Egypt. J. Rad. Sci. Applic., Vol. **24**, No. 1, pp. 153-164 (2011)

Effect of γ-Radiation on the Physical Properties of poly(vinyl alcohol) Dyed with Tetrabromophenolphthalein Ethyl Ester

M. El.Kelany

Radiation Protection Dept., National Centre for Radiation Research and Technology, P. O. Box; 29 Nasr City, Cairo, Egypt. Email;dr.moosh@hotmail.com

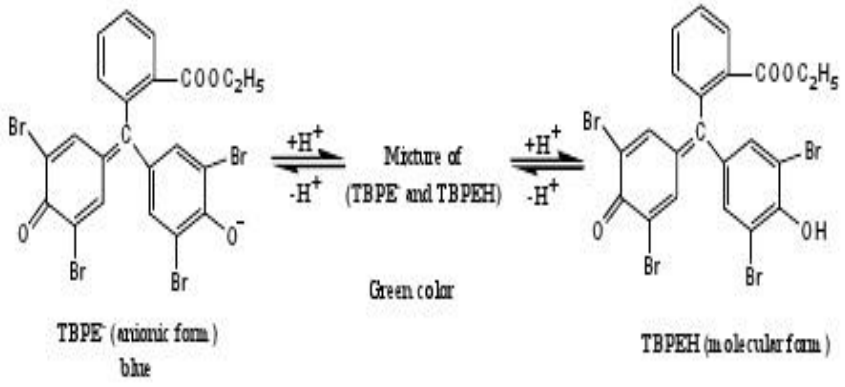
THE INVESTIGATION of the radiation sensitive indicators based on dyed poly(vinyl alcohol) (PVA) containing acid sensitive dye tetrabromophenolphthalein ethyl ester (TBPE) and trichloro acetamide (TCA) have been developed. These plastic film dosimeters undergo colour change from blue to green to pale green, indicating acid formation. These films can be used as dosimeters for food irradiation applications where the maximum of the useful dose ranges are between 1-5 kGy depending on TCA concentration in the film. The films have the advantage of negligible humidity effects on response in the intermediate range of relative humidity (RH) from 10-50% and good stability before and after irradiation under different storage conditions.

Keywords: Tetrabromophenolphthalein ethyl jester), poly(vinyl alcohol), γ-rays dosimeter, trichloro acetamide.

Many radiation sensitive indicators for qualitative indication of radiation exposure have been manufactured, to distinguish processed irradiation units from unprocessed irradiation units (Abdel-Rehim and Abdel-Fattah, 1993 and Abdel-Rehim *et al*., 1996). These indicators may be labels, papers, inks which undergo a visual colour change when exposed to ionizing radiation (Abdel-Rehim *et al*., 1985). These indicators based mainly on radiochromic dye (Akhava *et al*., 2002, Butson *et al*., 2001& 2003, Chen Wenxiu *et al*., 1985 and Kovacs *et al*., 2000). Other based on the pH-indicator dye (Abdel-Fattah *et al*., 1996 & 2002, Abdel-Fattah and El-Kelany, 1998 and Sidney *et al.*, 1990) and radiation sensitive diacetylenes (Ogawa, 1995). They are not used for quantitative dose measurements while label dosimeters may be used for quantitative dose measurements during radiation processing.

A new plastic film dosimeter has prepared from PVA incorporating an acid-sensitive dye bromophenol red (BPR) and water soluble chlorine containing substance [CCl_3COONa or chloral hydrate ($CCl_3CH(OH)_2$, 2,2,2-trichloroethan-1,1-diol)]. This film is easy to prepare in laboratory and can be used as a dosimeter in the relatively low dose range up to 5 kGy (Abdel-Fattah *et al*., 1996).

A new thin transparent cellophane film was developed for high-dose dosimetry by (Abdel-Rehim *et al*., 1993 and McLaughlin, 2003). This film containing disazo "Direct" dyes *e.g.*, blue Cellophane, have long been used as monitors of large absorbed doses of ionizing radiation (10-300 kGy) and especially for mapping electron-beam dose profiles. The radiation response is markedly dependent on temperature and RH during irradiation. 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 most commonly used as dosimeters, indicators (Abdel-Rehim and Abdel-Fattah, 1993) and for monitoring the absorbed dose delivered by electron beams and γ-rays (Kovaces *et al*., 2002). Ueno (1988) developed a radiation dosimeter from acid indicators by coating a high molecular wt 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 deals with the investigation of a new dyed PVA film to enable their use in food irradiation processing applications.



Experimental

Preparation of stock solution of TBPE

The stock solution of the indicator was prepared by dissolving 0.025 g of TBPE ($C_{22}H_{14}Br_4O_4$, M.W. = 661.96 g/mol) (Sigma-Aldrich, Inc., USA) in 25 ml ethanol.

Preparation of TBPE/PVA films

Films were prepared by dissolving 10 g of PVA powder (average M wt 25,000 fully hydrolyzed 99-100% product of J.T. Baker Chemical Co. USA) in 250 ml double distilled water at about 60^{o}C. The solution was kept well stirred at the temperature for about 48 h; then left to cool. To each 30 ml of PVA solution 2, 4, and 8 ml of dye stock solution were added and kept stirred for about 3h at room temperature in order to obtain a uniformly dyed solution. The TCA was added in certain concentration ranged from 0.2 to 0.8 phr to solution containing 0.66 phr of TBPE. The dyed PVA solutions were stirred, casted on a 10×10 cm horizontal glass plate and dried at room temperature for about 48 h. The film thickness was found to be 0.055± 0.02μm, 1σ.

Instrumental analysis

The absorption spectra of unirradiated and irradiated films were measured throughout the wavelength range 200-800nm using a UV4–visible 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 4000Å (product of India). The absorbed dose rate in the irradiation facility was measured to be 5 kGy/ h and the electronic equilibrium conditions were maintained during irradiation.

Results and Discussion

Absorption spectra

The absorption spectra of the unirradiated and irradiated films were measured throughout the wavelength range 300-800 nm. The absorption spectra of the TBPE/ PVA films (0.66 phr TBPE) without TCA recorded before and after irradiation to different doses are shown in Fig. 1. The absorption spectrum of unirradiated film shows a main absorption band in the visible region

characteristic of a blue colour peaking at 606 nm (Fig. 1). The amplitude of this band decreases gradually with the increase of absorbed dose of gamma ray photons. It is clear from the spectra of irradiated film that the TBPE dye degraded by applying of gamma rays on the film.

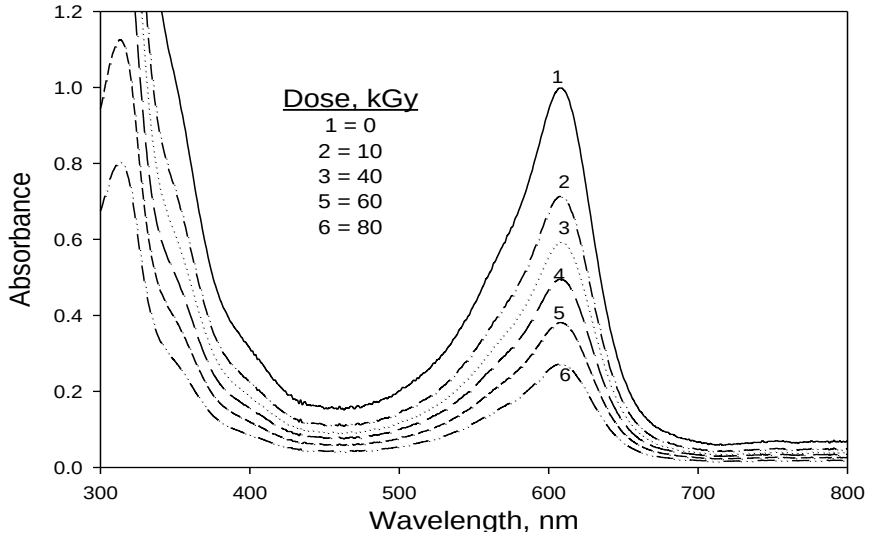


Fig. 1. The absorption spectra of TBPE/ PVA films unirradiated and irradiated to different doses.

Fig. 2. shows the absorption spectra of TBPE/ PVA films unirradiated and irradiated to different doses. These films contain 0.4 phr tri chloro acitamide and 0.66 phr TBPE. The spectrum shows a main absorption band peaking at 606 nm.

The amplitude of this band decreases gradually with the increase of γ-ray. Upon irradiation, these films change their colour from blue to green and finally to pale green indicating acid formation. The green colour is observed due to the visual sensation of mixed ratios of unchanged part of indicator and changed part. Four different TCA concentrations; 0.2, 0.4, 0.6, 0.8 phr with 0.66 phr TBPE were examined. It was found that the useful dose range of these films 1-5 kGy. It was noticed that the bleaching reaction takes place faster within films containing TCA than that without TCA (*i.e.*, TCA act as sensitizer).

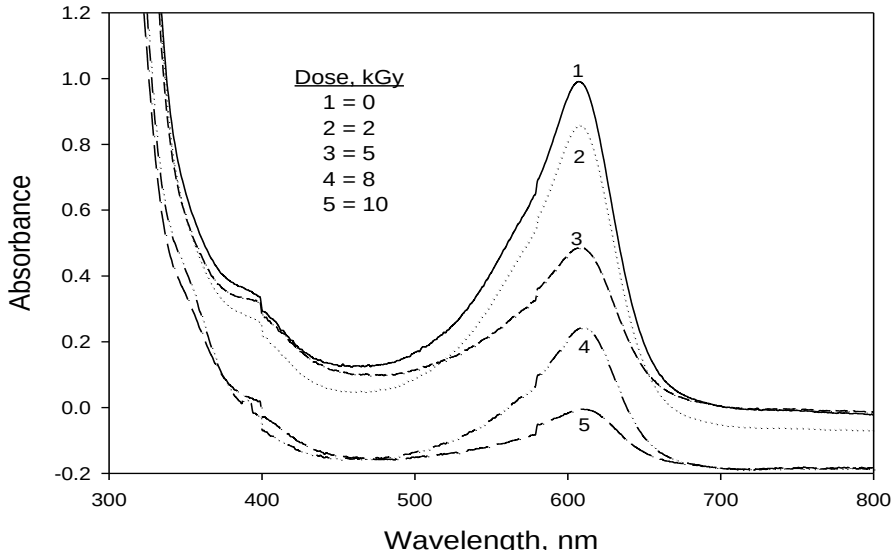


Fig. 2. The absorption spectra of TBPE/ PVA films unirradiated and irradiated to different doses [TCA]= 0.4 phr.

Response curves

Fig. 3. shows the response curves of TBPE/ PVA films containing different dye concentrations (0.16, 0.33, 0.66 and 1 phr). It can be noticed that the four curves have S-shape, characteristic of pH indicator in an acid base titration. Each curve reaches saturation at different dose depending on the concentration of TBPE. Its show the response curves in terms of change optical density per unit thickness in terms of change optical density per unit thickness $\Delta A = A_o - A_i$ and 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 40kGy.

By applying gamma ray to the films containing TCA, the response completely changed. Fig. 4. show that the response of the films containing different TCA concentrations (0.2, 0.4, 0.6 and 0.8 phr) was decreased to be ranged from 1-5 kGy, meaning the presence of TCA inside the matrixes of the polymer led to accelerate the degradation of TBPE dye ten folds than that one dose not containing TCA.

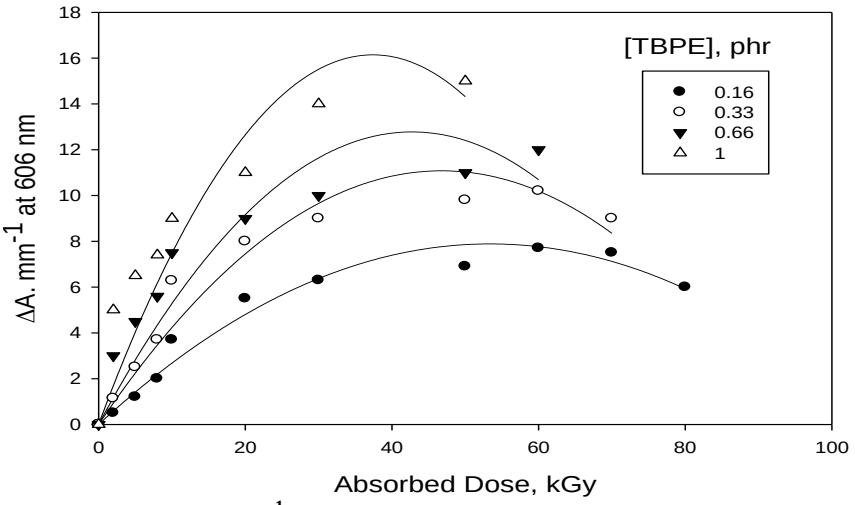


Fig. 3. Change of ΔA.mm^{-1} as a function of absorbed dose of TBPE/ PVA films with different concentrations of TBPE.

This means that the resulting species produced from the irradiation of TCA act as a major factor of the dye degradation in the case of TBPE/ PVA film. Fig. 5. shows the slope of the linear parts in response curves given in Fig. 3 as a function of TBPE concentration at absorption band, 606 nm. It can be seen that the radiation sensitivity of TBPE/ PVA film increases with increasing the TBPE concentrations.

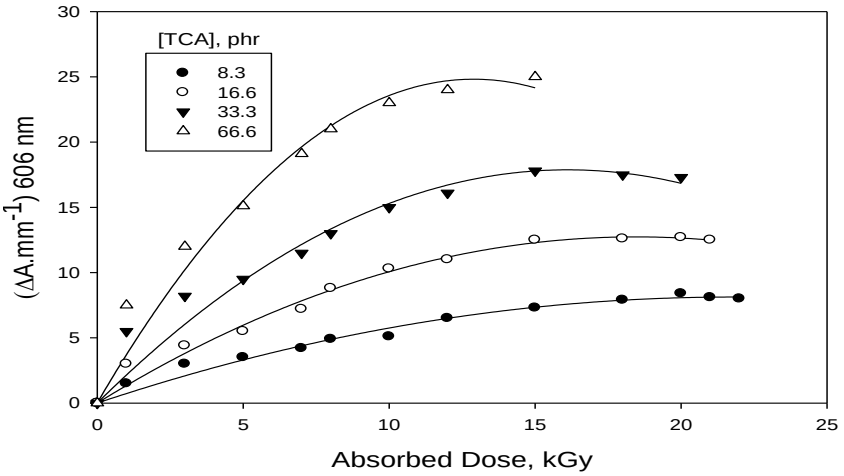


Fig. 4. Change of ΔA.mm-1 as a function of absorbed dose of TBPE/PVA films with different concentration of tri chloro acitamide, [TBPE]= 0.66 phr.

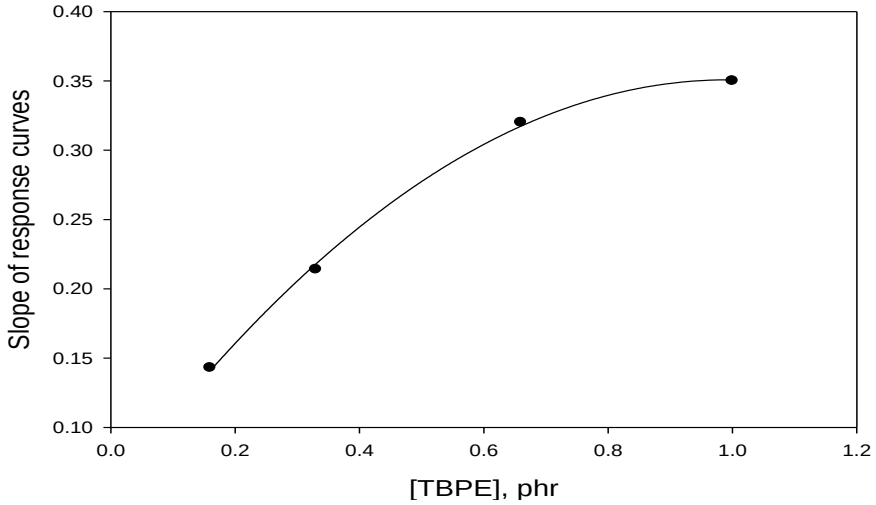


Fig. 5. Radiation sensitivity of TBPE/PVA films against the concentration of TBPE.

It can be seen that response curves at different concentrations of TCA are non-linear and tend to saturate at high doses of γ-ray. The response curves (Fig. 4) were fitted with third-order polynomial functions.

$$Y = ax + bx^2 + cx^3$$

Where, ***Y*** is absorbed dose, kGy for TBPE/PVA films, ***x*** is the change of absorbance as indicated by (ΔA mm^{-1}) at 606 nm of these films, ***a, b*** and ***c*** are constants. The calculated value of the constants ***a, b*** and ***c*** is tabulated in Table 1.

TABLE 1. The constants *a, b* and *c* for TBPE/ PVA films containing different conc. of TCA.

[TCA] phr	a	b	c
0.2	0.137	0.012	4.10×10^{-3}
0.4	0.031	0.023	6.81×10^{-5}
0.6	0.043	0.03	3.1×10^{-4}
0.8	0.047	0.04	-1.1×10^{-4}

Radiation-chemical yield

The radiation-chemical yield (G-value) is defined as the 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).

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

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 dosimeter (g.cm^{-3}) and D is the absorbed dose (Gy). By using the dye concentration in mol/L and the average value L mol^{-1} cm^{-1} of A_o/b., the molar extinction coefficient is calculated as 1030.05 L mol^{-1} cm^{-1} and the density of PVA 1.25 gm cm^{-3}. The G(-TBPE) for the different dye concentration 0.16, 0.26, 0.33 and 0.48 μmol/J. It can be seen that the G(-TBPE) values increase with the increase of TBPE concentration. In presence of TCA the G(-TBPE) values was calculated to be 0.54, 0.72, 1.2 and 2.6 μmol/J for 0.2, 0.4, 0.6 and 0.8 phr TCA concentrations respectively. It is clear that the presence of TCA accelerates the degradation of TBPE about 5 folds, which is very important to control the dose response range according to the kind of application needed.

Humidity during irradiation

The effect of RH during irradiation on the response was investigated by irradiating TBPE/ PVA films (10kGy) at different relative humidities (0, 12, 33, 54, 76 and 92%). Irradiation was carried out while the films were suspended over various saturated-salt solutions in an enclosed jar, except for the 0 % RH which was suspended over dried silica gel.

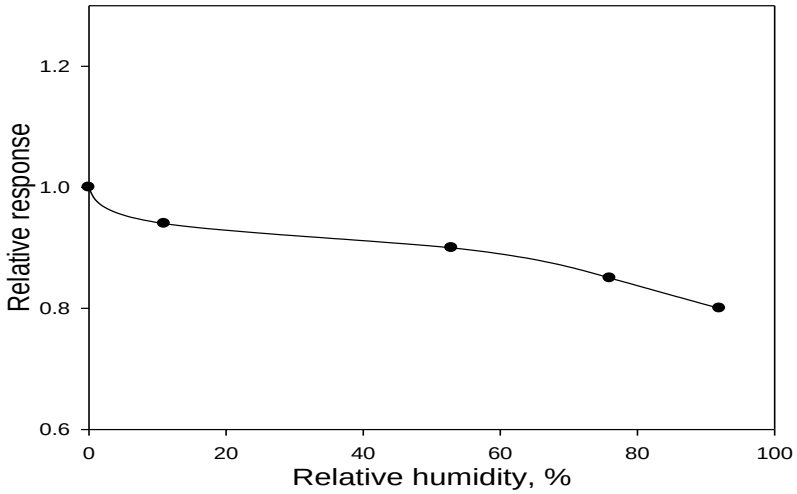


Fig. 6. Variation of response of TBPE/PVA films as a function of relative humidity during irradiation where response in ΔA.mm^{-1} at 5 kGy. [TBPE]= 0.66 phr.

Fig. 6. shows the variation in response ($\Delta A.\ mm^{-1}$) as a function of percentage RH during irradiation relative to that at 33%. It was found that, for these films there is no appreciable effect in the range of RH (10-50%), although the response shows somewhat different sensitivities at both higher and lower humidities.

Post-irradiation stability

The post-irradiation stability of TBPE/PVA films ([TCA= 0.4 phr]) irradiated to 5kGy is investigated by storing them in the dark at room temperature. The absorbance of these films was measured at 606 nm at different intervals of time during the post-irradiation storage period of 60 days, as shown in Fig. 7. The films show good stability, but we have to left films 7 days for stability requirements. The response of irradiated films decreases gradually for about one week, where the absorbance changes within ±10% overall the storage period. On the other hand, the film stored shows excellent stability overall the storage period.

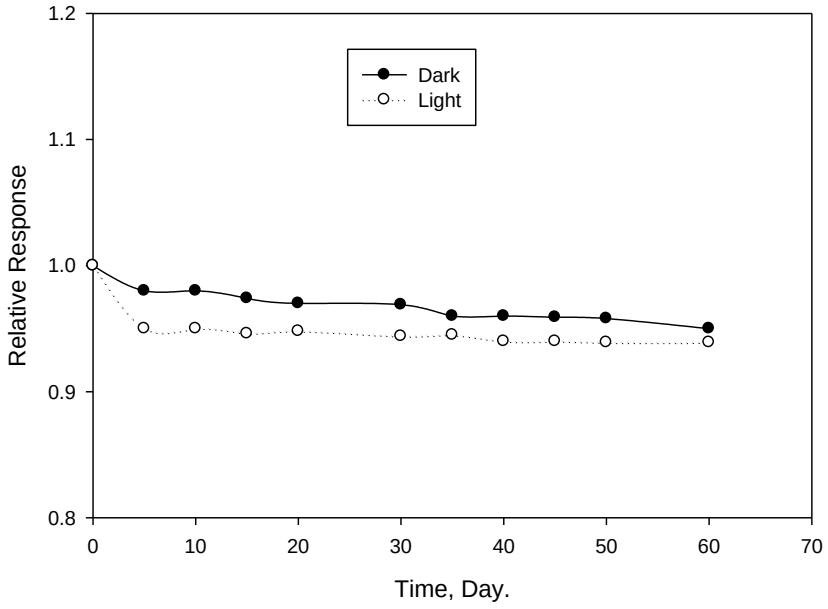


Fig. 7. Post-irradiation stability of TBPE/ PVA films stored in dark and light at room temperature.

Conclusion

On irradiating TBPE/ PVA films containing TCA, the colour of the films changes from blue to green and finally to pale green indicating acid formation. The amount of acid formed due to irradiation depends on the absorbed dose and the concentration of TCA. These films have clear visual change in colour in the dose 1-5 kGy reflecting their suitability for use as radiation indicators in some food irradiation applications. The response of this film was investigated spectrophotometrically at wavelength 606 nm. The response of these films has negligible humidity effects in the intermediate range of relative humidity from 10-50 % as well as good post-irradiation stability when stored in dark and light at room temperature.

References

Abdel-Fattah, A.A. and El-Kelany, M. (1998) Radiation sensitive indicators based on Bromophenol Blue and chloral hydrate dyed polyvinyl butyral. *Radiat. Phys. Chem.*, **44**, 317.

Abdel-Fattah, A. A. and Miller, A. (1996) Temperature, humidity and time combined effects on raiochromic film dosimeters. *Radiat. Phys. Chem.*, **47**, 611.

Abdel-Fattah, A. A., Ebraheem, S., El-Kelany, M. and Abdel-Rehim, F. (1996) High-dose film dosimeters based on bromophenol blue or xylenol orange dyed polyvinyl alcohol. *Appl. Radiat. Isot.*, **47**, 345.

Abdel-Fattah, A. A., Hegazy, E. S. A. and Ezz El-Din, H. (2002) Radiation chemical formation of HCl in poly(vinyl butyral) films containing chloral hydrate for use in radiation dosimetry. *Int. J. Polymeric. Material.*, **51**, 413.

Abdel-Rehim, F. and Abdel-Fattah, A. A. (1993) A thin-film radiation monitoring label and dosimetery system. *Appl. Radiat. Isot.*, **44**, 1047.

Abdel-Rehim, F., El-Sawy, N. M. and Abdel-Fattah, A. A. (1993) Dyed grafed films for large –ndose radiation dosimetry. *Appl. Radiat. Isot.*, **44**, 1055.

Abdel-Rehim, F., Miller, A. and McLaughlin, W. L. (1985) Response of radiation monitoring labels to gamma rays. *Radiat. Phys. Chem.*, **25**, 79.

Akhavan, A., Sohrabpour, A. and Sharifzadeh, M. (2002) Preparation of a new chemical radiochromic film dosimeter. *Radiat. Phys. Chem.*, **63**, 77.

Butson, M. J., Chueng, and Yu, K. (2001) GafChromic radiochromic dosimetery films information. *Phys. Med. Biol.*, **46**, 27.

Butson, M., Peter, J., Yu, K., Cheung, T. and Metealfe, P. (2003) Radiochromic film for medical radiation dosimetry. *Material Sci. Engineer.*, **41,** 61.

Chen, W., Jia, H. and McLaughlin, W. L. (1985) Response of film dosimeters to electron beams in different atmospheres. In High-Dose Dosimetry. *Vienna, International Atomic Energy Agency*, **41**, 345.

Chung, W. H., Kim, H. S., Kim, H. J. and Jung, H. T. (1985) Methylene blue-PVA dosimeter. *J. Korean Assoc. Rad. Prot*., **64**, 772.

Ebraheem, S. and Beshir, W. B. (2005) Investigation of dyed film based on 2, 6-dichlorophenol dyed poly (vinyl alcohol) and poly (vinylbutyral) for possible use in high-dose processing dosimetery. *Arab. J. Nucl. Sci. Applic.*, **38**, 661.

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

Kovacs, A. and Ebraheem, S. (2002) A new dyed poly(vinyl alcohol) film for high-dose application. *Radiat. Phys.Chem.*, **63**, 807.

McLaughlin, W. L. (2003) Radiation chemistry of anionic disazo dyes in Cellophane films applications for high-dose dosimetry. *Radiat. Phys. Chem.*, **67**, 56.

Ogawa, T. (1995) Diacetylenes in Polymeric Systems. *Prog. Polymer Sci.*, **20**, 934.

Sindey, L. N., Lynch, D. C. and Willet, P. S. (1990) A new radiochromic dosimeter film. *Radiat. Phys. Chem.*, **33**, 770**.**

Ueno, K. (1988) Development of a plastic dosimeter for industrial use with high doses. *Radiat. Phys. Chem.*, **31**, 467.

(Received: 08/12/2011;

accepted: 28/12/2011)

تأثير أشعة جاما على الخواص الفيزيائية لأفلأم البولى(فينيل كحول) المصبوغة برابع بروموفينولفثالين اثيل استر

مشيرة الكيلانى

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

فى هذة الدراسة يتم تناول تحضير أفلام بوليمرية من ألبولى(فينيل كحول) المصبوغة برابع بروموفينول فثالين اثيل والمحتوية على ثلاثى كلورو أسيتاميد . هذة الأفلام البلاستيكية يتغير لونها من الأزرق الى الأخضر ثم الأخضر الفاتح وذلك لتكون الحمض. تسخدم هذة الأفلام ككاشف اشعاعى لتشعيع الأغذية فى مدى يتراوح بين ١-٥ كيلو جراى. ومن مميزات هذا الفيلم أنة تم اهمال تأثير الرطوبة على استجابة الأفلام لأشعة جاما من ١٠ الى ٥٠ % كما تضمنت الدراسة تأثير ظروف التخزين فى الضوء والظلام عند درجة حرارة الغرفة على حساسية الأفلام وثباتها عند عملية التشعيع وبعدها.