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Quantitative analysis of FTIR Spectra of Acrylinitrile (AN) Methacrylate (MA) Copolymer

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ABSTRACT - FTIR spectroscopy is considered to be finger print technique to identify chemical structures of polymer. To prove this, FTIR spectra of unirradiated and irradiated ANMA are recorded under different conditions. The spectra show finger print absorption bands corresponding to both acrylonitrile and methacrylate groups. Radiation dose dependency on chemical structure of ANMA copolymer has been investigated by recording FTIR spectra at various radiation doses. Changes in intensity of some absorption bands are observed. Double integration methods are used to quantity the results. Based on the results chemical changes induced by gamma irradiation are identified.

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

I. INTRODUCTION

Reactivity ratios for the homogeneous free radical initiated copolymerization of acrylonitrile and methyl acrylate were measured by NMR and FTIR techniques. For this purpose azobisisobutyronitrile (AIBN) is used as initiator in dimethyl form amide (DMF) at 62°C. The FTIR technique allowed rapid generation of extensive copolymer compositions,. The, reactivity ratios were determined to be 1.29 ± 0.2 and 0.96 ±0.2 for acrylonitrile and methyl acrylate, respectively. The results are useful for the development of acrylonitrile (<90%) melt process able copolymer fibres and films, which could include precursors for carbon fibres (1).

Poly (acrylonitrile-co-methyl methacrylate), p (AN-co-MMA) copolymers were synthesized in DMF solution using AIBN as initiator and reaction was carried out at 90ºC for 5 hours. A yellow polymer solution was obtained which was precipitated in a large excess of water-methanol, filtered, washed with excess of water to remove unreached products and dried to a constant weight. Reaction scheme for the synthesis of p (AN-co-MMA) copolymer was proposed (2).

Several acrylonitrile (AN)copolymers were synthesized with co monomers (AN/M), such as methyl acrylate(MA), vinyl acetate (VAc) and acrylamide (AM) by aqueous precipitation. The copolymers were characterized by using Fourier transform infrared spectroscopy, nuclear magnetic resonance (1H NMR), differential scanning calorimetry, thermogravimetry (TG) and X-ray diffraction (XRD) analyses. 1H NMR studies revealed that the compositions of AN/MA agreed best with the feed molar ratios. Differential scanning calorimetry (DSC), thermogravimetry (TG) and X-ray diffraction (XRD) results showed that the effect on delaying cyclization reactions, depression of melting points and crystallinities, all ranged in the order MA > VAc > AM for various types of co monomers. With co monomer contents increasing, it was interesting to note that the decomposition temperature of AN/MA shifts continuously to higher temperatures. With increased co monomer content, the decomposition temperature of AN/VAc is initially increased and then decreased. For AN/AM, it shows an opposite trend to that of AN/VAc. Incorporating 15 mol% of MA, melting peak value (Tm) and crystallinity of the AN/MA drop to the lowest values of 174°C and 18.5%, respectively. The decomposition peak value (Td) of AN/MA with the feed molar ratio of 85/15 increases to 321°C. There is awider window of 147°C for melt processing of AN/MA. It is concluded that MA is the most suitable co monomer for enhancing the melt processing of PAN based copolymers (3).

Infrared resonance (IR) spectra of polystyrene (PST), polymethyl methacrylate (PMMA), polyacrylonitrile (PAN) and their co-mixtures were performed. Through this study the absorption peak area to weight ratios as well as

working curves were obtained to test for their reliability as well as their suitability. Satisfactory results were achieved and these working curves were then used to measure the polymerized components of binary and ternary co-polymers. By investigating the acquired data we conclude that the monomer prefers proposed in this work (4-6). Gamma irradiation effects in acrylonitrile ethyl methacrylate copolymer and acrylonitrile methacrylate copolymer have been investigated by ESR, FTIR, DSC techniques (7, 8).

II. 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 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 (9).

Table 1: AM Copolymers used in the present studies

Designation of Copolymer	Mole fraction of AN	Mole fraction of MA	Glass transition Temperature (^oC)	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

III. RESULTS AND DISCUSSION

FTIR spectra of unirradiated and irradiated AM_1 are as shown in Fig 5. Curve 1 corresponds to unirradiated Copolymers; while Curves 2, 3, 4, 5 and 6 correspond to the FTIR spectra of AM_1 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.

On irradiation intensities of some of the absorption bands is found to vary with radiation dose. Double integration methods are used to measure to calculate intensities of the bands (11-13). As these bands are assigned to chemical groups present in the co polymer, these groups are expected to be effected by gamma irradiation. As such intensity variation of 3400
3100,2980,2240,1720,1620,1450,1200,1170,1120, 1070, 990,840 and 760 Cm^{-1} absorption bands with radiation dose are as depicted in histograms shown as Fig2,Fig3,Fig 4, Fig5, Fig 6, Fig7, Fig8, Fig9, fig 10 Fig11,Fig 12,Fig13 and Fig14. Therefore these chemical groups are thought to be influenced by gamma irradiation. The main event of gamma irradiation are cleavage of inter molecular bonding, cleavage of carbonyl groups and change in bond position of some of the absorption bands.

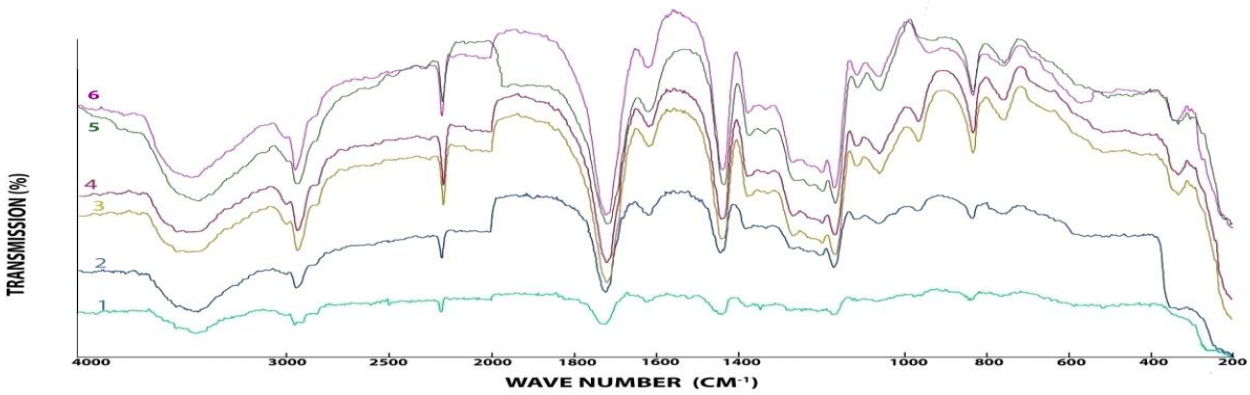

Figure1: FTIR spectra of irradiation ANMA copolymer at different doses.
Curve 1: Unirradiated Curve 2: 7.0 M rad Curve 3: 14.0 M rad
Curve 4: 3.5 M rad Curve 5: 10.5 M rad Curve 6: 17.5 M rad

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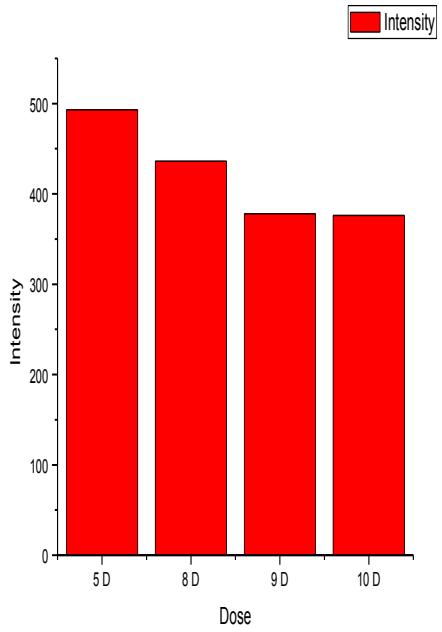

Figure2: Intensity radiation of 3400cm^{-1} Absorption bandwidth radiation dose.

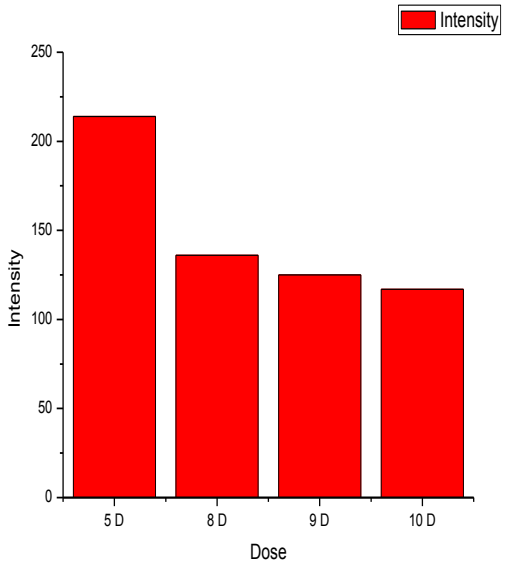

Figure3: Intensity radiation of 2980cm^{-1} Absorption bandwidth radiation dose.

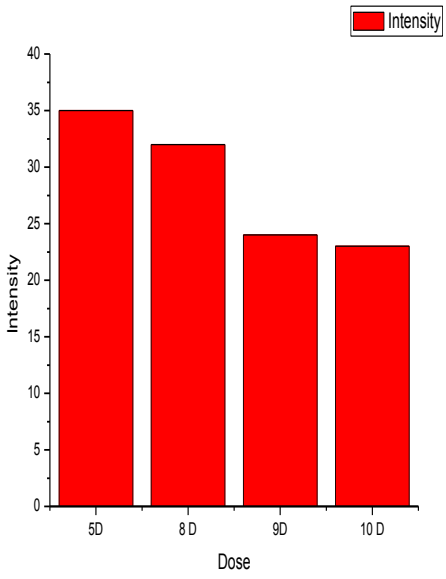

Figure4: Intensity radiation of 2240 cm^{-1} Absorption bandwidth radiation dose.

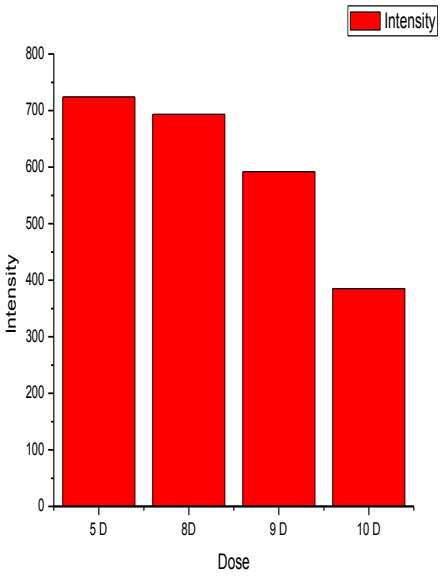

Figure5: Intensity radiation of 1730cm^{-1} Absorption bandwidth radiation dose.

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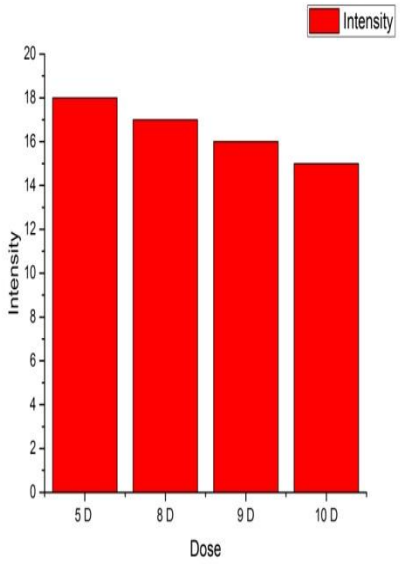

Figure6: Intensity radiation of 1620 cm^{-1} Absorption bandwidth radiation dose.

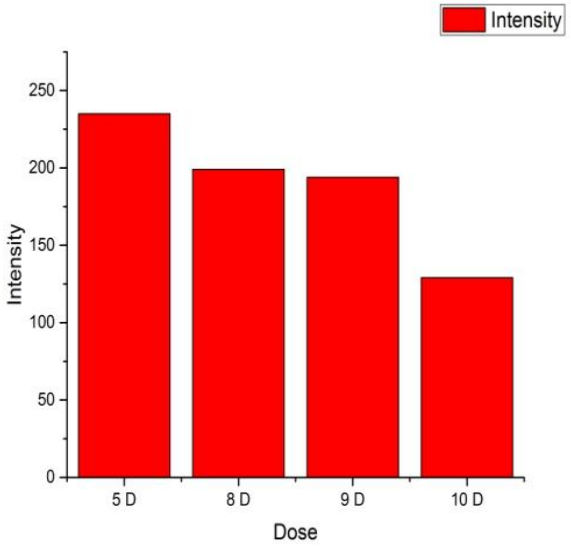

Figure7: Intensity radiation of 1450cm^{-1} Absorption bandwidth radiation dose.

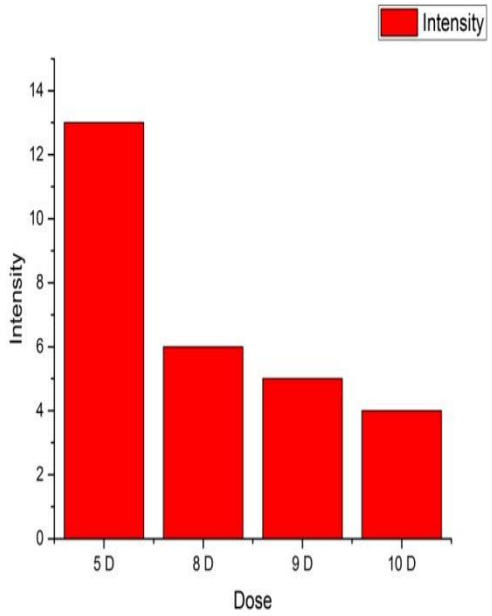

Figure8: Intensity radiation of 1200 cm^{-1} absorption bandwidth radiation dose.

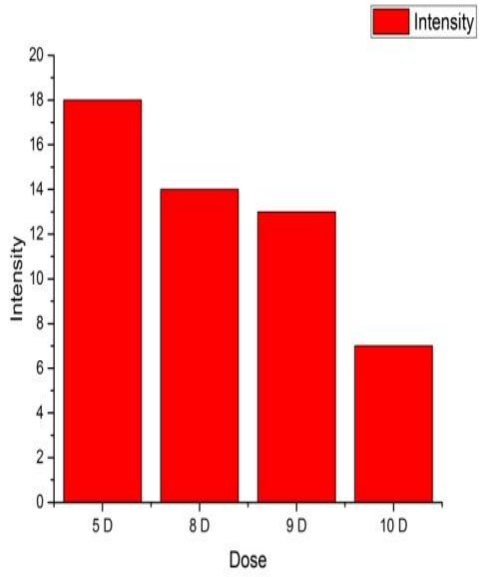

Figure9: Intensity radiation of 1170cm^{-1} Absorption bandwidth radiation dose.

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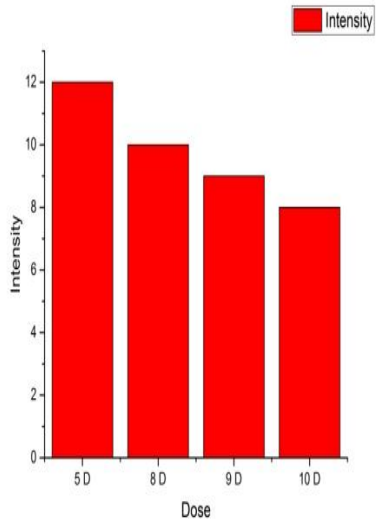

Figure10: Intensity radiation of 1120 cm^{-1} absorption bandwidth radiation dose.

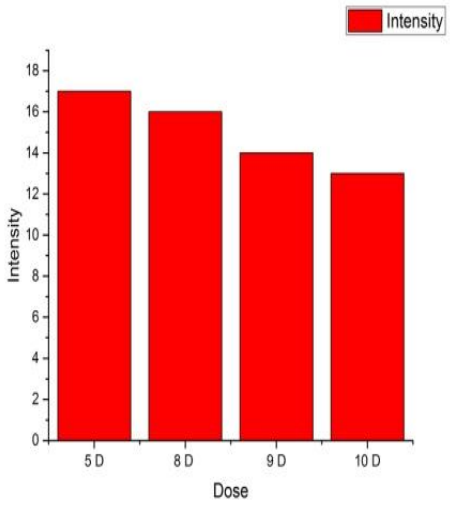

Figure11: Intensity radiation of 1070cm^{-1} Absorption bandwidth radiation dose.

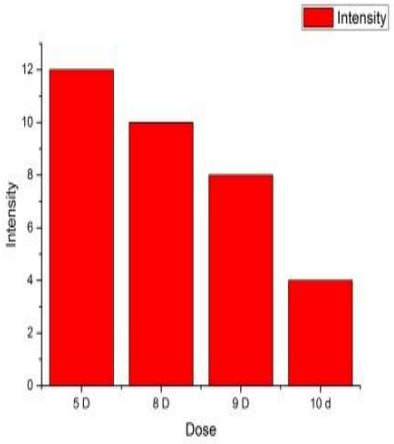

Figure12: Intensity radiation of 990 cm^{-1} absorption bandwidth radiation dose.

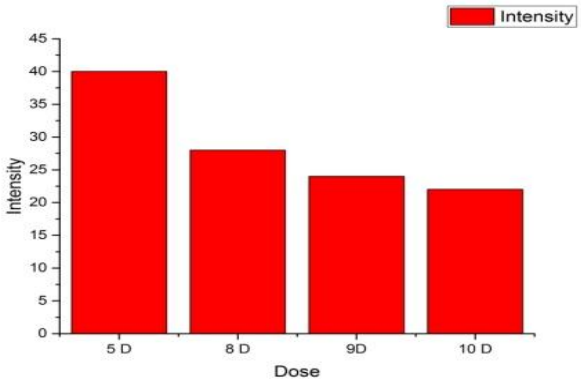

Figure13: Intensity radiation of 840cm^{-1} absorption bandwidth radiation dose.

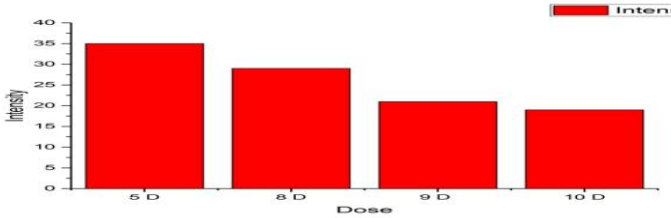

Figure14: Intensity radiation of 760cm^{-1} absorption bandwidth radiation dose.

V. CONCLUSION

In conclusion FTIR spectra are used to ascertain chemical changes induced by gamma irradiation. Quantitative methods are used to measure concentration of chemical groups of copolymer under different conditions. Based on the results it is proved that FTIR technique can be effectively used to identify chemical changes induced by gamma irradiation.

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