Dosimetric Evaluation And Radiation Induced Structural Change In Polymer Based Radiochromic Film

Dr. Muhammad Attique Khan Shahid[1], Arfa Mubashir[1*], Madeeha Mubashir[2] and Bushra Bashir[1]

1. Department of Physics, G.C. University, Faisalabad, Punjab, **PAKISTAN**
2. Department of Chemistry, G.C. University, Faisalabad, Punjab, **PAKISTAN**

Email: arfamubashir@gmail.com

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ABSTRACT

Polyvinyl-alcohol based reactive yellow 145-A films (PVA-Y) were irradiated by Cs^{137} γ-source in the range of 200 Gy-10^5 Gy. The effects of gamma irradiation on optical and mechanical properties of PVA-Y were studied using spectrophotometry and x-ray diffraction (XRD) technique to check its feasibility in radiation processing. The found values of the $λ_{max}$ and the molar extinction coefficient of the dye were 418 nm and 78 $Lgm^{-1}mm^{-1}$ respectively. Parameters such as effect of dye concentration and pH values, Electrical Conductivity, % decoloration, Strain , % crystallinity, crystallinity Index (C.I.) and crystallite size (d) have been selected for the dosimetric and mechanical strength evaluation. Linearity between specific absorbance and absorbed dose showed that PVA-Y films can be best chemical dosimeter in two different ranges i.e., 200 Gy-1 kGy and 10 kGy-100 kGy. At high dose 80-100 kGy of gamma irradiation, change in mechanical strength was found due to decrease in crystallinity, crystallite size and increase in strain values.

Keywords: Polyvinyl Alcohol, Reactive Yellow 145-A, gamma irradiation, Specific Absorbance, XRD, Crystallinity.

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INTRODUCTION

The chemical, biological and physical effects of radiation on materials are scientific establishment of the radiation technology [7]. A systematic attempt to measure such radiations is known as dosimetry and has become an active research area for scientists of the present era. One of the most effective and economical attempt of the researchers to design, manipulate, fabricate or to develop dosimeters in chemical dosimetry was to use dyes in form of their solutions[3], gels [4] or films [1,2]. Radiochromic films instantly changes color upon exposure to ionizing radiation and needs no chemical or physical process. Radiochromic dosimeters are prepared using different natural or artificial dyes and polymer materials. Artificial dyes are preferable over natural dyes due to their tincture strength, vast color range and good fastness properties, mainly, to ultraviolet light and different chemical and detergents. The first and foremost step to check the confirmation of the dosimetric calculations of any proposed material is Beer's Law which is related to the

absorption of light (A) with respect to the concentration(c) of dye present in solution and the thickness of material(l) as given by following equation 1.

$$A = \varepsilon c l \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where ε is a constant known as molar extinction coefficient.

The dosimetric response of reactive yellow in aqueous solutions has been determined [5] in the range limit of 0 Gy-100kGy, present study aims at to check out its response in PVA films. Moreover the use of high-energy radiation incident on polymer films may support the development of mechanically strong polymers [9]. One of the resulting processes of radiation interaction in polymers is cross linking which usually enhance the mechanical strength, environmental stability and radiation stability [15]. In order to check such changes, the calculations were made from continuous scans obtained from XRD; a best technique to study such mechanical changes along with the crystallinity and grain size of the sample under observation for dosimetric calculations. The overall objective of this work is to check for reactive yellow 145-A to respond to Gamma radiation as a dosimeter. Furthermore, the mechanical properties and morphological features will be obtained for un-irradiated and irradiated PVA-Y films using XRD to understand the overall effect of irradiation on the sample. The molecular structure of reactive yellow 145-A is shown in figure 1.
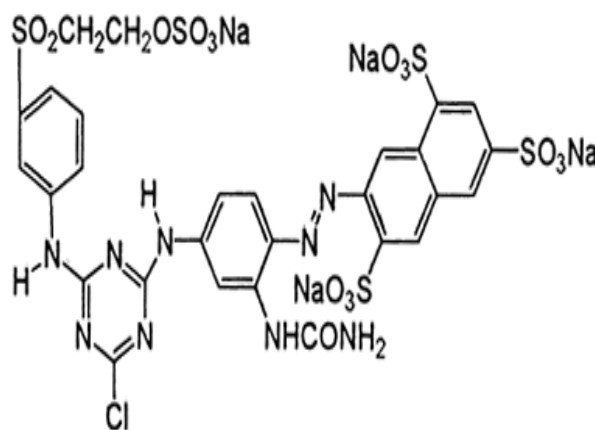
Figure 1. Molecular structure of reactive yellow 145-A

MATERIALS AND METHODS

Films were prepared by adding 3g of PVA in 50 ml distilled water [12] and was kept well stirred at a temperature of 60^0C followed by continuous stirring for 1hr at room temperature to make a homogeneous mixture. Three concentrations i.e., 1g L^{-1}, 0.5g L^{-1} and 0.25g L^{-1} of dye was dissolved in PVA solution until the formation of a uniform dyed solution [13]. pH of PVA-Y solutions was adjusted with the help of NaOH and HCl to get the samples of three different chemical natures i.e., acidic, alkaline and neutral (measured by pH-meter (3510 pH-meter (Jenway)) [11]. Electrical conductivity (EC) of all acidic and alkaline solutions was also measured using EC meter (KL-1388) which was found to be 1100μScm^{-1} and 1330 μScm^{-1} respectively. 0.5ml PVA-Y dyed solution was poured every time on a perfectly leveled horizontal glass plate for casting of film and let it to be dried for almost 48 hrs at room temperature. Uniform films having thickness of 0.03mm were obtained after detaching from glass plate, were stored at room temperature in dark, sealed in small dark plastic bags and stored under 1aboratory condition for further investigations [6]. Irradiation was carried out with the Mark-IV irradiator (Cs^{137}gamma ray source) having dose rate of 660Gy/h, confirmed by Fricke reference standard dosimeter prior to every run of film

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irradiation [8]. Range of dosimetry was characterized as low dosimetry (0-1 kGy), intermediate dosimetry (1-10 kGY) and high dosimetry (10-100kGY). The absorption band maxima (λ_{max}) of dye was explored using a UV/VIS spectrophotometer (Perkin Elmer Precisely Lambda 25 UV/VIS) and optical density of all films was find out at this λ_{max} for pre and post irradiation. The X-ray diffraction studies were carried out using diffractometer available at QU, Islamabad, Pakistan. % crystallanity, crystallanity index (C.I), stress and strain were calculated using following equations.

$$\% \text{ Crystallanity} = \frac{I_{max}}{I_{max}+I_{min}} \, 100 \ldots\ldots\ldots\ldots(2)$$

$$\text{Crystallanity index} = \frac{I_{max}-I_{min}}{Imax} \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\eta = \frac{Bcos\theta - K\lambda/d}{sin\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\varepsilon = \frac{Bcos\theta}{4tan\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

The working conditions of XRD used are shown in table 1.

Table 1. Working conditions of XRD

X-radiation	NI-filtered
X-ray tube voltage & current	35kV& 20mA
Divergent & Anti-scatter slits	1°
Receiving slits	0.13mm & 0.3mm
Goniometer Scanning speed/step width	$1^o min^{-1}/0.02^o$
Ratemeter time constant	1s
Detector	Scintillation counter
Start angle	^{70o}(2)
Stop angle	^{5o}(2)

RESULTS AND DISCUSSION

Spectrophotometric analysis: The spectrophotometric analysis and gamma radiation response for Reactive Yellow 145A in PVA films were studied in three phases of the dosimetry i.e., Low dosimetry (0 Gy–1 kGy), Intermediate dosimetry (1 kGy-10 kGy) and High dosimetry (10 kGy-100 kGy). Moreover, XRD technique was used in order to know the morphological changes in the films exposed to gamma radiations. Following is the scientifically and technically detailed discussion of the acquired data and the results obtained for the selected dye.

Absorption spectra of unirradiated and irradiated solutions were recorded in the range of 380-700nm. An absorption band maximum (λmax) for controlled samples was found to be 418nm. Radiation induced color changes found in PVA-Y films indicated its structural changes. To study the effect of pH on the dosimetric response of the films; two sets of the films having pH 4 and 10 were prepared and were exposed to gamma radiations. Maximum decoloration for PVA-Y films was found to be 73 % in acidic samples. %Decoloration was calculated by using following equation.

$$\% \text{ Decoloration} = \frac{A_0 - A_i}{A_0} \times 100 \ldots\ldots\ldots\ldots.(6)$$

Where A_0 and A_i are the absorbances of the dyes before and after irradiation [15].
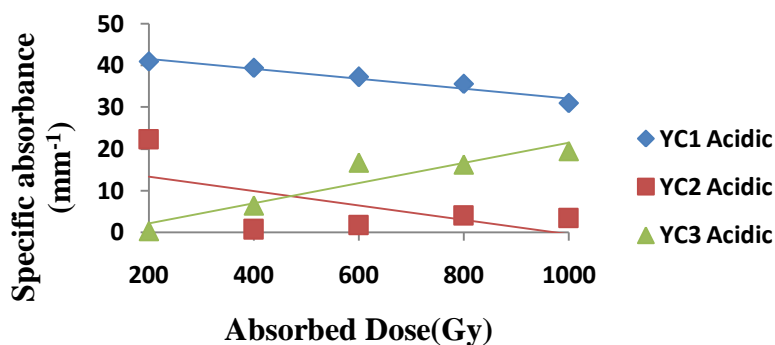
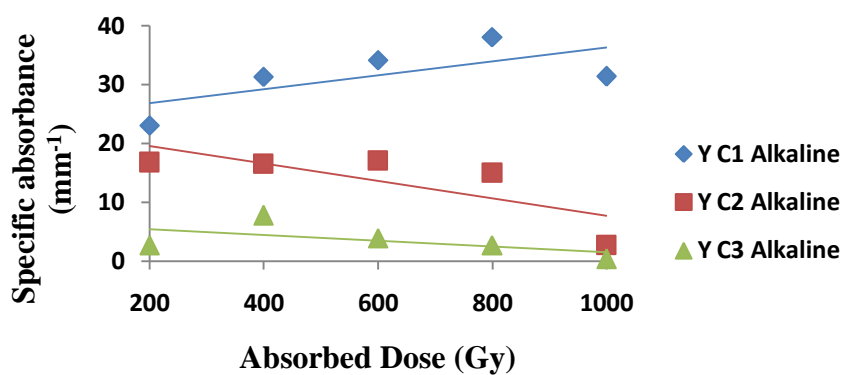**Figure 2.** The dosimetric response of PVA-Y acidic in dose range 200Gy-1kGy

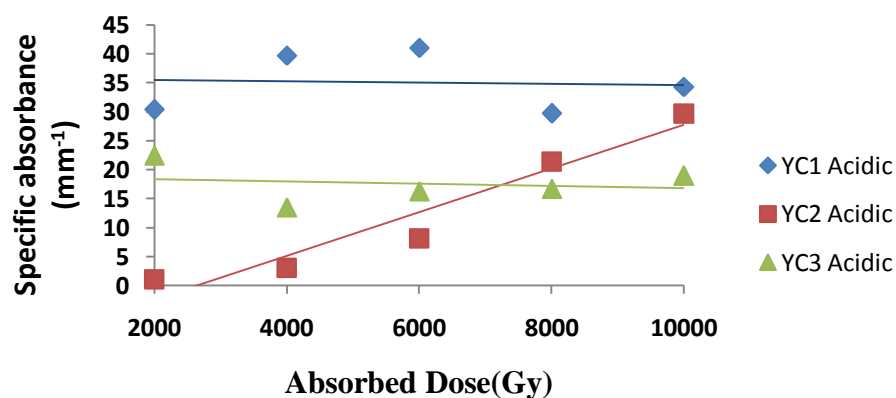**Figure 3.** The dosimetric response of PVA-Y alkaline in dose range 200Gy-1kGy

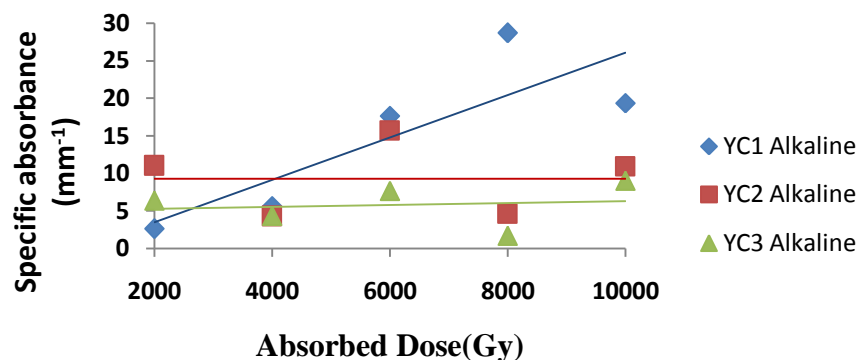**Figure 4.** The dosimetric response of PVA-Y acidic in dose range 2 kGy-10 kGy

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Figure 5. The dosimetric response of PAV-Y Alkaline in dose range 2 kGy-10 kGy
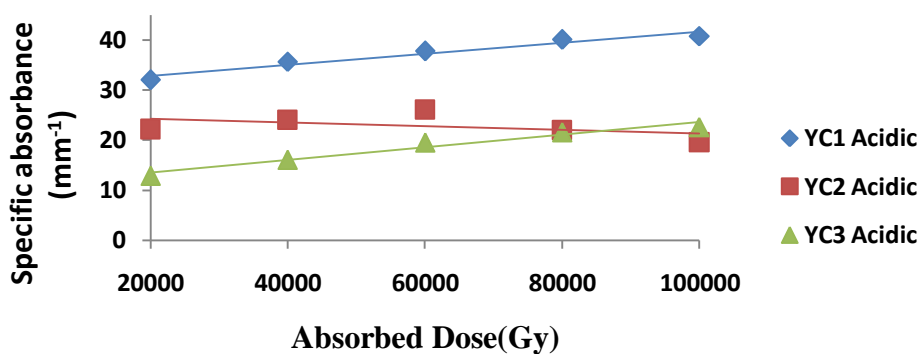

Figure 6. The dosimetric response of PVA-Y acidic in dose range 20 kGy-100 kGy

Low Dose Range: Figures 2 and 3 describe the specific absorbance at λ_{max} of irradiated acidic and alkaline films respectively, against absorbed dose 200 Gy-1 kGy. Among all acidic samples Figure 2, of reactive yellow 145 A, it was found that for low dose range specific absorbance of C_3 concentration sample increased linearly with absorbed dose providing good dosimetric response as compared to other concentrations. Among all alkaline samples Figure 3, specific absorbance of C_1 concentration satisfactorily increased linearly with absorbed dose.

Intermediate Dose Range: A deep look on Figure 4, describes that the C_1 and C_3 samples exist in saturation region however C_2 show good dosimetric response for gamma radiation. Among all alkaline samples Figure 5 of reactive yellow 145 A, it was found that for Intermediate dose range samples of C2 and C3 concentration showed slight variations in specific absorbance with respect to absorbed dose, they exist in saturation region while C_1 satisfactorily increased linearly with absorbed dose.

High Dose Range: Figures 6 and 7 shows the specific absorbance at λ_{max} of irradiated acidic and alkaline films respectively, against absorbed dose 20 kGy-100 kGy. Among acidic samples Figure 6, it was found that for high dose range specific absorbance of C1 and C3 concentration increased linearly with respect to absorbed dose providing good dosimetric response as compared to other C2 sample which was highly insensitive to gamma radiation. Figure 7, elaborates that all the alkaline PVA-Y samples show linear response with almost a negligible variation in high dosimetry phase.
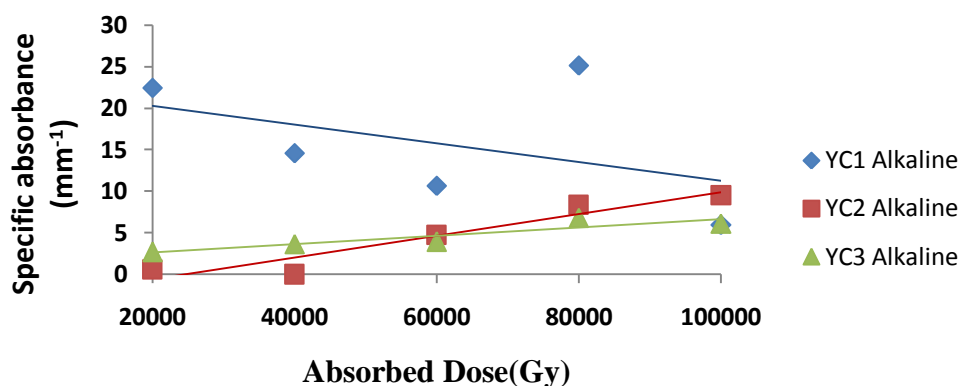
Figure 7. The dosimetric response of PVA-Y alkaline in dose range 20 kGy-100 kGy

X-ray Diffraction (XRD): X-ray diffraction (XRD) is a new technique planned to be used in routine dosimetry in order to notice the optical and structural properties of gamma irradiated PVA films, therefore, the parameters like Stress (η), Strain (ε), Modulus of Elasticity (Y), % Crystallinity, Crystallinity Index (C.I.) and Crystallite Size (d) have been selected for the dosimetric evaluation. From XRD pattern Figures 8 for PVA-Y, the crystallinity has been evaluated on behalf of the assumption that broadening of line is due to the increase in amorphousness whereas if crystallinity increases it results into the increase in peak intensity.
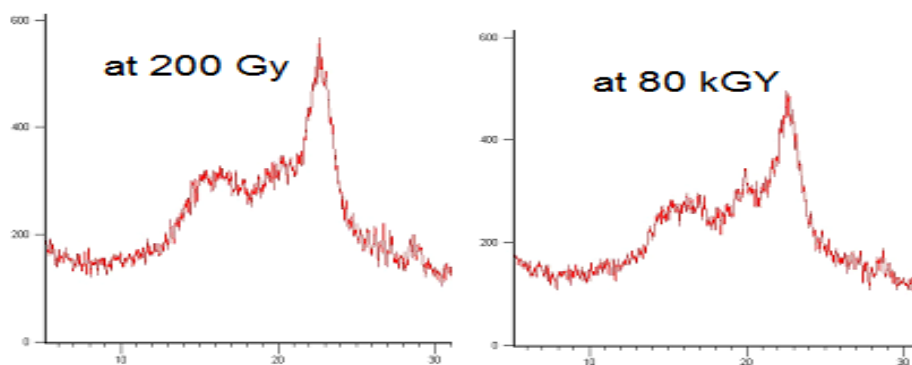

Figure 8. XRD pattern of PVA-Y at two different doses

Table 2, shows that the intensity for PVA-Y has been decreased. This decrease can be linked to the increase in the amount of amorphous phase in this material. As radiation dose increases, peaks get broadened up indicating that degree of crystallinity is decreased [10]. Following trend is observed for PVA-Y films

$$\text{Peak Intensity} \propto \% \text{ Crystallinity} \propto \text{Crystallite size} \propto \frac{1}{\text{FWHM}} \propto \frac{1}{\varepsilon}\ldots\ldots\ldots\ldots(7)$$

Where ε represents strain.

Table 2. Mechanical properties and crystallinity from XRD pattern for PVA-Y

Properties	PVA-Y	
	200 Gy	**80 kGy**
% crystallanity	64%	62%
FWHM (degrees)	2	2.25
Crystallie size d (nm)	4.6	4.0

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Stress η (Nm⁻²)	-8.6 X 10 ⁻⁸	-9.7 X 10 ⁻⁸
Strain $\mathcal{E}$	2.4	2.79
Modulus of ElasticityY (Nm⁻²)	3.5 X 10 ⁻⁸	3.4 X 10 ⁻⁸
Intensity (a.u)	575	475

APPLICATIONS

Radiochrmic film dye dosimetry is an active area of research which should be accompanied with the efforts to make it ecologically safe and less damaging for human health. By using different dose ranges and eco-friendly textile industrial procedures radiochromic film dye dosimetry can be used for proper dose delivery check up, enhancement of shelf life, sterilization and pasteurization and waste management techniques. The above said future objectives will only be achieved by getting proper knowledge of radiation protection and safety, documentation and dose assessment techniques.

CONCLUSIONS

Radiation induced color changes found in PVA-Y films indicated their structural changes. Effect of concentration, absorbed dose and pH for PVA-Y showed that both C_1 and C_3 provided good dosimetric response for low and high dose range while for intermediate dose ranges such PVA films could not provide good dosimetric responce. From XRD pattern obtained calculations for decrease in crystallinity, small crystallite size, less peak broadening and strain values in PVA-Y after gamma irradiation proved that this dosimeter has less mechanical strength as compared to unirradiated PVA-Y film.

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REFERENCES

[1]   A. Akhavan, M. Sohrabpour, & M. Sharifzadeh. *Radiation Physics and Chemistry*. **2002**, 63, 773– 775.

[2]   A. Akhavan, M. Sohrabpour, & M. Sharifzadeh. *Iranian Journal of Science & Technology,* **2007**, 31, 397-401.

[3]   M.F. Barakat, K.E. Salamawy, M.E. Banna, M. Abdel-Hamid, A.T. Abdel-Rehim ,*Radiat Phys Chem*.**2001**, 6: 129-36.

[4]   J.B. Davies, S.G. Bosi, & C. Baldock., *Radiation Physics and Chemistry*, **2012**, 81, 1263–1265.

[5]   T. Hussain, M.Y. Hussain, M. Shahbaz, Inam-ul-haq, H. Farooq, & S. Ali. *Journal of Basic & Applied Sciences*. **2012**, 8(2), 315-318.

[6]   M. Kattan, H. Alkassiri, &Y. Daher,*Applied Radiation and Isotopes*.**2011**, 69, 377–380.

[7]   H.N. Mai, N. D. Doung & T. Kojima. *Radiation Physics and Chemistry*. **2004**, 69, 439-444.

[8]   H.N. Mai, N. D. Doung & T. Kojima.,*Journal of Chemistry*. **2003,** 38, 87– 91.

[9]   S. Mishra, R. Bajpai1, R. Katare & A.K. Bajpai. *Express Polymer Letters*. **2007**, 1(7), 407–415.

[10]   N.S. Rani, J. Sannappa, T. Demappa & Mahadevaiah. *Advances in Applied Science Research*, **2013**, 4(3), 195-219.

[11]   G.E. Reynolds, A. Kovacs & J.J. Fletcher. *Radiation Physics and Chemistry*. **2007**, 76, 1519– 1522.

[12]   M.A.K. Shahid, N. Kousar, N. Akhtar, T. Hussain, M.S. Awan, A. Mubashir, B. Bashir B, A. Javed. *J.Basic and Applied Sci*. **2012**, 8, 508-512.

[13]   M.A.K. Shahid, A. Mubashir, B. Bashir, N. Mansoor. *International Journal of Chemistry and Material Science*. **2013**, 1(8), 195-200.

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[14]   M.A.K. Shahid, A. Mubashir, B. Bashir, N. Mansoor. *International Journal of Applicable Chemistry*. **2013**, 2(4), 922-926.

[15]   A. Wang, A.P. Essener, A. J. Zarnowski, Process for preparing selectively cross-linked polyethylene orthopedic devices, *U.S.Paten*, U.S.A, **2002**, 6,818, 171.