

Preparation of 4PNPAN Dyed Poly (vinyl butyral) Copolymer Films for Dosimetric Applications

Sayeda Elewa Eid*, Seif Ebraheem and Nehad Magdy

Radiation Protection and Dosimetry, Dept., National Center for Radiation Research and technology (NCRRT).

Egyptian Atomic Energy Authority P.O Box 029. Naser City 11371, Cairo, Egypt.

drsayed1@hotmail.com*

(Received on 10th July 2017, accepted in revised form 7th February 2018)

Summary: Poly (vinyl butyral co-poly vinyl alcohol co-vinyl acetate) (PVB-co-PVA/PVAC) combined with 4-(p-nitrophenyl-azo)-1-naphthol dye has been examined a promised dosimeter suitable for high dose ranges. The prepared films have yellow color. This color undergoes color bleaching upon irradiation with gamma rays. Different concentrations were prepared to obtain the suitable dosimeter in the dose range from 3 to 200kGy depending on the dye concentration. Chloral hydrate was then added in different concentrations, as a result the bleaching reaction expedites and in accordance the dose range diminishes to be 35kGy. The effect of chloral hydrate as well as dye concentration on response curve was studied. The radiation efficiency (G-value) was estimated for all the prepared films. Influence of relative humidity during irradiation was estimated as well as stability before and after irradiation.

Keyword: 4-P-nitrophenyl-azo-1-naphthol; Poly (vinyl butyral) copolymer; Film dosimeter; Gamma radiation; G-(value)

Introduction

Polymeric films containing dye are mostly containing organic dyes which are usually colored compounds have been examined and used as radiation dosimeters. They have been utilized in various polymeric films [1]. Azo dye films play acritical rule in radiation processing as high dose dosimeter [2-6]. Several studies have investigated the dosimetry characteristics of a poly vinyl alcohol based on nitro blue tetrazolium chloride dye for high dose applications. The useful dose range for the dosimeter film for gamma and electron beam irradiation is 5–50 kGy, depending on the dye concentration [7]. Poly vinyl alcohol (PVA) films dyed with methyl orange (MO) was investigated to allow their use in applications for high dose radiation processing in the dose range of 100-200kGy [8]. Cellophane films containing diazo dye for application to high – dose dosimetry have been reported [9], blue cellophane was examined as a monitor of high dose in the range (10–300 kGy). Numerous studies have attempted to explain the effect of gamma radiation on Radio-chromic dye film based on polyvinyl butyral (PVB) containing methyl red (MR) dye of different concentrations. The reported MR concentrations are 0.125, 0.25 and 0.5 mM as high dose dosimeter. The dosimeters were subjected to gamma ray from ⁶⁰Co source from 5 to 150 kGy [10]. Previous studies have reported that synthesis of a new film dosimeter based on Methyl red (MR) dye was introduced into poly (chloroprene) in various concentrations. The films were intensely red with λ_{max} 515 nm. The absorbance

value decreased linearly with the absorbed radiation dose up to 30 kGy [11].

The present work attempts to show that the radiation induced degradation of 4PNPAN/(PVB-co-PVA/PVAC) films to be a suitable dosimeter in high dose range, chloral hydrate was added in different concentrations and its effect was documented. . Also, the relative humidity during irradiation as well as storage time before and after irradiation was investigated

Experimental

Preparation of stock solution of (4PNPAN)

The stock solution of 4-(p-nitrophenyl-azo)-1-naphthol dye was prepared by dissolving 0.08 g in 50 ml N,N-dimethylformamide. The structural formula of 4-p-nitrophenyl-azo-1-naphthol is represented in Fig. (1):

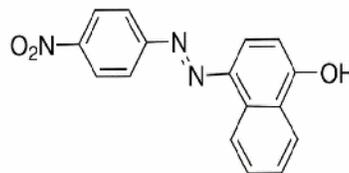


Fig. 1: Scheme structure of 4-(p-nitrophenyl-azo)-1-naphthol.

*To whom all correspondence should be addressed.

Preparation of 4PNPAN /copolymer dye films

Films were prepared by dissolving 9 g of Poly (vinyl butyral co-poly vinyl alcohol co-vinyl acetate) (PVB-co-PVA/PVAC) (average M.W. 70,000-100,000 product of Aldrich chemical company USA in 180ml n-butanol at about 60°C. The solution was kept well stirred at the same temperature for about 24 h; then left to cool. Solution was divided into 6 parts. To each 30 ml of the well mixed solution, the first three parts contain 1, 1.5 and 2 ml from the stock solution of 4PNPAN. The rest three parts contain 0.2, 0.4, and 0.6 g of chloral hydrate with 2 ml from the stock 4PNPAN solution. The Six solutions were kept well stirred at room temperature for about 3h in order to obtain a uniformly mixed solution. Six films were obtained; the first three of them contain 0.107, 0.16 and 0.213phr of 4PNPAN dye respectively, the rest three films contain 13.33, 26.67 and 40 phr of chloral hydrate and 0.213 phr of dye. Each solution was poured on 15x 15 cm horizontal glass plate and dried at room temperature for about 48 hours. After drying, the films were stripped from the glass plate, then cut into 1 x 1 cm pieces and stored for different investigations.

Apparatus

The absorption spectra of both unirradiated and irradiated films were measured throughout the wavelength range 200-800 nm using a UVIKON860 spectrophotometer. The film thickness was measured using Digitrix-MarkII thickness gauge; precision $\pm 1\mu\text{m}$. Gamma irradiation was carried out in the ^{60}Co gamma chamber 4000 Ao; product of India. The absorbed dose rate in irradiation facility was measured to be 1.67 kGy/h using reference alanine dosimeter and the measured films were placed between two polystyrene slabs of the same thickness to ensure that irradiation were performed under electronic equilibrium conditions which were maintained during irradiation.

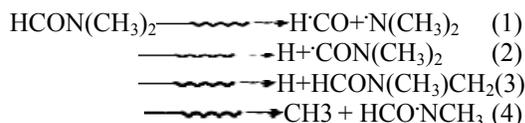
Results and Discussion

Absorption spectra

The spectral analysis of 4PNPAN/(PVB-co-PVA/PVAC) including 0.213phr of 4NPAN dye were represented before and after irradiation to different absorbed doses are cleared in Fig. 2. The unirradiated film shows a main absorption band in the visible

region peaking at 472 nm characteristic of yellow color.

The intensity of this peak is inversely proportional to the absorbed dose up to 200kGy. From point of view the structure of azo dyes assigned with the presence of one $-\text{N}=\text{N}-$ group or more binded to at least one aromatic group. The attached chromophores and auxochromes are considered to be the main source of azo dye color, the explanation of the decoloration process is that the radiolysis product of N,N-dimethylformamide by ^{60}Co γ -irradiated is the following [12]:



We can conclude that $-\text{N}=\text{N}-$ breakdown is accomplished by a reduction process from hydrogen radical produced as a result of N,N-dimethylformamide's fragmentation [13]. Accordingly, H-N-N-H was produced, leading to the absence of the main source of color. With increasing the absorbed dose, the number of free radicals increases, as a result, breaks down of the azo group takes place and the chromophores disappear which leading to color bleaching.

Response Curves

The response was established for 4PNPAN/(PVB-co-PVA/PVAC) films containing different dye concentrations in terms of difference in absorbance per unit thickness ($\Delta A \cdot \text{mm}^{-1}$) at 472 nm against the irradiation dose ($\Delta A = A_0 - A_i$), where A_0 and A_i are values of absorbance at 472 nm for unirradiated and irradiated films respectively). Each point on the dose response curve exemplifies the mean optical density measurement of three films which have an identical dose. From Fig. 3, it is clear that the dose range was affected by dye concentration, so the dose range reduced from 200 to 90 kGy according to dye concentration. The dose range is directly proportional to dye concentration. The conjunction between dose at saturation of 4PNPAN/(PVB-co-PVA/PVAC) and dye concentration is represented in Fig. 4. from which it is clear that the dose at saturation is directly proportional to its dye concentration.

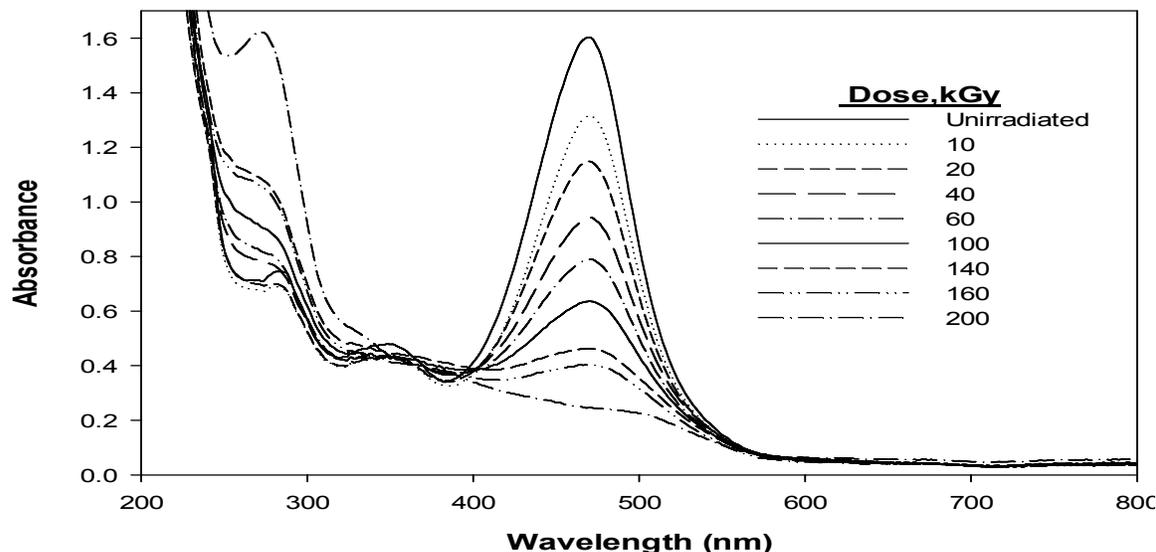


Fig. 2: The UV-absorption spectra of 4PNPAN/(PVB-co-PVA/PVAC) films before and after irradiation to different absorbed dose [4PNPAN]= 0.213 phr.

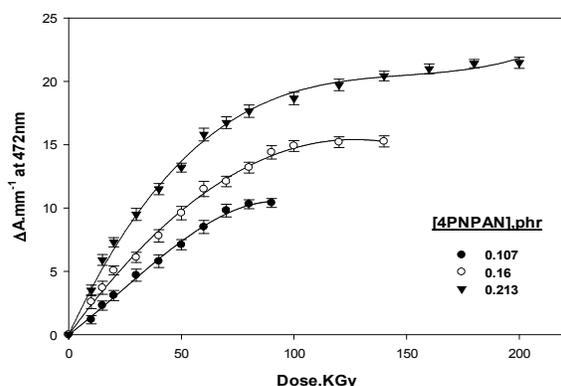


Fig.3: Variation of $\Delta A. mm^{-1}$ with the absorbed dose of 4PNPAN/(PVB-co-PVA/PVAC) films containing different dye concentrations.

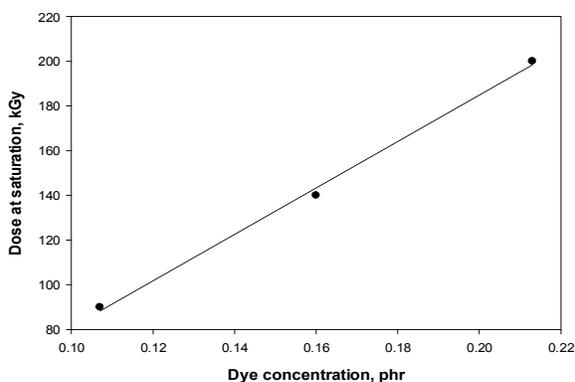


Fig. 4: Change of dose at saturation of 4PNPAN/(PVB-co-PVA/PVAC) films dye concentrations.

Effect of chloral hydrate concentration:

Absorption spectra

The spectral analysis of 4PNPAN/(PVB-co-PVA/PVAC) films including different chloral hydrate concentrations were estimated under the effect of γ -radiation to different doses. The result of film with 40 phr of chloral hydrate and 0.213 phr 4PNPAN are cleared in Fig. 5; In which the absorbance value at 472 nm undergoes significant decrement as a result of increasing the applied dose. It was noticed that the dose range was reduced from 200 to be 35 kGy for the same dye concentration with chloral hydrate, it was observed that chloral hydrate enhances the bleaching reaction of dye. So, the degradation process was accelerated, as expected. The radiolysis products of chloral hydrate [14] together with that from fragmentation of N,N-dimethylformamide decreases the dose range to be 35kGy.

Response Curves

Fig. (6). represents the response curves of 4PNPAN/(PVB-co-PVA/PVAC) films including 0.213 phr of 4PNPAN and different chloral hydrate concentrations in terms of variation in optical density per unit thickness, ($\Delta A. mm^{-1}$) at 472 nm. The results show that all the curves have the same trend but the difference in their sensitivity. The sensitivity is directly proportional to chloral hydrate concentration. It was noticed that chloral hydrate is influential factor in the bleaching rate of 4PNPAN, because the radiolysis products and free radicals are generated leading to breakage of azo group of 4PNPAN, resulting in the acceleration of disappearance of chromophore. As a result the color bleached.

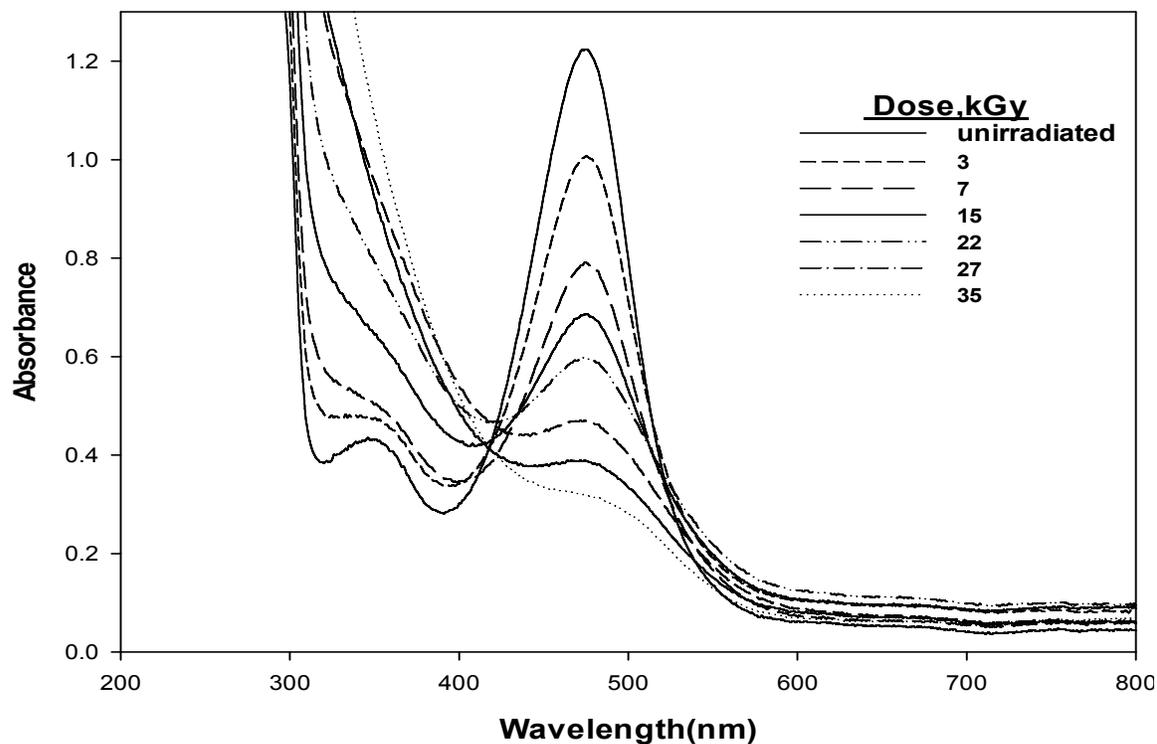


Fig. 5: The UV-absorption spectra of 4PNPAN/(PVB-co-PVA/PVAC) films before and after irradiation to different absorbed doses, [chloral hydrate] = 40 phr [4PNPAN]=0.213 phr

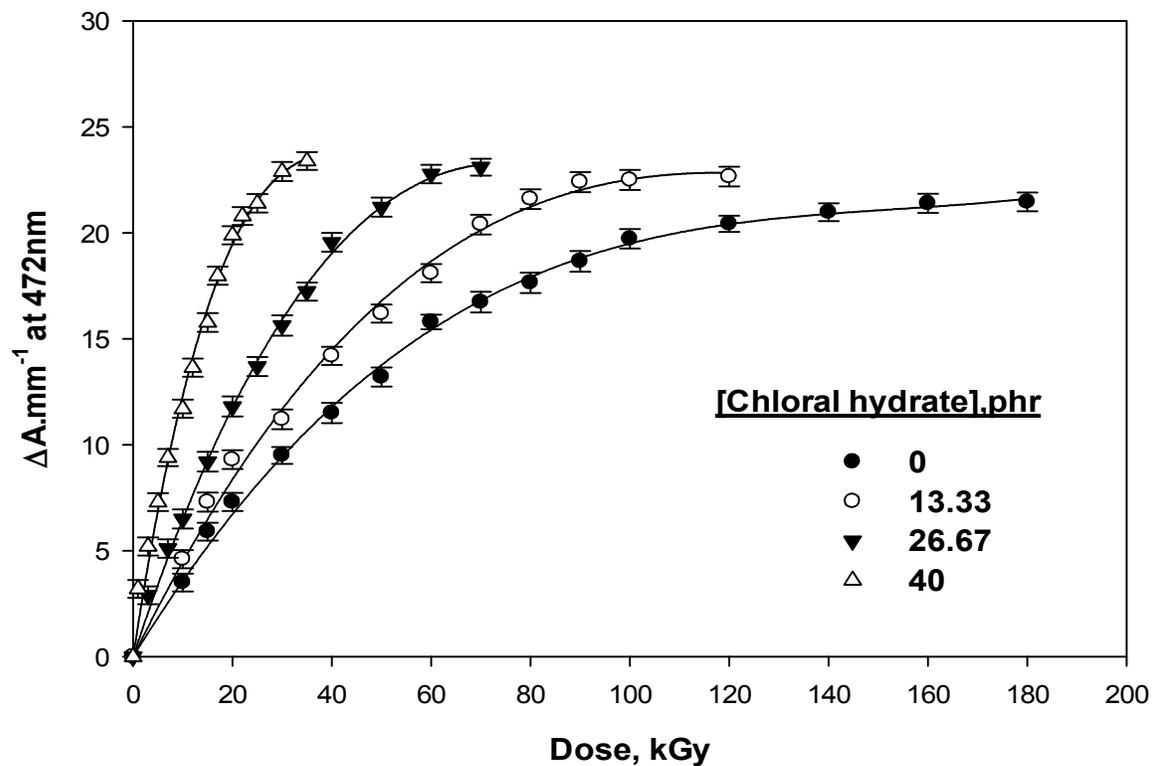


Fig. 6: Variation of $\Delta A \cdot \text{mm}^{-1}$ with the absorbed dose of 4PNPAN/(PVB-co-PVA/PVAC) films containing different chloral hydrate concentrations. [4PNPAN] = 0.213phr.

The conjunction between dose at saturation of 4PNPAN/(PVB-co-PVA/PVAC) and chloral hydrate concentration is represented in Fig. 7. from which it is clear that the dose at saturation is inversely proportional to chloral hydrate concentration.

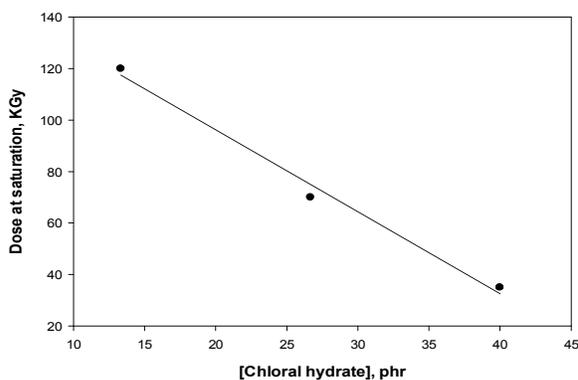


Fig. 7: Change of dose at saturation of 4PNPAN/(PVB-co-PVA/PVAC) films with chloral hydrate concentrations.

Radiation chemical efficiency

The radiation-chemical yield (G-value) is defined as the number of moles of dye degraded by the absorption of 1 J of energy (mol/J). The G-value is calculated from the general relation (15).

$$G(-\text{Dye}) = \frac{\Delta A}{D} \cdot \epsilon \cdot \rho \cdot b \left(\frac{\text{mol}}{\text{J}} \right) \quad (5)$$

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} ($\text{L mol}^{-1} \text{cm}^{-1}$), 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_0/b , the molar extinction coefficient is calculated as $27030.89 \text{ Lmol}^{-1}\text{cm}^{-1}$ where the density for PVB-co-PVA/PVAC is 1.083 g/cm^3 . G-values of 4PNPAN/(PVB-co-PVA/PVAC) films with different dye concentrations and chloral hydrate with 0.213 phr of 4PNPAN represented in Table (1). From the table G-value is directly proportional to both chloral hydrate concentrations and dye concentrations.

Table-1: G-values of 4PNPAN/(PVB-co-PVA/PVAC) films containing different concentrations of dye and chloral hydrate with 0.21 phr of 4PNPAN

Dye Conc. phr	Chloral hydrate phr	G-value ($\mu \text{ mol} \cdot \text{J}^{-1}$)
0.107	--	0.031
0.16	--	0.11
0.213	--	0.16
0.213	13.33	0.2
0.213	26.67	0.25
0.213	40	0.37

Influence of relative humidity during irradiation

The influence of relative humidity (RH) during irradiation on the response of 4PNPAN/(PVB-co-PVA/PVAC) films were examined by irradiating the films containing 0.213 phr 4PNPAN to an absorbed dose of 50 kGy at different relative humidities (0, 33, 54, 76, 92 and 100% RH). The relative humidities were maintained by using different saturated salt solution (16). 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. 8 represents the change in $\Delta A \cdot \text{mm}^{-1}$ at 472 nm as a function of percentage relative humidity during irradiation, relative to the response value at 33% relative humidity. It can be seen that the response of 4PNPAN/(PVB-co-PVA/PVAC) films exhibits no change till 76%, while it undergoes a gradual increase with ~5% for the relative humidity from (80 - 100%).

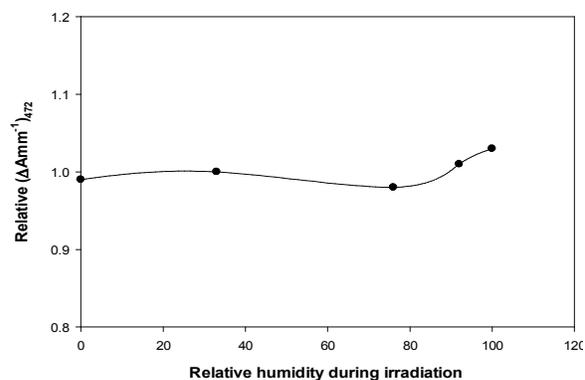


Fig. 8: Change of response of 4PNPAN/(PVB-co-PVA/PVAC) films with relative humidity during irradiation, $\lambda_{\text{max}472\text{nm}}$, irradiation dose 50K Gy.

Uncertainty in the estimated dose value

The uncertainty value of the film 4PNPAN/(PVB-co-PVA/PVAC) containing [4PNPAN] = 0.213 phr was analyzed at 472nm irradiated at dose range (10-200kGy) was found to be 1.57. The estimated value was calculated by using the following formula [17].

$$u = \sqrt{\frac{\sum_i (n_i - 1)(\sigma_i)^2}{\sum_i (n_i - 1)}} \quad (3)$$

Where n_i and σ_i are the number of dosimeters and the standard deviation of the dose measurements at a given dose level, respectively.

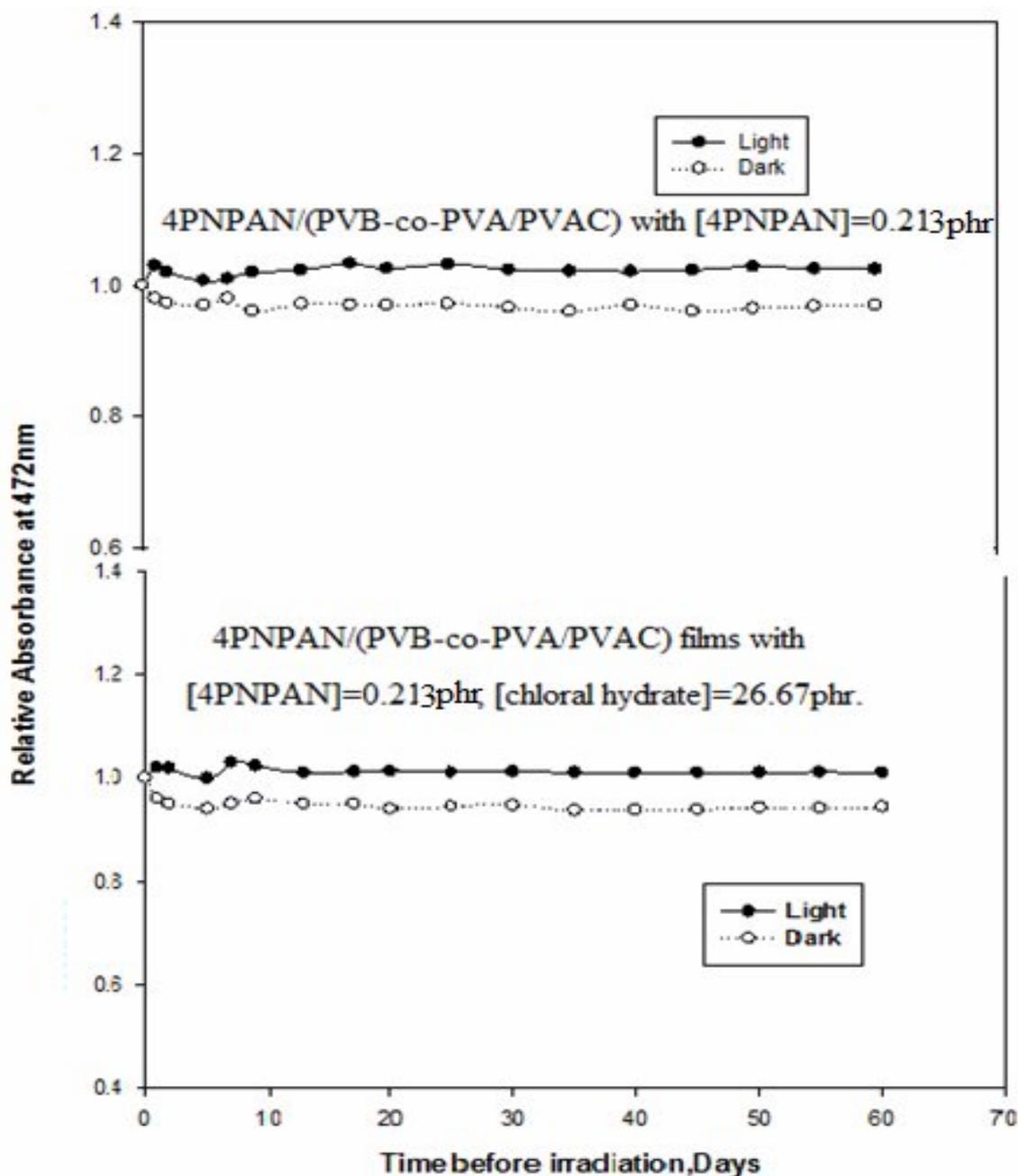


Fig. 9: stability before irradiation of 4PNPAN/(PVB-co-PVA/PVAC) films $[4PNPAN]=0.213\text{ phr}$ and $[4PNPAN]=0.213\text{ phr}$, $[\text{chloral hydrate}]=26.67\text{ phr}$ were in dark and light at room temperature at λ_{472} .

Pre-irradiation stability

Stability measurements before irradiation were carried out by storing both 4PNPAN/(PVB-co-PVA/PVAC) and 4PNPAN/(PVB-co-PVA/PVAC)/[chloral hydrate] films in dark and light at 25 °C. The films were measured spectrophotometrically at different interval times during storage period of 60 days. Fig. 9 represents the

stability of 4PNPAN/(PVB-co-PVA/PVAC) containing $[4PNPAN]=0.213\text{ phr}$. And the stability of 4PNPAN/(PVB-co-PVA/PVAC)/[chloral hydrate] containing $[4PNPAN]=0.213\text{ phr}$ and $[\text{chloral hydrate}]=26.67\text{ phr}$. From Fig. 9 it could be noticed that the films exhibit change in absorbance during the first 10 days in dark and light after that the films tend to be stable to the end of storage time period.

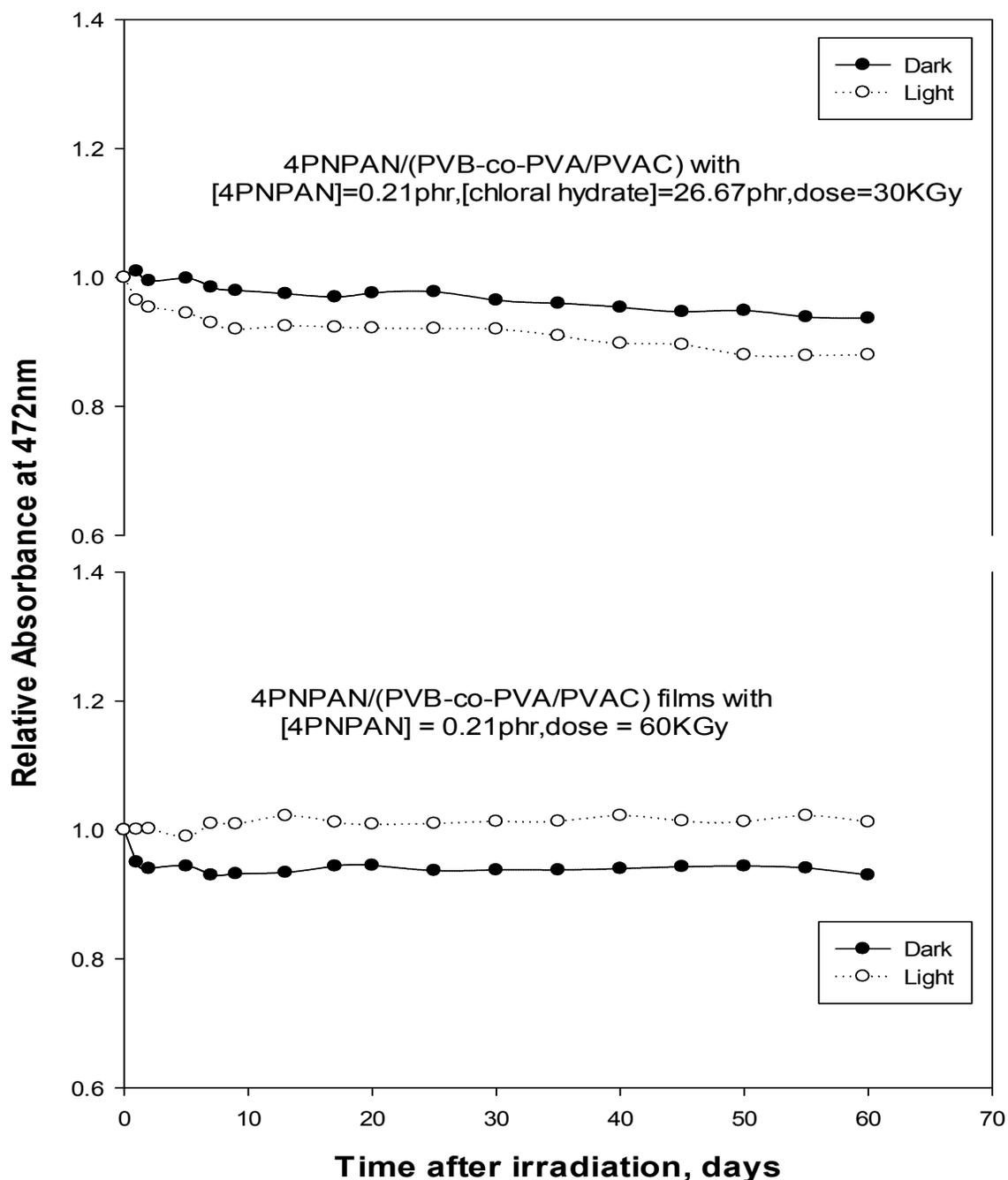


Fig. 10: Stability after irradiation of 4PNPAN/(PVB-co-PVA/PVAC) films at λ_{472} , [4PNPAN]=0.21 phr, dose=60kGy and [4PNPAN]=0.213 phr, [chloral hydrate]=26.67 phr, dose=30KGy.

Post irradiation stability

4PNPAN/(PVB-co-PVA/PVAC) and 4PNPAN/(PVB-co-PVA/PVAC)/[chloral hydrate] films undergo gamma radiation to a dose of 30kGy were stored at dark and light at temperature 25°C. The optical density of these films at 472nm was measured at different interval times during the

storage period of 60 days after irradiation. Fig. 10 represents the stability of 4PNPAN/(PVB-co-PVA/PVAC) containing [4PNPAN]= 0.213 phr the response decreases gradually by ~3 % in dark and in light increases gradually by ~1 % at the first 10 days then the response tends to be stable to the end of the storage period, and also the stability of 4PNPAN/(PVB-co-PVA/PVAC)/[chloral hydrate]

containing [4PNPAN]= 0.213 phr and [chloral hydrate]= 26.67phr, which indicates that immediately after irradiation the response was gradually decreases by ~ 3% in dark and ~1% in light through the first 10 days, then the response tends to be stable to the end of the storage time period.

Conclusion

Radiation-induced decoloration of 4PNPAN/(PVB-co-PVA/PVAC) film dosimeter with different concentrations of 4PNPAN dye was investigated. The bleaching of color increases gradually with the increase of absorbed dose and this prepared film can be used as dosimeter in the dose range from 3 to 200KGy. Addition of chloral hydrate accelerates the bleaching process of the dye. G-value was calculated for both 4PNPAN/(PVB-co-PVA/PVAC) and 4PNPAN/(PVB-co-PVA/PVAC) with chloral hydrate and its value was found to directly proportional to both dye concentration and chloral hydrate concentration. The films can be used in the range of relative humidity during irradiation from 0 to 76%. The irradiated films were found to have a good stability before and after irradiation in dark and light at room temperature over 60 days storage period. Finally this film can be used as dosimeter for high dose applications.

Acknowledgment

The authors would like to acknowledge all members of dosimetry department, NCRRT for their helpful assistance.

References

- M. A. Rauf, and S. S. Ashraf, Radiation induced degradation of dyes—An overview, *J. of Hazardous Mater.*, **166**, 6 (2009).
- W. L. McLaughlin, Flims dyes and photographic systems In Holm, N.W., Berry, R.J., (Eds), Manual on Radiation Dosimetry. *Marcel Dekker Inc., New Yourk*.p. 313 (1970).
- A. Miller, Dosimetry for radiation processing, *Radiant. Phys.Chem.*, **28** (5/6) 321.
- A. Kovács, K. Wojnarovits, C. Kurucz,, M. AL-Sheilkhy and W. L. McLaughlin, Lage scale dosimetry using dilute methylene blue dye in aqueous solutions, *Radiat. Phys. Chem.*, **52**, 539 (1998).
- M. F. Barakat, K. El-Salamawy, M. EL-Banna, M. Abdel- Hmid, and T. A. Abdel-Rehim, Radiation effects on some dyes in non-aqueous solvents and in some polymeric films., *Radiat. Phys. Chem.*, **61**, 129 (2001).
- Y. P. Chen, S. Y. Liu, H. Q. Yu, H. Yin, and Q. R. Li, Radiation induced degradation of Methyl Orange in aqueous solutions, *Chemosphere.*, **72**, 532 (2008).
- A. Moussaa, M. Baranyaib, L. Wojnarovits, A. Kovacs and W. L. McLaughlin, Dosimetry characteristics of the nitro blue tetrazolium poly vinyl alcohol film for high dose applications. *Radiat. Phys. and Chem.*, **68**, 1011 (2003).
- S. Akhtar, T. Hussain, A. Shahzad, Q.ul-Islam, M. Y. Hussain and N. Akhtar, Radiation Induced Decoloration of Reactive Dye in PVA Films for Film Dosimetry. *J.of Basic & Appl. Sci.*, **9**, 416 (2013).
- W. L. McLaughlin, Radiation chemistry of anionic diazo dyes in cellophane films applications for high dose dosimetry, *Radiat. Phys. Chem.*, **67**, 561 (2003).
- A. A. Al Zahrany, K. A. Rabach, and A. A. Basfar, Radiation-induced color bleaching of methyl red in polyvinyl butyral film dosimeter, *Radiat. phys. and chem.*, **80**, 1263 (2011).
- S. K. Suman , K.A. Dubey, B. B. Mishra, Y. K. Bhardwaj, R. K. Mondal, M. Seshadri, V. Natarajan, and L. Varshney, Synthesis of a flexible poly(chloroprene)/methyl red film dosimeter using an environment-benign shear compounding method. *Appl. radiat. isotopes.*, **98**, 60 (2015).
- N. Colebourne, E. Collinson and F. Dainton, ⁶⁰Coy-Radiolysis of N,N-dimethylformamide. Transactions of the faraday society. **50**, 886 (1963).
- N. Bhat, M. Nate, R. M. Bhat and B. C. Bhatt, Effect of γ - irradiation on polyvinyl alcohol films doped with some dyes and their use in dosimetric studies. *Indian J. of pure & appl. Phys.*, **45**, 545 (2007).
- A. A. Abdel-fattah, A. I. F. Said, S. Ebraheem, M. El-kelany and A.A. El Miligy, Dyed acrylic-acid grafted polypropylene films for high-dose radiation dosimetry, *Radiat. phys. Chem.*, **54**, 271 (1999).
- W. L. McLaughlin, A. W. Boyd, K. H. Chadwick, J. C. McDonald, and A. Miller, Dosimetry for Radiation processing. (London: Taylor & Francis) (1989).
- H. Levine, W. L. McLaughlin and A. Miller, Temperature and humidity effects on the gamma-ray response and stability of plastic and dyed plastic dosimeters. *Radiat. Phys. Chem.*, **14**, 551 (1979).
- P. Sharpe and A. Miller, guidelines for the calibration of routine dosimetry systems for use in radiation dosimetry. National Physical Laboratory NPL Rep.CIRM., **29**, (2009).