Egypt. J. Chem. **Vol. 64** No 6 pp. 3161 - 3165 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Possible Using of Acid Sensitive Dyes Embedded in Poly(vinyl alcohol) in Determination the Irradiation Doses

M. El-Kelany[a] A.Sobhy[a*], M. Sadek[b] and H. Bader[a]

a Radiation Protection and Dosimetry Dept.,National Center for Radiation research and Technology (NCRRT). Atomic Energy Authority (AEA).P.O Box8029. Naser City, Cairo, Egypt.

b Faculty of Science (girls), Al-Azhar University, Cairo.

Abstract

Study a new film prepared via casting a mixture of aqueous solutions consists of Orange IV and Indigo Carmine dyes embedded poly (vinyl alcohol) for dose monitoring. The prepared film may be beneficial in low and moderate dose monitor range from 0 to 60 kGy. The film undergoes an obvious color change from green to red color on exposure to gamma photons nominated it to be used as label dosimeter. The range of response curve in the target film depends on the concentration of the added chloral hydrate. The film shows good stability pre and after irradiation. There is no effect of humidity in the range of (10-70 % RH). The overall combined uncertainty measured is 6.32%.

Keywords: Orange IV; Indigo Carmine; poly (vinyl alcohol); PVA, Gamma ray; Dosimetry

1. Introduction

Ionizing radiation is commonly used in many industrial applications such as food preservation, blood irradiation, medical devices sterilization and others. Indicators and dyes are sensitive towards radiation inducing change in their colors after irradiation; they have been used commercially in the area of medicines, radiation sterilization and food irradiation, water and other mineral purification, crosslinking of polymers [1-5]. Such applications require dosimeters with high accuracy to quantify the absorbed doses and indicators to detect visually the radiation exposure. Dosimeter plays essential role in determination of absorbed dose where it absorbs the dose prompting a visual response in the form of coloration in the visible region bringing a physical change there within [6]

The change measured for low or high dosimetry is attributed to the "absorbed dose which is proportional to intensity of the color and also proportional to the character of the color"[7]. Due to simplicity and easy preparations, many dyed plastic films were investigated asking to cover all needed applications in irradiation field. Some of the related researches are addressed in the following review, radio chromic thin films based on polyvinyl alcohol (PVA) containing different concentrations of methyl red (MR) and methylene blue (MB) dyes were studied for the determination of high doses up to 200 kGy [8]. The effect of irradiation on optical properties of the polyvinyl chloride film based on dimethyl yellow dye using a phthalate free plasticizer was investigated. The color changes from yellow to red at dose range up to 30 kGy [9]. Furthermore, dosimeters made up of polystyrene (PS) binder containing different concentrations of dithizone (Dz) dye are investigated for high dose applications [10]. Preparation of a mixture of two dyes namely chlorophenol red and Quinaldine Red have different sensitivity to radiation were investigated as label dosimeter film in the dose range of 2-30 kGy, the color of these films changes from deep red to yellow on exposure to gamma radiation[11]. Gathering two pH indicator dyes m-cresol purple and tetrabromophenolphthalein ethyl ester previously studied as individual dosimeter each at low dose application in the same polymer matrix (PVA) asking to cover a higher dose range , this flexible plastic film changes its color from

*Corresponding author e-mail: asmaa.sobhy@hotmail.com
Received date 28 September 2020; revised date 6 February 2021; accepted date 25 February2021
DOI: 10.21608/ejchem.2021.44378.2898

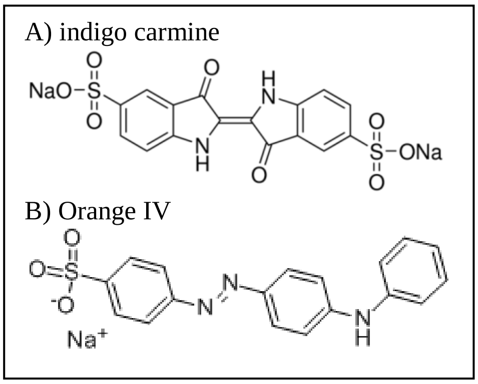
green to red passing through yellow color on exposure to γ-rays photons due to the consequent lowering of pH caused by HCl generated from the radiolysis of chloral hydrate [12]. Mixed dyes film containing 2,6-dichlorophenol indophenol sodium salt and Cresol Red was inspected to be useful dosimeter in dose range up to 50 kGy[13]. The de-colorization of aqueous solutions of Indigo Carmine dye which is primarily used as pH indicator was tested to be used in dose monitoring [14].

In the current work , mixing of Orange IV dye to the Indigo Carmine dye which both was previously studied individually, in the same matrix (PVA) aiming to manufacture a new label dosimeter film, possing dosimetry behavior in low dose applications and labeling behavior in low and moderate dose ranges as well.

2. Experimental

2.1Preparation of stock dye solutions of Orange IV and Indigo Carmine

Stock solution of the Orange IV dye was prepared by dissolving 0.1 g of the dye (product of sigma-Aldrich)) in 50 ml distilled water and 0.05 gm of Indigo Carmine dye (product of sigma- aldrich) in 100 ml distilled water. Structure of Orange IV and Indigo Carmine are shown in scheme 1



Scheme 1: Molecular Structure of Orange IV and Indigo Carmine dyes.

2.2 Preparation of Mixed dyes/PVA film

The mixed dyes/PVA film was prepared by dissolving 6.25g of PVA powder (average MW= 25000) fully hydrolyzed (99-100%) (product of G.T baker chemical Co. USA) in 125 ml double distilled water at about 60°C, the solution was kept well stirred for about 48h, then left to cool. Five equal volumes of mixed dyes/ PVA solutions were taken, then adding 2 ml of (OIV) and 0.1 g chloral hydrate on the first flask and 1ml (IC), 0.2 chloral hydrate in the second flask. The other three flasks contain the same concentrations of the two dyes (i.e 2 ml Orange IV and 1 ml indigo carmine) and different concentrations of chloral hydrate (0.05, 0.15, 0.2, g). After preparing the five solutions, they were kept well stirred at room temperature for about 3hr's in order to obtain a uniform homogeneous mixed solution. Each solution was poured on a 15x15 cm^3 horizontal glass plate, left to dry at room temperature for about 48h. After drying, the films were stripped off from the glass plate, then cut into 1x1cm^2 pieces and stored for further investigation. The thickness of the obtained films was found to be 0.049± 0.005mm (1δ).

2.3Apparatus

The absorption spectra of the un-irradiated and irradiated films were measured throughout the wavelength range (200-800nm) using a UVKON 860 spectrophotometer. The film thickness was measured using a Digitrix-Mark thickness Gauge (precision≠1um; 1δ).

Irradiation was carried out with gamma rays using Gamma cell-220 Excel ^{60}Co irradiation facilities (Manufactured by MDS Nordian, Canada). The absorbed dose rate in water was measured by Frike dosimeter to be 2.35161 kGy/h. The temperature during gamma ray irradiation was 30^{0}C, and the electronic equilibrium conditions were maintained during irradiation through keeping the films between two polystyrene slabs of 3mm thickness.

3. Results and discussion

3.1UV/VIS absorption analysis

Absorption spectra addressed in both figures (1a & 1b) reveals main peaks at 448 nm and 616 nm respectively related to the yellow color characteristic of (O IV) [O IV= 0.32 phr] and the blue color characteristics of (IC) [IC = 0.04 phr].

It is clear from figure (1a) that the main peak at 448 nm decreases by increasing the absorbed dose. At 30 kGy a small peak at 562 nm began to appear and slightly increases in intensity upon increasing dose exposure till 55 kGy. The appearance of this peak at 570 nm is accompanied by change in the color of the film from yellow to red color. Figure . (1b) illustrates the change in the absorption spectra at 612 nm which decreases gradually by irradiation till colorless end at 80 kGy. Both above mentioned absorption spectra were drawn in the presence of 8 and 16 phr chloral hydrate for (O IV) and (IC) respectively. Gathering of 0.32 phr of (O IV) and 0.04 phr of (IC) in presence of 16 phr of chloral hydrate PVA matrix led us to characteristic absorption spectra which is addressed in Figure 2. As shown there are two main peaks at 448 and 612 nm characteristics for (O IV) and (IC), In the dose range of (0- 15 kGy) the amplitude of these peaks decreases in systematic manner when dose exposure increased. At 20 kGy a new peak appears at 585 nm which increased with little deviation in wave length accompanied with each indicated dose (i.e 20, 30, 55, 60kGy). The color changes from green to red passing through yellow and orange as shown in scheme 2. The behavior of gamma radiation on the combined dyes is discussed as follows. The first step of reaction is the degradation of (IC), i,e (IC) more sensitive than (O IV). Secondly, all radiolysis species are directed to transformation of (O IV) to its acidic form i.e the appearance of the red color of (O IV). This change in color is due to the effect of radiation resulting species that affected both dyes in the presence of HCL resulting from dissociation of chloral hydrate salts [12]. So the pattern demonstrated in figure 2 focused on the possibility of using this film as a dosimeter at 448nm in low doses range (0- 15 kGy) and as a label in extended dose range reach to 60 kGy.

Scheme 2 : Change in color of O IV/ IC/ PVA film containing chloral hydrate at different absorbed dose

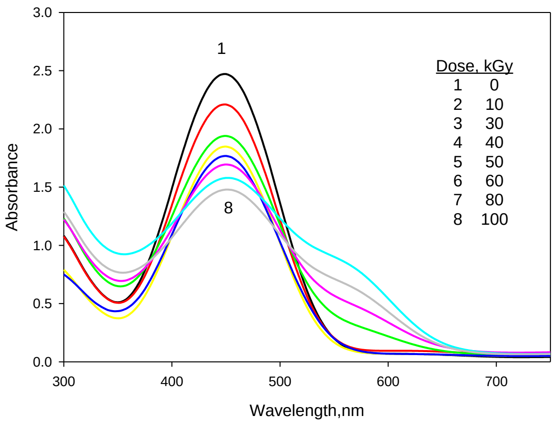


Fig.1a Absorption Spectra of unirradiated and irradiated O IV/ PVA film containing chloral hydrate at different absorbed doses. [O IV= 0.32 phr], [CH= 8 phr]

.

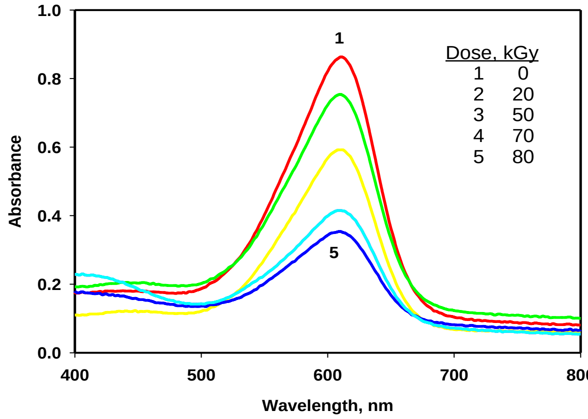


Fig.1b Absorption Spectra of unirradiated and irradiated IC/ PVA film containing chloral hydrate at different absorbed doses. [IC= 0.04 phr], [CH= 16 phr]

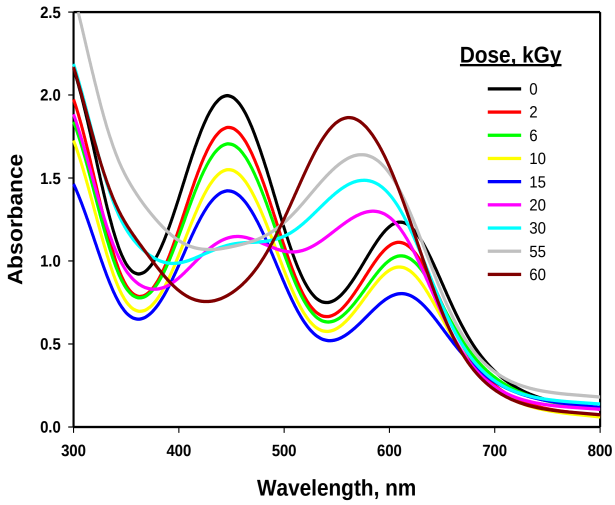


Fig 2: Absorption Spectra of unirradiated and irradiated O IV/ IC/ PVA film containing chloral hydrate at different absorbed dose.[O IV= 0.32 phr], [IC= 0.04 phr], [CH= 16 phr]

3.2 **Response Curve**

The effect of the absorbed dose on the films containing different concentrations of chloral hydrate can be estimated through studying their response curves. Figure 3 shows the dose response curves of three films containing 0.32 phr of (O IV) and 0.04 phr of (IC) in presence of different concentrations of chloral hydrate [4, 12, 16 phr]. The response curves were established in terms of change in optical density measured at 448 nm (ΔA), ($\Delta A = A_0 - A_i$) against the absorbed dose, where A_0 and A_i are values of optical absorbance at 448 nm for un-irradiated and irradiated films respectively. It can be noticed that all the curves show the same trend, but they differ in slope value. The slope value increases with increasing chloral hydrate concentrations.

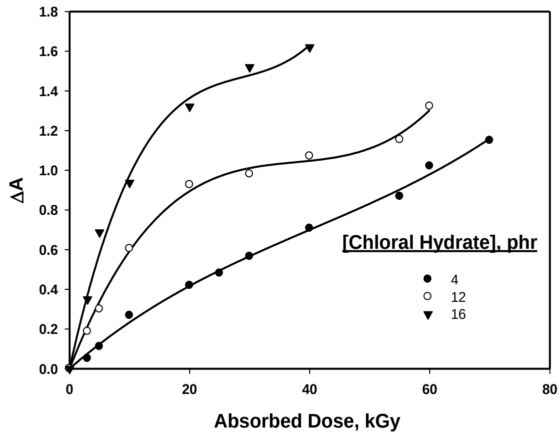


Fig 3. Change of ΔA. of O IV/ IC/ PVA films containing different chloral hydrate concentrations. [O IV]= 0.32 phr, [IC] = 0.04 phr, at λmax= 448 nm.

3.3 Humidity during irradiation

The effect of RH during irradiation on the response was investigated by irradiated O IV/ IC/ PVA films (16 phr Chloral hydrate), (0.32 phr O IV, 0.04hr IC) at 448 nm by 20 kGy at different relative humidity (0%, , 33%, 54%, 76%, 92%, 100%). 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 embedded over dried silica gel [15]. Fig. 4. shows the variation in optical density after irradiation (Ai) to optical density before irradiation (Ao) as a function of percentage RH during irradiation relative to that at 33%. It was found that, the films have no appreciable effect in the range of RH (10-70%), although the response shows somewhat different sensitivities at both higher and lower humidity.

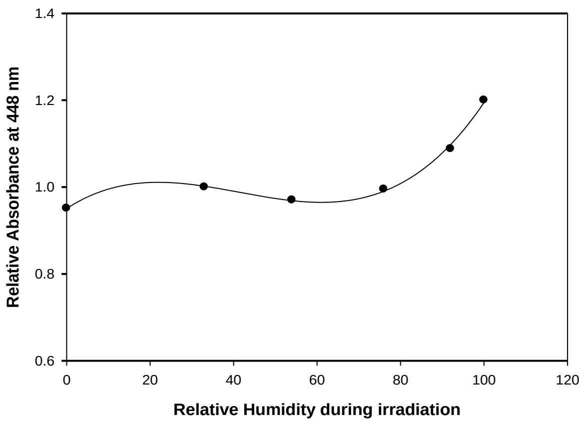


Fig. 4 Variation of response of O IV/ IC/PVA film as a function of relative humidity during irradiation

3.4 Pre-irradiation stability

The stability of Orange IV/ IC/ PVA films containing (16 phr chloral hydrate, 0.32 phr O IV, 0.04 phr IC) at 448nm before irradiation were investigated by storing the films at 35% RH at room temperature (25± 3^0C) in the dark and under laboratory fluorescent light. The absorbance of the films was measured at 448nm wavelength at different time intervals during the pre-irradiation storage period of 35 days. The change in absorbance at 448 nm as a function of storage time is shown in Figure 5. It can be observed that the films have excellent stability, just 3% decrease through 35 days.

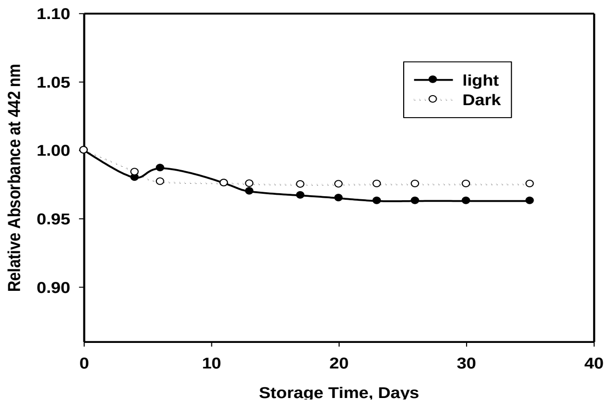


Fig. 5. Pre-irradiation stability of O IV/ IC/ PVA films stored in diurnal cycles of day light at room temperature in 25ºC at 424nm.

3.5 Post irradiation stability

The stability of O IV/ IC/ PVA films containing (16 phr chloral hydrate, 0.32 phr O IV and 0.04 phr IC, 0.16phr CH) at 448 nm was investigated immediately after irradiation then, storing the films at 35% RH at room temperature (25± 3^0C) in the dark and under laboratory fluorescent light. The change in absorbance at 448 nm as a function of storage time is shown in Figure 6. It can be noticed that the films have excellent stability, just 5 % decrease through 35 days storage time in dark and 7 % decrease in light.

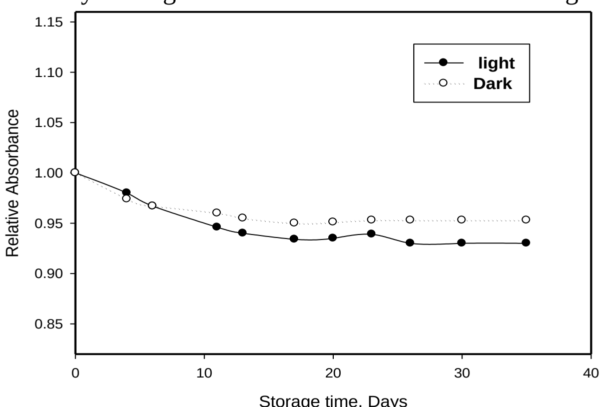


Fig. 6. Post-irradiation stability of O IV/ IC/ PVA films stored in diurnal cycles of day light at room temperature in 25ºC at 448 nm.

3.6 Assessment of uncertainties

To be meaningful, measurement of gamma rays should be accompanied by an estimation of the uncertainty in the measured value. Factors contributing to the total uncertainty can be separated into two types[16], type A and type B[17]. 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 UVKON spectrophotometer was determined by reading the absorbance value (at 448 nm wavelength and absorbance level 0.8) of irradiated films several times (one hundred readings per film). From the data obtained, it was found that the coefficient of variation (1σ) is ±0.2%, reflecting the precession of the spectrophotometer. The reproducibility of the measurements of several films (10 times for film) was found to be 1.88% (1 σ). On the other hand, the type "A" uncertainties (at one standard deviation, 1σ) arising during calibration over the useful response range were found to be ± 2.6%. The combined uncertainties (Uc) can be obtained by combining all the components in quadrature at one standard deviation (1σ) as follow:

$$Uc=\sqrt{(0.2)^2 + (2.6)^2 + (1.88)^2} = 3.214$$

The combined uncertainty (at two standard deviations, i.e 2σ, approximately equal to 95% confidence level) is found by multiplication of Uc at (1σ) by two. Hence the combined uncertainty is 6.43%.

4.Conclusion

Studying the data obtained from irradiated O IV/IC/PVA films containing chloral hydrate for dose monitoring nominates these films for dose monitoring in low dose range extended from 0-15 kGy beside the possibility of its usage as label in wider range that reaches 60 kGy since its color changes from green to intense bright red. The dose range depends on the chloral hydrate concentrations. The films have negligible humidity effects in range of 0-70 % RH as well as good pre and post irradiation stability. These films are easy to prepare so they are useful to be utilized in large scale production and application for routine irradiation processes in low and moderate dose irradiation range.

5. **Conflicts of interest**

"There are no conflicts to declare".

6. **Acknowledgments**

The authors gratefully acknowledge to National Center for Radiation research and Technology (NCRRT). Egyptian Atomic Energy Authority and El Azhar university for supporting this research work.

7. References

1- Bhat N. V., Nate M. M., Bhat R. M. , Bhatt B. C., "Effect of γ-irradiation on polyvinyl alcohol films doped with some dyes and their use in dosimetric studies," *Indian J. Pure Appl. Phys.*, **45,** 545–548 (2007) .

2- Shahid M.,A. , Kousar N, Akhatr N, . Hussain T, Awan M.,S., Mubashir A, Beshir B., and Javed A., . "Dosimetry characterization of unknown dye polyvinyl alcohol films," *J. Basic Appl. Sci.*, **8** , 508–512 (2012).

3- Hussain, "The Feasibility of Reactive Dye in PVA Films as High Dosimeter," *J. Basic Appl. Sci.*, **9**, 420–423 (2013).

4- Mathad R. D., Harish Kumar H. G. , Sannakki B. , Ganesh S. , Sarma K. S. S. , Badiger M. V. , "High energy electron irradiation effects on polystyrene films," *Radiat. Eff. Defects Solids*, **164** (10), 656–664, (2009).

5- Kovács A. , Baranyai M. , Baranyai L., Slezsák I. , McLaughlin W. L. , Miller A. , Moussa A., "Dose determination with nitro blue tetrazolium containing radiochromic dye films by measuring absorbed and reflected light," *Radiat. Phys. Chem.*, **57**, 711–716, (2000).

6- Laranjeira J. M. Khoury G., H. J., De Azevedo W., De Vasconcelos M., E. A., Da Silva E. F., "Polyaniline nanofilms as a monitoring label and dosimetric device for gamma radiation," *Mater. Charact.*, **50,** 127– 130 (2003).

7- Artandi C., Stonehill A. A., "Rigid vinyl fim dosimeter," *Nucl. Instruments Methods*, **6,** 279–282 (1960).

8- Akhtar S., Shahzad A., Bashir S., Hussain M.Y. and Akhtar N. "Improved performance of radiochromic films for high-doseDosimetry**,** *Radioprotection* **51**(2), 129-133, (2016).

9- Oberoi P., Maurya C. and Mahanwar P., Effect of gamma irradiation dose on phthalate free PVC dyed thin film dosimeter, *J. Mater. Environ. Sci*., **10 (**6), 533-542, (2019).

10-Rabaeha K. A. , Basfarb A.A. "A polystyrene film dosimeter containing dithizone dye for high dose applications of gamma-ray source" *Radiat. Phys. Chem.*, ***170*,** 108646–108651, (2020).

11- Eid S., Rabie A. , Ebraheem S. and Sobhy A. " Effect of Gamma Radiation on a Mixed Dyed Film and its Possible Use as a Radiation Dosimeter" *Eur. Chem. Bull.*, **6**(11), 510-513, (2017).

12- Faheem E., Abdel-Moniem Sh. And El Ahdal M.A. " High Dose Film Dosimeter Based on a Mixture of m-cresol Purple and Tetrabromo phenolphthalein Ethyl Ester Dyed Poly (vinyl alcohol)". *Egypt. J. Rad. Sci. Applic.*, **28**, No. 1-2, 49-60 (2015).

13- Ebraheem S.., Eid S., , Kovacs A., A new poly (vinyl alcohol) film for high- dose applications, *Radiat. Phys. Chem.*, **63**, 807-811,(2002).

14- Anoop P.Fartode , Swati A. Fartode, Tushar R. Shelke " Gamma Radiation Induced Decolorization of Indigo Carmine Dye Solutions" *International journal of current engineering and scientific research*. **6** (1), 1363-1368, (2019).

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

16- ISO/ASTM 51707, Standard guide for estimating uncertainty in dosimetry for radiation processing. Annual book of ASTM standards ASTM International, West Conshohocken. PA.(2004)

17- AEA, Guidelines for the development. Validation and Routine control of Industrial Radiation Processes. IAEA Radiation Technology Series No. 4. International Atomic Energy Agency. Vienna. Austria. (STI/PUB/1581). (2013)