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

D Suresh¹, B Sanjeeva Rao^{2*}, S Kalahasthi³, S Ramesh⁴, and V Ashok Babu⁵.

¹Research Scholar, Department of Physics, Rayalaseema University, Kurnool, AP, India.

²Department of Physics, Government of India, TS, India.

³Department of Physics, Kakatiya University, Warangal, TS, India.

⁴Department of Mechanical Engineering, KITS, Warangal, TS, India.

⁵Department of Physics, Andhra Layola College Vijayawada, AP, India

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.

**Corresponding author*

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)- CH_2 (I) COOC_2H_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^oc corresponding to the T_g of copolymer, while exothermic peak is observed at 285^oC. 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 ₁	0.50	0.50	70.43	2.45
AM ₂	0.60	0.40	76.96	2.57
AM ₃	0.70	0.30	71.20	2.53

RESULTS AND DISCUSSION

ESR spectrum of irradiated AM₁, AM₂ and AM₃ 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 AM₁, AM₂ and AM₃ near glass transition temperature. When compared to the spectra at RT, the spectra of T_g 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.

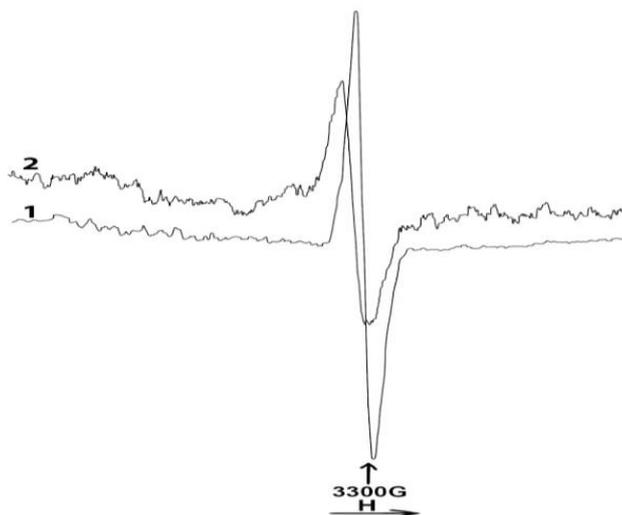


Figure 1: ESR Spectra of irradiated AM₁ Copolymer
 Curve 1: spectra of RT Curve 2: spectra of near T_g

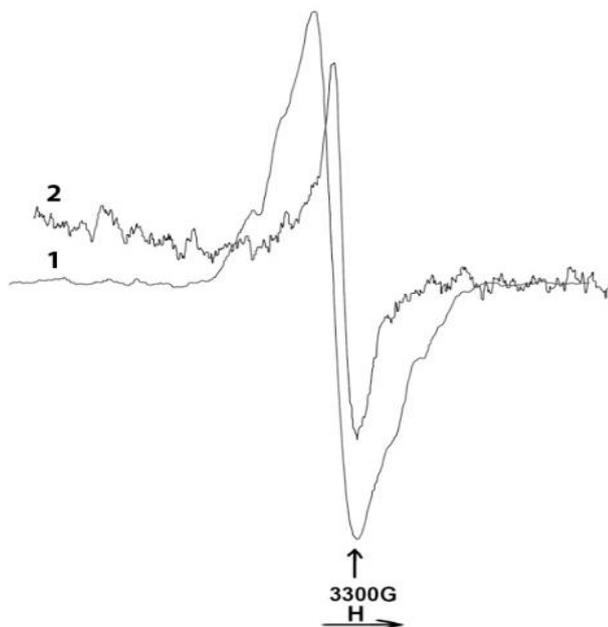


Figure 2: ESR Spectra of irradiated AM₂ Copolymer
 Curve 1: spectra of RT Curve 2: spectra of near T_g

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).

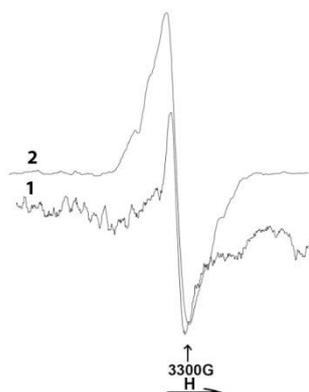


Figure 3: ESR Spectra of AM₃ Copolymer
Curve 1: spectra of RT Curve 2: spectra of near T_g

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 cm^{-1} absorption band of C \equiv N groups and 1730 cm^{-1} , 1620 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 cm^{-1} , 2960 cm^{-1} absorption bands corresponding to CH₂/CH₃ group as linked in Table 2.

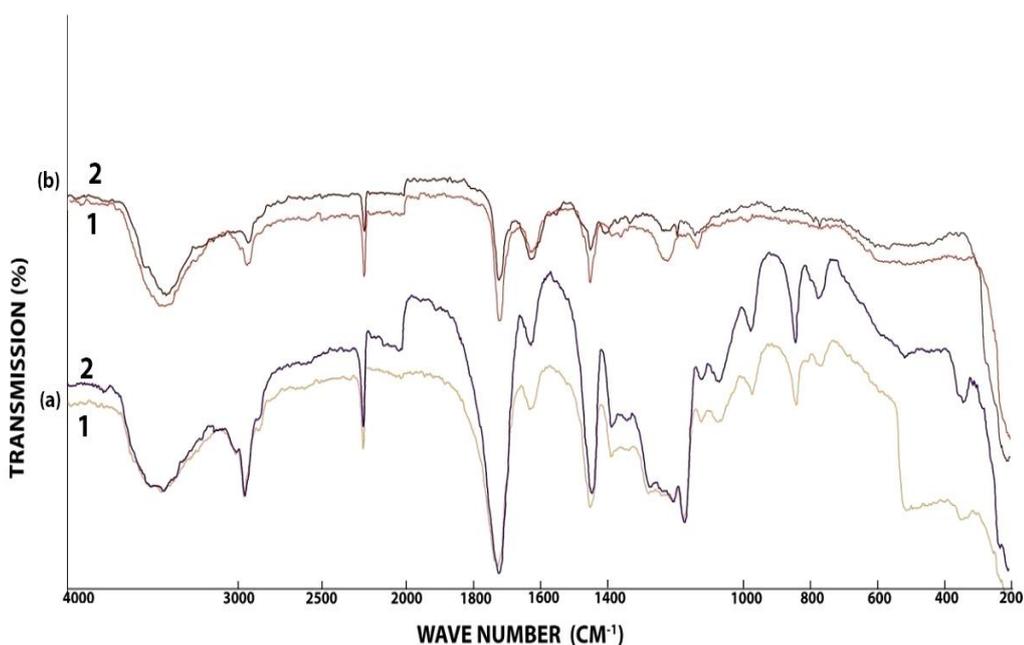


Figure 4: FTIR spectra of unirradiated and irradiated AM Copolymers
 Curve 1: AM₂ Curve 2: AM₃

Additionally a 3400-3100 cm⁻¹ is observed in the FTIR spectra of copolymer.

Table 2: FTIR absorption bands of AN and MA Copolymers

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

Further upon increase of AN content, intensity of 2240 cm⁻¹ absorption band, and on increase in MA content, intensity of 1730 cm⁻¹ and 1620 cm⁻¹ absorption bands is increased; as expected. Additionally an absorption band on 3400-3100 cm⁻¹ 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 AM₂ and AM₃ are shown as Curve 2. Fig 4a and Fig 4b only small changed are observed when compared to the spectra of unirradiated copolymer.

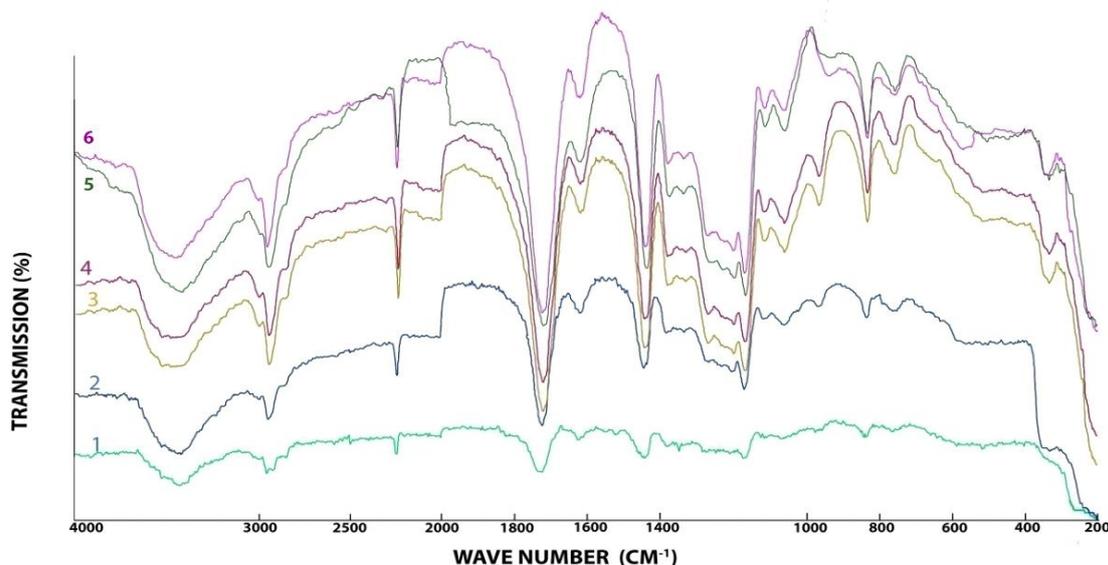


Figure 5: FTIR spectra of unirradiated and irradiated AM₁ Copolymer at different doses.

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 AM₁ 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 AM₁ at different radiation dose. Intensity of 3400-3100 cm⁻¹ 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.

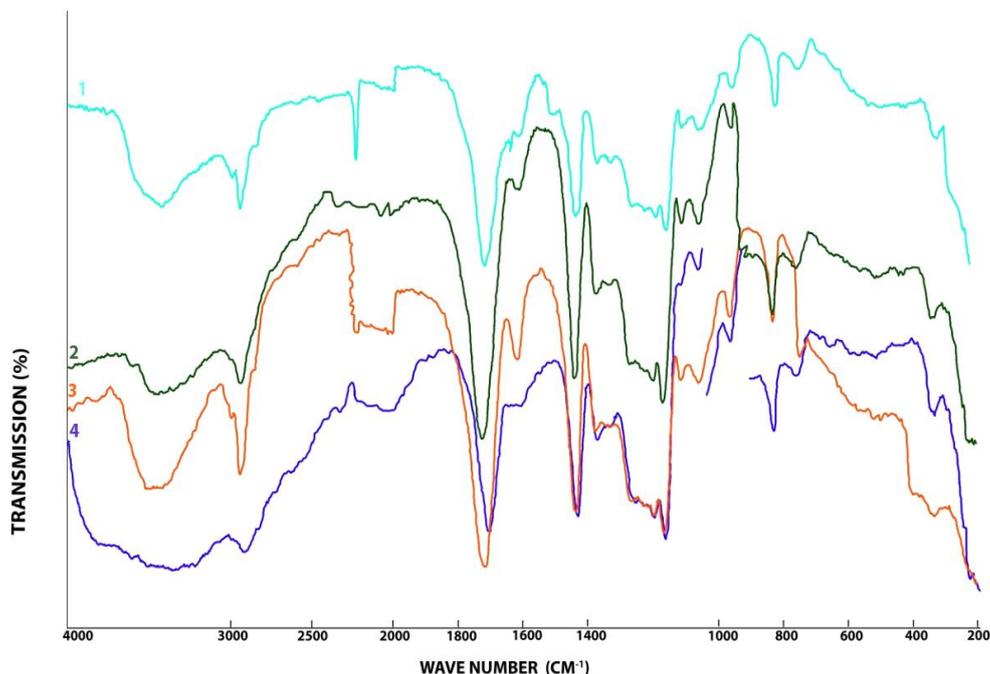


Figure 6: FTIR spectra of irradiated and aged AM₁ Copolymer
 Curve 1: 24 hours Curve 2: 48 hours Curve 3: 72 hours Curve 4: 120 hours

FTIR spectra of irradiated and aged AM₁ Copolymer are as shown in Fig 6.

Curves 1, 2, 3 and 4 represent the spectra of irradiated AM₁ 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⁻¹ absorption bands of irradiated and aged FTIR spectra.

REFERENCES

- [1] Throat BH, Prabhu CS, Suresh Kumar K, Pandhya MV. Gamma Ray induced Degradation in Ethylene – Propylene Copolymer. J. Appl. Polym. Sci. 1996; 59:1769.
- [2] Hill DJT, Lang AP, O'Donnell JH, Pomery P. The effects of gamma radiation on Copolymers of Styrene and Acrylonitrile. J. Polym. Degrad. Stab. 1992; 38(3): 209.
- [3] Alexander P, Charlesby A, Ross M. The degradation of Solid Poly (methylmethacrylate) By ionizing Radiation. Proc. Phy. Soc A. 1954; 223:392.
- [4] Busfield WK, O'Donnell JH. Radiation degradation of Poly (Styrene-co- methylmethacrylate) 2. Protective effects of Styrene on Votale products chain scission and flexural strength. Polymer 1982; 23: 431.
- [5] Parkinson WW, Bopp CD, White JE. A Comparison of fast Neutron and γ -irradiation of Polystyrene I. Cross-linkingrates. J. Phys. Chem. 1965; 69(3): 827.
- [6] Chen H, Qu RJ, Liang Y, Wang CG. Kinetic of diffusion in Polyacrylonitrile fiber formation. J. Appl. Polym. Sci. 2005; 96: 1529.
- [7] Nuguyen TQ, Kaush HH, Jud K, Detternmaier M. Cracking – healing in Cross linked Styrene-co-acrylonitrile. Polymer 1982; 23: 1305.
- [8] Sanjeeva Rao B, Srinivasa Rao N, Suresh Babu B, Papi Reddy M.Characterization and Gamma irradiated ME-EMA Copolymer by ESR and FTIR Techniques. J. Polym. Comp. 2016; 4(3): 40-44.
- [9] Hill DJT, Lang AP, O'Donnell JH, Pomery P. The effects of Gamma Radiation Polyacrylonitrile. J. Polym. Degrad. Stab. 1992; 38(3): 193.
- [10] Shashidhar GVS. Ph.D. Thesis. Synthesis and Characterization of some Copolymers.Kakatiya University, Warangal 1989.
- [11] Ramakrishna Murthy M., Sanjeeva Rao B. Computer simulated ESR Spectra od Irradiated polyoefin oxides- effect of glass transition temperature. J. Polym. Sci B. 1990; 28(2): 133-138.
- [12] Sanjeeva Rao B, Sudersanna Reddy Y, Subbarami Reddy N, Fasiul Hasan Md. Electron Spin Resonance study gamma irradiated Poly (metha acrylic acid).J. Polym. Sci B. 1994; 34: 1789.
- [13] Madhukar K, Sainath AVS, Biksamaiah N, Srinivasa Rao Y, Babu NM, Ashok B. Thermal properties of single walled carbon nanotubes composite of the Polymaide6/Poly (methyl methacrylate) blends system.J. Therm. Eng. Sci. 2014; 53(2): 397.
- [14] Nirav Gupta, Roopali Rai, Arun Sikder Sangita Nandi, Akhilsh Tanwer, Rukimini Khatokar, Stephen D. Pask, Susanta Mitra. Design and Development of Poly (acrylonitrile-co-methylmethacrylate) Copolymer to improve viscoelastic and Surface properties Critical to Scratch Resistance (ID: RA-ART-10-2015-022264).Electronic Supplementary Material (ESI) for RSC Advance. J. Roy. Soc. Che. 2016.