

Dosimeter Film Based on Ethyl Violet-Bromophenol Blue Dyed Poly (vinyl alcohol)

S. Ebraheem and M. El-kelany#

Radiation Protection and Dosimetry Dept., National Centre for Radiation Research and Technology (NCRRT), P. O. Box; 29 Nasr City, Egypt, #E.mail; dr.moosh@hotmail.com.

DYED POLY(VINYL ALCOHOL) (PVA) films, prepared by a simple technique of casting aqueous solutions of PVA containing a mixture of ethyl violet and bromophenol blue (EV-BPB) on a horizontal glass plate, are useful as routine high-dose dosimeter in the 1-30 kGy range. The colour of films changes from violet to yellow when exposed to gamma radiation. The response of this dosimeter depends up on the concentration of chloral hydrate (CH) in the polymer material. The radiation chemical yield (G-value) of PVA dyed film was calculated and found to increase by increasing concentration of chloral hydrate. Post-irradiation storage on the response of the films are discussed.

The overall combined uncertainty (at 2σ) associated with measurement of response ($\Delta A \text{ mm}^{-1}$) at 600 nm for dose range 1-15 kGy is 5.6 %.

Keywords: Ethyl-violet and bromo-phenol blue, Poly(vinyl alcohol, gamma ray dosimeter.

Treatment of food by radiation has rendered routine dosimeters and labels in the 1-30 kGy range necessary. There are few solid-state dosimeters known to be applicable in this dose range e.g., amber and gammachrome perpex (Glover *et al.*, 1985 and Whittaker, 1988) and analnine dosimeters (Regulla and Deffiner, 1982). Radiation-sensitive indicators may be used to show that products have been exposed to radiation source. A new label dosimetry system based on the idea of mixing more than one dye having different sensitivities to radiation has been developed (Abdel-Rehim and Abdel-Fattah, 1993). Radiation sensitive materials consisting of a chlorine-containing polymer and an acid-sensitive dye are known (Matsumoto *et al.*, 1973 and Hori *et al.*, 1975). The chlorine-containing polymer is dehydro-chlorinated when the material is irradiated there by reducing pH and causing the acid-sensitive dye to change colour. A similar colour can be produced if a halogen-containing substance is present in the dye-containing matrix (Whittaker, 1987). Many other films

containing a radiation sensitive pH indicator dye with chloral hydrate have been prepared to be used as γ -radiation monitoring dosimeters and indicators (Yasser, 2005). Ueno (1988) developed a radiation dosimeter from acid indicators by coating a high molecular weight polymer support (e.g. polyester film) with a composition containing a halogen-containing polymer (e.g. PVC), a pigment which changes colour with the changes of pH and basic material (e.g. KOH in EtOH). A chlorine-containing polymer is not necessary for this reaction to occur.

The current work describes the initial investigations of films which combine PVA, mixture of EV and BPB and chloral hydrate to give dosimeter films.

Materials and Methods

Preparation of stock solutions of EV and BPB dye

The stock of the dye was prepared by dissolving 0.08 g of EV (product of RIEDEL DEHAEN, Germany) in 50 ml distilled water. Also, the stock solution of the dye was prepared by dissolving 0.08 g of BPB (product of CHAMPOL, Czech Republic) in 50 ml distilled water. These two stock solutions were used in the preparation process of the mixed dye dosimetry film.

Preparation of (EV-BPB)/PVA mixed dye films

Fully hydrolyzed poly vinyl alcohol; 99-100% (10g) from J. T. Baker chemicals Co, USA were dissolved in 250 ml doubly-distilled water at about 60°C. The solution was kept well stirred at the same temperature of about 24h, then left to cool. To this solution 2 mg of EV-BPB mixture was added and further stirred for 3 h so as to obtain a uniformly coloured PVA solution. To each 30 ml of the well mixed solution 0.2, 0.5, 0.8 and 1 g of chloral hydrate CH (from Merck Co.) were added. The dyed PVA solution are poured onto a 15× 15 cm polyester sheet (0.1 mm thickness) fixed on a horizontal levelled glass plate and kept to dry in dark room at temperature (25± 2°C). After stripping the films they were stored in dark at relative humidity of 35%. The thicknesses of the films were measured using Digitrix-MarkII thickness gauge at 5 randomly selected places with a thickness gauge having an accuracy of 0.055± 0.002 mm.

Measurement and dosimetry

The absorption spectra of un-irradiated and irradiated films were measured throughout the wavelength range 200-800 nm using a UVIKON 860
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spectrophotometer. The film thickness was measured using a Digitrix-Mark II gauge (precision $\pm 1\mu\text{m}$, 1σ). Irradiation was carried out with gamma radiation in the ^{60}Co gamma chamber 4000A irradiation facility (product of India). The absorbed dose rate in the irradiation facility was measured to be 6.334 kGy/h, using reference Alanine dosimeters. The electronic equilibrium conditions were maintained during irradiation.

Results and Discussion

Absorption spectra

The absorption spectra of EV-BPB/ PVA films without chloral hydrate recorded before and after irradiation to different doses are shown in Fig. 1. The main absorption band in visible region is characteristic to violet colour peaking at 600 nm. The amplitude of this band decreases gradually with the increase of dose of γ -ray photon, at λ_{max} 600 nm. The absorption spectra of unirradiated and irradiated films were measured throughout the wavelength range 200-800 nm. The absorption spectra of these films with chloral hydrate recorded before and after irradiation to different doses are shown in Fig. 2. The amplitude of this band, decreases gradually with the increase of dose of γ -ray photon. It is clear from the spectra of irradiated film that, the mixed dyes V-BPB degraded by applying of gamma rays on the film. Four different chloral hydrate concentrations 16.6, 41.6, 66.6 and 83.3 phr with 0.3 phr of EV-BPB were examined.

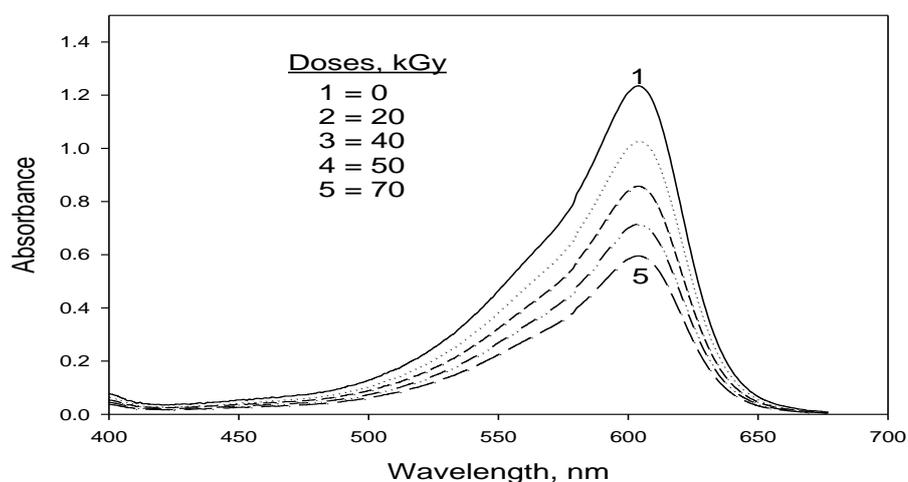


Fig. 1. The absorption spectra of EV-BPB/ PVA films unirradiated and irradiated to different absorbed doses

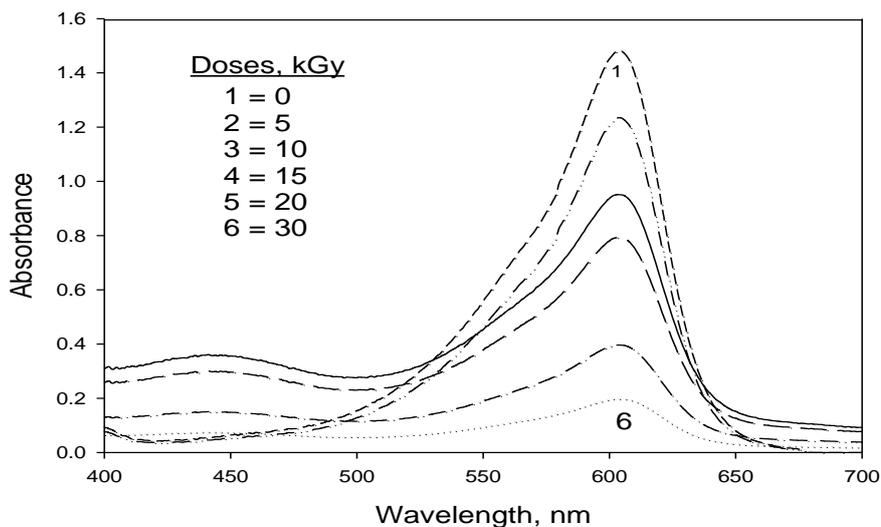


Fig. 2. The absorption spectra of EV-BPB/ PVA films containing chloral hydrate unirradiated and irradiated to different absorbed doses (Chloral hydrate= 66.6 phr).

The acid sensitive dye in the film changes its colour from violet to yellow by irradiation due to consequent lowering of the pH of the film caused by the HCl generated from the radiolysis of chloral hydrate (Abdel-Fattah *et al.*, 1996).

Response curves

For dosimetry, optical density read out was carried out at 600 nm for EV-BPB/ PVA films for different concentration of chloral hydrate (16.6, 41.6, 66,6 and 83.3 phr). Fig. 3. show the response curves in terms of change optical density per unit thickness $\Delta A = A_o - A_i$, where A_o and A_i are values of optical density for the unirradiated and irradiated films, respectively. The curves show that the useful dose range extends up to 30 kGy. It can be noticed that all curves show the same trend where they are linear up to about 15 kGy, then tend to saturate at higher doses. But, all curves differ in the response value (initial curve slope). Fig. 4. shows the relation between the response value (initial curve slope) and the concentration of chloral hydrate. It can be seen that, the response increases by increasing the concentration of chloral hydrate.

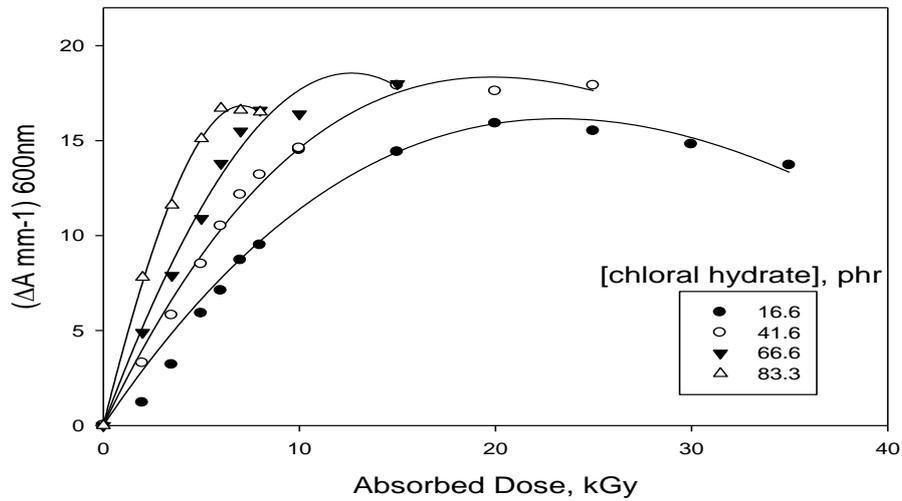


Fig. 3. Change of ΔA . mm-1 as a function of absorbed dose of EV-BPB/ PVA films with different concentration of CH (measured at 600 nm).

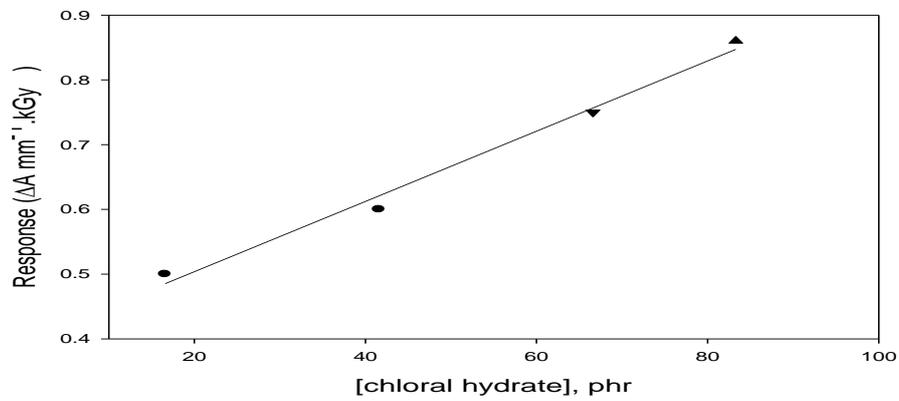


Fig. 4. Change of response ($\Delta A \cdot \text{mm}^{-1} \cdot \text{kGy}^{-1}$) of EV-BPB/ PVA film as a function of concentration of chloral hydrate.

Fig. 5. shows the relation between the dose at saturation (reach saturation more than 95% of indicator changes its colour) and the concentration of chloral hydrate. It can be seen that, the dose at saturation decreases linearly with the increase of [CH] from 16.6 to 83.3 phr. The obtained straight line which can be expressed as follows:

$$D = 21.8 - 0.23 [\text{chloral hydrate}]. \quad D \text{ is the dose at saturation in kGy.}$$

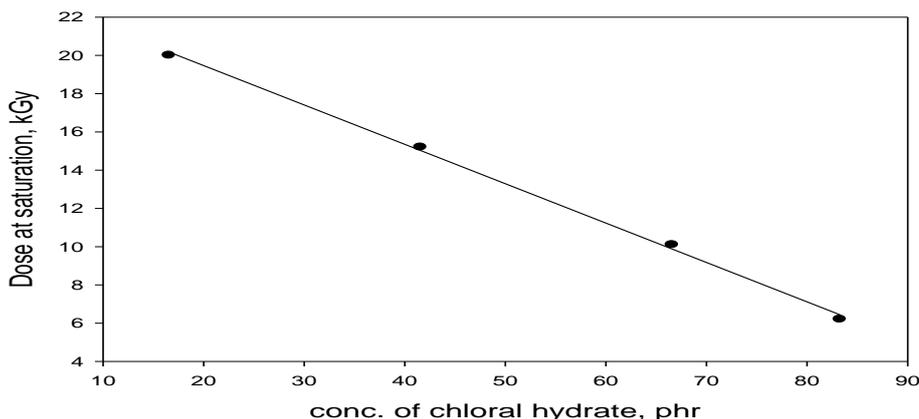


Fig. 5. Variation of dose at saturation, kGy of EV-BPB/ PVA films as a function of concentration of CH ($\lambda_{\max} = 600$ nm).

Calculation of concentration of hydrogen ion

Fig. 6. show the total amount of H^+ ion in films containing different concentrations of chloral hydrate as a function of absorbed dose at 600 nm wavelength (Abdel-Fattah and El-Kelany, 1998). It can be seen that the amount of acid formed increases gradually with the increase of absorbed dose. The rate of increment of acid increases with the increase of both absorbed dose and concentration of chloral hydrate.

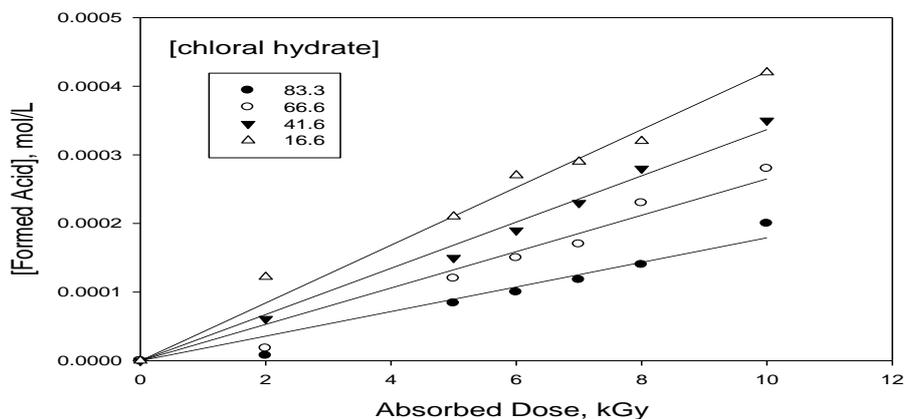


Fig. 6. Concentration of radiation formed HCl in EV-BPB/ PVA films containing different concentrations of chloral hydrate as a function of absorbed dose. $\lambda_{\max} = 600$ nm.

Radiation-chemical yield

The radiation-chemical yield (G-value) is defined here as the number of moles of dye degraded by the absorption of 1J of energy (unit: mol/ J). The G-value has been carried out by using the equation (McLaughlin *et al.*, 1989).

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

Using the dye concentration in mol/L and the average value $L \text{ mol}^{-1} \text{ cm}^{-1}$ of A_0/b , the molar extinction coefficient (ϵ) is calculated as $1230.07 \text{ L mol}^{-1} \text{ cm}^{-1}$. The density of PVA is 1.25 g.cm^{-3} . Fig. 7. shows the obtained G(-dye) values as a function of chloral hydrate concentration. It can be seen that the G(value) increases with the increase of chloral hydrate concentration.

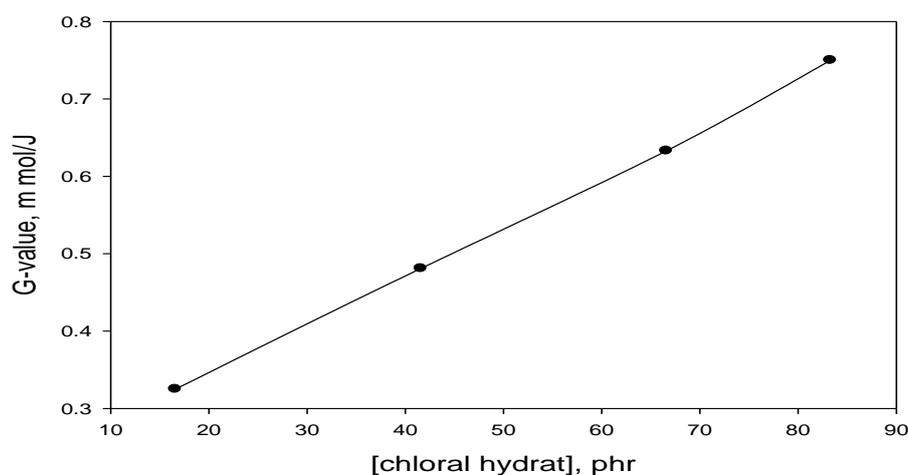


Fig. 7. Change of G-value of EV-BPB/ PVA as a function of chloral hydrate concentration.

Assessment of uncertainties

To be meaningful, a measurement of gamma ray shall be accompanied by an estimate of the uncertainty in the measured value. Factors contributing to the total uncertainty may be separated into two types, type A and type B (ISO/ASTM, 2002 and Taylor *et al.*, 1994). The first factor is associated mainly with the measuring equipment and the film while the second is mainly related to the calibration.

The reproducibility of the Unicam UV-4 spectrophotometer was determined by reading the absorbance value (at 600 nm wavelength and

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absorbance level 0.8) of irradiated films several times. From the data obtained, it was found that the coefficient of variation (1σ) is $\pm 0.23\%$, reflecting the precision of the spectrophotometer. The reproducibility of the Digitrix-Mark II thickness gauge was determined by reading the thickness value for EV-BPB/PVA films several times. From the data obtained, it was found that the coefficient of variation (1σ) is $\pm 0.7\%$. The reproducibility of the measurements of several films (10 times for film) was found to be 0.9% (1σ).

On the other hand, the type A uncertainties (at one standard deviation, i.e. 1σ) arising during calibration over the useful response range were found to be $\pm 2.6\%$. The combined uncertainties can be obtained by combining all the components in quadrature at one standard deviation (1σ) as follows:

$$U_c = \sqrt{(0.23)^2 + (0.7)^2 + (2.6)^2 + (0.9)^2} = 2.8\%$$

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 EV-BPB/PVA film is 5.6% .

Post-irradiation stability

The post irradiation stability for EV-BPB/PVA films containing 66.6 phr of CH and irradiated to 20 kGy is investigated by storing them in dark at 25°C and under laboratory fluorescent lights at the same temperature.

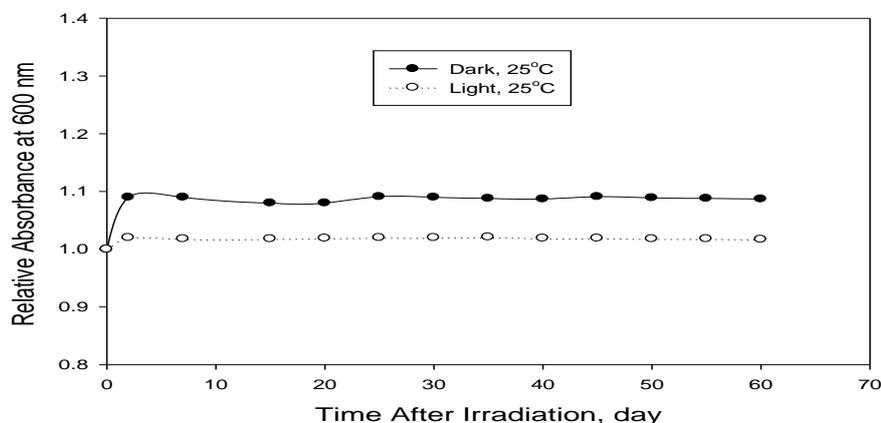


Fig. 8. Post-irradiation stability of EV-BPB/PVA film stored under different storage conditions, [CH]= 66.6 phr.

The absorbance of these films was measured at 600 nm at different intervals of the time during the post-irradiation storage period of 60 days, as shown in Fig. 8. The films show excellent stability under all storage conditions.

Conclusion

Films made of PVA dyed with ethyl violet and bromophenol blue are useful radiation dosimeters in the dose range up to 70 kGy while these films containing chloral hydrate (16.6-83.3 phr) are useful in the range 5-30 kGy. The films are highly stable for long times after irradiation under different storage conditions. These properties suggest them to be useful for routine monitoring and dose mapping in radiation processing. They are easy to prepare in a laboratory and do not require toxic solvents in the preparation.

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استخدام أفلام البولي فينيل كحول المحتوية صبغة الايثيل البنفسجي-بروموفينول الزرقاء كمقياس للجرعات الإشعاعية

سيف الدين إبراهيم و مشيرة عبد القادر الكيلاني

قسم الوقاية و الجرعات الإشعاعية ، المركز القومي لبحوث وتكنولوجيا الإشعاع
ص. ب : ٢٩ مدينة نصر ، مصر.

لقد تم في هذا البحث تحضير أفلام بلاستيكية ملونة بطريقة بسيطة وذلك بتحضير محلول مائي من عديد فينيل الكحول و الذي يحتوي على خليط من صبغة الايثيل البنفسجي - البروموفينو الزرقاء ثم فرد هذا المحلول على لوح زجاجي أفقي للاستعمال كمقياس للجرعات الإشعاعية بالطرق الروتينية في المدى 5 - ٣٠ كيلو جراى. كما تم دراسة استجابة هذا الفيلم للإشعاع تعتمد على تركيز المادة التي تحتوى على الكلور. وقد تم حساب الناتج الكيميائي وتكنولوجيا الإشعاعي (G-value). و وجد أنه يزيد بزيادة تركيز الكلور الهيدرات في مادة الفيلم. كما تضمنت الدراسة تأثير ظروف التخزين المتباينة على حساسية الأفلام وثباتها بعد عملية التشعيع.