Gamma Irradiation Effect on Mixed Dye Film; its Possible Use as a Radiation Dosimeter

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Summary: The polymer films under investigation include poly (vinyl alcohol) in a combination with mixture of two dyes, namely, 2,6-dichlorophenol indophenol sodium salt (DCP), and tetrabromophenol blue (TBPB) as pH indicator in presence of various chloral hydrate concentrations. These films undergo color change from the blue to the yellow color passing through green as an intermediate state. The decoloration of DCP started first in the beginning of reaction, followed by the transformation of TBPB to its acidic form as a result of the delivery of HCl from the radiolysis of chloral hydrate. The dosimetric parameters, eg; dose response, effect of relative humidity on response as well as before and after irradiation stability of these films were inspected. The energy band gap value of the prepared films decreased from 1.83 to 1.75 against absorbed dose. These films can be used as dosimeters for food irradiation applications where the useful dose range is recorded from 1 to 15 kGy.

Keywords: Dyed Poly (vinyl alcohol); Radiation dosimetry; Mixed polymeric films; Energy gap; γ-radiation.

Introduction

Recent developments in routine dosimetry have lightened the need for polymeric films for using as monitors and indicators [1-6]. All these polymeric films are bleached when exposed to gamma radiation. Previous studies have developed a labeled dosimetry system on the basis of mixing poly (vinyl alcohol) with two dyes having different sensitivities to radiation [7]. Surveys such as that conducted have shown that polymeric dyed films which contain a combination of two mixed dyes, the color change of the film occurs in two steps from green to yellow as a starting step followed by change to red color, these films are suitable for using in various dosimetric applications with two different dose ranges [8]. A radiation-sensitive indicator composed of poly (vinyl alcohol) film containing pH-indicator dye and chloride-incorporating material has been investigated [9]. A detectable decrease in the pH value leads to change the color, the extent of decreasing the pH value depends on the chloral hydrate concentration. Recently, investigators have examined the influence of gamma irradiation on the color change of tetrabromophenol blue, the color change is influenced by the addition of chloral hydrate. [10]. Dyed polymer films, with two different polymer PVA or PVB and quinaldine red (QR) were examined, these films are useful as routine high-dose dosimeters. These polymeric film dosimeters undergo decoloration when subject to gamma rays [11]. Similar system of poly (vinyl butyral) film containing bromo cresol green in the presence of chloral hydrate has been examined as a radiation sensitive indicator [12]. 2,6-dichlorophenol-inodophenol dyed with two different polymer was investigated for possible use as high-dose dosimeter. These dosimetric films undergo decoloration when subjected to radiation [13]. Several studies have shown that measurements of reflectance with diffuse а UV-visible spectrophotometer is a standard technique in the estimation of the absorption properties of material and calculation of the band gap energy from the diffuse measurement of the reflectance [14,15]. Tellurium dioxide thin film (TeO₂) were examined for γ -radiation dosimetry purposes. Absorption spectra for tellurium dioxide were documented and the energy gap values were determined. It was noticed that the values of energy gap were inversely proportional to the radiation dose [16]. Numerous studies have attempted to explain the effect of gamma radiation on the optical and electrical properties of both manganese phthalcyanine polymer (MnPC) thick films and polystyrene doped by methylene blue were examined for dosimetry applications [17, 18]. Many studies detect the value of $E_{\rm g}$ from measuring the diffuse reflectance of radiation sensitive indicator and its value was reported [19].

The main goal of the present work paper is the investigation of mixed dye films of two dyes TBPB and DCP to be a dosimeter for food irradiation. Also, it describes the influence of humidity during irradiation as well as the before and after irradiation stability on the film response. Optical energy gap value was determined for the polymeric films which exposed to gamma rays.

Experimental

Preparation of stock solution of 2,6 dichlorophenolindophenol sodium salt

The stock solution of the dye was prepared by dissolving 0.04 gm of 2,6-dichlorophenol indophenol sodium salt (DCP-Na) (mo.wt.=290.06 product of RIEDEL-DEHAEN, Germany) in 50 ml ethanol.

Preparation of stock solution of tetrabromophenol blue

The stock solution of the sodium salt of the indicator was prepared by dissolving 0.08 gm of tetrabromophenol blue indicator (TBPB). (mo.wt = 985.55 product of MP Biomedicals, Inc) in 1.2 ml of an aqueous solution of 0.1M NaOH and then the volume was completed by ethanol in 50 ml volumetric flask. The following scheme represents the acidic and basic form of TBPB.



Preparation of (TBPB- DCP)/PVA mixed dye films

Films were prepared by dissolving 6 gm of poly (vinyl alcohol) PVA powder (average mo.wt 25.000 fully hydrolyzed 99–100% product of J.T. Baker Chemical Co. USA) in 120 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 four parts each of 30 mL, the first three parts contain 4ml of DCP and 4ml of TBPB indicator with different concentrations of chloral hydrate as 0.2, 0.4,0.6 gm respectively, the fourth contains 4ml of DCP and 2ml of TBPB with 0.4 gm of chloral hydrate. The four solutions were kept mixed and threw on a 15×15 cm flat glass plate and left to dry at room temperature for around 48 h. four films were obtained, The first three films contain different concentrations of chloral hydrate as 13.33, 26.67, 40phr (part per hundred parts of resin) and the dye concentration was, (0.43phr TBPB and 0.21phr DCP), the fourth film contains 0.21phr of both DCP and TBPB with 26.67phr of chloral hydrate concentration. After drying, the films were stripped from the glass plate, then cut into 1 x1cm pieces and stored for different investigations.

Apparatus

Irradiation was carried out with gamma radiation in the 60Co gamma chamber 4000A (product of India). The absorbed dose rate in the irradiation facility was measured to be 2.688kGy/h using reference alanine dosimeter. Three 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. Uvikon 860 spectrophotometer (product of KONTRON Co. Ltd, Switzerland) was used to measure the absorption spectra of the unirradiated and irradiated films. Evolution 600 UV-VIS was used to measure the reflectance of the prepared films. The film thickness was measured using a Digitrix-Mark II thickness gauge (precision $\pm l \mu m$, 1σ).

Results and Discussion

Absorption spectra

The absorption spectra of the PVA film including 0.43phr TBPB with 0.21phr DCP in the presence of 13.33phr chloral hydrate were measured before and after irradiation. The spectra is depicted in Fig. (1). The absorption spectra of the unirradiated film shows a main characteristic absorption band specific to blue color peaking at 623 nm .The intensity of this absorption band is inversely proportional to the absorbed dose of y-ray photons. A absorption band peaking at 447 nm, new characteristic of yellow color, is formed at 10.5 kGy and its intensity is directly proportional to the applied dose until complete alteration to acidic form at 15 kGy, the explanation of this is that the beginning of irradiation gradual decrease in absorbance at λ_{max} 623 nm takes place due to the radiolysis products cause bleaching of DCP molecules, followed by gradual

transformation of TBPB to its acidic form at 15 kGy. From the previous studies complete transformation to acidic form for TBPB occurs at 8 kGy [10], and complete bleaching of DCP takes place at high dose [13]. In the present work, the dose range of TBPB was extended to be 15 kGy and the dose range of DCP was accelerated to be 9kGy. Most of radiolysis products were consumed in the degradation reaction of DCP causing the retardation of alternation of TBPB to its acidic form. This behavior reflects the high sensitivity of DCP towards radiation better than TBPB.



Fig. 1: Absorption spectra of (TBPB/DCP)/PVA films before and after irradiation to different absorbed doses. [TBPB] = 0.42phr, [DCP] = 0.21phr [chloral hydrate] = 13.33 phr.

Response Curves

Fig. 2 maintains the response curves of three dye films comprise 0.43phr TBPB and 0.21phr DCP in presence of different concentrations of chloral hydrate (13.33, 26.67 and 40phr). The response curves were established in terms of change in optical density measured at λ_{max} 447 nm versus the absorbed dose. It was cleared that the presence of chloral hydrate plays an important role in the transformation of TBPB to its acidic form. This is because HCl was released as a result of radiolysis product of chloral hydrate [20]. As we can see all curves have the same shape but they differ in sensitivity i.e. the sensitivity increases with the increase of chloral hydrate.

Fig. 3 affirms the response curves of three dye films comprise 0.43phr TBPB and 0.21phr DCP in presence of different concentrations of chloral hydrate (13.33, 26.67 and 40phr). The response

curves were established in terms of change in optical density measured at λ_{max} 623 nm versus the absorbed dose. From the Fig we noticed that the rate of decoloration of the blue color is directly proportional to chloral hydrate as it acts as sensitizer to decoloration process [21].



Fig. 2: Variation of $\Delta A.mm^{-1}$ with the absorbed dose of (TBPB/DCP)/PVA films containing different chloral hydrate concentration. λ_{max} 447 nm, [TBPB] = 0.43phr, [DCP] = 0.21phr.



Fig. 3: Variation of Δ A.mm⁻¹ with the absorbed dose of (TBPB/DCP)/PVA films containing different chloral hydrate concentrations. $\lambda_{max}623$ nm, [TBPB] = 0.43phr, [DCP] = 0.21phr.

Fig. 4 represents that the absorption spectra of mixed dye film contains an equal concentration of DCP dye and TBPB indicator (0.21phr of each) and 26.67phr of chloral hydrate. It was noticed that, no peak appears at 447 nm. i.e the transformation to acidic form not happened, this behavior is an evidence that DCP is more sensitive toward gamma radiation than TBPB. From the present study we can conclude that the preferred concentration of both dyes is 0.43phr TBPB and 0.21phr DCP, in which the decoloration reaction of DCP dye and also the appearance of the acid form of TBPB occurs.



Fig. 4: Absorption spectra of (TBPB/DCP)/PVA films before and after irradiation to different absorbed doses. [TBPB] = 0.21phr, [DCP] = 0.21 [chloral hydrate] = 26.67 phr.

Optical Energy Gap Determination

The energy band gap refers to energy difference between the bottom of the conduction band and the top of valance band. The combination between the optical band gap, absorption coefficient and energy hu of the incident photon is controlled by the following equation [22, 23]: (How to calculate α) (inserted in separate word document)

$$\alpha h \upsilon = B(h \upsilon - E_g)^r \tag{1}$$

where, E_g is the optical energy gap; α is the absorption coefficient; B is a constant; and r is an index which determines the type of transition 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 [18]. According to Urbach rule [24] the absorption coefficient α can be calculated as follows:

$$\alpha = \frac{1}{d} ln \frac{(100-R)^2}{T}$$
(2)

T is the transmittance, R is the reflectance, and d is the thickness of the sample in (cm). The representation of transmittance spectra is addressed in Fig. 5 for film contains [TBPB] = 0.43phr, [DCP] = 0.21phr and [chloral hydrate] = 26.67phr. On the other hand the reflectance spectrum of the same combined ratios was recorded in Fig. 6. The obtained results were found to obey equation (1) with value r =2 for all films, which indicate indirect, allowed transitions. Values of the absorption coefficient were taken between 10 to 10^3 cm⁻¹. $(\alpha h\nu)^{1/2}$ yielded a linear dependence which describes the allowed indirect transition [17,24,25]. Fig. 7 represents $(\alpha h v)^{1/2}$ against hv for (TBPB/DCP)/PVA films unirradiated and irradiated to different doses. The optical band gap can be determined 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 is inversely proportional to absorbed dose. Fig. 8 indicates the value of E_{g} for indirect transition for (TBPB/DCP)/PVA containing (TBPB) = 0.43 phr, [DCP] = 0.21phr and [chloral hydrate] = 26.67phr. From the Fig. it can be seen that the E_g is inversely proportional to absorbed dose. Explanation of this decrease in the band gap energy with increasing dose may be attributed to an increase in structural disorder causing detachment of ions and unsaturated groups (-C = C-) of the irradiated dyed films. These contributed to the structural defects, which decrease the band gap with increasing dose [17, 19, 25]



Fig. 5: Transmittance spectra of (TBPB/DCP)/PVA films before and after irradiation to different absorbed doses containing, [TBPB] = 0.43phr, [DCP] = 0.21phr and [chloral hydrate] = 26.67phr.



Fig. 6: The reflectance spectra of (TBPB/DCP)/PVA films before and after irradiation to different absorbed doses containing, [TBPB] = 0.43phr, [DCP] = 0.21phr and [chloral hydrate] = 26.67phr.



Fig. 7: Change of $(\alpha h\nu)^{1/2}$ with hv for (TBPB/DCP)/PVA irradiated to different absorbed dose [TBPB] = 0.43phr ,[DCP] = 0.21phr and [chloral hydrate] = 26.67phr.



Fig. 8: Change in optical band as a function of absorbed dose [TBPB] = 0.43phr, [DCP] = 0.21phr and [chloral hydrate] = 26.67phr.

Effect of Relative Humidity During Irradiation

The effect of relative humidity (RH) during irradiation on the response of TBPB/DCP/PVA films, [TBPB] = 0.43 phr, [DCP] = 0.21 phr and [chloral]hydrate] = 26.67phr were examined by irradiating the films to a dose of 4 kGy at different relative humidities (0, 33, 76, 92and100% RH). The different relative humidity percentage was maintained by using different saturated salt solution [26]. Films were stored before irradiation for two days period under the same relative humidity conditions as when irradiated, so that the equilibrium moisture content in dosimeter is established during irradiation. Fig. 9 represents the change in $\Delta A.mm^{-1}$ at 623nm as a function of percentage relative humidity during irradiation, relative to the response value at 33% relative humidity. The response of films is almost flat in the range of relative humidity from 0-76%. It can be concluded that TBPB/DCP/PVA films can be used at negligible humidity effects on response of humidity from 0 to 76% to avoid the effects of high humidity levels. It may also be possible to reduce the humidity influences by using sealed films under controlled intermediate humidity conditions.



Fig. 9: Variation of response of TBPB/DCP/PVA films at 623 nm with relative humidity during irradiation.

Uncertainty in the Estimated Dose Value

The uncertainty value of the film13.33phr chloral hydrate with 0.43phr TBPB and 0.21phr DCP analyzed at 623nm irradiated at dose range (1-15kGy) was found to be 4.14. The estimated value was calculated by using the following formula [27].

$$u = \sqrt{\frac{\sum_{i} (n_{i} - 1)(\sigma_{i})^{2}}{\sum_{i} (n_{i} - 1)}}$$
(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.

Stability

Pre-irradiation stability

Fig. 10 represents the change in relative absorbance of the tested film by measuring the absorbance at 623nm at various time intervals during the storage time of 60 days. From which it is cleared that, the film exhibits a good stability before irradiation.





Post Irradiation Stability

(TBPB/DCP)/PVA films [chloral hydrate] = 26.67phr irradiated to 8 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 λ_{max} 447 nm at different times during the post irradiation storage period of 60 days. Fig. 11 shows the relative change in absorbance at 447 nm relative to the value at zero time, as a function of storage time. It can be seen that absorbance of the film stored in the light increases during the first four days after irradiation then tends to be stable. On the other hand, the storage period of 60days.



Fig. 11: Stability after irradiation of (TBPB/DCP)/PVA films in dark and light at room temperature, λ_{max} 447 nm [TBPB] = 0.43phr, [DCP] = 0.21phr, [chloral hydrate] = 26.67phr.

Conclusion

irradiating TBPB/DCP/PVA films Bv containing chloral hydrate, the color changes from blue to green (intermediate color) and finally to yellow. The obvious change in color is in reference to the presence of chloral hydrate which is main reason for the appearance of acidic form of TBPB. Gathering the two dyes effects on the dose range of each other if it was used separate. The dose range of TBPB extends to be 15 kGy instead of 8kGy, on the other hand the dose of DCP was reduced to be 9 kGy. These films are useful dosimeter in the dose range from 1 to 15 kGy, depending on chloral hydrate concentration. The response of these films have negligible effect in the humidity range from 0 to 76%, in addition exhibit excellent stability before and after irradiation when stored in dark and light at room temperature. Further advantage is that it is easily prepared and inexpensive. Optical energy gap was determined and its value is inversely proportional to absorbed dose. Finally, the documented date suggests the suitability of TBPB/DCP/PVA films as a dosimeter for food irradiation applications.

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