DEVELOPMENT OF TWO DOSIMETERS FOR INDUSTRIAL USE WITH LOW DOSES

by

Moshira A. EL-KELANY and Sameh M. GAFAR *

National Center for Radiation Research and Technology,
Egyptian Atomic Energy Authority, Nasr City, Cairo, Egypt

Scientific paper
http://doi.org/10.2298/NTRP1702148E

The present study involves a comparison between two dosimetry systems. The first system depends on victoria blue B (incorporating polyvinyl alcohol) as a thin-film dosimeter. The second system depends on the same dye as a liquid dosimeter, which is more sensitive to gamma rays. The prepared film/liquid has a considerable signal that increases upon irradiation and the intensity of the signal decrease with increasing radiation dose. The gamma ray absorbed dose for these dosimeters was found to be up to 25 kGy for the thin film and 700 Gy for the liquid form. Radiation chemical yield, additive substance, dose response function, radiation sensitivity, also before and after-irradiation stability under various conditions were discussed and studied.

Key words: victoria blue B, dye, gamma ray, film, liquid dosimeter

INTRODUCTION

Radiation dosimeter is a material, or a device, or a system that measures absorbed doses, when exposed to gamma radiation, a change occurs that can be recorded by any instrumental analysis technique such as UV-spectrophotometer, EPR, IR, and electrical conductivity. One of its advantages is stability over a long time [1]. A lot of polymers are used in preparation of dosimetric films due to their flexibility, clarity, and ease of availability. In recent developments in radiation dosimetry a new thin plastic film dosimeter has been prepared from polyvinyl alcohol (PVA) mixing with dyes. On the other hand, this film is simple to prepare in the laboratory and is considered to be a promised radiation dosimeter [2]. Moreover, a lot of other thin dyed plastic films containing various radiation sensitive indicator dyes, incorporating with active chlorine substance, have been prepared to be applied as dosimeters and indicators [3]. These dyed plastic films significantly change their colors upon exposure to γ-rays [4]. This change is related to the decomposition or degradation of the active substance chlorine atom producing H^+ ion that induces a color change of the pH indicator dye. The authors investigated the effect of adding alanine to an organic dye, incorporated with a transparent polymer film, for radiation dosimetry applications [5]. Moreover, pH indicator dyes can exist in "keto-enol form" having different colors [6]. There are recent studies on some organic dyes, which decolorized and bleached under the effect of gamma radiation [7, 8] and radiochromic films [4, 9]; liquid dosimetry systems [10, 11]. Previous studies have primarily concentrated on the effect of radiation on the solution which causes the formation of transient active species such as free radicals, free ions and excited molecules, which can then be monitored by using optical spectrum, electric spin resonance spectra, conductivity detection or some other suitable techniques [12]. Free radicals H and OH, which are produced in the radiolysis of aqueous solution, are considered to be the main oxidizing species [13]. In recent years, several studies have concentrated on the radiation-induced degradation of dyes [14].

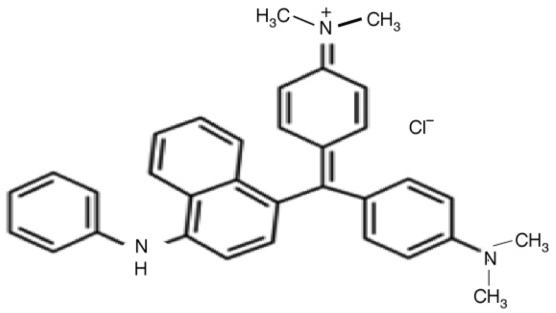
This paper attempts to provide a more detailed investigation of the effects of gamma radiation on victoria blue B (VBB) in both forms, as film and gel dosimetry systems, giving a comparison study between the two-dosimetry systems developed for high and low-dose dosimetry applications.

EXPERIMENTAL WORK

Preparation of stock solution of victoria blue B

The stock solution of the indicator was prepared by dissolving 0.025 g of VBB, (Sigma-Aldrich, Inc., USA) in 25 ml of distilled water. Scheme (1) shows the structure of the dye.

* Corresponding author; e-mail: gafarsameh@yahoo.com



Scheme 1. Molecular structure of VBB

Preparation of VBB/PVA films

Dyed polymeric films were prepared by dissolving 5 g of PVA powder (average M.W. 25 000 totally hydrolyzed 99-100 % J.T. Baker Chemical Co. USA) in 125 ml double distilled water at about 60 °C. The solution was kept fully stirred at that temperature for about 24 h; there after left to cool. Moreover, 1.1, 2.5, and 3 ml of dye stock solution (0.2, 0.4, and 0.5 phr*) were added to each 15 ml of PVA solution and kept stirred for about 3 h at room temperature to get a homogenous colored solution. Finally, the dyed PVA solutions were stirred, casted on a 10 cm × 10 cm horizontal glass plate and dried at room temperature for about 48 h. The film thickness was found to be 0.049 0.03 mm, (1σ).

Preparation of the VBB liquid dosimeter

A stock solution of the VBB without any changes was used to prepare aqueous solutions of different concentrations ($1.5\ 10^{-4}$, $3.3\ 10^{-4}$, and $5.1\ 10^{-4}$ mol L^{-1}) in distilled water.

Instrumental analysis

Absorption spectra of both unirradiated and irradiated films and liquid samples were measured in the wavelength range 200-800 nm using a UV4-visible spectrophotometer (KONTRON Co. Ltd., Switzerland). The film thickness was measured using Digitrix-Mark II thickness gauge (precision 1 µm, 1σ). Gamma irradiation process was carried out using a ^{60}Co Gamma Cell GC-220 Excel (manufactured by MDS Nordion, Canada) with absorbed dose rate of 5.9 kGyh^{-1}.

RESULTS AND DISCUSSION

Absorption spectra

The discussion of the results begun with the absorption spectra of the unirradiated and irradiated films which were measured over the wavelength range 300-800 nm. The absorption spectra of the VBB/PVA films/liquid (0.5 phr VBB) recorded before, and after irradiation by different doses are shown in figs. 1 and 2. The findings suggest that the absorption spectra of unirradiated and irradiated films display a central absorption peak in the visible region, with distinctive of a blue color peaking at 612 nm (fig. 1), and at 617 nm (fig. 2) for dyed liquid. The amplitude of this peak decreases progressively with the increase of absorbed dose of gamma ray photons. This study indicates that the spectra of irradiated film with the VBB dye bleached by exposing the film to gamma rays.

Response curves

For dosimetry, optical density was read-out at 612 nm for VBB/PVA films. Figure 3 demonstrates the response curves of VBB/PVA films containing various concentrations of the dye (0.2, 0.4 and 0.5 phr) in terms of variation in an absorption coefficient, A mm^{-1} at 612 nm, against the absorbed dose, D, where (A =

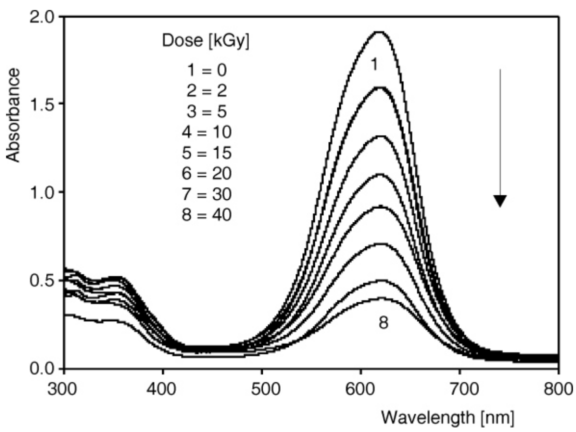


Figure 1. The absorption spectra of un-irradiated and irradiated VBB film, according to different absorbed doses; VBB = 0.5 phr , λ_{max} = 612 nm

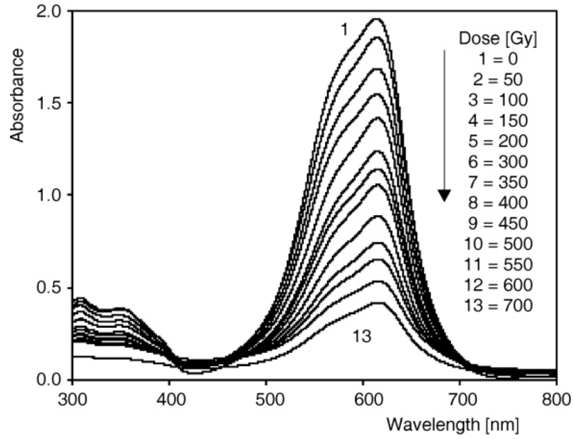


Figure 2. The absorption spectra of the un-irradiated and gamma irradiated VBB liquid, according to different absorbed doses; VBB = $5.1\ 10^{-4}$ molL^{-1}, λ_{max} = 617 nm

*phr = part per hundred parts of substrate polymer

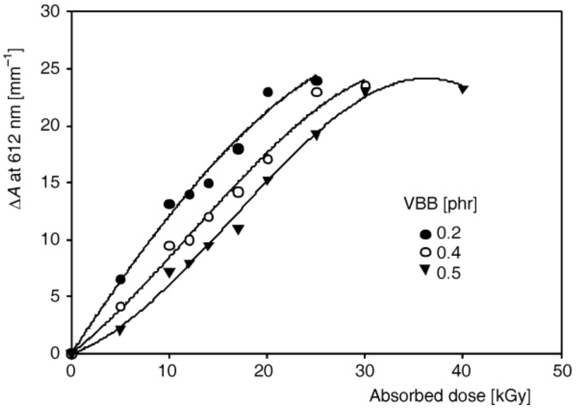


Figure 3. Change of ΔA as a function of absorbed dose for different VBB concentrations in PVA films

$= A_o - A_i$) and A_o and A_i are values of an absorption coefficient for the un-irradiated and irradiated films, respectively. From the response curve, it is clear that the useful dose range of the system, between 1-40 kGy depends up on the dye concentration. A group of liquids was irradiated at a dose rate of 5.9 kGyh^{-1} in the dose range up to 700 Gy. Through that dose range, the response tends to saturate. Under the effect of gamma radiation the resulting liquid color has an absorbance peak at 617 nm, which bleaches upon irradiation as the liquid bleaches. Figure 4 illustrates the dose response functions of the samples prepared with four concentrations of VBB (1.5 10^{-4}, 3.3 10^{-4}, and 5.1 10^{-4} mol L^{-1}) dyed liquid. In general, as observed from prior documented studies, the effect of gamma radiation on water is production of a lot of radicals H_2, H_2O_2, H^+, H^-, and hydrated electrons (e_{aq-}). Hydroxyl radicals (OH), as intermediate active species, accelerate the decolorization reaction [14]. This revealed higher sensitivity of VBB in a liquid system than the in case of VBB as a film dosimeter, which was due to free mobility of all free radicals in the liquid form and opposite, the rigidity of free ions and radicals in a solid system

$$H_2O \quad OH, H, {}^{\bullet}e_{aq-} \tag{1}$$

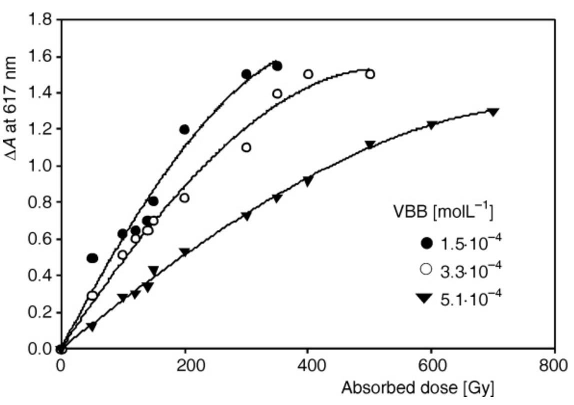


Figure 4. Dose response of the (VBB -liquid) at 617 nm in the full dose range of 0-700 Gy. $\Delta A = A_0 - A_i$, where A_0 and A_i are absorbances of the irradiated and un-irradiated samples, respectively

Rate of degradation reaction (bleaching process) of VBB

UV-V is absorption spectra of VBB were studied at different intervals of irradiation dose. Absorbance at 300-800 nm was attributed to *n* transition of benzene and naphthalene rings of the dye. The absorption peak at 617 nm corresponds to the chromophore part of VBB. Under optimum conditions, absorbed dose (0.7 kGy) of irradiation is required for complete mineralization of VBB. The photocatalytic degradation can be performed as

$$R \quad R_1 \quad R_2 \tag{2}$$

where R, R_1, and R_2 are total bleaching, photocatalytic and photolysis rates, respectively. Under chosen experimental conditions, photolysis had no effect on the degradation process. Equation 2 reduced to

$$R \quad \frac{d[VBB]}{dD} \quad R_1 \tag{3}$$

A simple power law model was examined to determine the rate of photocatalytic degradation as

$$R \quad k_1 [VBB]_1^n \tag{4}$$

where n_1 and k_1 are appropriate order and rate constant of the reaction. In order to obtain the appropriate parameters in eq. 4, differential methods of analysis based on data about the dye concentration *vs*. absorbed dose

$$\log R \quad \log k_1 \quad n_1 \log[VBB] \tag{5}$$

The rate order of the reaction increases with increasing the absorbed dose

$$\log D \quad \log k_1 \quad n_1 \log[VBB] \tag{6}$$

Figure 5 demonstrates the order of degradation reaction indicating the intricacy of the degradation process. Rate constant for the degradation of VBB was found to be 9.4 10^{-2}. Under chosen experimental con-

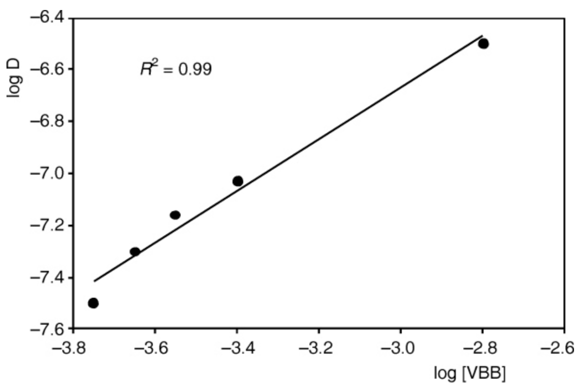


Figure 5. Variation of VBB degradation rate *vs*. its concentration (1.5 10^{-4}, 2.5 10^{-4}, 3.3 10^{-4}, 4.3 10^{-4}, 4.4 10^{-4}, and 5.1 10^{-4})

ditions, the net rate of the degradation of VBB can be expressed as

$$R \quad 9.4 \quad 10^{-2}[\mathrm{VBB}]^{2.2} \tag{7}$$

Radiation chemical yield (G-value)

Radiation-chemical yield (G-value) is defined as the number of moles of dye degraded by absorption of 1 J of energy (unit: $\mathrm{molJ^{-1}}$). The G-value is calculated from the general relation [15]

$$\mathrm{G(value)} \quad \frac{\Delta A}{D\varepsilon\rho b} \; [\mathrm{molJ}^{\;\;1}] \tag{8}$$

where ΔA is the change in absorbance at $\lambda_{\max}$, b [1 cm] – the optical path length , ε [$\mathrm{Lmol^{-1}\,cm^{-1}}$] – the linear molar extinction coefficient for the solution at $\lambda_{\max}$, ρ [$\mathrm{gcm^{-3}}$] – the density of the dosimeter, and D [Gy] – the absorbed dose. Using the dye concentration in $\mathrm{molL^{-1}}$ and the average value of A_0/b, the molar extinction coefficient had been found to be 71625.1 $\mathrm{Lmol^{-1}\,cm^{-1}}$ for VBB films. Using the density of VBB/PVA to calculate the G-value in terms of $\mu\mathrm{molJ^{-1}}$, the calculated G-value for these films and the concentration of the dye inside the film's matrix were tabulated in tab. (1). From the table, it could be observed that the G-value increases with the increase in the dye concentration. Moreover, this may be due to the number of radiolysis products of liquid/PVA. Based on the results, these data reflect the significant role of the polymer matrix in the degradation process.

Humidity during irradiation

The effect of relative humidity (RH) during irradiation, on the response, was inspected by irradiating VBB films (0.8 kGy) at various relative humidities (0, 12, 33, 54, 76, and 92 %). Irradiation was carried out while the films were pending surrounded by different super saturated-salt solutions in jar. Relative humidity of 0 % RH was achieved by surrounding the VBB film by dried silica gel. The difference in response (A $\mathrm{mm^{-1}}$) as a function of RH percentage RH through irradiation proportional to that at 33 %. These results revealed that these films have no ratable effect in the range of relative humidity RH (10-50 %), however, the response shows slightly various sensitivities at both high and low humidity values.

Table 1. The calculated G-value for VBB/PVA at different dye concentrations

Dye concetration phr	G-value (VBB/PVA) [$\mu\mathrm{molJ^{-1}}$]
0.2	0.0093
0.4	0.0116
0.5	0.0168

Assessment of uncertainty

In addition, a measurement of gamma radiation shall be taken by an assessment of the uncertainty in the measured value. Factors contributing to the total uncertainty may be divided into two types, type A and type B [16]. The first factor is related at most with the measuring instrument and the film, but the second is mainly related to the calibration.

One of the first factors the reproducibility of the Unicam UV4 spectrophotometer was determined by reading the absorbance value (at 600 nm wavelength and absorbance level 0.8) of irradiated films several times. From the data obtained, it was found that the coefficient of variation (1) is 0.22 %, indicating the accuracy of the spectrophotometer. The reproducibility of the Minitest thickness gauge was examined by reading the thickness value for VBB/PVA films many times. Obviously, from the data obtained it was found that the coefficient of variation (1) is 0.5 %. The reproducibility of the measurements of several films (10 times for a film) was found to be 0.7 % (1) [16].

On the other hand, the type A uncertainties (at one standard deviation, *i. e.* 1) arising during calibration over the useful response range were found to be 2.4 % [16](ISO/ASTM 51707, 2004). Combining all the components in squares at one standard deviation 1σ leads to

$$U_{\mathrm{c}} \quad \sqrt{(0.22)^{2} \quad (0.5)^{2} \quad (2.4)^{2} \quad (0.7)^{2}} \quad 3.2\% \tag{9}$$

The expanded uncertainty (at two standard deviations, *i. e.* 2σ, approximately equal to a 94 % confidence level) is set up by multiplication of U_{c} (at 1σ) by two. Therefore, the combined uncertainty using VBB/PVA film is 6.4 %.

Pre-irradiation stability for VBB /PVA films

The color fading stability of (0.5 phr) VBB/PVA films was examined by storing the films at 33 % RH and at room temperature (25 °C 2) in the dark and under laboratory fluorescent light. In order to investigate the possible effects of pre-irradiation storage on the manufactured films samples, we observed absorbances of un-irradiated film samples stored under various conditions. These film samples, manufactured about one month before the experiment started, were stored under different conditions, and their absorbances at 612 nm were observed for 30 days. One of the groups was stored at room temperature in the dark; another group was stored at room temperature exposed to laboratory fluorescent light. Measured absorbances *vs*. time (days) are shown in fig. 6. Pre-irradiation stability was very good, with the absorbance of the films decreasing by only

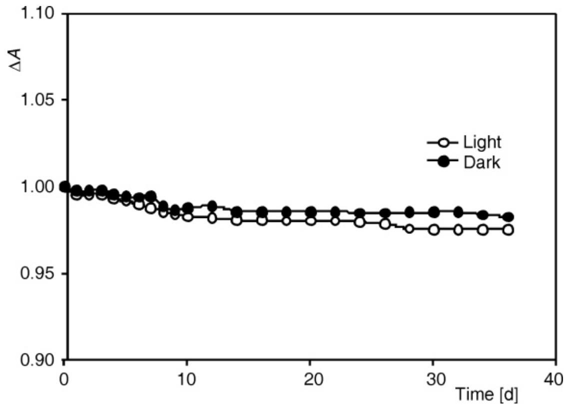


Figure 6. Pre-irradiation stability of (VBB film) stored under different storage conditions

about 8% over the first 10-days in storage pre-irradiation period.

Post-irradiation stability for VBB /PVA films

In case of VBB/PVA films containing [VBB] = = 0.5 phr irradiated to 30 kGy, the samples were stored at room temperature (25 °C   2) in the dark and under laboratory fluorescent light. The absorbance of these films was measured at 612 nm wavelength at different time intervals during the pre-irradiation storage period of 60 days. The change in the absorbance at 612 nm as a function of storage time relative to that before storage (immediately after stripping) is shown in fig. 7. It can be seen that the irradiated films show good stability under storage conditions.

Self-life of VBB dyed liquid dosimeters

VBB solution containing 5.1 10^{-4} µmolL^{-1} VBB irradiated to 400 Gy, was stored at room temperature (25 °C   2) in the dark and light. The absorbance of this solution was measured at 617 nm wavelength for various time intervals through the post-irradiation storage period of 63 days. It is clear from this figure that the irradiated solutions exhibit good stability under different storage conditions.

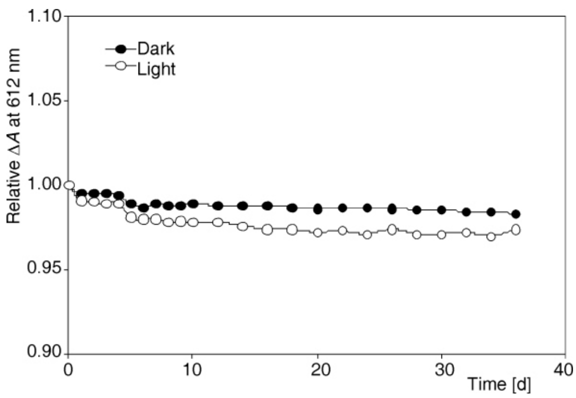


Figure 7. Post-irradiation stability of (VBB films) stored under different storage conditions

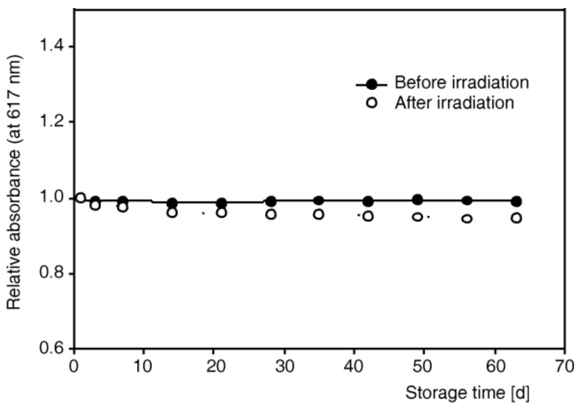


Figure 8. Post-irradiation stability of VBB solutions [TR] = 4.1 10^{-4} µmoll^{-1} and [CH] = 66.6 phr) stored in direct and indirect light at room temperature, as a function of storage time, at 100 Gy

Comparison between VBB/PVA films and VBB/gelatin gels dosimetry systems

A comparative study with other dye dosimeters is also developed in our lab. We published many papers in the field of radiation dosimetry [2, 4, 7, 9], in case of dyed-film dosimetry applications. Moreover, the author published two papers in the field of gel dosimetry and liquid dosimetry; respectively [10, 11]. Consistent with previous findings, we found that the following tab. 2 summarizes the differences between the two-dosimetry systems used for VBB dye (films, liquid) with wavelength, sensitivity, dose range and applications. From this table, one can easily choose the suitable conditions for a specific application. These liquids have clear visual change in color for the dose up to 700 Gy reflecting their suitability for use as radiation indicators in some food irradiation applications. The sensitivity of this film was investigated spectrophotometrically at a wavelength of 612 nm, change in color for the dose up to 25 kGy reflecting their suitability for applications as radiation indicators in food irradiation, medical sterilization and polymer cross link-

Table 2. Comparison between different dosimetry systems used for VBB dye

System	Film	Liquid
Wavelength [nm]	612	617
Sensitivity	Sensitive	More sensitive
Dose range	(0-25) kGy	(0-0.7) kGy
Applications	Food irradiation, medical sterilization, polymer cross linking and degradation	Food irradiation, water treatment and medical sterilization

ing applications, as well as good post-irradiation stability when stored in dark and light, at room temperature. By comparing, the results, previously published [6], of the rhodamine b liquid and [7] of 2.6 DNP/PVA and this prepared VBB liquid and films it was found that, the radiation sensitivity in the present study of VBB liquid system is more sensitive than rhodamine b liquid system. Moreover, the sensitivity of VBB/PVA film is higher than 2.6 DNP/PVA that published by [7]. This revealed the possibility of applications in a wide dose range, more than the two previous dosimetry systems, especially in medical sterilization, food irradiation processing, radiotherapy and blood irradiation.

CONCLUSION

From the data presented in this study, the dosimetric characteristics of VBB films and liquid containing different concentrations of dye, were studied. The useful dose range for these films was found to be from 2 to 25 kGy and for liquid was found to be from 50 to 700 Gy. Moreover, these film dosimeters have insignificant dependence on the change of relative humidity during irradiation. It is recommended to calibrate these dosimeters at the conditions of use or at humidity values less than 50 %. These liquids have clear visual change in color for the dose up to 700 Gy reflecting their suitability for use as radiation indicators in some food irradiation applications. Furthermore, the response of these dosimeters show excellent stability when stored at room temperature and the overall uncertainty VBB/PVA film is 6.4 %. The properties of the prepared films and liquid suggest their usefulness in medical and industrial applications.

ACKNOWLEDGMENTS

This work was financially supported by National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA), Nasr City, Cairo, Egypt for basic research in the field of radiation technology applications.

AUTHORS' CONTRIBUTIONS

S. M. Gafar and M. A. El Kelany carried out the experiments, calculations and analysis on results, and participated in preparation of the final version of the manuscript.

REFERENCES

[1] ***, IAEA, Absorbed Dose Determination in Photon and Electron Beams, Technical Reports Series No. 277, IAEA, Vienna, 1987

[2] El-Kelany, M., *et al*., Preparation of Radiation Monitoring Labels to γ Ray, *Optik, 127* (2016), pp. 6746-6753

[3] Abdel-Fattah, A. A., *et al*., Radiation Chemical Formation of HCl in Poly(Vinyl Butyral) Films Containing Chloral Hydrate for use in Radiation Dosimetry, *International Journal of Polymer Materials, 51* (2002), 2, pp. 413-419

[4] Gafar, S. M., El-Ahdal, M. A., A New Developed Radiochromic Film for High-Dose Dosimetry Applications, *Dyes. and Pigments, 114* (2015), 1, pp. 273-277

[5] Ebraheem, S., *et al*., Formyl Violet Cyanide Liquid Dosimetry System, *Radiation Physics and Chemistry, 76* (2007), 2, pp. 1218-1221

[6] Beshir, W. B, Radiation Sensitive Indicator Based on Tetrabromophenol Blue Dyed Poly(Vinyl Alcohol), *Radiation Physics and Chemistry, 86* (2013), 1, pp. 129-135

[7] Gafar, S. M. El-Ahdal, M. A., Dosimetric Characteristics of 2,6 Di-Nitro Phenol for High Dose Dosimetry, *Dyes and Pigments, 109* (2014), May, pp. 67-71

[8] Mahmoodi, N. M., Arami, M., Modeling and Sensitivity Analysis of Dyes Adsorption Onto Natural Adsorbent from Colored Textile Wastewater, *Applied Polymer Science, 109* (2008), 2, pp. 4043-4048

[9] Antar, E. M., *et al*., Suitability of Gafchromic EBT2 Films for Dosimetry of Low Gamma-Rays, *International Journal of Low Radiation, 9* (2014), 5-6, pp. 317-326

[10] Beshir, W. B., *et al*., Application of Solutions of Rhodamine B in Dosimetry, *Applied Radiation and isotopes, 89* (2014), Nov., pp. 13-17

[11] El-Ahdal, M. A., *et al*., Comparison between New (Gel/Liquid) Dosimeter for Radiation Dosimetry Applications, *International Journal of Science and Engineering Research, 5* (2014), 11, pp. 954-959

[12] Krapfenbauer, K., *et al*., Pulse Radiolysis and Chemical Analysis of Azo Dyes in Aqueous Solution I. p-phenylazoaniline, *Radiation Physics and Chemistry, 58* (2000), 1, pp. 21-27

[13] Taguchi, M., Kojima, T., Yield of OH Radicals in Water under Heavy Ion Irradiation, Dependence on Mass, Specific Energy, and Elapsed Time, *Nuclear Science and Technology, 18* (2007), 3, pp. 35-38

[14] Foldvary, Cs. M., Wojnarovits, L., Role of Reactive Intermediates in the Radiolytic Degradation of Acid Red1 in Aqueous Solution, *Radiation Physics and Chemistry, 78* (2009), 2, pp. 13-18

[15] McLaughlin, W., *et al*., Dosimetry for Radiation Processing, 1989 Taylor & Francis, London

[16] ***, ISO/ASTM 51707, Standard Guide for Estimating Uncertainties in Dosimetry for Radiation Processing, in: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Penn., USA, 2004

Received on November 7, 2016
Accepted on May 24, 2017

Мошира А. ЕЛ-КЕЛАНИ, Самех М. ГАФАР

РАЗВОЈ ДВА ДОЗИМЕТРА У ОПСЕГУ НИСКИХ ДОЗА ЗА ПРИМЕНУ У ИНДУСТРИЈИ

Овај рад обухвата поређење два дозиметријска система. Први систем заснива се на боји *Victoria Blue B* (уз присуство поливинил алкохола), у облику дозиметра са танким филмом. Други систем заснива се на истој боји у облику течног дозиметра који је осетљивији на гама зрачење. Припремљени филм и течност, имају значајан сигнал увећан при озрачивању, са интензитетом сигнала који опада са порастом дозе зрачења. Апсорбована доза гама зрачења овим дозиметрима износила је до 25 kGy за дозиметар са танким филмом и до 700 Gy за течни дозиметар. Такође су проучавани хемијски принос зрачења, адитивне супстанције, функција одзива дозе, радијациона осетљивост и стабилност пре и после озрачивања, под разним условима.

Кључне речи: Victoria Blue B, боја, гама зрачење, филм, течни дозиметар