

Investigation of Dyed Film Based on Quinaldine Red Dyed Poly(Vinyl Alcohol) and Poly(Vinyl Butyral) for High Dose Dosimetry Applications

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Received May 14, 2012; revised June 15, 2012; accepted June 26, 2012

ABSTRACT

Dyed polymer films, prepared by a simple technique of casting aqueous solutions of poly(vinyl alcohol) PVA or poly(vinyl butyral) PVB containing quinaldine red (QR) on a horizontal glass plate, are useful as routine high-dose dosimeters. These flexible plastic film dosimeters are bleached when exposed to gamma rays. The response of these dosimeters depends on the concentration of QR and the polymer material. The radiation chemical yield (G-value) of both PVA and PVB dyed films was calculated and was found to increase with increasing dye concentration. The effect of relative humidity during irradiation as well as pre- and post-irradiation storage, on the response of the films is examined. These films are not affected by humidity change in the intermediate range of 10% - 50%.

Keywords: Quinaldine Red; Dosimetry; High Dose

1. Introduction

Many dyed poly films had been developed and investigated for possibility of their being used to measure absorbed doses in nuclear reactors and doses of X-rays, gamma rays and electron beam [1-6].

All these dyed PVA systems are bleached by irradiation the extent being to which the colour change is used for determining the absorbed dose. Radiation bleachable organic dyes were widely investigated [7]. For dose monitoring in radiation processing, the polymeric dyed flexible films are considered to be the most commonly used as dosimeters, indicators [8] based on the idea of mixing poly(vinyl alcohol) with two dyes having different sensitivities to radiation, a new label dosimetry system has been developed [9]. Dyed polymeric films containing organic dyes have been investigated to be a useful dosimeter in the high dose application [10].

In the current work, thin films of PVA or PVB coloured with different concentrations of quinaldine red were investigated to be used as dosimeters for radiation processing. The effect of humidity during irradiation as well as pre and post irradiation stability is examined.

2. Experimental

2.1. Materials

Quinaldine red indicator (product of E-Merck) molecular weight 430.352, PVA (average mo.wt 25.000 fully hydro-

lyzed 99% - 100% product of J.T baker chemical Co. USA) and poly(vinyl butyral) PVB, (piloform BM18) average molecular weight 36.000, product of wacker Co., USA.

2.2. Preparation of Stock Dye Solution

The stock solution of quinaldine red indicator was prepared by dissolving 0.08 gm in 50 ml absolute ethanol.

2.3. Preparation of Quinaldine Red Films

Films were prepared by dissolving either 4.5 gm of PVA (Average mo.wt 25.000 fully hydrolyzed 99% - 100% product of J. T baker chemical/CO. USA), in 90 ml double distilled water or poly(vinyl butyral) in 90 ml n-butanol. Complete dissolution was attained by stirring 3 hours at 60°C followed by continuous stirring for 24 hours at room temperature then left to cool. For PVA and PVB films, polymer solution was divided into 3 parts each one of 30 ml volume and 0.2, 0.4, 0.6 ml of quinaldine red were added to each part. Each solution was poured on to 15 × 15 cm horizontal glass plate and dried at room temperature for about 48 h. After stripping the films were cut into 1 × 1 cm pieces and were stored in the dark at (RH) of 33%, the film thickness was measured using digitrix-mark I thickness gauge to be 0.054 ± 0.005 mm. Six polymer films were obtained, three PVA films and three PVB films. Containing 0.021, 0.042 and

0.063 phr (phr = part per hundred parts by weight of resin).

3. Instruments

The absorption spectra of the unirradiated and irradiated films were measured in the wavelength range of 200 - 800 nm using a UVIKON 860 spectrophotometer. The film thickness was measured using a Digitrix-Mark II thickness gauge (precision $\pm 1 \mu\text{m}$, 1σ). Irradiation was carried out with the ^{60}Co Gamma chamber 4000A irradiation facility (manufactured at Bahabha Atomic Research Center, India). The absorbed dose rate in water was measured to be 3.75 kGy/h using reference alanine dosimeters. The temperature during gamma-ray irradiations was maintained at $37^\circ\text{C} \pm 2^\circ\text{C}$ and the electronic equilibrium conditions were during irradiation.

4. Results and Discussion

The absorption spectra of quinaldine red QR/PVA with 0.063 phr dye were recorded before and after irradiation to different doses and are shown in **Figure 1**. **Figure 2** shows the absorption spectra of QR/PVB with 0.042 phr dye recorded before and after irradiation.

The absorption spectrum of the unirradiated quinaldine red film shows a main absorption band in the visible region characteristic to pink colour peaking at 547 nm for both PVA and PVB film **Figure 1** curve (1), **Figure 2** curve (1) the amplitude of this absorption band decreases gradually with the increase of gamma-ray-dose it can be noticed that the bleaching per unit dose of QR/PVA is much higher than that of QR/PVB.

4.1. Response Curves

For dosimetric purposes, optical density measured at 547 nm for both QR/PVA and QR/PVB films for different

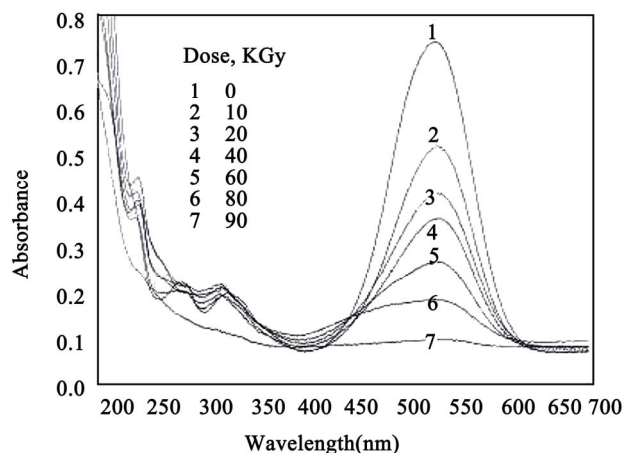


Figure 1. The absorption spectra of QR/PVA unirradiated and irradiated to different absorbed doses (QR) = 0.063 phr.

dye concentrations 0.021, 0.042 and 0.063 phr **Figures 3** and **4** shows the response curves in terms change in optical density per unit thickness, $\Delta A \cdot \text{mm}^{-1}$, versus the absorbed dose D , where $\Delta A = A_0 - A_i$ and A_0 and A_i are values of

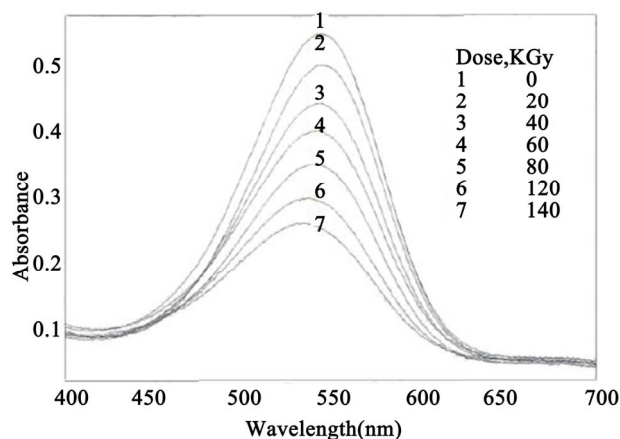


Figure 2. The absorption spectra of QR/PVB unirradiated and irradiated to different absorbed doses (QR) = 0.042 phr.

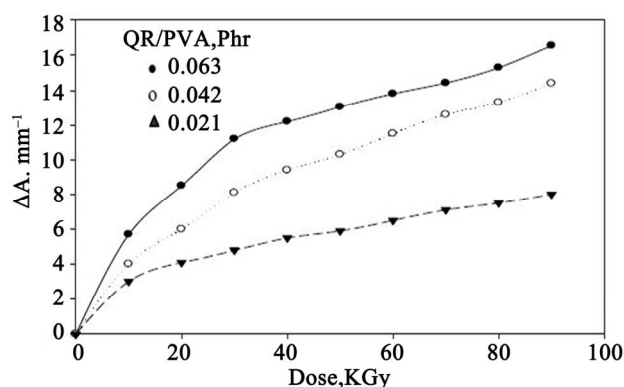


Figure 3. Change of $\Delta A \cdot \text{mm}^{-1}$, as a function of absorbed dose for different (QR) concentrations in PVA films.

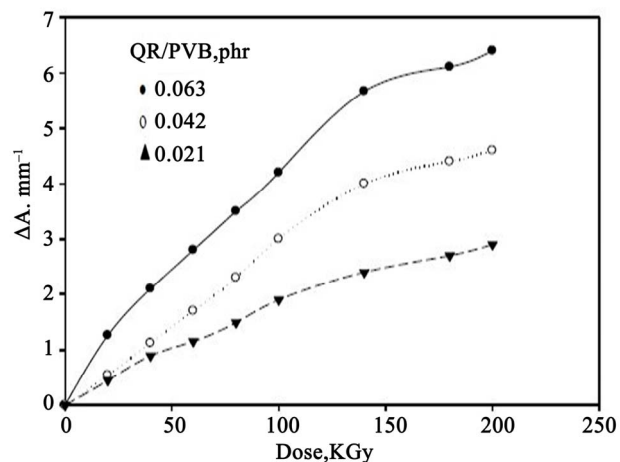


Figure 4. Change of $\Delta A \cdot \text{mm}^{-1}$, as a function of absorbed dose for different (QR) concentration in PVB films.

optical densities for the unirradiated and irradiated film respectively. The curves show that the maximum dose range extends up to 90 kGy for QR/PVA films and 200 kGy for QR/PVB films, it can be seen that all curves have the same trend but differ in their slopes depending on dye concentration.

4.2. Radiation-Chemical Yield

The radiation chemical yield (G-value) is defined as the number of moles of dye degraded by the absorption of 1 J of energy (unit, mol/J). The G-value is calculated from the general relation [11].

$$G(-\text{dye}) = \Delta A / D \varepsilon \cdot b \rho$$

where ΔA is the change in the absorbance at λ_{max} , b is the optical path length (cm), ε is the linear molar or extinction coefficient at λ_{max} ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), ρ is the density of the dosimeter $\text{gm} \cdot \text{cm}^{-3}$, D is absorbed dose (Gy). Using the dye concentration in mol/L and the average value of A_0/b , the molar extinction coefficient, ε is calculated as $108384.44 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for QR/PVA and $104480.63 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for QR/PVB. Using the density of either PVA ($1.25 \text{ gm} \cdot \text{cm}^{-3}$) or PVB ($1.1 \text{ gm} \cdot \text{cm}^{-3}$) to calculate the G-value in terms of $\mu\text{mol}/\text{J}$. The calculated G-value for both kinds of films and the concentration of the dye inside the film matrix were tabulated in **Table 1**.

From the table it could be noticed that for the same dye concentrations the G-value in PVA is higher than that in PVB films. This may be due to the number of radiolysis products of PVA compared with that in PVB, this result reflects the important role of the polymer matrix in the bleaching process.

5. Humidity during Irradiation

The effect of relative humidity (RH) during irradiation on the response of these films was investigated by irradiating QR/PVA (30 kGy) and QR/PVB (60 kGy) films at the different relative humidities (0%, 12%, 23%, 54%, 76% and 92% RH). The different relative humidity was maintained by using different standard salts [12]. The films were stored before irradiation for three days period under the same relative humidity conditions as when irradiated, so that equilibrium moisture content in dosimeter is established during irradiation.

Table 1. The calculated G-value for both QR/PVA and QR/PVB at different dye concentration.

Dye conc. phr	G-value	
	QR/PVA $\mu\text{mol} \cdot \text{J}^{-1}$	QR/PVB $\mu\text{mol} \cdot \text{J}^{-1}$
0.021	0.02096	0.189×10^{-2}
0.042	0.02795	0.21018×10^{-2}
0.063	0.04325	0.429×10^{-2}

Figure 5 represents the relative variation in A_i/A_0 at 547 nm for QR/PVA and QR/PVB as function of percentage relative humidity during irradiation, relative to that at 33% one it can be seen that for PVB films, the response of the films are almost flat in the range of relative from 0% - 95%, where the variation in response over the whole RH range, never exceeds 5%. While in QR/PVA films, there is a gradual decrease in Response with the increase of RH. This film can be used in the RH range from 10% - 50% RH.

6. Stability

6.1. Pre-Irradiation Stability

The colour stability of QR/PVA and QR/PVB films were tested before irradiation by storing the films at 35% RH at room temperature under laboratory fluorescent light. **Figure 6** represents the change in A_i/A_0 of the tested films, were measured at 547 nm for both PVA and BVB films at different intervals time during the storage period of 30 days. It can be seen that, both films exhibit excellent stability before irradiation, where the variation in absorbance during the 30 days storage period is less than $\pm 2\%$.

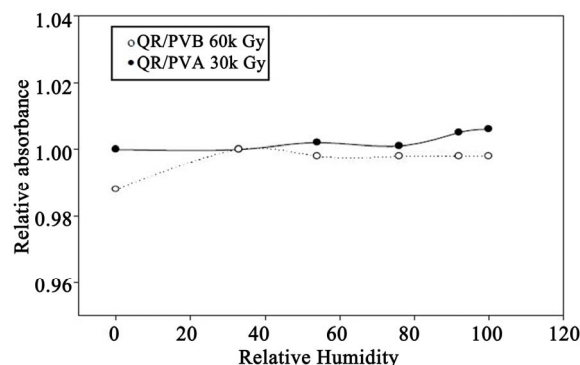


Figure 5. Variation of relative response A_i/A_0 of both QR/PVA and QR/PVB as a function of relative humidity during irradiation, QR/PVA and QR/PVB irradiated to 30 and 60 kGy.

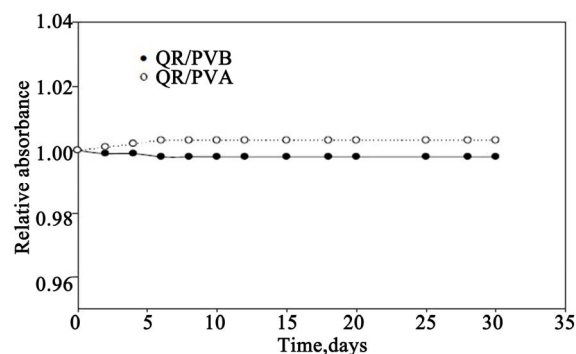


Figure 6. Pre-irradiation stability of both QR/PVA and QR/PVB films in terms of relative change in absorbance as a function of storage time.

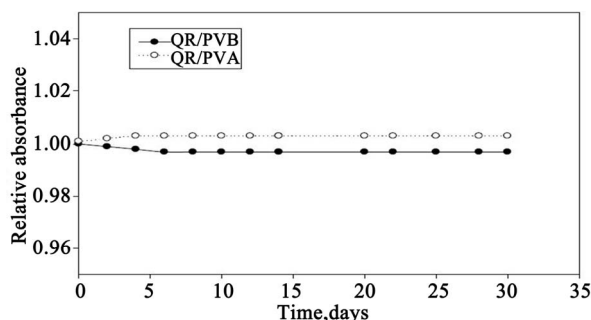


Figure 7. Post-irradiation stability of both QR/PVA and QR/PVB films in terms of relative change in absorbance as a function of storage time, where QR/PVA and QR/PVB films irradiated to and 40 kGy.

6.2. Post-Irradiation Stability

QR/PVA and QR/PVB films containing 0.063 phr of dye irradiated to a dose of 40 kGy, then stored at 35% RH at room temperature $25^{\circ}\text{C} \pm 30^{\circ}\text{C}$ in the laboratory fluorescent light the absorbance these films were measured at 547 nm for both PVA and PVB films at different intervals of time during the storage period of 30 days. The change in absorbance as a function of storage time relative to that zero time immediately after irradiation are showing in **Figure 7**. From this figure, it can be seen that, QR/PVB films shows a good stability, while QR/PVA films show a gradual decrease in absorbance with around 3% during the first 10 days then tends to be stable to the end of the storage period.

7. Conclusions

Films of PVA or PVB dyed with Quinaldine Red are useful dosimeters in the dose ranges 10 - 90 and 30 - 200 kGy respectively.

The films considered being highly stable for long times before and after irradiation and have negligible humidity effects in the range of 0% - 50% RH as well as they are easy to prepare in a laboratory and do not require toxic solvents in the preparation, the above properties suggest there to be useful for routine monitoring and dose mapping in radiation processing.

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