirradiated Copolymer; while Curves 2, 3, 4, 5 and 6 correspond to the FTIR spectra of AM<sub>1</sub> at different radiation dose. Intensity of 3400-3100 cm<sup>-1</sup> absorption band is found to decrease suggesting the cleavage of these groups on irradiation of Copolymer. Additionally some of the absorption bands are found to shift either higher/lower wavelength side.

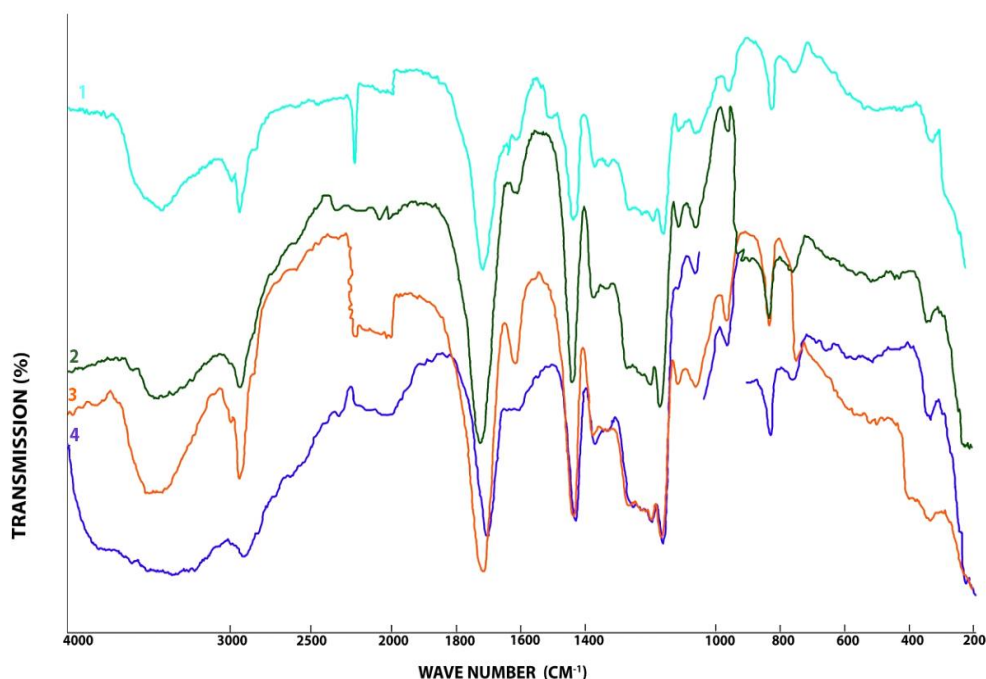


Figure 6: FTIR spectra of irradiated and aged AM<sub>1</sub> Copolymer  
 Curve 1: 24 hours    Curve 2: 48 hours    Curve 3: 72 hours    Curve 4: 120 hours

FTIR spectra of irradiated and aged AM<sub>1</sub> Copolymer are as shown in Fig 6.

Curves 1, 2, 3 and 4 represent the spectra of irradiated AM<sub>1</sub> aged to 24 hr, 48hr, 72hr and 120hr of post irradiation times. The absorption bands are found to be broadened. Broadening of the absorption bands is attributed to the hydroxylation of co polymer.

### CONCLUSION

In conclusion, effect of composition, radiation dose and post irradiation time on radiation behaviour of AM Copolymer is investigated by ESR and FTIR technique confirm AM the presence of functional groups corresponding to AM and MA suggesting the formation of Copolymer. Gamma irradiation induces chain cleavage of N-H/O-H bonds forming free radicals which produce ESR spectra with smaller splittings. Correspondingly chemical changes induced by gamma irradiation are also observed by monitoring intensities of 3400- 3100, 1730, 1620 cm<sup>-1</sup> absorption bands of irradiated and aged FTIR spectra.

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