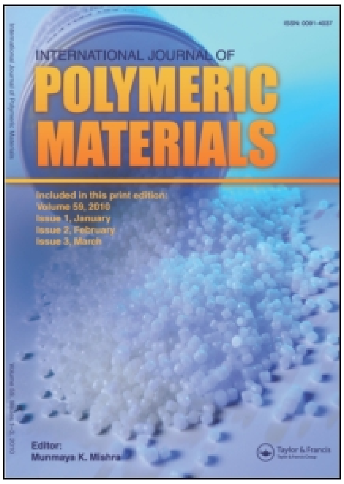

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Rhodamine B and Methylene blue dyed grafted poly(vinyl butyral) films for high-dose radiation dosimetry

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RHODAMINE B AND METHYLENE BLUE DYED GRAFTED POLY(VINYL BUTYRAL) FILMS FOR HIGH-DOSE RADIATION DOSIMETRY

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Gamma radiation-induced polymerization of acrylic acid (AAc) onto poly(vinyl butyral) (PVB) film has been carried out under nitrogen atmosphere. The resulting grafted film of PVB-g-PAAc was allowed to react with solutions of two ionic dyes, namely Rhodamine B (RB) or Methylene Blue (MB). The radiation-induced color bleaching has been analyzed with visible spectrophotometry, either at the maximum of the absorption band peaking at 552 nm (for PVBRB) or that peaking at 651 nm (for PVBMB). The investigations show that these dosimeter films may be useful for high-dose gamma radiation applications. The useful absorbed dose range of the dyed films extends up to 600 kGy for PVBRB and 300 kGy for PVBMB, with a minimum useful dose of about 10 kGy. The type A uncertainty of dose measurements using PVBRB and PVBMB films at two standard deviations (2σ, approximately equal to 95% confidence limit) was found to be $\pm$ 8.8 and 9.4%, respectively. The effects of temperature and relative humidity during irradiation as well as pre- and post-irradiation storage, on the radiation response of films are studied. These films are highly stable before and after irradiation and have no appreciable effect of temperature or humidity on response in the relative humidity range 0–60% and temperature range 15–60°C.

Keywords: thin film dosimeters, rhodamine B, methylene blue, poly(vinyl butyral), dyed grafted films

INTRODUCTION

Modification or introduction of new characteristics to those based on synthetic polymers such as poly(vinyl butyral), can be achieved by several methods. Grafting, whether initiated chemically or by ionizing radiation, constitutes one of the methods that is being applied successfully. The graft copolymer will be formed from the main macromolecule of the parent polymer to which is attached branches of varying length of the grafted polymer. It would be expected that the new attained property to be a function of

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the length of the grafted monomer. Most graft copolymers are formed by radical polymerization and hence the suitability of ionizing radiation such as gamma rays in their preparation.

Saturated polymers such as poly(vinyl butyral) are usually resistant to direct dyeing. This difficulty can, however, be overcome by grafting suitable branches onto the backbone of PVB macromolecules. This may be accomplished by grafting at first acrylic acid onto poly(vinyl butyral) and then subjecting the obtained graft-copolymer of PVB-g-PAAc to the dye material. As a matter of fact, this technique has proved to be very efficient in preparation of suitable films for radiation dosimetry [1, 2].

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 [3 – 5]. In polymeric film dosimeters, the relationship between the radiation-induced signal and the radiation dose depends on the absorbed energy of ionizing radiation and may also depend on the dose rate or fractionation of dose [6], on the temperature during the irradiation and handling, on the presence or absence of oxygen in the surrounding atmosphere or in the dosimeter [7, 8], and on the ambient humidity or rather on the amount of water in the dosimeter [9 – 15].

In the present work, dyed grafted PVB films have been prepared by grafting acrylic acid onto poly(vinyl butyral) and subjecting the resulted grafted films to dyeing by two ionic dyes, namely, Rhodamine B (RB) and Methylene blue (MB); these were evaluated as radiation dosimeters. The assessment of uncertainties, effect of both humidity and temperature during irradiation as well as pre- and post-irradiation stability at different storage conditions have been investigated.

EXPERIMENTAL

Preparation of PVB Film

5 grams of PVB (Pioloform BM18, average molecular weight of about 36,000, product of Wacker Co., USA) were dissolved in 100 mL of *n*-butanol at about 50°C and kept well stirred at that temperature for about 24-h for complete dissolution. Each 30 mL of this solution were poured onto a 15×15 cm glass plate and dried at room temperature for about 48 h. After drying, the films were stripped from the glass plates, then cut into 5×10 cm strips and stored for different investigations. The thickness of the obtained films was found to be $65 \pm 4\,\mu m$ (1σ).

Radiation-Induced Graft Polymerization

Strips of PVB films were washed with acetone, dried in an oven at 50°C, weighed and then immersed in a mixture of acrylic acid (99%, product of

Merck, Germany) and distilled water in glass ampoules. Mohr'salt (ammonium ferrous sulfate) (2.5 wt%) was added to minimize the homopolymerization of acrylic acid during radiation grafting process. The reactants mixtures in glass ampoules were dearated by bubbling nitrogen gas for 5–7 minutes, sealed and then subjected to gamma rays irradiation for a dose of 5 kGy. The grafted films, thus obtained, were removed and washed thoroughly with distilled water and then soaked overnight in distilled water to eliminate the residual monomer and homopolymer contained in the films. The films were then dried in oven for 24 hours at 50–60°C and then weighed. The degree of grafting was calculated using the following relation:

$$\text{Degree of grafting (\%)} = (W_g - W_o/W_o) \times 100$$

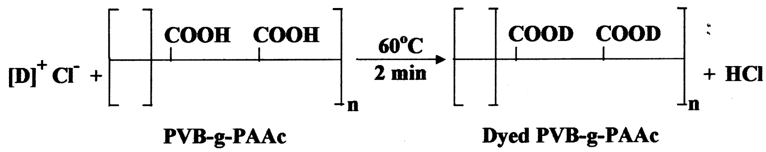
where, W_o and W_g represent the weights of the initial and grafted films, respectively.

Synthesis of Dyed Graft Copolymer Films

Acrylic acid was thus grafted onto PVB films and the grafting percentage was fixed at about 15% by weight. These graft copolymer PVB-g-PAAc films were immersed for about two minutes in 60°C solution of either $0.05\,g \cdot L^{-1}$ Rhodamine B (product of BDH Chemicals Ltd, England) or Methylene Blue (product of REIDEL DE HAEN AG, Germany) to produce PVBRB or PVBMB films, respectively. These treated films were removed, washed, dried and then investigated.

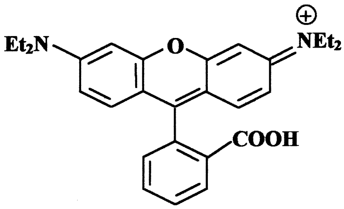
Reaction of Dye with Polymer

In the present study, Rhodamine B and Methylene Blue dyes, $D^+ Cl^-$, were reacted in a cationic exchange with PVB grafted-PAAc films obtained by the direct radiation induced grafting method. In light of previous works [1, 2, 16], the proposed structure of each dye with PVB-g-PAAc can be represented as follows (Scheme 1):



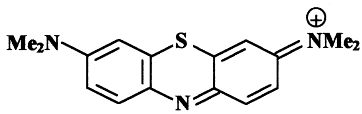
SCHEME 1

where $[D]^+$, is the dye cation and the two dye cations have the following schematic diagrams (Scheme 2):



$[\text{Rhodamine B}]^+$

$C_{28}H_{31}N_2O_3$



$[\text{Methylene Blue}]^+$

$C_{16}H_{18}N_3S$

SCHEME 2

where $Me = CH_3$ and $Et = C_2H_5$.

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 9.0 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. The temperature during irradiation was ca 30°C.

Unicam UV4 spectrophotometer (product of Unicam Co. Ltd., England) was used to measure the absorption spectra of the unirradiated and irradiated films.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of both PVBRB and PVBMB films recorded before and after irradiation are shown in Figures 1 and 2, respectively. The absorption spectra of the unirradiated film show a main absorption band in the visible region peaking at 552 nm for PVBRB (Fig. 1, curve 1) and at 651 nm for PVBMB (Fig. 2, curve 1). The absorption bands at 552 nm (PVBRB) and 651 nm (PVBMB) arise from the excitation of an electron from the non-bonding molecular orbitals (NBMO) to the lowest antibonding orbitals, ($n \rightarrow \pi^*$ transition). It is shown that the amplitudes of both absorption bands in the visible spectra decrease gradually with the increase of the dose of gamma-ray photons, and the decrease at 651 nm (in the case

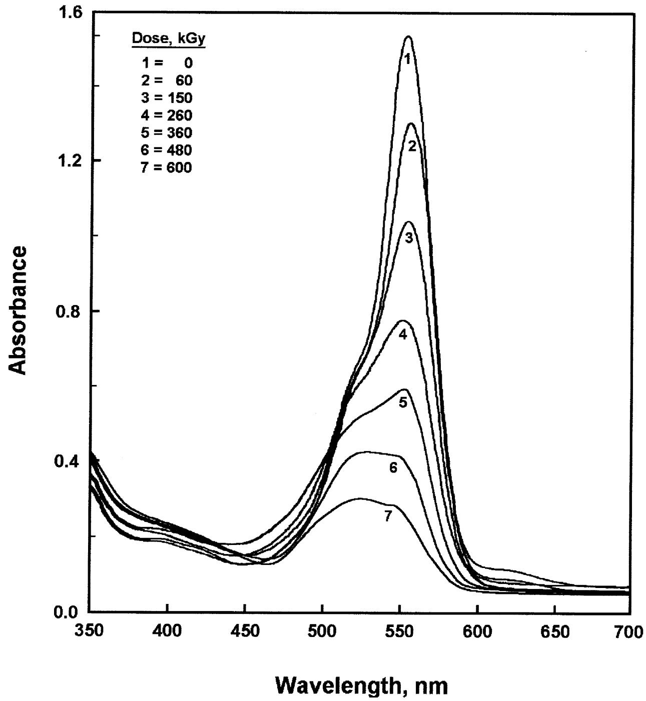


FIGURE 1 The absorption spectra of PVBRB films unirradiated and irradiated to different absorbed doses.

of PVBMB) is more pronounced than that at 552 nm (in the case of PVBRB). See also, Figure 3, where the response curves for the two films are plotted.

Response Curves

The results that were obtained by Abdel-Rehim *et al.*, 1993 and Abdel-Fattah *et al.*, 1999 [1, 2] show that the reproducibilities of the responses of these types of films are independent of the thickness within the standard deviations for responses of 50 and 100 μm films, namely ± 5%, whereas the sensitivities are mainly dependent on the initial optical densities of the films. Moreover, the initial optical density (A_o) was reported to depend on the grafting percent of the film, the concentration and temperature of the dye solution used in the synthesis of the films [1, 2]. Therefore, the response functions of these films were established in terms of change in absorbance divided by the absorbance before irradiation at ($\Delta A/A_o$) at λ_{max} as a function of absorbed dose.

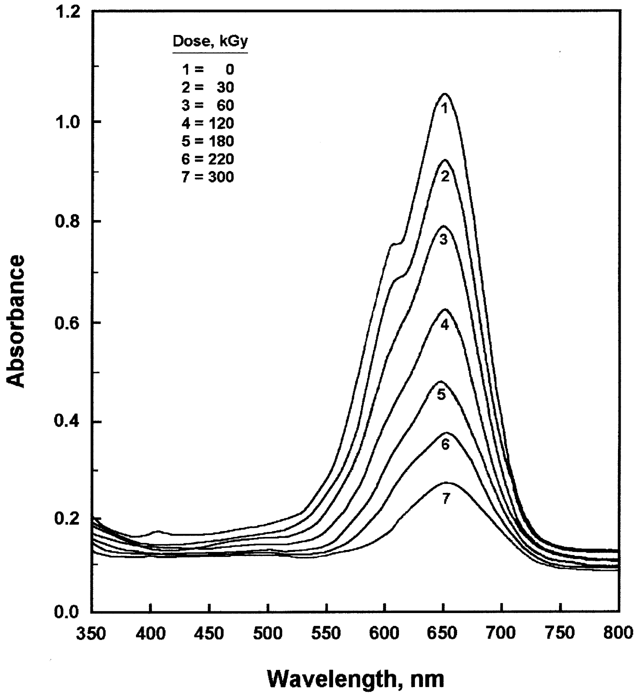


FIGURE 2 The absorption spectra of PVBMB films unirradiated and irradiated to different absorbed doses.

Figure 3 shows the changes of $(\Delta A/A_o)_\lambda$ values at 552 and 651 nm (for PVBRB and PVBMB, respectively) as a function of absorbed dose (where, $\Delta A = A_o - A_i$, and A_o and A_i are the absorbances of the film before and after irradiation, respectively). Sublinear relationships were obtained for both films. Regression expressions for these two lines are represented by the following relationships:

$$D = 465x - 196x^2 + 648x^3 \quad (1)$$

and

$$D = 298y - 205y^2 + 438y^3 \quad (2)$$

where, D is the absorbed dose in kGy, x is $(\Delta A/A_o)_{552}$ for PVBRB film and y is $(\Delta A/A_o)_{651}$ for PVBMB film.

The above relations can be used for the evaluation of the absorbed dose corresponding to a radiation-induced decrease in absorbance of these films (PVBRB and PVBMB) where the average deviation of the experimental

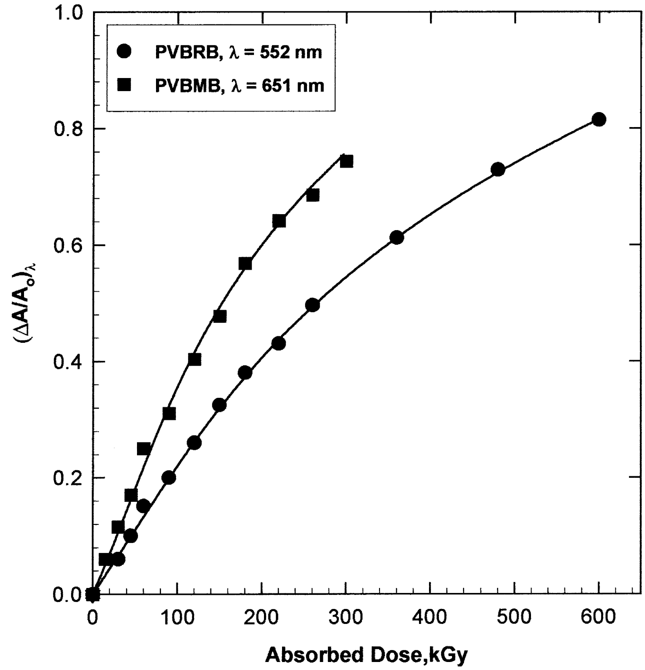


FIGURE 3 The response $(\Delta A/A_o)_\lambda$ of both PVBRB and PVBMB films as a function of absorbed dose, when measured at the indicated wavelength.

points from the response curves given in Figure 3 is about ± 4%. The use of these two relationships is restricted to the dose range up to 600 kGy for PVBRB and 300 kGy for PVBMB.

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 Unicam UV-4 spectrophotometer was determined by reading the absorbance values of two films (PVBRB at 552 nm and PVBMB at 651 nm with a bandwidth of 2 nm) several times (one hundred readings per film). From the data obtained, it was found that the coefficient of variation (1σ) is ± 0.3%, 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 ± 2% for both dyed films.

On the other hand, the type *A* uncertainties (at one standard deviation, *i.e.*, 1σ) arising during calibration of dyed grafted-PVB films were calculated,

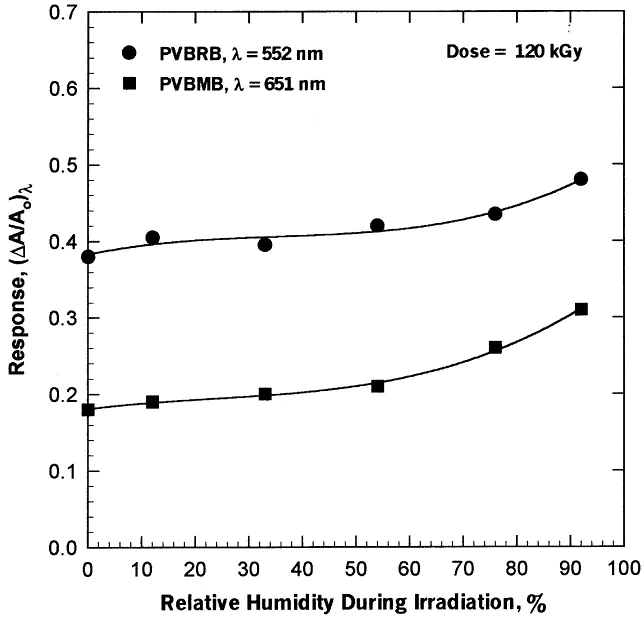


FIGURE 4 Variation of response of both PVBRB and PVBMB as a function of relative humidity during irradiation. Absorbed dose = 120 kGy.

where the measurements were made under conditions of repeatability [17]. Five replicate measurements of radiation-induced change were made at each value of absorbed dose (11 doses were applied, *i.e.*, 55 replicates). By pooling the sets of $(\Delta A/A_o)_\lambda$, a single value for uncertainty was found by using the following equation [17]:

$$\mathrm{CV\%} = \sqrt{\frac{\sum_i (n_i - 1)(\sigma_{i-1}/\overline{X_i})^2}{\sum_i (n_i - 1)}} \times 100 \tag{3}$$

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; $(n_i - 1)$ is the degrees of freedom for *i*th set of data; $\overline{X_i}$ 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 $\pm 3.9\%$ for PVBRB and $\pm 4.3\%$ for PVBMB. The combined uncertainty (U_c) is calculated through combining all components in quadrate at one standard deviation (1σ) as follows:

For PVBRB film,

$$U_c = \sqrt{(0.3)^2 + (2)^2 + (3.9)^2} = 4.4\% \quad (4)$$

and that for PVBMB is 4.7%.

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 using PVBRB films is 8.8% and that using PVBMB films is 9.4%.

Effect of Humidity during Irradiation

To investigate the humidity effects during irradiation of PVBRB and PVBMB films, the films were irradiated to a dose of 120 kGy at different relative humidities (RH). These irradiations were made at 25 ± 3°C, while the films were suspended over various saturated salt solutions in an enclosed jar except for the two extreme values of relative humidities [18]. The 0% RH value was

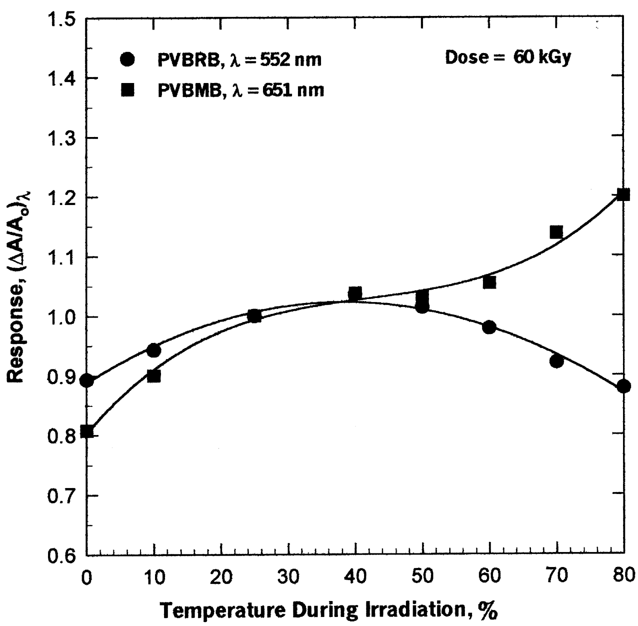


FIGURE 5 Variation of response of both PVBRB and PVBMB as a function of temperature during irradiation. Absorbed dose = 60 kGy.

made with films suspended over dried silica gel and 100% RH was made with films suspended over water. All films were conditioned before irradiation under each specific condition of well defined moisture content for 48 hours. The results of this study are given in Figure 4; in terms of response $(\Delta A/A_o)_\lambda$ as a function of percent relative humidity. It was found that, the response of both PVBRB and PVBMB films does not affect with the change in relative humidity in the range 0 – 60% where the response is almost flat (within ± 5%). Therefore they can be used at any relative humidity in this range without any correction. For irradiations at higher humidities than 60% a correction should be applied.

Effect of Temperature during Irradiation

The temperature during irradiation was investigated by irradiating PVBRB and PVBMB films to a dose of 60 kGy at different temperatures (0, 10, 25, 40, 50, 60 and 70°C) using liquid thermal baths [19]. Figure 5 shows the variation in response, $\Delta A/A_o$, as a function of temperature during

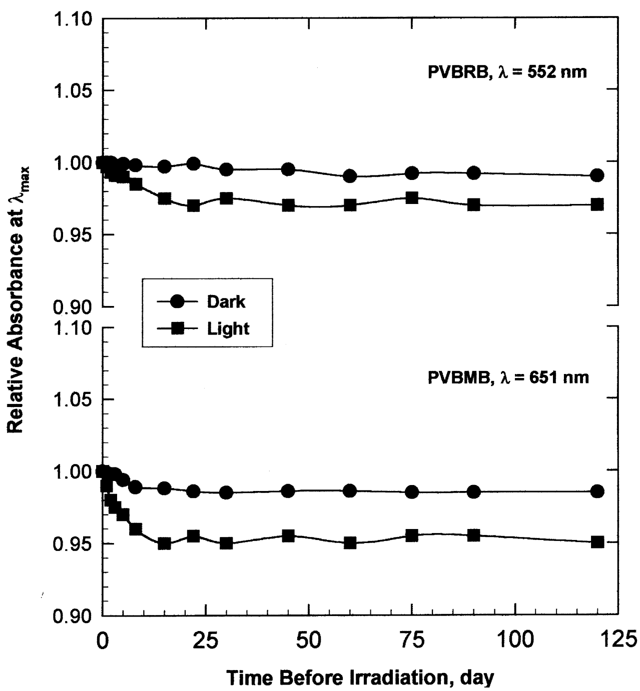


FIGURE 6 Pre-irradiation stability of PVBRB and PVBMB films stored in dark or indirect daylight.

irradiation. It can be seen that there is no appreciable effect of temperature on response in the range of temperature from ~15 to ~60°C, where the variation of response in this range is less than 5%. Accordingly, these films can be used successfully in this range without any correction, while a correction should be applied to the measurements at lower and higher irradiation temperatures.

Shelf-Life

Stability measurements before irradiation of PVBRB and PVBMB films were made by storing two films, one in the dark and the other in light at ambient temperature (25 ± 3°C) and reading the films spectrophotometrically at different times during the pre-irradiation storage period of 120 days (Fig. 6). It can be seen that the films stored in the dark show excellent stability, where ± 2% change in absorbance was obtained overall the 120-day storage period. On the other hand, the absorbance of PVBRB and

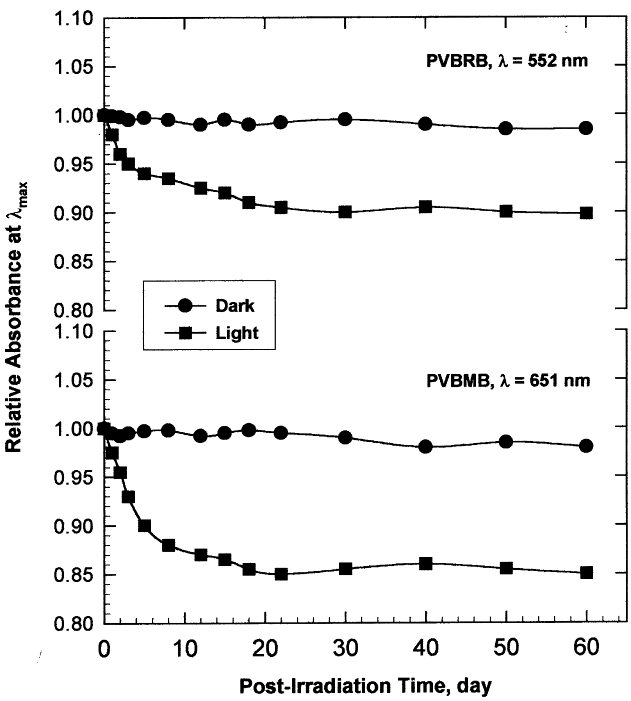


FIGURE 7 Post-irradiation stability of PVBRB and PVBMB films stored in dark or indirect daylight. Absorbed dose = 120 kGy.

PVBMB films stored in indirect daylight decreases gradually during the first two weeks after preparation with about 3% and 5%, respectively, and after that tend to be stable to the end of storage period. The unirradiated PVBRB and PVBMB films were then read spectrophotometrically after a storage period of 12-months in dark and only a decrease in absorbance of about 3% and 5% of their initial values were noticed, respectively.

Post-Irradiation Stability

PVBRB and PVBMB films irradiated to a dose of 120 kGy were stored for different periods after irradiation in dark and indirect daylight at ambient temperature ($25 \pm 3°C$). These films were read spectrophotometrically (at 552 nm for PVBRB and 651 nm for PVBMB) at different intervals of time during the post-irradiation storage period of 60 days. Representative results are shown in Figure 7. It can be seen that, over this storage period (60 days) the irradiated PVBRB and PVBMB films exhibited excellent stability in dark, namely less than $\pm 2\%$ change in absorbance was obtained. On the other hand, the absorbance of irradiated PVBRB and PVBMB films stored in indirect daylight decreases gradually with about 10% and 15%, respectively, during the first three weeks of storage and after that the films tend to be stable to the end of the 60-day storage period.

SUMMARY AND CONCLUSION

This new approach for producing dyed plastic film dosimeters by graft polymerization has proved to be promising. The results indicate that the dye has a fairly uniform distribution within the grafted layer of the plastic films. The responses of these films are independent of thickness variations. The useable response of PVBMB film covers an absorbed dose range of 20 – 300 kGy, which is approximately twice as sensitive to gamma radiation as the PVBRB film.

The response of both PVBRB and PVBMB films is not affected by the change in relative humidity during irradiation in the range 0 – 60% or the change in temperature in the range from 15 to 60°C, where the response is almost flat (within $\pm 5\%$).

Irradiated PVBRB and PVBMB films exhibited excellent stability in the dark, where less than $\pm 2\%$ change in absorbance was obtained, while the absorbance of the films stored in indirect daylight decreased gradually with about 10% and 15%, respectively, during the first three weeks of storage. It is possible for these films to be produced in large quantities and inexpensively, which could make them suitable for high-dose applications as routine dosimeters in radiation processing.

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