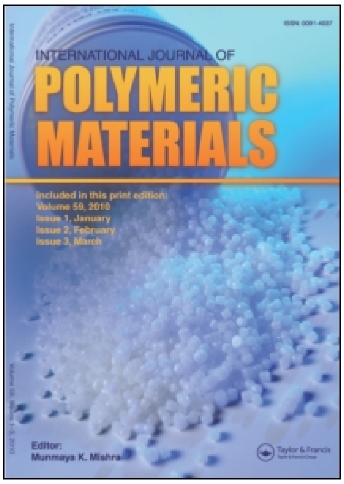

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Use of Bromocresol Green Dyed Poly(Vinyl Butyral) Film for Dosimetric Applications

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Use of Bromocresol Green Dyed Poly(Vinyl Butyral) Film for Dosimetric Applications

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A system consists of a poly(vinyl butyral) film containing acid-sensitive dye, bromocresol green (BCG), in presence of chloral hydrate has been investigated as a radiation-sensitive indicator. The acid-sensitive dye in the film changes its color from blue to yellow by irradiation due to the consequent lowering of the pH of the film caused by HCl generated from the radiolysis of Cl-containing substance. This film can be used as a dosimeter in a relatively low dose range up to 6 kGy. The radiation chemical yield (G-value) of films was calculated, where it increases with increase of both concentration of bromocresol green film and concentration of chloral hydrate. This response range makes this system useful in some food irradiation applications. The effects of humidity during irradiation and post-irradiation storage on the response of the film are discussed.

Keywords: bromocresol green, pH indicator, poly(vinyl butyral), thin film dosimeter

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, the irradiation process is designed so that all parts of the product receive an absorbed

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dose within prescribed limits. In radiation processing the absorbed dose is frequently measured with calibrated passive dosimeter 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 gamma rays [1–7]. Poly(vinyl butyral) has previously been used successfully to make free-standing dye 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 system [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 also depends on the dose rate or fractionation of the dose [14], on the temperature during irradiation, and on the ambient humidity or, rather, on the amount of water in the dosimeters [15–21].

In the present work, thin films of PVB were colored with bromocresol green dye in absence or presence of chloral hydrate to give dosimeter films. The effects of humidity during irradiation as well as the post-irradiation stability on the film response are described.

EXPERIMENTAL

Preparation of Stock Solution of Indicator

A stock solution of sodium salt of the indicator was prepared by dissolving 0.08 g of bromocresol green indicator (BCG) in 1.2 ml of an aqueous solution of NaOH ([NaOH] = 0.1 ml/L) and then the volume was completed by ethanol in a 50 ml volumetric flask. It should be noted that the BCG stock solution is almost neutral (the pH was found to be 6.8) because the NaOH in its preparation is used in equi-molar concentration.

Preparation of the Film

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 [8,13]. 12.5 g of poly (vinyl butyral), PVB (Pioloform BM18, product of Watcker Co., USA) were dissolved in 250 ml of n-butanol at about 50°C. The solution was kept well stirred at the same temperature for about 24 h, left to cool and then divided into 8 parts, each one 25 ml volume.

To five parts of the polymer solution, 2 ml of BCG stock solution was added. Then, 0.1, 0.2, 0.3, or 0.4 g of chloral hydrate (product of Merck, Germany) were separately added to 4 parts and the fifth one was left without chloral hydrate.

To each solution of the rest three parts, 0.2 g of chloral hydrate and 5, 6, or 7 ml of BCG stock solution were added, separately. The eight solutions were kept well stirred at room temperature for about 3 h in order to obtain uniformly mixed solutions. Each solution was poured onto a 15 × 15 cm horizontal glass plate and dried at room temperature for about 48 h. Eight films were obtained, four of them containing the same concentration of BCG (0.64 phr) and different concentrations of chloral hydrate (40, 30, 20, 10 phr). The other four films contained the same concentration of chloral hydrate (20 phr) and different concentrations of BCG (1.12, 0.96, 0.8, 0.74 phr). After drying, the films were stripped from the glass plate, then cut into 1 × 1 cm pieces and stored for future use.

Apparatus

Irradiation was carried out with gamma radiation in the ^{60}CO gamma chamber 4000 A (product of India). The absorbed dose rate in the irradiation facility was measured to be 1.3 kGy/h, using Fricke dosimetry [$G(Fe3^{+}) = 1.62\,\mu mol/J$] [14]. Five films at each dose are grouped together, sandwiched between two PMMA plates of 3 mm thickness (to maintain electronic equilibrium conditions) and irradiated at the control spatial position of the sample chamber using a specially designed holder made from polystyrene. The temperature during irradiation was 30°C.

Unicam UV4 spectrophotometer (product of Unicam Co. Ltd. England) was used to measure the absorption spectra of 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 different BCG/PVB films were recorded before and after irradiation to different doses. The results with films containing 0.8 phr of BCG indicator and 20 phr of chloral hydrate are shown in Figure 1. The absorption spectrum of unirradiated film shows a main absorption band in the visible region, characteristic of blue color, peaking at 631 nm (Figure. 1, curve 1). The amplitude of this absorption band decreases gradually and shifts to lower wavelength with the increase of absorbed dose of γ-ray photons.

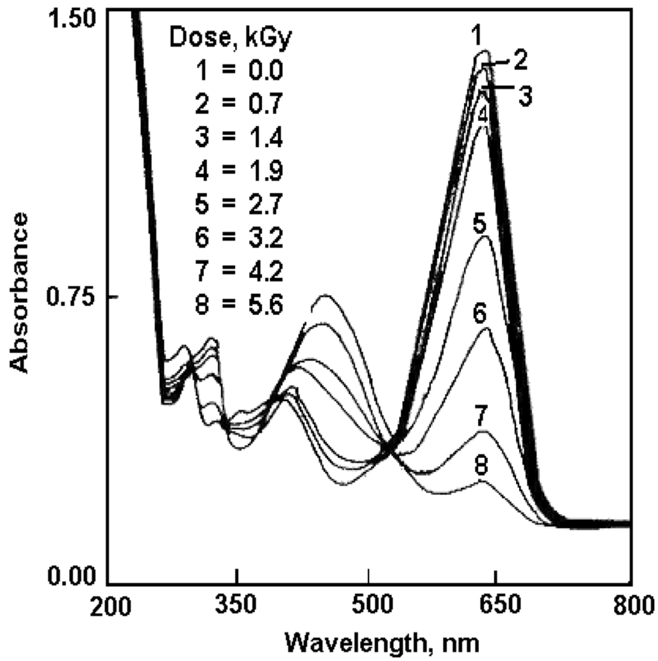

FIGURE 1 The absorption spectra of (BCG/PVB) films unirradiated and irradiated to different absorbed doses, [BCG] = 0.8 phr and [chloral hydrate] = 20 phr.

A new absorption band peaking at 435 nm, characteristic of a yellow color, is formed and its amplitude increases gradually with the increase of absorbed dose. That is, upon irradiation these films change their color from blue (the alkaline form of BCG with $\lambda_{\max} = 631$ nm) to yellow (the acidic form of BCG with $\lambda_{\max} = 435$ nm), indicating acid formation due to gamma irradiation.

Figure 2 shows the absorption spectra of BCG/PVB films without chloral hydrate unirradiated and irradiated to 2.3, 5.6, and 33.4 kGy absorbed doses. The absorption band at 631 nm decreases slowly with the increase of absorbed dose, however, no apparent bleaching occurs at dose of 33.4 kGy. Also, this figure indicates the absence of any absorption band at 435 nm, that is, there is no appreciable radiation formed acid to change the color.

Response Curves

Figure 3 shows the response curves of BCG/PVB films containing 0.64 phr of BCG and different concentrations of chloral hydrate. The

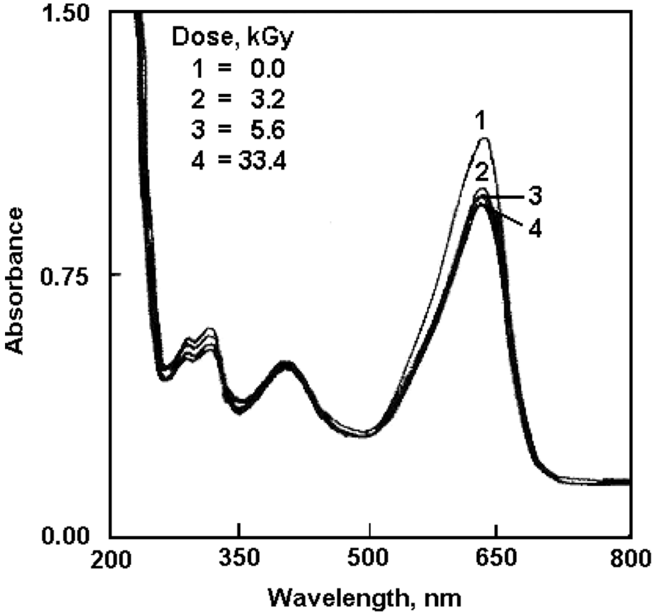

FIGURE 2 The absorption spectra of (BCG/PVB) films unirradiated and irradiated to different absorbed doses, without chloral hydrate.

response curves were plotted in terms of change in optical density per unit thickness, (ΔA mm^{-1}) measured at 631 nm wavelength versus the absorbed doses, ($\Delta A = Ai - Ao$), where Ao and Ai are the optical densities of unirradiated and irradiated films, respectively. It can be noticed that all curves have the same S shape, characteristic of irradiation response of a pH indicator in an acid base titration with different sensitivities. It may be observed from the data illustrated in Figure 3, that the initial part of all curves depends on the concentration of chloral hydrate. As a matter of fact, the flattening of this portion of curves decreases with increasing the concentration of chloral hydrate. Accordingly, this behavior may be attributed to the [H^+] formed on irradiation as its concentration would be expected to increase with increasing chloral hydrate concentration. A certain [H^+] ought, therefore, to be present, corresponding to certain pH value, for indicator BCG, to start changing its color. After reaching this pH value the indicator starts to change color linearly within its specific range, giving the linear sections in the curves. The occurrence of flattening off end section of the curves may be ascribed to complete transformation of the indicator form its basic form to acidic one.

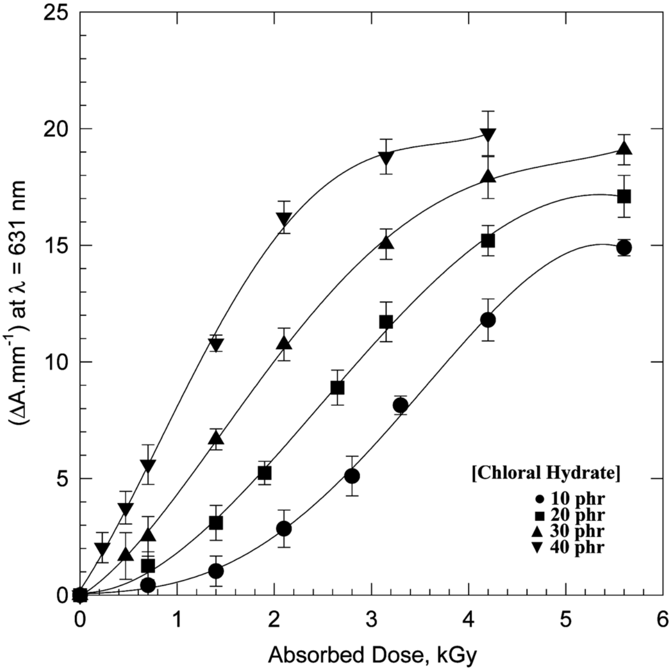

FIGURE 3 Change of $\Delta A \cdot mm^{-1}$, as a function of absorbed dose for different chloral hydrate concentrations in BCG/PVB films. [BCG] $= 0.64$ phr. $\lambda_{max} = 631$ nm.

Figure 4 shows the response curves of BCG/PVB films containing 20 phr chloral hydrate and different concentrations of BCG indicator. It can be seen that all curves have the same S shape, which reaches saturation doses proportional to the concentration of BCG.

Radiation Chemical Yield

The radiation-chemical yield (G-value) is defined as the number of moles of reactant consumed by the absorption of 1 J of energy (unit: mole/J). The G-value is calculated from the general relation (McLaughlin et al., 1989) [13]:

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

where ΔA is the change in the absorbance at λ_{max}, b is the optical path length (cm), ε is the linear molar extinction coefficient at λ_{max} ($L\,mol^{-1}cm^{-1}$), ρ is the density of the dosimeter (g/cm^3), D is the absorbed dose (Gy).

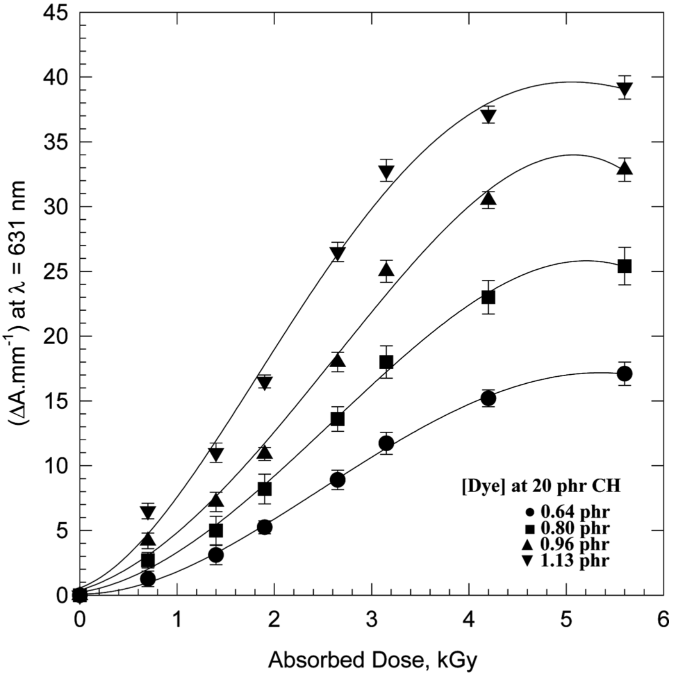

FIGURE 4 Change of $\Delta A{\cdot}mm^{-1}$, as a function of absorbed dose for different BCG concentrations in PVB films. [CH] = 20 phr. $\lambda_{max} = 631\,nm$.

The calculated G-values at different doses are shown in Figure 5 as a function of both dye concentrations and chloral hydrate concentrations. It is clear that G-values increase with constant slope, calculated to be $2.53\,e^{-5}$ by increasing dye concentrations and $2.1\,e^{-7}$ by increasing chloral hydrate concentrations. These results indicate that the effect of dye on the G-value is larger than that of the chloral hydrate.

Effect of Humidity During Irradiation

The effect of relative humidity (RH) on response of BCG/PVB films (0.8 phr BCG, 20 phr chloral hydrate) was investigated by irradiation of the BCG/PVB films to a dose of 2.7 kGy at different humidities (0, 12, 33, 54, 76, and 93%).

Irradiation was carried out while the films were suspended over various saturated-salt solutions in an enclosed jar [21], except for 0% RH, which was suspended over dried silica gel. Figure 6 shows the variation of response ($\Delta A\,mm^{-1}$) as a function of

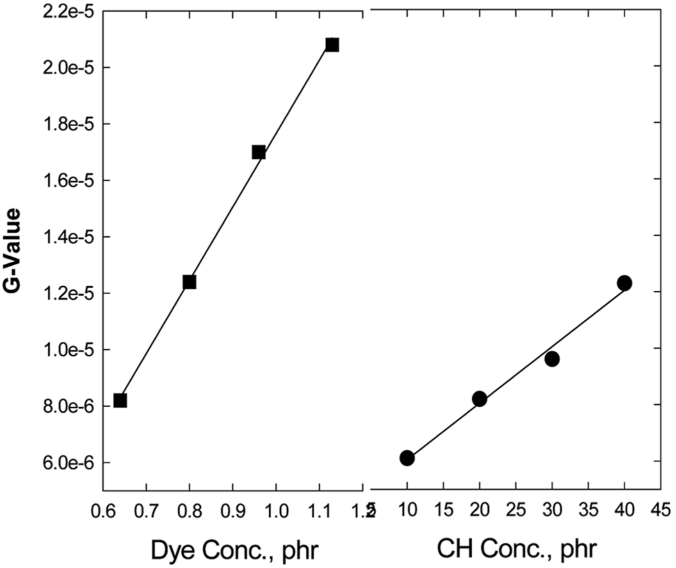

FIGURE 5 The calculated G-values at different doses as a function of both dye concentrations and chloral hydrate concentrations.

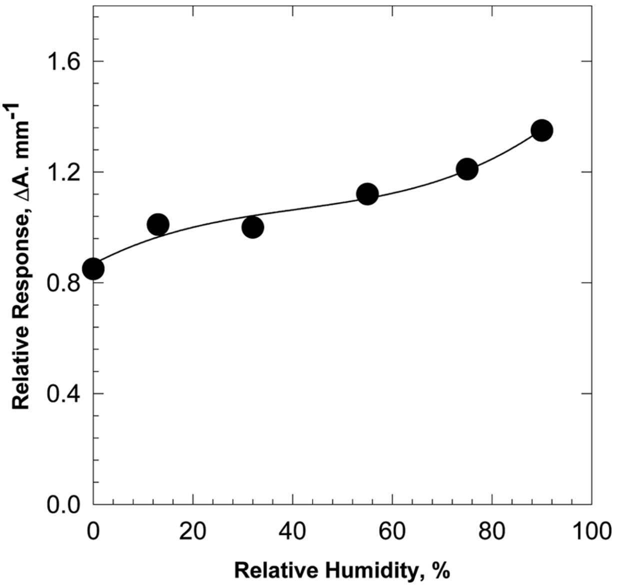

FIGURE 6 Variation of response of BCG/PVB films as a function of relative humidity during irradiation at $\lambda_{\max} = 631\,\text{nm}$.

percentage relative humidity during irradiation relative to that at 33% RH.

It is clear from Figure 6 that the response increase gradually with the increase of relative humidity up to 50% RH. Above it, the increase is larger.

Shelf Life

Stability measurements before irradiation were made by storing films in the dark and under laboratory fluorescence lights at ambient relative humidity (35–40% RH) and room temperature (25°C), and reading the films spectrophotometrically at different times during the pre-irradiation storage period of 60 days. The films exhibited excellent stability before irradiation.

Post-Irradiation Stability

Figure 7 shows BCG/PVB films (irradiated to 2.92 kGy) were stored in the dark and under laboratory fluorescence light at 25°C. The

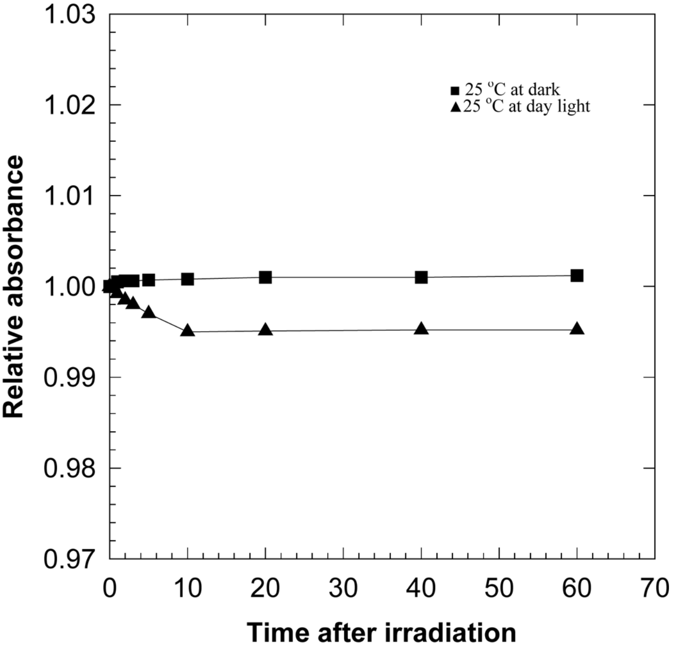

FIGURE 7 Post-irradiation stability of BCG/PVB film stored under different storage conditions at $\lambda_{max} = 631\,nm$, time in days.

absorbance of these films (at 631 nm for BCG/PVB) was measured at different intervals of time during the post-irradiation storage period of 60 days. The irradiated films show satisfactory stability under all storage conditions, with less than 5% increase in absorbance over this period.

CONCLUSION

Films made of PVB dyed with BCG are useful as radiation dosimeters in the dose ranges 1–6 kGy, if properly calibrated. The radiation chemical yield (G-values) increase with constant slope, calculated to be $2.53\,e^{-5}$ for increasing dye concentrations and $2.1\,e^{-7}$ for increasing chloral hydrate concentrations. The films are highly stable for long times before and after irradiation under different storage conditions and are not affected by humidity changes during irradiation in the intermediate range of humidity.

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