Optical Band Gap and Radiation Chemical Formation of HCl in Polyvinyl Alcohol Films Containing Chloral Hydrate for Use in Radiation Dosimetry

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Summary: Radiation sensitive indicator based on dyed polyvinyl alcohol (PVA) containing acid – sensitive dye (bromo-chloro-phenol blue, BCPB) and chloral hydrate has been developed. These plastic film dosimeters undergo color change from blue (the alkaline form of bromo-chloro-phenol blue, BCPB) to yellow (the acidic form of bromo-chloro-phenol blue, BCPB), indicating acid formation. The concentration of formed acids in the films containing different concentrations of chloral hydrate was calculated at different doses. These films can be used as dosimeters for food dosimetry applications where the maximum of the useful dose ranges are between 1-10 kGy depending on chloral hydrate concentration in the film. The films have the advantage of negligible humidity effects on response in the range of relative humidity from 0 to 100% as good post irradiation stability when stored in the dark at room temperature. The energy band gap of the prepared films was calculated and the effect of gamma radiation on its value was determined. Direct and indirect transitions were illustrated from the absorption spectra.

Keywords: Thin films, Energy band gap, Polyvinyl alcohol (PVA), Gamma radiation.

Introduction

Several thin polymeric film dosimeters have been successfully developed and used as dosimeters for routine use in radiation processing by electron beam and gamma rays [1-3].

Radiation–sensitive materials consisting of chlorine-containing polymers and an acid sensitive dye are widely known [4]. The chlorine containing polymer is de-hydro-chlorinated when the material is irradiated, thereby decreasing the pH and causing the acid-sensitive dye to change color. Polyvinyl butyral films mixed with xylenol blue (XB) indicator and hexachloro ethane (HCE) were prepared for possible application in food irradiation [5]. A similar color change can be produced if halogen-containing compounds are present in the dye-containing matrix [6,7]. A new dyed film contains a mixture of two dyes, the color of the film changes in two steps from green to yellow and finally to red color, these films can be used as a dosimeter in two dose ranges [8].

Radiation sensitive indicator based on tetra-bromo phenol dyed polyvinyl alcohol was developed to be use in food irradiation where the dose between 1-8 kGy [9]. Similar system of polyvinyl butyral film containing acid- sensitive dye, bromo cresol green in presence of chloral hydrate has been investigated as a radiation sensitive indicator [10].

Absorption spectra for TeO_2 films were recorded and the values of the optical band gap of γ irradiated samples were calculated, it was found that the optical band gap values were decreased as the radiation dose was increased [11]. The effect of gamma irradiation on the optical and electrical properties of manganese phthalcyanine polymer (MnPC) thick films were investigated for dosimetry applications [12], the effect of gamma irradiation on the optical properties of polystyrene doped by methylene blue have been investigated, the optical band E_g was determined and was found to decrease after irradiation [13].

The main target of the present study is to introduce films that combine a pH-indicating dye, Bromo-chloro-phenol blue dyed polyvinyl alcohol and a Cl-containing substance, chloral hydrate to evaluate and assess the dosimetric characteristics of the prepared films. The radiation formed acid concentration was calculated, the effect of irradiation dose on the optical energy gap was studied, and also the humidity during irradiation as well as post irradiation stability on the response was reported.

The structural formula of bromo-chloro-phenol blue is represented in the following scheme.

Experimental

Preparation of Stock Solution of Bromo-Chloro-Phenol Blue

The stock solution of the sodium salt of the indicator was prepared by dissolving 0.04 g of bromo-chloro-phenol blue, BCPB (From ACROS organics. M.W. =581.06) in 0.69 ml of an aqueous solution of NaOH ([NaOH] = 0.1 mol L^{-1}) and then the volume was completed by ethanol in 50 ml volumetric flask.

Preparation of bromo-chloro-phenol blue films

Films were prepared by dissolving 7.5 g of PVA Polyvinyl alcohol powder (average M.W. 25.000 fully hydrolyzed 99-100% product of J.T. Baker Chemical Co. USA) in 150 ml double distilled water at about 60°C. The solution was kept well stirred at the same temperature for about 48 h; then left to cool. Polymer solution was divided into 5 parts. To each 30 ml of the well mixed solution, 2 ml of stock solution of bromo-chloro-phenol blue, BCPB and 0, 0.4, 0.8, 1.2 and 1.6 g of chloral hydrate (product of Merck, Germany) was added, stirred and casted on a 15 x 15 cm horizontal glass plate and dried at room temperature for about 48h. Five films were obtained containing same concentration of bromo-chloro-phenol blue, BCPB [0.1066 phr] (phr = part per hundred parts by weight of resin) and different concentrations of chloral hydrate [0, 26.66, 53.33, 79.98 and 106.64 phr]. After drying, the films were stripped from the glass plate, then cut into 1 x 1cm pieces and stored for different investigations.

Apparatus

Irradiations were carried out with gamma radiation in the ^{60}Co gamma chamber 4000A (product of India). The absorbed dose rate in the irradiation facility was measured to be 2.688 kGy/h using reference alanine dosimeters. Five films at each dose are grouped together, sandwiched between two PMMA plates of 3 mm thickness (to maintain electronic equilibrium conditions) and irradiated at the central spatial position of the sample chamber using a specially designed holder made from polystyrene. The temperature during irradiations was maintained at 37±2°C. The UV-Vis spectral analysis of unirradiated and irradiated films dosimeter was performed using UV-Vis Uvikon 860 spectrophotometer (product of KONTRON Co. Ltd, Switzerland). The film thickness was measured using a Digitrix-Mark II thickness gauge (precision ±l μm, 1σ). Analysis of absorption coefficient was also carried out to determine the optical band gap and nature of transition.

Results and Discussion

Absorption Spectra

The absorption spectra of bromo-chloro-phenol blue, BCPB/PVA films containing different concentrations of chloral hydrate were recorded before and after irradiation to different doses. The results with films containing 53.33 phr of chloral hydrate are shown in Fig. 1. The absorption spectra of unirradiated films show a main absorption band in the visible region characteristic of a blue color located at 604 nm which corresponds to blue color (Fig. 1). The amplitude of this absorption band decreases gradually with increase of absorbed dose of γ-ray photons.
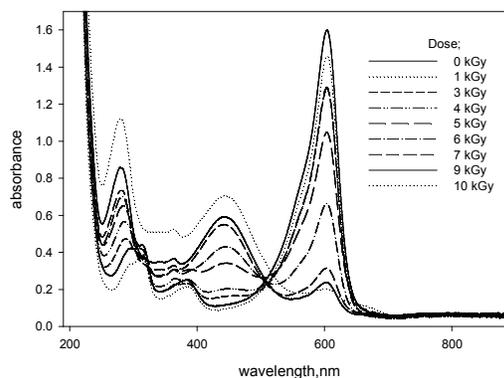

Fig. 1:   The absorption spectra of BCPB /PVA films unirradiated and irradiated to different absorbed doses, [chloral hydrate] = 53.33 phr [BCPB]=0.1066 phr.

A new absorption band locates at 440 nm, characteristic of a yellow color, is formed and increases gradually with increase of absorbed dose. Upon irradiation, these films change their color from blue (the alkaline form of the dye with $λ_{max}$ = 604 nm) to green and finally to yellow (the acid form of the dye with $λ_{max}$ = 440 nm) indicating acid formation. The green color is observed due to the visual sensation of the mixed ratios of unchanged part of indicator (blue) and changed part (yellow).

The absorption spectra of BCPB /PVA films without chloral hydrate ([BCPB] = 0.1066phr) were recorded before and after irradiation to different doses and are shown in Fig. 2. Absorbance at 604nm decreases slowly with the increase of absorbed dose. Also, this Fig indicates the absence of any absorption

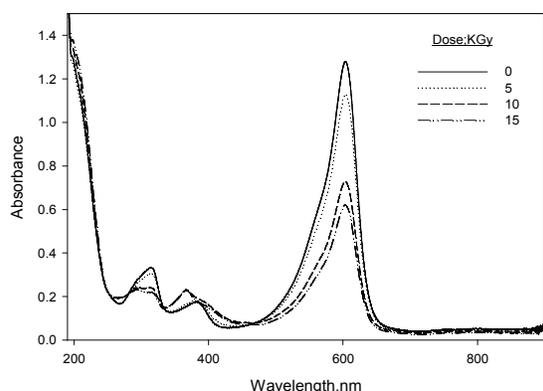band at 440nm, *i.e.* there is no appreciable radiation–formed acid to change the color.

Fig. 2: The absorption spectra of BCPB /PVA films (without chloral hydrate) unirradiated and irradiated to different doses, [BCPB] = 0.1066 phr.

Response Curves

The absolute difference ΔA of the absorbance of unirradiated and irradiated films were taken as the measure of the dose response. Fig. 3 and 4 show the response curves of BCPB/PVA films containing different concentrations of chloral hydrate in terms of change in optical density per unit thickness, (ΔA.mm^{-1}) at 604 and 440 nm wavelengths respectively, versus the absorbed dose. It can be noticed that all curves have the same S–Shape, characteristic of the irradiation response of a pH indicator in an acid–base titration with different sensitivities.
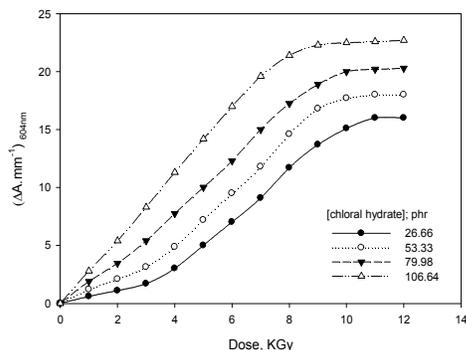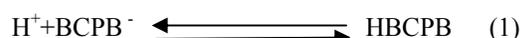

Fig. 3: Change of ΔA.mm^{-1} as a function of absorbed dose of BCPB /PVA films with different concentrations of chloral hydrate. λ_{max} = 604 nm, [BCPB] = 0.1066 phr.

Calculation of Acid Concentration

The results indicate that in the dose range up to 10 kGy, radiation induced bleaching of BCPB/PVA indicator (i.e. the decrease in the absorbance of BCPB/PVA films without chloral hydrate at 604 nm) is about 40% Fig. 2. Therefore, it can be concluded that radiation induced change in color of BCPB/PVA films containing chloral hydrate is due to decrease of pH. It is known that acid–base indicators exist in equilibrium between two tautomeric forms and the ratio of the two forms depend on the concentration of hydrogen ions in the medium. The equilibrium between the two forms of BCPB indicator is represented as follow in equation 1:

$$H^+ + BCPB^- \rightleftharpoons HBCPB \quad (1)$$

The concentration of acid formed due to irradiation of BCPB /PVA films to a dose D is given by the sum of hydrogen reacting with BCPB$^-$, [H BCPB]$_D$, and the free hydrogen percent in the medium, [H$^+$]$_D$ [9] , to maintain the equilibrium given by equation 1,

$$[\text{Total acid formed}]_D = [HBCPB]_D + [H^+]_D \quad (2)$$

Where, [HBCPB]$_D$ is the concentration of changed BCPB due to the irradiation to a dose D, and [H$^+$]$_D$ is the concentration of free acid present in equilibrium after irradiation to a dose D.

Using the reported density of PVA (1.25 g.cm^{-3}), the concentration of BCPB before irradiation in the films containing 106.6 phr of sodium salt of BCPB is calculated as 2.294 x 10^{-3} mol/L. Assuming that Beer's law is valid in the used range of concentration of BCPB indicator, [BCPB]$_D$ may be calculated using increase in response at 440 nm due to irradiation to a dose D as follows

$$[HBCPB]_D = 2.2940 \times 10^{-3} \frac{[(\Delta A.mm]^{-1})_D}{[(\Delta A.mm]^{-1})_S} \quad (3)$$

where, (ΔA.mm^{-1})$_D$ is the increase in response at 440 nm due to irradiation to a dose D, and (ΔA.mm^{-1})$_S$ is the response at 440nm at saturation, i.e. when all BCPB$^-$ is changed to H BCPB. From Fig. 4, it can be seen that the average of (ΔA.mm^{-1})$_S$ is equal to 8.4 ΔA.mm^{-1}. Substituting the value of (ΔA.mm^{-1})$_S$ in equation (3), gives

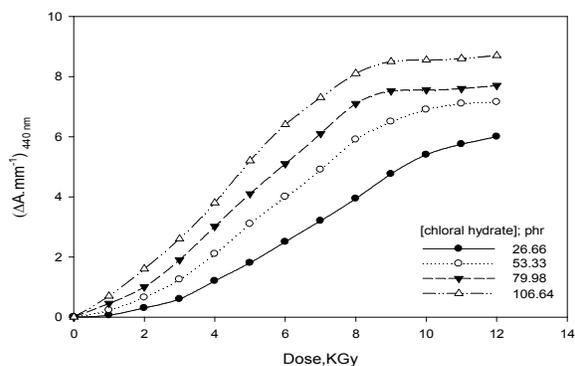$$[HBCPB]_D = 0.273 \times 10^{-3} (\Delta A.mm^{-1})_D \quad (4)$$

Fig 4:   Change of $\Delta A.mm^{-1}$ as a function of absorbed dose of BCPB/PVA films with different concentrations of chloral hydrate. λ_{max} = 440 nm. [BCPB]=0.1066 phr.

Fig (5) represents the concentration of radiation–formed acid HCl in BCPB/PVA films containing different concentrations of chloral hydrate as a function of absorbed dose.
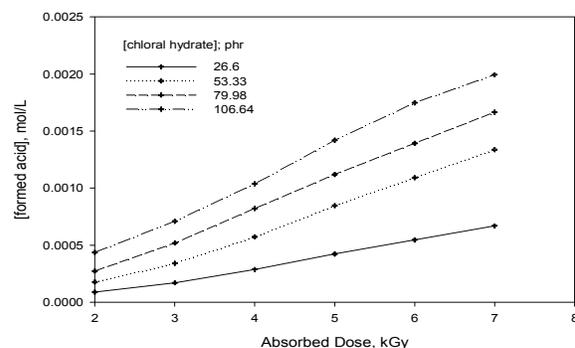

Fig. 5:   Concentration of radiation –formed HCl in BCPB/PVA films containing different concentrations of chloral hydrate as a function of absorbed dose, [BCPB]=0.1066phr.

Radiation Chemical Yield

The radiation chemical yield of [H⁺] in BCPB /PVA films containing chloral hydrate is calculated as follows:

$$G\ (H^+) = \frac{[[H]^+]}{D.\rho}\ mol.J^{-1} \qquad (5)$$

Where, [H⁺] is the concentration of radiation–formed H⁺ in the film (mol/L)
D is the absorbed dose in Gy (Gy = J.kg⁻¹)
ρ is the density of the film (kg.L⁻¹)

Using the density of PVA (1.25 g.cm⁻³), G (H⁺) is calculated at different concentrations of chloral hydrate and the results are shown in Fig. 6. It can be seen that the radiation chemical yield increases with the increase of chloral hydrate concentration.
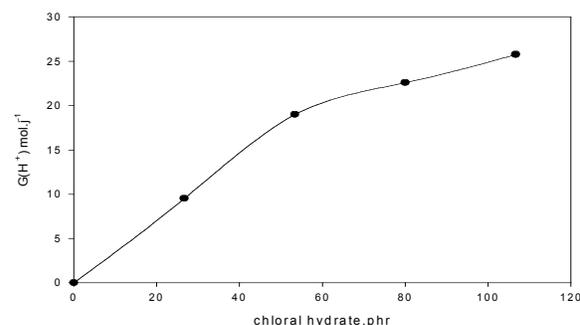

Fig. 6:   The radiation chemical yield, G (H⁺), versus the initial concentration of chloral hydrate in BCPB /PVA films

Optical Energy Gap

For the optical energy gap in which, the minimum of the conduction band and the maximum of the valance band. The relation between the optical band gap, absorption coefficient and energy $h\nu$ of the incident photon is given by [14, 15]

$$\alpha h\nu = B(h\nu - E_g)^r \qquad (6)$$

where, E_g is the optical energy gap; α is the absorption coefficient; B is a constant; and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. r = 1/2 for allowed direct transition, r = 3/2 for forbidden direct transition and r = 3 for forbidden indirect transition, and r = 2 refers to indirect allowed transitions. The absorption coefficient for direct transition takes the values from 10^4 to 10^5 cm⁻¹, while the absorption coefficient for indirect transition takes the values from 10 to 10^3 cm⁻¹.

According to Urbach rule [16] the absorption coefficient α can be calculated as follows:

$$\alpha = \frac{1}{L}\ \ln\frac{I_o}{I_t} \qquad (7)$$

where, I_o and I_t are the intensities of incident and transmitted light respectively, L is the thickness of the sample (cm).

The present results were found to obey equation (6) with $r = 2$ for all films, which indicate indirect, allowed transitions. Values of the absorption coefficient were taken between 10 to 10^3 cm^{-1}. The $(\alpha h v)^{1/2}$, yielded a linear dependence which describes the allowed indirect transition [13-15].

Fig. 7 shows $(\alpha h v)^{1/2}$ as a function of hv for BCPB/PVA films un-irradiated and irradiated to different doses. The optical band gap can be evaluated from the extrapolations of these plots to the point at which they cross the abscissa give the indirect allowed optical band gap. The plots show E_g decreases with increasing absorbed dose. Table-1 represents the value of E_g for both direct and indirect transition for PVA dyed BCPB containing different chloral hydrate concentrations. From the table, it can be seen that the E_g decreases with the increase of absorbed dose.
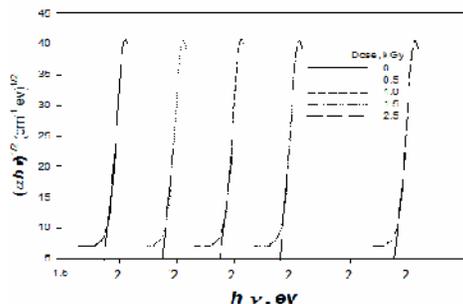

Fig. 7:   Variation of $(\alpha h v)^{1/2}$ as a function of hv for dyed PVA/BCPB at different absorbed dose[BCPB]=0.1066phr [chloral hydrate]=79.98phr.

The decrease in the band gap energy with increasing dose may be attributed to an increase in structural disorder of the irradiated dyed films. Irradiation of the dyed Polyvinyl alcohol induces bromo-chloro-phenol blue, $C_{19}H_{10}Br_2Cl_2O_5S$ causing detachment of ions and unsaturated groups in bromo-chloro-phenol blue and so produces the structural defects, which reduce the band gap with increasing dose [12, 17].

Humidity During Irradiation

The effect of relative humidity (RH) during irradiation on the response of BCPB/PVA films was investigated by irradiating the films of 0.1066 phr BCPB and 53.33 phr chloral hydrate to a dose of 4kGy at different relative humidities. The different relative humidities were maintained by using different saturated salt solutions [18].

The films were stored before irradiation for three days period under the same relative humidity conditions as when irradiated, so equilibrium moisture content in dosimeter is established during irradiation. Fig. 8 shows the variation in response $(\Delta A. \text{mm}^{-1})$ at 440nm as a function of percentage relative humidity during irradiation relative to the response value 33% relative humidity. The response is flat within 5% for relative humidities in the range of 0-100 %.
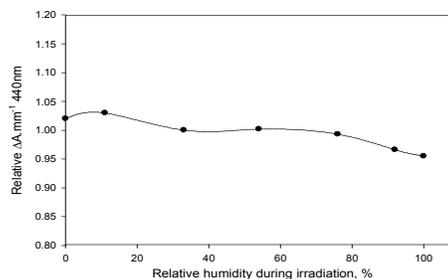

Fig. 8:   Variation of response of BCPB/PVA films (at 440 nm) as a function of relative humidity during irradiation where response in ΔA mm^{-1} at 4kGy.

Post Irradiation Stability

BCPB/PVA films ([chloral hydrate] = 53.33phr) irradiated to 4 kGy were stored immediately after irradiation, one in dark and the other in indirect sunlight, both at room temperature. The films were measured spectrophotometrically at 440 nm wavelength at different intervals of time during the post irradiation storage period of 30 days. Fig. 9 shows the relative change in ΔA_{440} relative to the value at zero time, as a function of storage time. It can be seen that ΔA_{440} of the film stored in the light decreases sharply during the first five days after irradiation then tends to stabilize. On the other hand, the film stored in dark shows excellent stability overall the 30 days storage period.
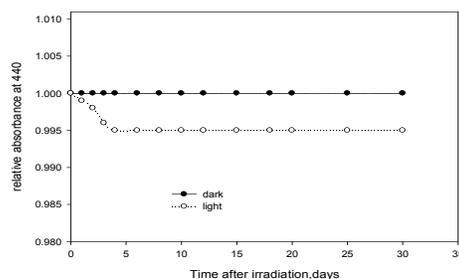

Fig. 9:   Post-irradiation stability of BCPB/PVA films stored, in dark and light at room temperature. Wavelength of analysis is 440 nm.

Table-1: The value of E_g for direct, and indirect transitions.

Dose, kGy	Chloral hydrate concentration, phr							
	26.66 phr		53.33phr		79.98phr		106.64phr	
	E_g (ev)		E_g (ev)		E_g (ev)		E_g (ev)	
	direct	indirect	direct	indirect	direct	indirect	Direct	Indirect
0	1.982	1.945	1.982	1.945	1.982	1.945	1.981	1.945
0.5	1.976	1.902	1.976	1.936	1.976	1.871	1.978	1.761
1.0	1.959	1.885	1.971	1.901	1.972	1.841	1.981	1.686
1.5	1.955	1.846	1.968	1.887	1.972	1.811	1.980	1.661
2.0	1.953	1.822	1.967	1.859	1.971	1.748	1.980	1.621
2.5	1.951	1.798	1.964	1.856	1.969	1.720	1.980	1.571
3.0	1.941	1.775	1.961	1.829	1.968	1.707	1.979	1.525
4.0	1.931	1.748	1.959	1.805	1.964	1.689	1.976	1.437

Conclusion

BCPB /PVA films have clear visual change in color (blue – green – yellow) in the dose range 1-10 kGy reflecting their suitability for use as radiation indicators in some food irradiation applications. The amount of acid formed due to irradiation depends on the absorbed dose and the concentration of chloral hydrate. The response of these films has negligible humidity effects in the range of relative humidity from 0-100 % as well as good post – irradiation stability when stored in dark and light at room temperature. The optical energy gap was found to be decrease with the increase of absorbed dose, may be attributed to an increase in structural disorder of the material.

Acknowledgment

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