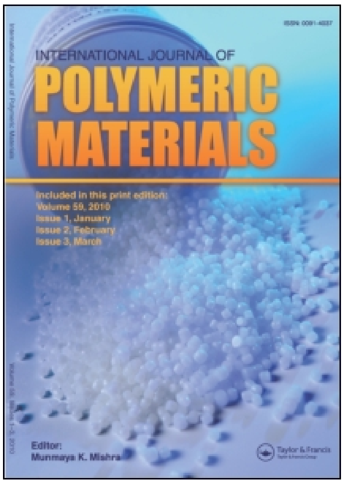

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EOSIN DYED POLY(VINYL BUTYRAL) FILMS FOR HIGH-DOSE RADIATION DOSIMETRY

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Eosin dyed poly(vinyl butyral) (PVB) films were prepared by casting the alcoholic solutions of PVB incorporating Eosin dye with or without chloral hydrate on a horizontal glass plate. These flexible plastic film dosimeters are bleached when exposed to γ-ray photons. Eosin/PVB films are useful as routine high-dose dosimeters where the maxima of the useful dose ranges are between 120 and 450 kGy, depending on Eosin and chloral hydrate concentrations in the film. The radiation-chemical yield (G-value) of films was calculated to be in the range from 0.01 to 0.03 μmol/J, where it increases with the increase of concentration of Eosin in the film. The type A uncertainty of dose measurements using Eosin/PVB films at two standard deviations (2σ, approximately equal to 95% confidence limit) was found to be ±5.4%. The effects of relative humidity during irradiation as well as pre-and post-irradiation storage on the radiation response of films are studied. Although the response of these films depends on relative humidity during irradiation, they are highly stable for long times after irradiation when stored in dark or light.

Keywords: eosin, poly(vinyl butyral), radiation dosimetry, thin polymeric films

INTRODUCTION

Radiation processing is a rapidly developing technology with numerous applications in, for example, sterilization of medical products, food irradiation, water purification and radiation treatment of polymers and semiconductors. The effectiveness of the process depends, however, on the proper application of dose and its measurement. In general, regulatory authorities require the processor to control the

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irradiation process so that all parts of the product receive an absorbed dose within prescribed limits. In radiation processing, absorbed dose is frequently measured with calibrated passive dosimeters in either solid or liquid forms. Several thin polymeric film dosimeters have been successfully developed and used as dosimeters for routine use in radiation processing by electron beam and γ-rays [1–7]. Poly(vinyl butyral) has previously been used successfully to make free-standing dyed films cast on a flat glass surface, from which they can be stripped as flexible foils [8–10]. Chloral hydrate has previously been used as an acid-releasing agent in indicator dosimetry systems [9, 11–13]. In polymeric film dosimeters, the relationship between the radiation-induced signal and the dose depends on the absorbed dose of ionizing radiation by the dosimeter and may also depend on the dose rate or fractionation of the dose [14], on the temperature during the irradiation and on the ambient humidity or, rather, on the amount of water in the dosimeter [15–21].

In the present work, thin films of PVB colored with Eosin dye in absence or presence of chloral hydrate as a radiation sensitizer are investigated to be used as dosimeters for radiation processing. The assessment of uncertainties, the effects of relative humidity during irradiation as well as pre- and post-irradiation stability on the response of the films are discussed.

EXPERIMENTAL

Preparation of Stock Solution of Eosin Dye

The stock solution of Eosin dye was prepared by dissolving 0.15 g of Eosin dye (product of Riedel De-Haen) in 50 mL butanol.

Preparation of Eosin/PVB Films

6 g of poly(vinyl butyral) powder, PVB, (Pioloform BM18, product of Wacker Co., USA) were dissolved in 120 mL n-butanol at about 50°C. The solution was kept well stirred at the same temperature for about 48-h, left to cool and then divided into four parts each of 30 mL volume. 1, 3 or 5 mL of Eosin stock solutions were added to three parts of the 30-mL polymeric solution. 1 g of chloral hydrate and 1 mL of dye stock solution were added to the fourth part of the polymeric solution. The four solutions were kept well stirred at room temperature for about 3 hours in order to obtain a uniformly mixed solution. Each solution was poured onto a 15 × 15 cm horizontal glass plate and dried at room temperature for about 48 h. Four films were obtained, three of them

contains different concentrations of Eosin (0.2, 0.6 and 1 phr)[1]. The fourth film contains 0.2 phr of Eosin and 66.7 phr of chloral hydrate. The films were then cut into pieces (1 × 1 cm) and stored for the purpose of this study. The thickness of the obtained films was found to be 0.065 ± 0.003 mm (1σ).

Apparatus

Irradiations were carried out with gamma radiation in the ^{60}Co gamma chamber (product of Russia). The absorbed dose rate in the irradiation facility was measured to be 8.5 kGy/h, using dichromate dosimeters (supplied and measured by National Physical Laboratory, England). Five films at each dose are grouped together, and sandwiched between two PMMA plates of 3 mm thickness to maintain electronic equilibrium conditions. Before irradiation, the films and the plates were preconditioned at 33% relative humidity for 24 h in a glass box, enclosed in and sealed by aluminum polyethylene laminate foil, then irradiated at the central spatial position of the sample chamber using a specially designed holder made from polystyrene. Uvikon 860 spectrophotometer (product of KONTRON Co. Ltd., switzerland) was used to measure the absorption spectra of the unirradiated and irradiated films. The film thickness was measured using a Digitrix-Mark II thickness gauge (precision $\pm 1\,\mu m$, 1σ).

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of Eosin/PVB film without chloral hydrate ([Eosin] = 0.2 phr) were recorded before and after irradiation to different doses, and are shown in Figure 1. The absorption spectrum of the unirradiated Eosin/PVB film shows a main absorption band in the visible region peaking at 533 nm, which is characteristic of red color (Fig. 1, curve 1). The amplitude of this peak at 533 nm decreases gradually with the increase of dose of γ-ray photons.

Figure 2 shows the absorption spectra of Eosin/PVB films containing chloral hydrate ([chloral hydrate] = 66.7 phr, [Eosin] = 0.2 phr) before and after irradiation to different γ-doses. It can be noted that in the films containing chloral hydrate, there is a fast radiation-induced bleaching of the red color of the films. In other words, the presence of chloral hydrate in the films increases the rate of bleaching of Eosin dye, *i.e.*, chloral hydrate acts as a sensitizer.

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[1] phr = part per hundred parts by weight of resin.

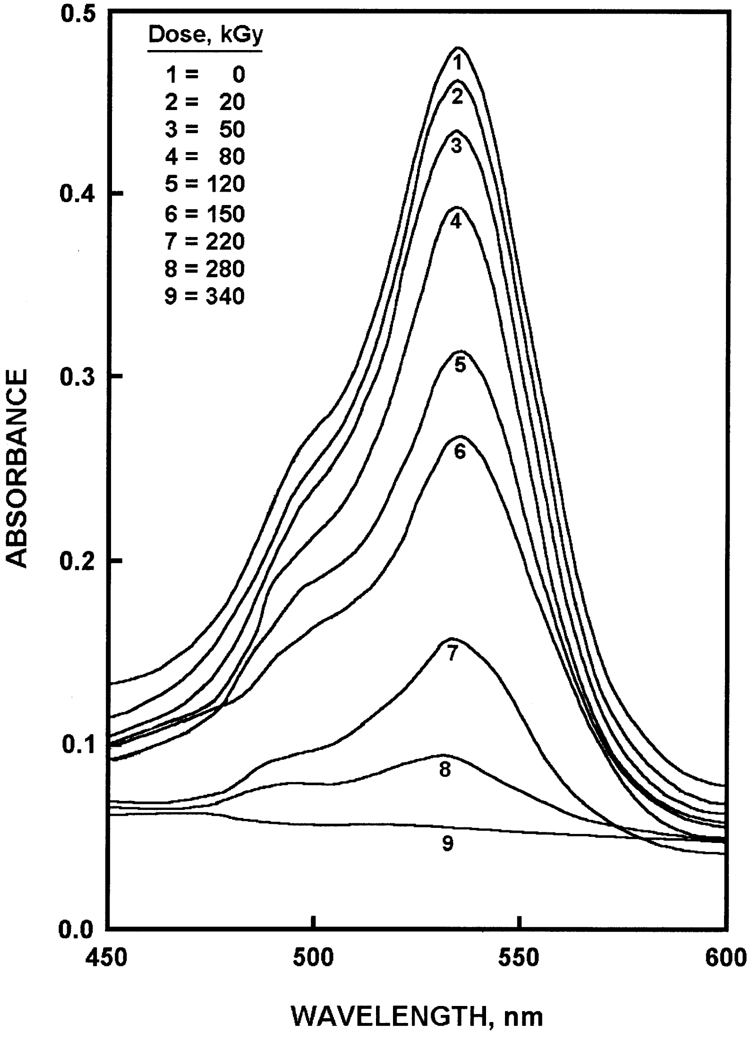

FIGURE 1 The absorption spectra of Eosin/PVB films (without chloral hydrate) unirradiated and irradiated to different absorbed doses. [Eosin] = 0.2 phr.

Response Curves

Figure 3 shows the response curves of Eosin/PVB films containing different concentrations of Eosin in terms of change in optical density divided by film thickness, (ΔAmm^{-1} at 533 nm wavelength *versus* the absorbed dose ($\Delta A = A_o - A_i$, where A_o, and A_i are optical densities of

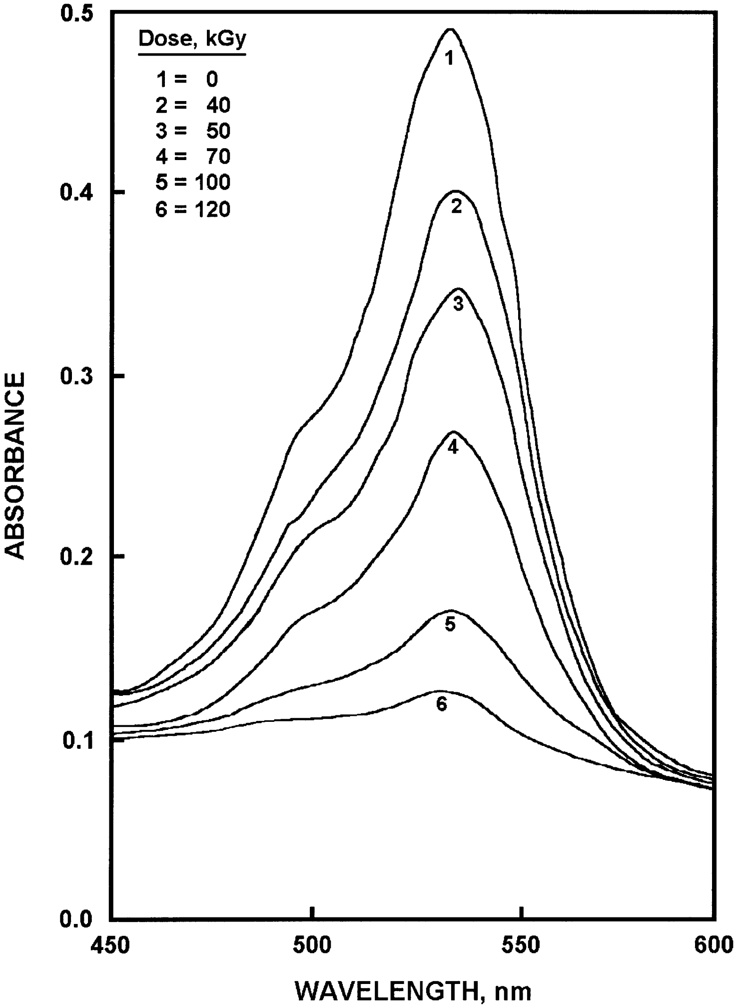

FIGURE 2 The absorption spectra of Eosin/PVB films containing chloral hydrate unirradiated and irradiated to different absorbed doses. [Eosin] = 0.2 phr; [chloral hydrate] = 66.7 phr.

the unirradiated and irradiated films, respectively. It can be seen that all curve show the same trend of almost straight lines and tend to reach saturation at high doses, but all curves differ in their response value (slope of the straight part in the curve). Figure 4 shows the relationship between the slope of the straight parts of the curves in

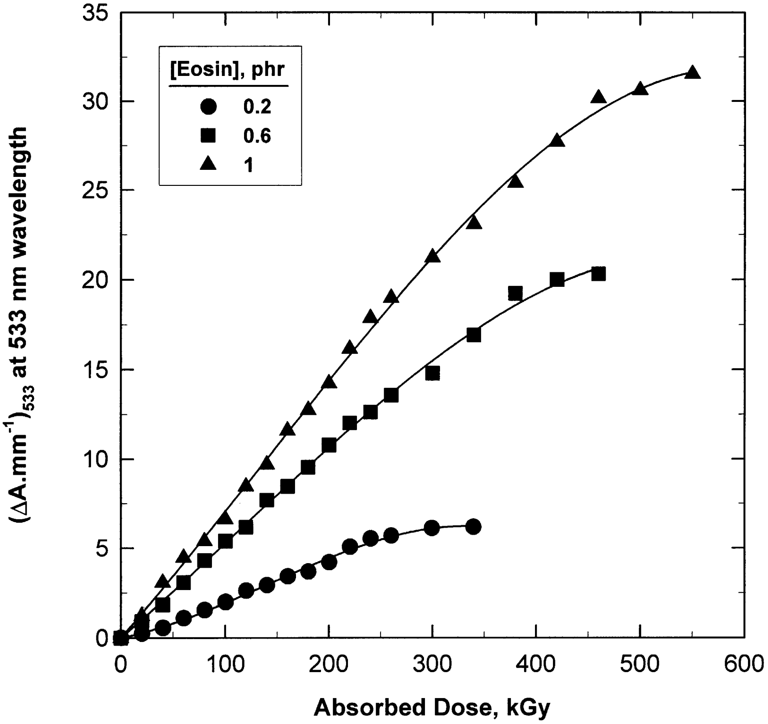

FIGURE 3 Change of $\Delta A.mm^{-1}$ as a function of absorbed dose of Eosin/PVB films containing different concentrations of Eosin. $\lambda_{max} = 533\,nm$.

Figure 3 and the concentration of Eosin. It can be seen that the slope increases almost linearly with the increase of Eosin concentration.

The curves in Figure 3 reach saturation at different doses, depending on the concentration of Eosin in the film. Figure 5 shows the relationship between the dose at saturation and the concentration of Eosin. It can be seen that the dose at saturation increases exponentially with the increase of Eosin concentration. The insert in Figure 5 shows the same relation on a semi-log scale. The maximum range of dose varies from 250 to 450 kGy depending on the concentration of Eosin in the film. From this Figure one can predict the suitable concentration of Eosin in a film for a specific range of application.

The effect of presence of chloral hydrate in the film was studied by irradiating two films having the same concentration of Eosin; one film without chloral hydrate and the another containing 66.7 phr chloral hydrate. The representative results are shown in Figure 6. It can be

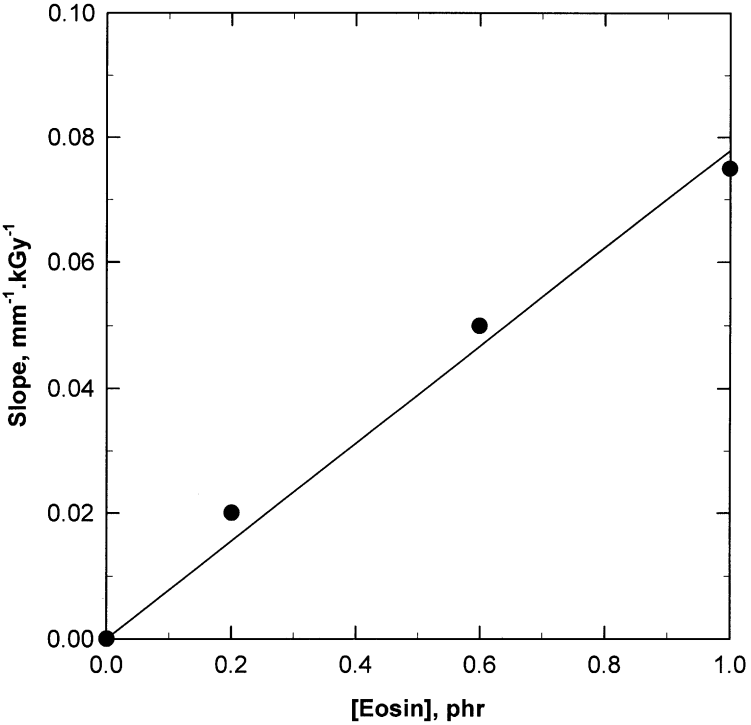

FIGURE 4 Change of response, slope of straight sections of curves given in Figure 3, as a function of the concentration of Eosin in the films.

noticed that the radiation-induced bleaching of the red color of the Eosin dye is faster in the films containing chloral hydrate. In fact, the rate of bleaching of films containing chloral hydrate is almost twice that of films without chloral hydrate. It can be concluded that the radiolysis products of chloral hydrate enhance the bleaching reactions of Eosin.

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 [18] as follows:

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

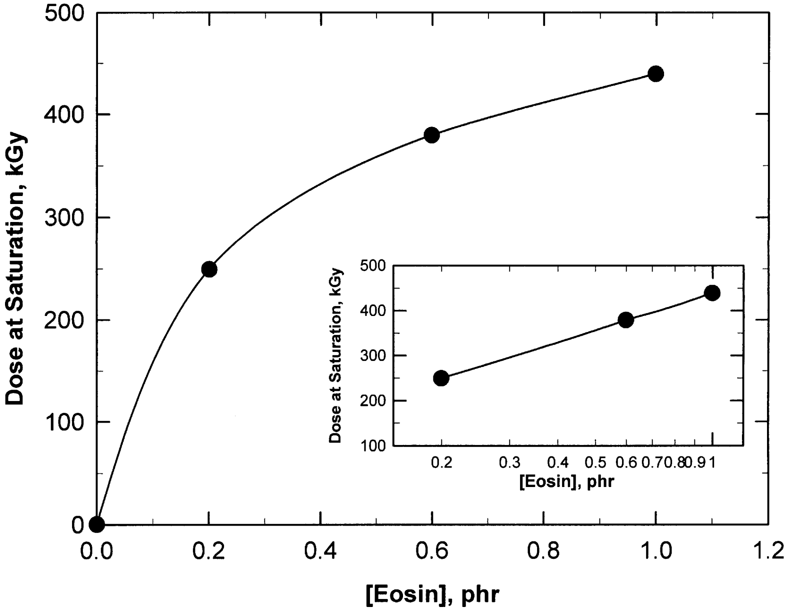

FIGURE 5 Variation of dose at saturation of Eosin/PVB films as a function of concentration of Eosin. The insert gives the same relation on a semi-log scale.

where

ΔA = the change in the absorbance at λ_{max}.
b = the optical bath length (cm).
ε = the linear molar extinction coefficient at λ_{max}($Lmol^{-1}cm^{-1}$).
ρ = the density of the film (gcm^{-3}).
D = the absorbed dose (Gy).

Figure 7 shows the relation A_o/b (cm^{-1}) as a function of concentration of Eosin (in mol/L) giving a straight line; its slope is the molar extinction coefficient, ε, and it was found to be 19759.5 $Lmol^{-1}$ cm^{-1}. Using the density of PVB (1.1 gcm^{-3}), the *G*(-Eosin) was calculated for different films containing different concentrations of Eosin and chloral hydrate and the results are tabulated in Table 1. It can be seen that, *G*(-Eosin) increases gradually with the increase of concentration of Eosin and the value of the film containing 66.7 phr chloral hydrate is almost double that of the film without chloral hydrate.

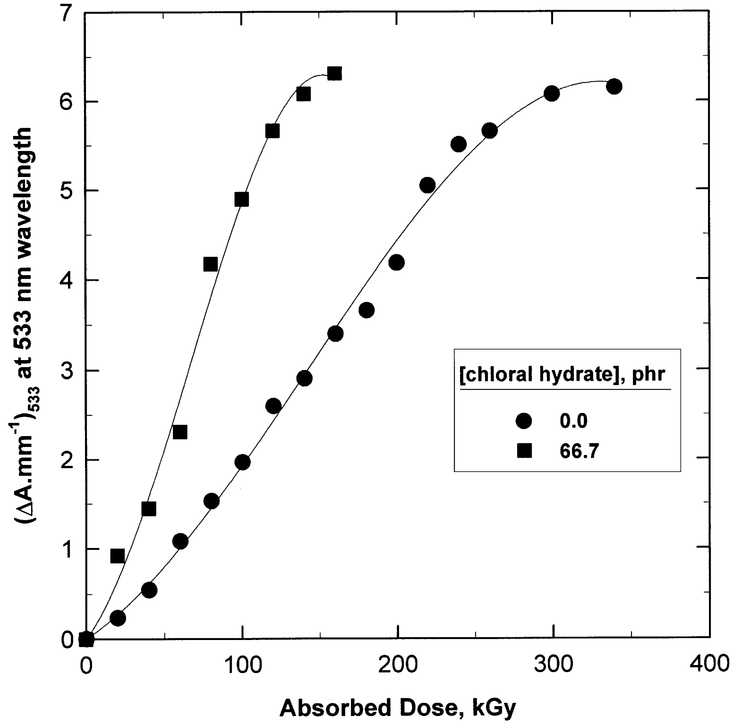

FIGURE 6 Comparison between response of Eosin/PVB films with and without chloral hydrate. [Eosin] = 0.2 phr. $\lambda_{max} = 533$ nm.

Effect of Relative Humidity during Irradiation

The effect of relative humidity (RH) during irradiation on the response of Eosin/PVB films with and without chloral hydrate ([Eosin] = 0.2 phr) was investigated by irradiating the films to doses of 80 and 140 kGy, respectively, at different relative humidities (0, 12, 33, 54, 76, and 92%). Irradiation was carried out while the films were suspended over various saturated-salt solutions in an enclosed jar [22], except for the 0% RH, which was made with films suspended over dried silica gel. The films were stored before irradiation for a 48-h period under the same RH conditions as when irradiated, so that equilibrium moisture content in the dosimeter could be established during irradiation. Figure 8 shows the variation in response (ΔAmm^{-1}) as a function of percentage relative humidity during irradiation relative to that at 33%. It can be seen that the response increases gradually with the increase of % RH over all the studied range of relative humidity. For dosimetry, it may be possible to reduce the influence of humidity by

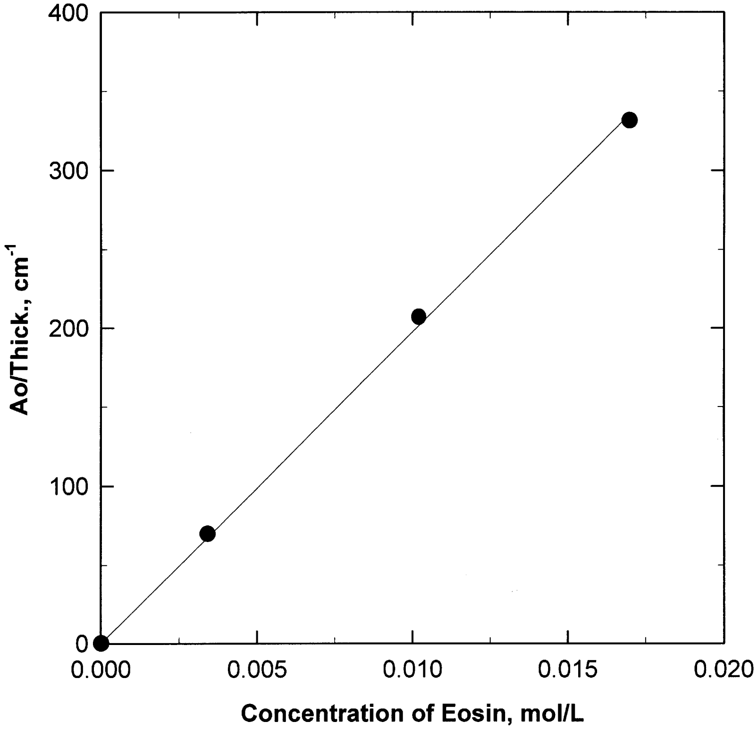

FIGURE 7 The relation between A_o/Thick., as a function of concentration of Eosin.

preconditioning the films at about 33% RH and sealing them in vapour-tight pouches before irradiation or, if that is impractical, one should maintain conditions of calibration as close as possible to the conditions of use.

TABLE 1 *G*-value of PVB/Eosin Films at Different Concentrations of Eosin Dye and Chloral hydrate

Film composition		
[Eosin], phr	[chloral hydrate], phr	G-value, μmol/J
0.2	0	0.01
0.2	66.7	0.0216
0.6	0	0.0237
1	0	0.0315

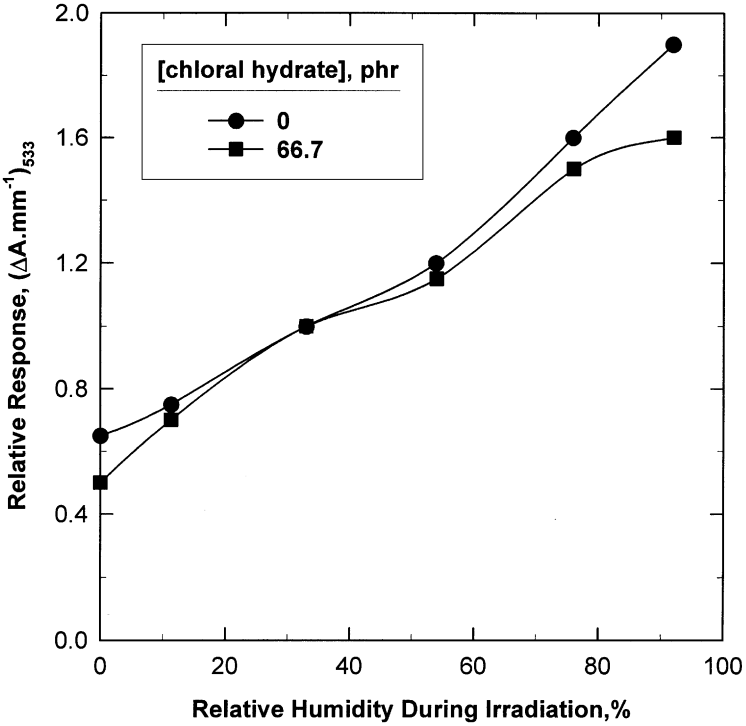

FIGURE 8 Variation of relative response of Eosin/PVB films with and without chloral hydrate (ΔA.mm^{-1}, at 533 nm) as a function of relative humidity during irradiation. [Eosin] = 0.2 phr.

Uncertainty

Factors contributing to the total uncertainty may be separated into two types, type A and type B. Type A is mainly related to the calibration and type B is associated mainly with the measuring equipment and the films. The reproducibility of the Uvicon 860 spectrophotometer was determined by reading the absorbance values of a film at 533 nm several times (one hundred readings per film). From the data obtained, it was found that the coefficient of variation (1σ) is ±0.4%, reflecting the precision of the spectrophotometer. The variation of the absorbance values of about 50 films before irradiation (10 times for each film) was found to be about ±1.2%.

On the other hand, the type A uncertainty (at one standard deviation, *i.e.*, 1σ) arising during calibration of Eosin/PVB films was calculated, where the measurements were made under conditions of repeatability [23]. Five replicate measurements of radiation-induced change were made at each value of absorbed dose (15 doses were applied, *i.e.*, 75 replicates). By pooling the sets of $(\Delta\text{Amm}^{-1})_{533}$, a single value for uncertainty was found by using the following equation [23]:

$$\text{CV\%} = \sqrt{\frac{\sum_i (n_i - 1)(\sigma_{i-1}/\bar{\text{X}}_\text{i})^2}{\sum_i (n_i - 1)}} \times 100 \tag{3}$$

where CV% is the percentage of coefficient of variation; σ_{i-1} is the sample standard deviation of a spectrophotometric quantity for *i*th set of data; $(\text{n}_i - 1)$ is the degrees of freedom for *i*th set of data; $\bar{\text{X}}_i$ is the average value of a spectrophotometric quantity for *i*th set of data and n_i is the number of replicate measurements for *i*th set of data.

The type A percent uncertainties (at one standard deviation, 1σ) were found to be $\pm 4\%$. The combined uncertainty (U_c) is calculated through combining all components in quadrate at one standard deviation (1σ) as follows:

$$U_\text{c} = \sqrt{(0.4)^2 + (1.2)^2 + (2.4)^2} = 2.7\% \tag{4}$$

The combined uncertainty (at two standard deviations, *i.e.*, 2σ, approximately equal to a 95% confidence level) is found by multiplication of U_c (at 1σ) by two. Hence, the combined uncertainty at 2σ using Eosin/PVB films is 5.4%.

Post-Irradiation Stability

A study of the stability of the radiation-induced changes in Eosin/PVB films in presence or absence of chloral hydrate was carried out by storing films in dark and under laboratory fluorescence lights at ambient relative humidity (35–40% RH) and room temperature. Films containing 66.7 phr chloral hydrate were irradiated to 80 kGy and films without chloral hydrate were irradiated to 140 kGy. These films were readout spectrophotometrically at 533 nm wavelength at different intervals of time during the post-irradiation storage period of 75 days, and the change of response (ΔAmm^{-1}) as a function of storage time is shown in Figure 9. It can be seen that the films show excellent stability overall the 75-day storage period.

CONCLUSION

Eosin/PVB films made from PVB incorporating Eosin dye with and without chloral hydrate are useful as radiation dosimeters in different dose ranges. Although the response of these films depends on the

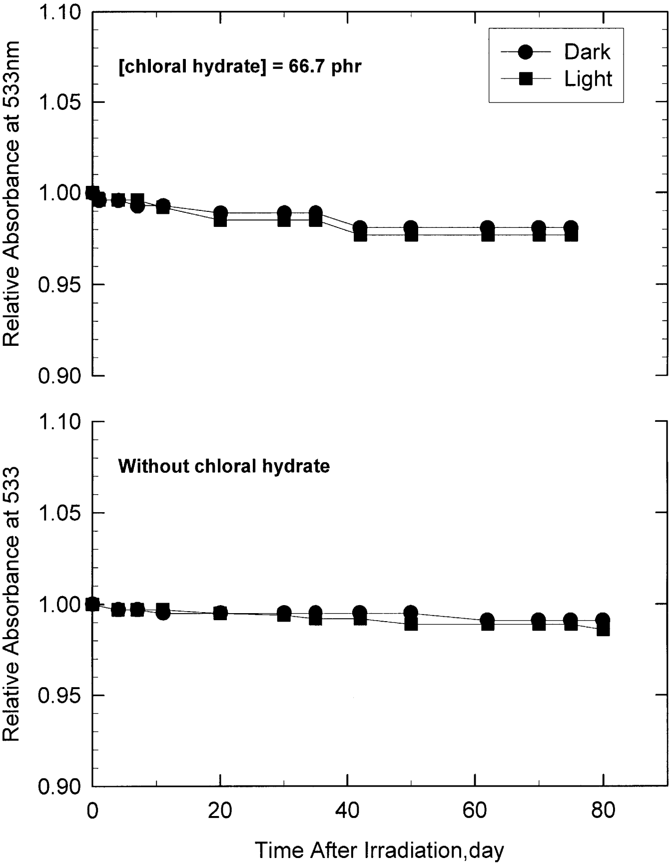

FIGURE 9 Post-irradiation stability of Eosin/PVB films stored in dark and light at room temperature. [Eosin] = 0.2 phr. $\lambda_{\max} = 533\,\text{nm}$.

relative humidity during irradiation, they are highly stable for long times after irradiation when stored in dark and light. The combined uncertainty at 2σ using Eosin/PVB films was found to be 5.4%. The properties of the prepared films suggest their useful application for routine monitoring and dose mapping in radiation processing.

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