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Investigation of Polymeric Films Based on Brilliant Green Dyed Poly (Vinyl Alcohol) and Poly (Vinyl Butyral) for Use in High Dose Processing Dosimetry

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DYED POLYMER FILMS prepared by simple technique of casting aqueous solution of poly vinyl alcohol (PVA) or poly vinyl butral (PVB) containing Brilliant Green (BG) on horizontal glass plate were studied to be used for high dose dosimetry. Both films were bleached with different rates on exposure to gamma ray. Chloral hydrate was added to both polymeric films and the effect of its concentration as well as dye concentration on response was studied. Wavelength of analysis is 633 nm. The radiation chemical yield (G-values) was calculated in presence and absence of chloral hydrate. The films exhibit negligible humidity effect during irradiation. Pre- and post- irradiation stability was examined.

Keywords: Poly vinyl alcohol, poly vinyl butral, Brilliant green, dosimetry

Radiation bleachable organic dyes were widely investigated (Ebraheem *et al*., 2005). For dose monitoring in radiation processing, the polymeric dyed flexible films are considered to be the most commonly materials used as dosimeters and indicators (Abdel-Rehim and Abdel-Fattah, 1993) and for monitoring the absorbed dose delivered by electron beams and gamma rays (Kovacs *et al*., 2002). Many dyed films had been developed and investigated for possibility of using in measuring absorbed doses in nuclear reactors, X- rays, gamma rays and electron beam (Kovacs *et al*., 2000). 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 (Soliman, 2005). Kattan *et al*., (2011) studied the using of Polyvinyl chloride (PVC) dyed with bromocresol purple was investigated as a high-dose radiation dosimeter.

In the current work, a distinct comparison for responses behaviour of BG dye in different polymer materials PVA and PVB were carried. The effect of dye

concentrations and chloral hydrate was studied; also pre and post irradiation stability as well as humidity effect during irradiation was examined from dosimetric point of view.

Materials and Methods

Preparation of stock solution of BG

Stock solution of BG dye prepared by dissolving 0.08 g of BG; $C_{27}H_{34}N_2O_4S$ M.Wt= 482.63 g/mol, Sigma-Aldrich, Inc., USA in 50ml Ethanol. The solution was kept well stirred for about 24 h to obtain a homogenous dye solution. The structure formula of BG was represented in Fig.1.

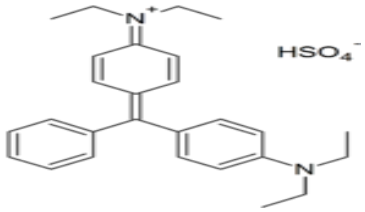

Fig.1. Structure formula of Brilliant Green.

Preparation of BG films

Films were prepared by dissolving either 9g PVA powder; average M.wt 25,000 fully hydrolysed 99-100% product of J.T baker chemical Co., USA in 180 ml double distilled water or 10.5g PVB; average M.wt 36,000 product of Wacker Co., USA in 210ml n-butanol. Complete dissolution done by stirring for 3h at about 60^{o}C followed by continuous stirring for 24h at room temperature then left to cool. PVB polymer solution was divided into seven parts each part is 30ml volume. 2.2ml, 3.3ml and 4.4ml of the BG stock solution were added to the first three parts. The rest four parts contain the same dye concentration 3.3ml and (0.1g, 0.2g, 0.3g, 0.4g) chloral hydrate was added. Seven films were obtained; three of them contain (0.23phr, 0.35phr, 0.46phr) of BG dye without chloral hydrate. The rest four films contain (7.4phr, 14.8phr, 22.2phr and 29.6phr) of chloral hydrate and 0.35phr of dye. For PVA films, polymer solution was divided into six parts each of its 30ml volume. BG was added to three parts of polymer solution as (1.1ml, 2.2ml and3.3ml). The rest three parts contain the same dye concentration 3.3ml and (0.1g, 0.2g, 0.3g) Chloral hydrate was added, respectively. Six films were obtained; three of them contain (0.11phr, 0.23phr, 0.35phr) of BG dye. The rest three films contain (7.4phr, 14.8phr, 22.2phr) of chloral hydrate and 0.35phr of dye. Each solution was poured on to 15x 15cm

horizontal glass plate and dried at room temperature for about 48h. After drying, the films were stripped from the glass plate then, cut into 1x 1cm pieces and stored for different investigation. The thickness of the obtained film was found to be 0.04 0± 0.01mm (1σ) for PVB and 0.042± 0.01mm (1σ) for PVA.

Instruments

The absorption spectra of un-irradiated and irradiated films were measured throughout the wavelength range 200-800nm using a UVIKON860 spectro-photometer. The film thickness was measured using Digitrix-Mark II thickness gauge; precision± 1µm. Gamma irradiation was carried out in the ^{60}Co gamma chamber 4000 A^{o}; India. The absorbed dose rate in irradiation facility was measured to be 3.75kGy/h using reference alanine dosimeter and the electronic equilibrium conditions were maintained during irradiation, through stuffing the films in the middle of5 mm thickness of poly methylmethaccrylate from both sides.

Results and Discussion

Absorption spectra

The absorption spectra of the BG/ PVB films containing 0.35phr BG and 22.2phr chloral hydrate were recorded before and after irradiation to different doses are shown in Fig. 2. The absorption spectra shows main absorption band in the visible region peaking at 633nm characteristic of a blue colour.

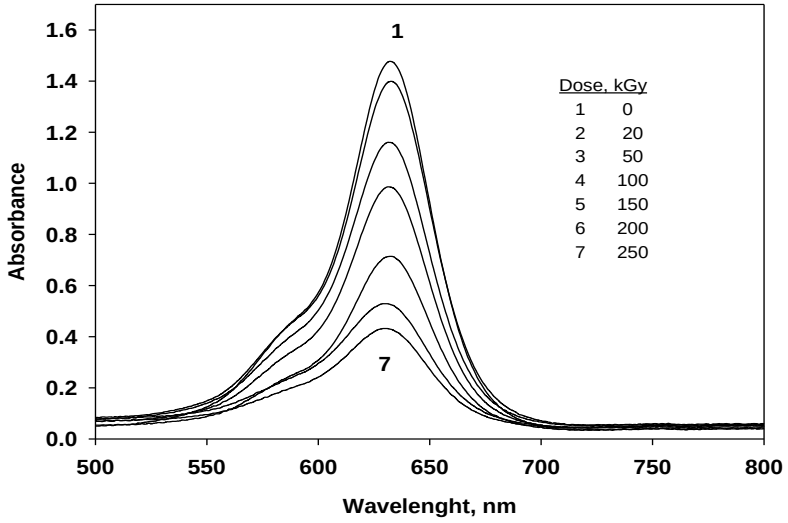

Fig. 2. The absorption spectra of (BG/ PVB) films unirradiated and irradiated at different absorbed doses. [BG]= 0.35phr.

The blue colour intensity of this band decreases gradually with the increase of absorbed dose until complete bleaching at 250kGy. BG/ PVA films have the same absorption band peaking at 633nm but differ in sensitivity towards γ radiation (i.e., PVA films are more sensitivity to γ-radiation). This reflects the sensitive to dye towards γ-radiation.

Response curves

Fig. 3&4. represent the response curves of both BG/ PVB and BG/ PVA films containing different dye concentrations. The response were established in terms of change in absorbance per unit thickness ($\Delta A.mm^{-1}$) at 633nm against the absorbed dose ($\Delta A = A_o - A_i$, where, A_o and A_i are values of absorbance at 633nm for un-irradiated and irradiated films, respectively). Each point on the dose response curve represents the mean optical density measurement of 3 dosimeter films irradiated to the same dose. The curves show that the useful dose range extend up to~70 kGy for BG/PVA film and up 250 kGy for BG/ PVB films. From the two Fig. we can conclude that PVA accelerates the bleaching reaction of BG dye.

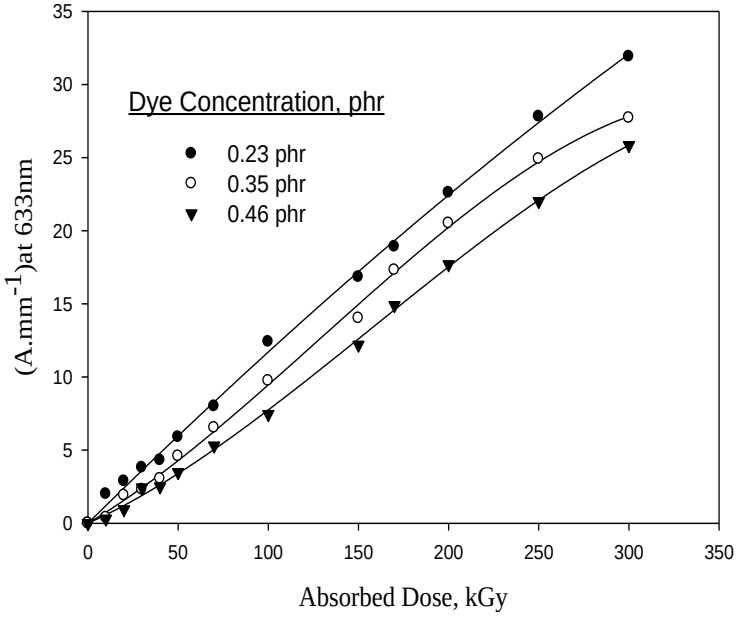

Fig. 3. Change of absorbance at 633nm as a function of absorbed dose of (BG/ PVB) films containing different dye concentrations.

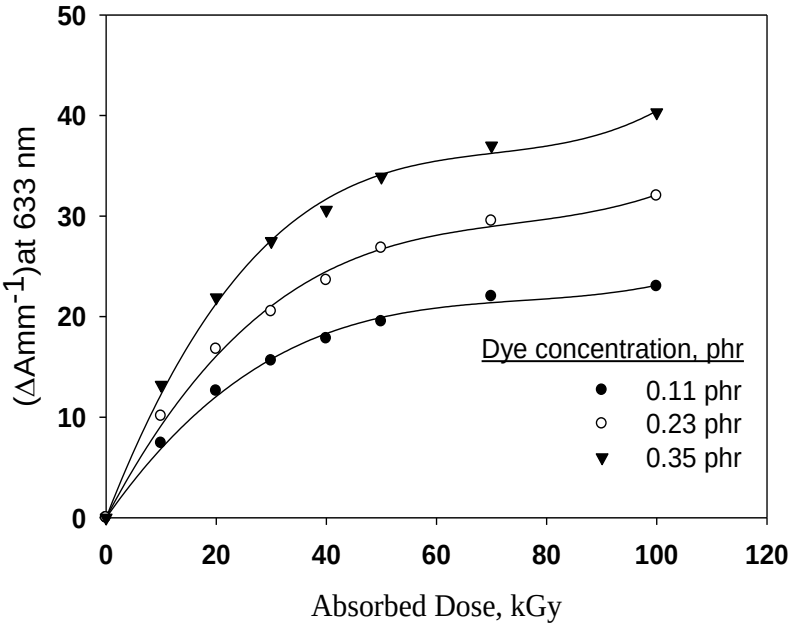

Fig. 4. Change of absorbance at 633nm as a function of absorbed dose of (BG/PVA) films containing different dye concentrations.

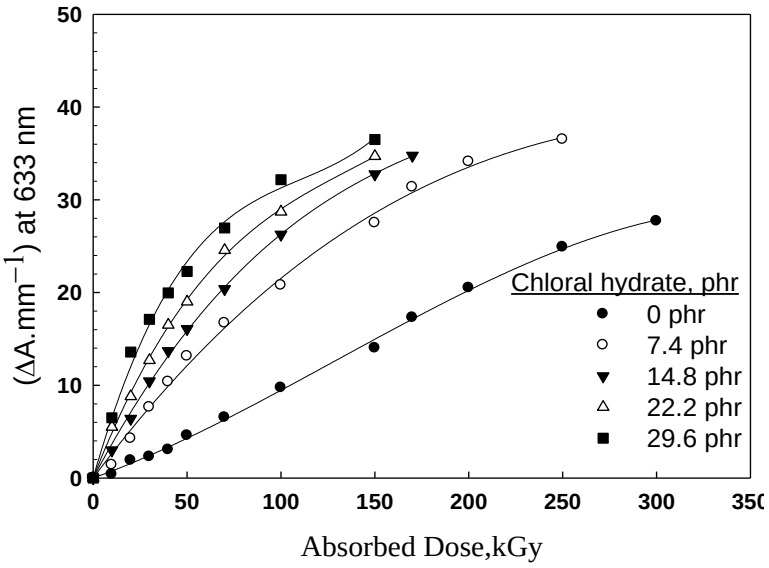

Fig. 5. Change of absorbance at 633nm as a function of absorbed dose of (BG/ PVB) films containing 0.35phr dye with different chloral hydrate concentrations.

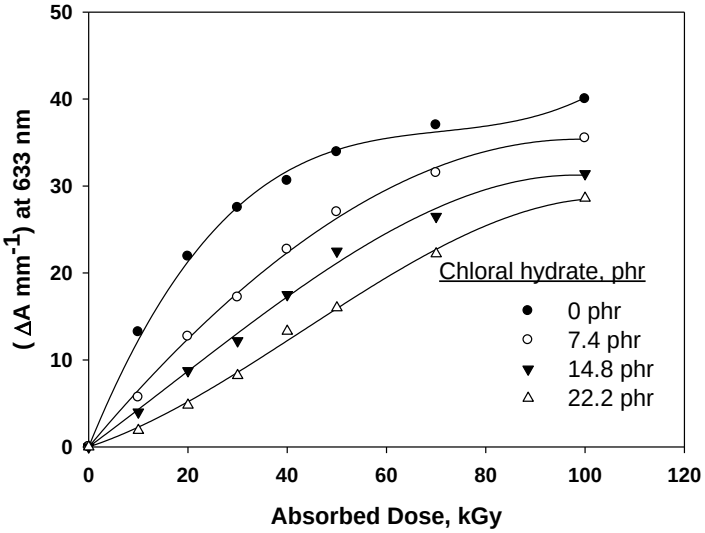

Fig. 6. Change of absorbance at 633nm as a function of absorbed dose of (BG/ PVA) films containing 0.35phr dye with different chloral hydrate concentrations.

Fig. 5&6. show the response curve of BG/ PVB and BG/ PVA films containing 0.35phr of BG and different concentration of chloral hydrate. In Fig. 5. all curves have the same trend but they differ in the slope value; slope of the initial part of the curves. The slope increase with increase of the choral hydrate concentrations in PVB films. The useful dose range extended up to 200kGy for lowest chloral hydrate concentration but goes down to 50kGy to the highest chloral hydrate concentration. In Fig. 6 it is clear that the increase in the chloral hydrate may be contributed in the complex formation with BG, this retards the bleaching reaction. Therefore, the slope decreases with the increase the chloral hydrate concentration. From the two Fig. it is clear that, chloral hydrate have a high effect on the bleaching process of both films, where it accelerates the bleaching reaction in PVB films, while in case of PVA films chloral hydrate acts as a shield for BG molecule.

Radiation chemical yield

The radiation-chemical yield is defined as a number of moles of dye degraded by the absorption of 1 J of energy. The G-value is calculated from the general relation (McLaughlin *et al*., 1989).

$$G(-\mathrm{Dye}) = \Delta A / D.\varepsilon.\rho.b \ (\mathrm{mol/J})$$

Where, ΔA is the change in absorbance at λ_{max}, b is the optical path length (cm),

ε is the molar extinction coefficient at λ_{max} (L mol $^{-1}$ cm $^{-1}$), ρ is the density of the dosimeter (g.cm^{-3}) and D is the absorbed dose (Gy).

By using dye concentration in mol/L and the average value of A_o/b, the molar extinction coefficient is calculated as 44153.52 L mol^{-1} cm^{-1} for PVB and 73668.03 Lmol^{-1} cm^{-1} for PVA where the density is 1.25 and 1.1 g cm-3 for PVB and PVA, respectively. Table 1. represents the G-value for PVB and PVA films containing different dye concentration.

TABLE. 1. The calculation G-value for both BG/ PVA and BG/ PVB at different dye concentration.

Dye conc. (phr)-	**G-value (BG/ PVB)** (μmol J^{-1})	**G-value (BG/ PVA)** (μmol J^{-1})
0.11	------	0.099
0.23	0.0250	0.1293
0.35	0.0150	0.1710
0.46	0.0114	--------

From the Table .1 it could be noticed that G-value (BG/ PVB) films decrease by increase the dye concentration and G-value (BG/ PVA) increase by increase the dye concentration. For the same dye concentration; 0.35phr, 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. Table 2. represent the G-value of both PVA&PVB films containing different concentrations of chloral hydrate and the same dye concentration; 0.35phr.

TABLE.2. The calculated G-values for BG/ PVA and BG/ PVB films containing different concentrations of chloral hydrate.

Chloral hydrate (phr)	**G-value (BG/ PVB)** (μmol J^{-1})	**G-value (BG/ PVA)** (μmol J^{-1})
7.4	0.0558	0.0806
14.8	0.0784	0.0557
22.2	0.1062	0.0237
29.6	0.1453	------

From Table 2. it can be seen that G-value increase by increase chloral hydrate concentration for BG/ PVB films. While it decrease by increase chloral hydrate concentration for BG/ PVA films.

Effect of humidity during irradiation

The effect of relative humidity (RH) during irradiation on the response of both BG/ PVA and BG/ PVB films were investigated by irradiating the films containing 0.35phr BG and 22.2phr chloral hydrate to a dose of 50kGy at

different relative humidity (0, 23, 54, 76, 92 and 100% RH). The different relative humidity was maintained by using different saturated salt solution (Levine *et al*., 1979). The films were stored before irradiation for three days period under the same relative humidity conditions as when irradiated so, that the equilibrium moisture content in dosimeter is established during irradiation.

Fig. 7. represents the variation in ΔAmm^{-1} at 633nm for PVA&PVB films, as a function of percentage relative humidity during irradiation, relative to that at 33% one. It can be seen that for PVA films the relative absorbance increase until 80% relative humidity with 2.5%, then it shows a decrease with 3.6% till relative humidity. In addition, PVB films exhibit a slight decrease until 45% relative humidity then a gradual decrease with 5% to 90% relative humidity.

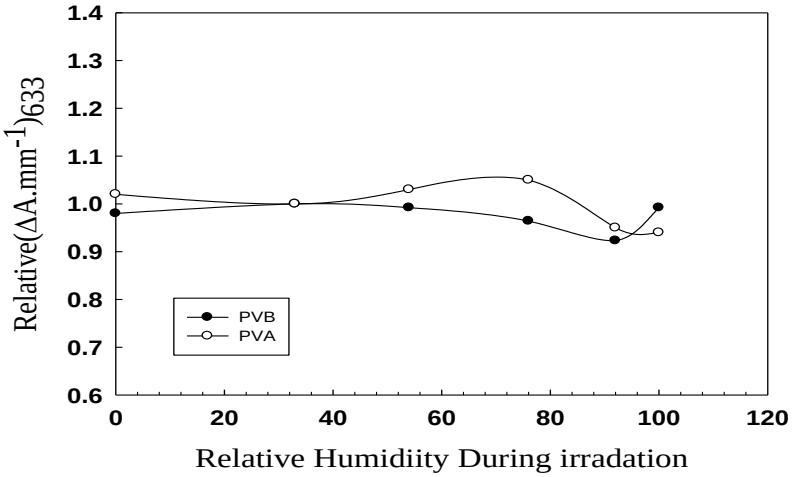

Fig. 7. Variation of response of (BG/ PVA) films as a function of relative humidity during irradiation, λmax 633 and irradiation dose 50kGy.

Shelf life

Stability measurements before irradiation were made by storing (BG/PVA) and (BG/ PVB) films in dark and light at temperature 25^{o}C and measured the absorbance of films spectrophotometrically at different interval times during the pre-irradiation storage period of 30 days as shown in Fig. 8&9. It can be seen that, after 30 days of conditioning at temperature 25^{o}C, both films exhibit excellent stability before irradiation where the variation in absorbance during the 30 days storage period is less than± 1% in light.

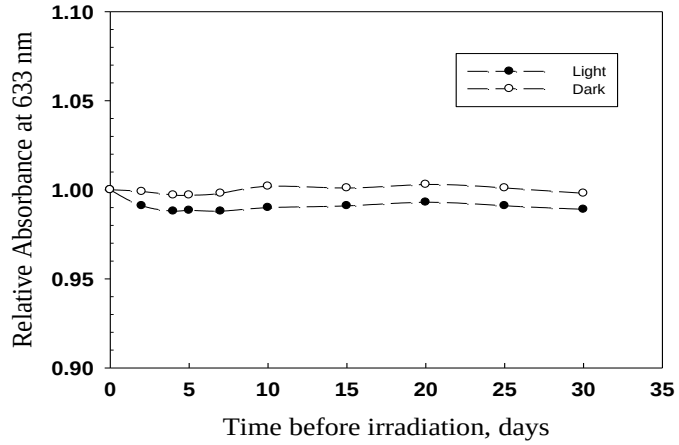

Fig. 8. Pre irradiation stability of BG/ PVB films stored in dark and light at room temperature at λ= 633nm.

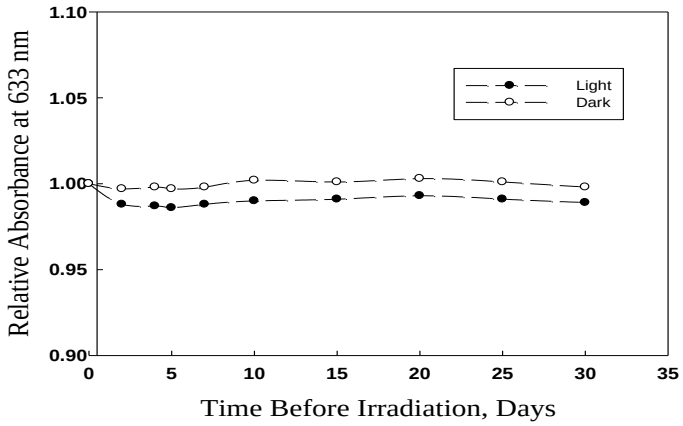

Fig. 9. Pre irradiation stability of BG/ PVA films stored in dark and light at room temperature at λ= 633nm.

Post irradiation stability

BG/ PVB and BG/ PVA films [BG]= 0.35phr and [chloral hydrate]= 22.2phr irradiated to 50kGy were stored at dark and light at temperature 25^{o}C. The absorbance of 3 films at 633nm was measured at different interval time during the post irradiation storage period of 30 days. Fig. 10&11. indicate that after irradiation the response decreases gradually in absorbance with around 3% in dark and 3.8% in light for PVB through the first 10 days then stable till the end of the storage period (30 days) for both films. The same trend observed in PVA

films the response decrease gradually in absorbance with around 2% in dark and 4.8% in light through the first 10 days then stable till the end of the storage period (30days).

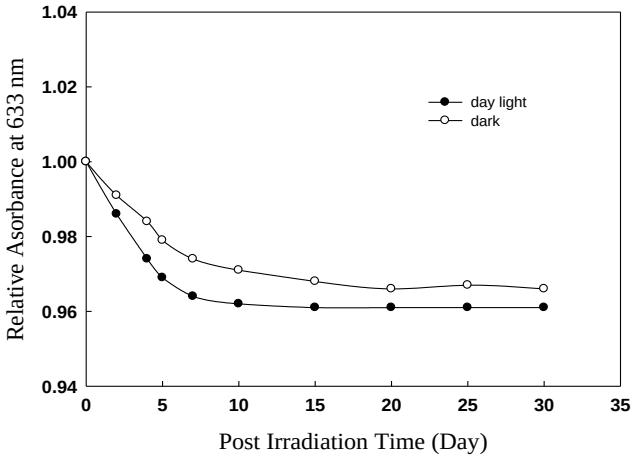

Fig. 10. Post irradiation stability of BG/ PVB films stored in dark and light at room temperature at λ= 633nm.

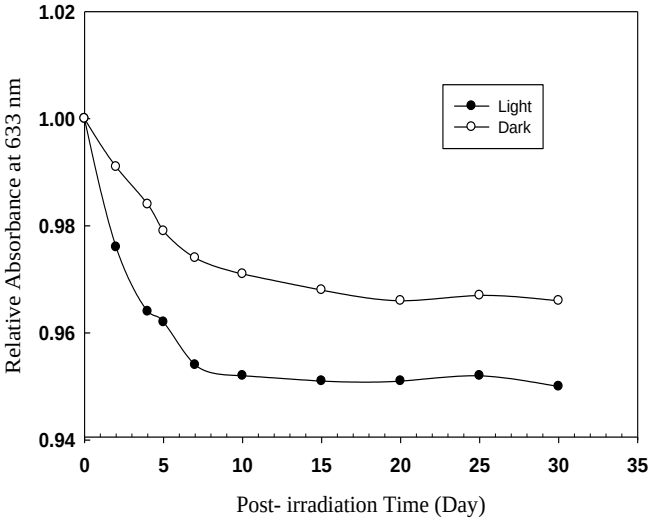

Fig. 11. Post irradiation stability of BG/ PVA films stored in dark and light at room temperature at λ= 633nm.

Conclusion

BG/ PVB and BG/ PVA films were bleached under the effect of gamma radiation. Different dye concentrations were prepared and the dose range was

affected by concentration. Chloral hydrate was added to both polymeric films, it was found that chloral hydrate accelerates the bleaching reaction in BG/PVB films and inhibits the reaction in PVA films. The radiation chemical yield G (BG) was calculated and its value increase with the increase of chloral hydrate in PVB films while it decrease by increase chloral hydrate concentration in PVA films. G-value is 0.106 in PVB film and 0.0237 in PVA films; the two films have the same concentration of BG [0.35]phr and [22.2]phr chloral hydrate. Both films have negligible humidity effect in range 0-50% RH as well as pre and post irradiation stability after five days to the end of storage period.

References

Abdel-Rehim, F. and Abdel-Fattah, A. A. (1993) A thin-film radiation monitoring lable and dosimetry system. *Appl. Radiat. Isotop.,* **44**, 1047.

Ebraheem, S., Beshir, W. B. and Eid, S. (2005) investigation of dyed film based on 2, 6-dichlorophenol-indophenol dyed poly (vinyl alcohol) and poly (vinyl butyral) for possible use in high –dose processing osimetry. *Arab. J. Nucl. Sci. Applic.,* **38**, 1.

Kattan, M., Daher, Y. and Alkassiri, H. (2011) using of Polyvinyl chloride (PVC) dyed with bromocresol purple was investigated as a high-dose dosimeter. *Appl. Radiat. Isotop.,* **69**, 377.

Kovacs, A., Baranyai, M., Wonjnarovits, L., McLaughlin. W. L., Miller, S. D., Miller, A., Fuochi, P. G., Lavalle, M. and Slezsak, I. (2000) Application of the sunna dosimeter film in gamma and electron beam radiation processing. *Radiant. Phys. Chem.,* **57**, 691.

Kavacs, A., Ebraheem, S. and Eid, S. (2002) a new dyed poly (vinyl alcohol) film for high application. *Radiant. Phys. Chem.,* **63**, 807.

Levine, H., McLaughlin, W. L. and Miller, A. (1979) Temperature and humidity effect on the gamma ray response and stability of plastic and dyed plastic dosimeters. *Radiant. Phys. Chem.,* **14**, 551.

Mclaughlin, W. L., Boyd, A. W., Chadwick, K. H., McDonald, J. C. and Miller, A. (1989) Dosimetry for Radiation Processing. London: Taylor & Francis, p. 116.

Soliman, Y. S. (2005) Development of some polymeric materials for possible use as radiation dosimetry system. M.Sc thesis: Chemistry Department. Faculty of Science, Beni-Suef Branch, Cairo Univeristy, p.53.

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دراسة امكانية استخدام الافلام البلاستيكية للبولي فينيل الكحول و البولى فينيل بيوترال المصبوغه بالبريلينت الاخضر كمقياس للجرعات الاشعاعيه العاليه

سيده عيد و عصماء صبحى و سيف الدين ابراهيم

قسم الوقاية و الجرعات الإشعاعية ، المركز القومي لبحوث و تكنولوجيا الاشعاع ، ص.ب.٢٩ مدينة نصر ، مصر.

هذه الدراسه تتناول تحضير افلام متبلمره من البولى فينيل الكحول و البولى فينيل بيتورال و التي تحتوى على صبغة البريلينت الاخضر و التى يتم تحضيرها عن طريق الصب على لوح زجاجى افقى و تعتبر من الافلام الجيده في مجال الاستعمال كمقياس للجرعات الاشعاعيه العاليه. تم تحضير تركيزات مختلفه من الصبغه و دراسة تأثير التركيز على المدى الاشعاعى. و أيضا تم اضافة الكلورال هيدرات و دراسة تأثيره على المدى الاشعاعى ووجد ان هذه الافلام يختفى لونها عند تعرضها للجرعات العاليه من اشعة جاما و بجرعات تختلف حسب تركيز الصبغة و ايضا حسب تركيز الكلورال هيدرات المضاف. و قد تم أيضا تقدير الناتج الكيميائى الاشعاعى للافلام التى تحتوى على الصبغه بمفردها و الصبغه المضاف اليها الكلورال هيدرات. كما تم دراسة تأثير الرطوبة النسبية أثناء التشعيع بالإضافة الى ظروف التخزين قبل و بعد التشعيع على حساسية الافلام لاشعة جاما.