A STUDY ON PHOTO DEGRADATION OF POLY (ACRYL AMIDE)

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ABSTRACT

Photo degradation of commercial plastics is always a point of technical and scientific interest. Poly acrylics are important class of polymers finding applications as paints and colors. During the course applications, they have been subjected to sun light and undergo photo degradation process. Due to photo degradation, many changes like color decrease of mechanical durability occurs. Therefore study on these processes is needed. In the present studies the authors investigated photo degradation process in polyacrylamide(PAM) using electron spin resonance (ESR) spectroscopy. ESR spectra of photo degraded PAM show ill-resolved hyperfine structure at the wings; while the central part is clear. Free radicals responsible for spectra are identified. Temperature radiation dose dependent ESR spectra are recorded and spectral changes are explained. Block analysis is applied to evaluate activation energy associated with free radical decay. Radiation dose dependency of free radical formation is also studied by recording ESR spectra at different radiation doses. FTIR spectra of non-irradiated and irradiated PAM are compared. The spectra show three important groups of vibrational bands 3400 – 3000 cm^{-1} region corresponding to symmetric and asymmetric N – H vibrations, 1600 cm^{-1} band corresponding to amide carbonyl (C = O) band and CH_2 , CH vibrations at 2900, 2800,1250,1080cm^{-1} positions. Due to irradiation reduction intensity of 3400-3000 cm^{-1} and 1620 cm^{-1} absorption bands is observed indicating reduction in intensity of N-H and C = O groups on irradiation.

Keywords: Poly acryl amide (PAM), Photo degradation, ESR spectra, radiation dose, free radical decay, Bloch analysis.

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INTRODUCTION

Polyacrylamide (PAM) is water soluble polymer used as floccutlant in water purification technologiesEffect of different types of radiation on PAAm have reported in literature. Ueda and Kuri (1,) have reportedon polymerization processes in acryl amide polymer. Photo degradation of PAM has been reported by Ramelow and Baysal(2) and they have reported on resultant processes. Gamma irradiation studies of polyacrylamide have been reported by SanjeevaRao et al (3) using electron spin resonance (ESR) spectroscopy. The ESR spectrum at RT is a triplet but at low temperatures a quintet like structure is observed. Both the spectra are attributed to the same free radicals, with inter-convertible forms and cause different resonances. Besides of this radical another radical giving singlet spectrum is also to be present (3). Srinivas et al (4) have reported on thetemperature dependent ESR spectra of gamma irradiated PAM and proposed that the observed quintet is to be due to macro-radicals, which has four interacting beta protons. These authors have evaluated the activation energy associated with the decay of free radicals. These authors have used Bloch analysis to evaluate activation energy associated with free radical decay. Gamma irradiation effects in PAM have been reported by Srinivas using ESR, FTIR, DSC and SEM techniques. The studies suggest the presencecharacteristicFTIR absorption band of N-H stretching and bending vibrations (3400 – 3000 cm^{-1}) and amide carbonyl vibrations(1650 – 1600 cm^{-1}), which were influenced by gamma irradiation. ESR studies indicate the presence macro radicals of the type $– CH_2 – C (CONH_2) – CH_2 –$ at room temperature. On annealing the free radicals decay below the glass transition temperature (4). DSC data also confirmed the results.

Caulfield etal (5) have reported on photo degradation (Light of 254 nm Wavelength) and stability of linear PAMby measuring different solution properties like viscosity. Up on irradiation decrease in viscosity is observed. The results suggest that small amounts of monomer (AM) were released during the photolysis. It is further reported that degradation polymerdoes not takes place by unzipping of molecular chains: instead it is chain scission process. Xiong et al (6) Mechanical degradation of polyacrylamide during hydraulic fracturing causes changes in size of the polymer. This will lead to the formation of smaller fragments. IR spectra of irradiated PA-PAM copolymer was reported by Moharram (7). FIIR spectra of the copolymer exhibited absorption bands corresponding to both polyacrylamide and poly acrylic acid. Shivanathan et al have (8)reported on structural investigations of gamma-irradiated polyacrylamide hydrogels using small-angle neutron scattering and ultraviolet–visible spectroscopy experimental methods.

Similarly catalytic degradation of PAM has been reported by Yang et al (9). Thermal degradation of soft PAM hydrogels(10) and photo chemical degradation has been reported(11) Kinetic study of photo chemical oxidation of PAMhas been reported (12)Though gamma irradiation effects on PAM are reported in literature,there is a need to probe photo degradation of PAM under different conditions. The authors made an attempt in this regard with ESR, FTIR, DSC and XRD as experimental techniques.

EXPERIMENTAL

Polyacrylamide (PAM) in the form of powder has been supplied by CDH laboratories, New Delhi. Photo degradation of PAM has been carried out by UV lamp with a power of 1m W. The samples are exposed to different time intervals. For the irradiated samples ESR spectra have been recorded under different conditions on JEOL spectrometer at X band frequencies and 100 KHz modulation.Un- irradiated PAM has not shown any ESR signal indicating free radicals are absent in it. FTIR spectra of Un- irradiated and irradiated PAM are recorded for pellets containing with KBr.

RESULTS AND DISCUSSION

Since ESR spectroscopy is useful in detection of free radicals formed on irradiation of PAM, the spectra are recorded under two different conditions. They are i) radiation dose dependency and ii) temperature dependency

i) **Dose dependency** :

Exposure of PAM to 1hr of UV light results in the ESR spectrum as shown in curve1 Fig1. The central part of spectrum is appeared to have doublet shape with some structures in the wings. Intensity of the spectrum gradually increased with dose of irradiation. Further the spectrum at higher doses has more resolved structure than the spectrum at low doses. Variation of ESR intensity against radiation dose is as shown in Fig2

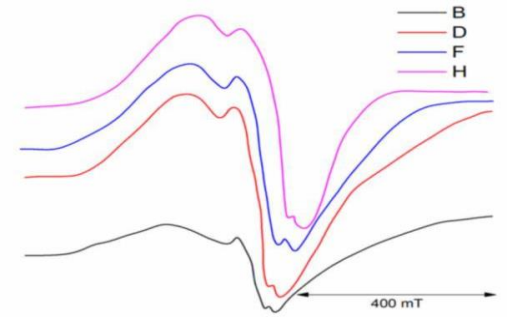

Figure 1: Dose dependent ESR spectra of irradiated Polyacrylamide

The graph suggests that variation is not linear in case of photo degradation. This is due to the fact that in low dose irradiated polymers chain cleavages are lesser producing low intense spectrum while at high doses chain scissions cumulatively increase producing high intense spectra.

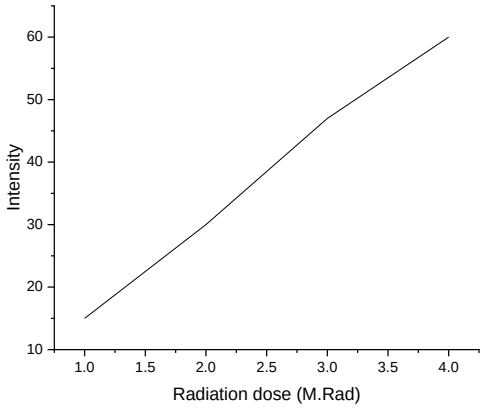

Figure2: Variation of ESR Intensity against radiation dose

ii) **Temperature dependency**: To study the effect of annealing on free radical behavior, ESR spectra are recorded as shown in Fig 3.

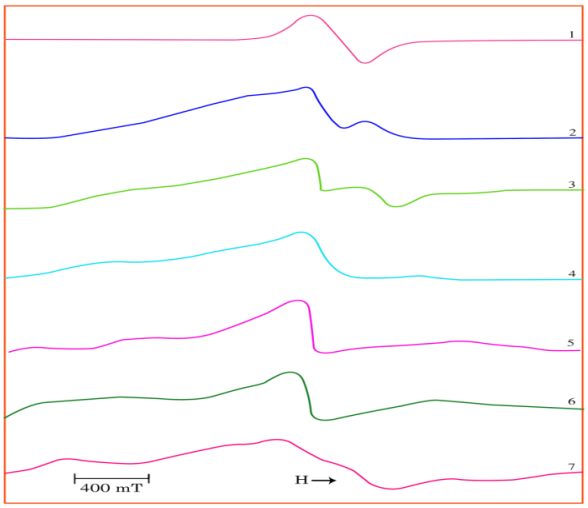

Figure 3: Temperature dependent ESR spectra of irradiated PAM
Curve 1: 300K, Curve2: 330K, Curve3: 350K, Curve4: 370K,
Curve5: 390K , Curve6: 400K Curve7: 405K

Computer simulations

ESR spectra of photo degraded PAM is appeared to have three central lines together with two hidden lines in the wings with total number of hyperfine lines being five. Intensity distribution and line separation of the spectrum is indicative of anisotropic interactions and presence of more than one free radical species. Gamma irradiated PAM is reported give triplet spectrum with splitting of 20 G at RT and quintet spectrum at LNT. The spectra are assigned to $CH_2 – C = O$(I) and $CH_2 – C (CONH_2) – CH_2$ (II) free radicals. With two protons in beta position the triplet spectrum at RT and four protons in beta position, which cause quintet spectrum in case of II at LNT is expected. While the spectrum observed in case of Photo degraded PAM has a distinct shape. Efforts have been made to analyze spectrum by computer simulation technique (14). The studies the presence of macro radicals observed earlier (15) but with different magnetic parameters as listed in table 1. The component quintet shown in Fig 2 together with component singlet shown as Fig 2 result in the experimental spectrum at RT. The magnetic parameters (listed in table 1)suggest the presence of $– CH_2 – C (CONH_2) – CH_2 –$ radicals. The value ofni = 2 suggest that the protons present in amide group will also participate in hyperfine interactions in addition to the four beta protons participating in hyperfine interactions. Component spectra are as shown in Fig 3. Curve 1 is component multiplet and curve 2 is singlet

Table 1 Magnetic Parameters of Photo degraded PAM

S. No	Relative Intensity	Line width	Centre of spectrum	Hyperfine splitting	n_i	m_i
1	10	10	32320	25	2	4

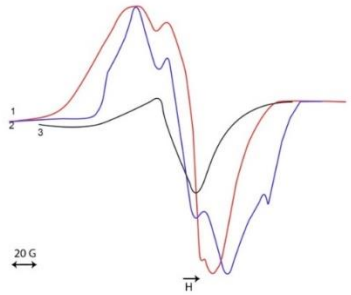

Figure4: Component spectra of irradiated PAM

Curve1 Experimental, Curve 2 Component Multplet, Curve3 difference singlet

Bloch analysis:

Bloch analysis is used to nature of free radical decay and evaluation activation energy associated with free radical decay (4). Using the line widths at different temperatures, plot of 1 /T against Log ($1/\tau$) is plotted as shown in Fig 5. The parameters used in Bloch analysis are given in table2. The activation energy for PAM is estimated to be around 30 KJ/ mole.

Table2: Bloch analysis of PAM

S.No	Temp K	1/T x 10^{-3}	Line width	τ	$1/\tau$	$\log(1/\tau)$
1	310	3.22	10.5			
2	330	3.03	10	0.0069	152.89	2.184
3	350	2.85	9.4	0.0081	130.13	2.114
4	370	2.70	8.9	0.0093	120.59	2.081
5	390	2.56	8.3	0.0117	109.47	2.039
6	400	2.5	7.7	0.01609	98.71	1.994
7	405	2.46	7.2	0.01985	96.44	1.984

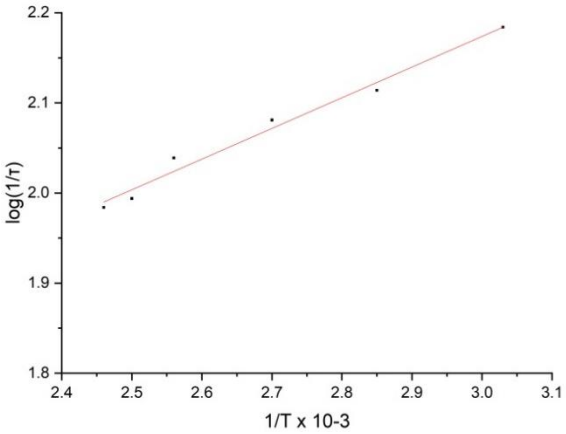

Figure5: Plot of 1/T x10^{-3} against $\log(1/\tau)$

FTIR Spectra:

FTIR data (listed in table 3) is used to identify changes induced by gamma irradiation on chemical structure of PAM. As such the absorption bands of un - irradiated and irradiated PAM are recorded and compared as shown in Fig 6. The absorption bands can be broadly classified into three categories. The first category is in the wave length region of 3400 – 3000 cm^{-1} assigned to symmetric N –H (3250) and asymmetric N – H stretching (3150) vibrations(16). In addition to this, hydrogen bonding existing between C = O and N – H groups of adjacent chains of PAM also show absorption in this region (17). AS a result a broad absorption band is noticed in the wave length region of 3400-3000 cm^{-1}. Such type of broad absorption is also reported previously for gelatins (18, 19) and several copolymers (20).

Table 3: FTIR Absorption Bands of irradiated PAM

S. No	**absorption band cm^{-1}**	**Intensity**	**Band Assignment**
1	(3356)3429- 3000/ 3288	Strong/ broad	NH/NH_2Vibrations
2	3150	Weak	NH_2 NH
3	(2936) / 2800	Strong	CH_2 /CH_3 Vibrations
4	(1720-1500) / 1800	Weak	CH_3/ CH_2 Vibrations / carbonyl
5	1408 / 1350/ 1325/ (1350)	Medium	CH_2 Vibrations
6	1240/ 1119/ 800 (1150)	Medium	CH_3/ CHVibrations
	Bands given in bracket are reported	Bands without brackets are redrawn figure	

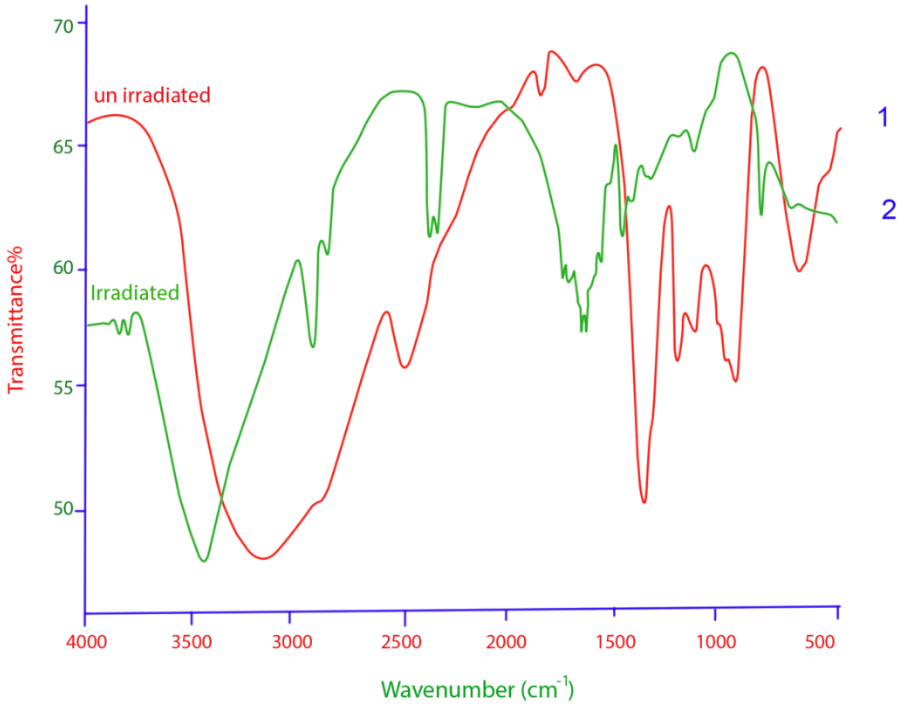

Figure6: FTIR of Un/irradiated PAM

XRD Studies:

X ray diffractogram of PAM show broad peak centered around 2 $\boldsymbol{\theta}$ = 8° and a broad peak centered on 2$\boldsymbol{\theta}$ = 20°. Efforts have been made to separate the peaks by deconvolution methods described (21). Two peaks resolved are as shown in figure7 and 8. The peaks are similar to the observed earlier (XRD ref) and suggest amorphous nature of polymer. Pam is amorphous polymer and hence does not show well defined peaks. The parameters used to simulate the XRD peaks as given in the Table4.

Table4: Deconvolution parameters used in XRD analysis

S.No	Condition of recording	a_i		Y_{max}		X_{OI} (deg)	
1	Irradiated	2	8	3.5	8	7	18
2	Non Irradiated	1.5	6,5	4.5	10	8	20

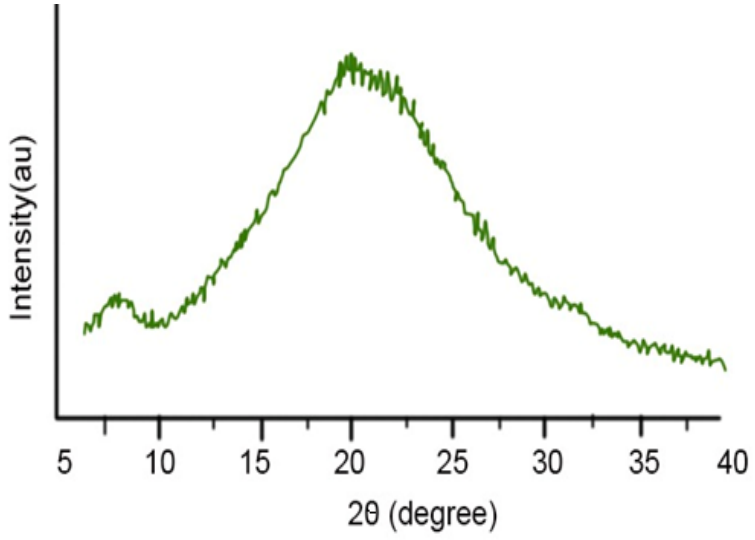

Figure7: XRD of PAM

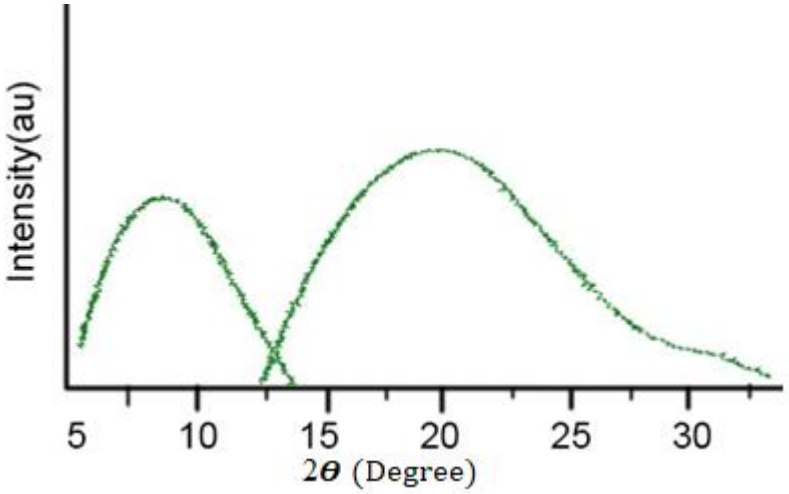

Figure8: Deconovelutionof XRD peaks.2$\boldsymbol{\theta}$ (Degree)

DSC Studies of PAM: Differential scanning calorimetry is used to investigate effect of photo degradation on thermal properties of PAM, Un-irradiated PAM show first order Transition around 145°C and exothermal peaks at 165° C.On irradiation the first order peak shifted to 135° C; while exothermic peak shifted to 145° C. PAM exhibited peculiar glass transition behavior due to presence water present in it and the Tg values reported in literature varied in the range of 120° C – 180° C (22). Further presence water in polymer matrix promotes relaxation translation behavior (18). Therefore presence both first orders shift as well as exothermic peak are thought to be associated with glass transition behavior of the polymer. On irradiation both the peaks have shifted to low temperatures as expected.

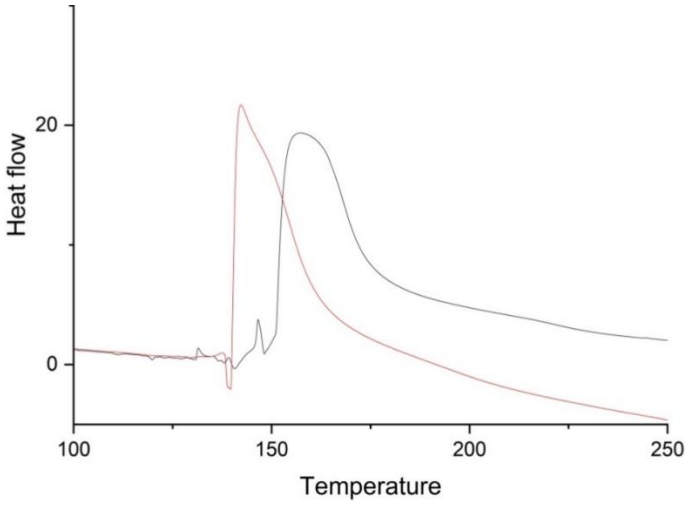

Figure9: DSC theromograms of PAM.

Conclusion:

In conclusion photo degradation of PAM alters chemical structure forming macro radicals giving ESR quintet spectrum. The spectrum is analyzed by computer simulations suggesting formation of macro-radicals. FTIR studies suggest reduction in concentration of N – H and C = O groups. DSC studies indicate the shift of glass transition temperature on irradiation.

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