Radiation Dosimetry by 4PNPAN/PVB Thin Films in High Dose Ranges

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Summary: Poly (vinyl butyral) combined with 4-(p-nitrophenyl-azo)-1-naphthol has been examined to be a dosimeter suitable for applications in the high dose range. Different concentrations were prepared to obtain the suitability of the dosimeter in the dose range 5-100 kGy in which the yellow color of the dye was bleached. Magnesium chloride was then added and its effect on the response was studied. The response is independent on the variation of relative humidity during irradiation. The radiation chemical yield for the prepared films was calculated. Films reveal excellent stability before and after irradiation. Optical energy gap was determined and the effect of gamma radiation on its value was studied.

Keyword: 4-p-nitrophenyl-azo-1-naphthol, Poly vinyl butyral, Film dosimeter.

Introduction

There is evidence that azo dye films play a crucial role in radiation processing as high dose dosimeters [1-5]. Several studies have documented the suitability of methyl red dyed polyvinyl alcohol in the dose range 10-55 kGy [6], as the film was exposed to gamma radiation it changes from the yellow color to colorless and its complete decoloration occurred at irradiation dose of 30 kGy. Cellophane films containing diazo dye for application to high – dose dosimetry have been reported [7], blue cellophane was examined as a monitor of high dose ranges from 10 to 300 kGy and also in electron beam dose profiles. Several examples of diazo dyes are direct blue, direct violet and direct orange, in which the bleaching of color was determined spectrophotometrically. Poly vinyl butyral incorporated with methyl red was investigated as a dosimeter in the dose range from 5 to 150 kGy. The sensitivity is directly proportional to methyl red concentration [8].

This paper provides an overview of radiation induced degradation of 4-p-nitrophenyl-azo-1-naphthol/Poly vinyl butyral (4PNPAN/PVB) films for dosimetry in high dose range. Different concentrations of MgCl2 were added and its influence on the degradation process was reported. Gamma radiation effect on the value of energy gap was determined. Also, the influence of relative humidity as well as pre and post irradiation stability was investigated.

The structural formula of 4-p-nitrophenyl-azo-1-naphthol is represented in fig. (1):

![Structural formula of 4-p-nitrophenyl-azo-1-naphthol.](image)

Experimental

Preparation of 4PNPAN/PVB dye film

Casting polymeric solution containing poly (vinyl butyral) (piloform BM18), average molecular weight 36,000 product of Wacker Co.,USA in butanol combined with 4PNPAN (product of BHD laboratory chemicals division, England) in dimethylformamide. The solution was kept well stirred at 60 °C for 3h to obtain homogeneous solution then left to cool at room temperature. To each 30ml of PVB solution 0.105, 0.210 and 0.315phr (part per hundred parts of resin) of 4PNPAN stock solution were added. MgCl2 was added as 0.66, 1.32 and 2.64phr in combination with 0.21phr of 4PNPAN. The solutions were poured onto a15x15 cm horizontal glass plate and left to dry at room temperature, then cut into 1x1 cm pieces and stored for different investigations. The obtained thickness was 0.05 ± 0.01 mm (1 σ).

Apparatus

The absorption spectra of unirradiated and irradiated films were measured throughout the wavelength range 200-800 nm using a Kontron UVIKON860 spectrophotometer. The film thickness was measured using Digitrix-MarkII thickness gauge;
precision ±1µm. Gamma irradiation was carried out in the 60Co gamma chamber Model 4000 A; product of India (we only interest the measurement of the dose rate by the organized system here accordingly samples irradiated to the required dose). The absorbed dose rate in irradiation facility was measured to be 3.75 kGy/h using reference alanine dosimeter. Electronic equilibrium conditions were maintained during irradiation, through stuffing the films in the middle of 5 mm thickness of poly methylmethacrylate (PMMA) from both sides.

Results and Discussion

Absorption spectra

The optical absorption spectra of 4PNPAN/PVB containing 0.21phr of 4PNPAN dye were recorded before and after irradiation at different doses, these spectra are shown in Fig. 2. The absorption spectrum of an unirradiated film shows a main absorption band in visible region peaking at 472 nm, which is characteristic of yellow color. The amplitude of the peak is inversely proportional to absorbed dose up to 100 kGy. A possible explanation for this might be that the structure of azo dyes assigned with the presence of one –N=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 dimethylformamide by 60Co γ-irradiated is the following [9]:

\[
\begin{align*}
HCON(CH_3)_2 &\rightarrow HCO+ N(CH_3)_2 \quad (1) \\
&\rightarrow H + CON(CH_3)_2 \quad (2) \\
&\rightarrow H + HCON(CH_3)CH_2 \quad (3) \\
&\rightarrow CH_3 + HCONCH_3 \quad (4)
\end{align*}
\]

We can conclude that –N=N-breakdown is accomplished by a reduction process from hydrogen radical produced as a result of N,N-dimethylformamide’s fragmentation [10]. Accordingly, H-N-N-H was produced, leading to the absence of the main source of color. As a result of exposure to gamma radiation more radiolysis products and free radicals are created causing the breakage of azo group of 4PNPAN dye, resulting in dissipation of chromophore. As a result the color bleached.

![Absorption spectra graph](image)

Fig. 2: The absorption spectra of 4PNPAN/PVB films before and After irradiation at different absorbed dose [4PNPAN] = 0.21phr.
Response Curves

The response was studied for 4PNPAN/PVB films containing different dye concentrations in terms of the change in absorbance per unit thickness (ΔA.mm⁻¹) at 472 nm against the absorbed dose (ΔA= A₀−Aᵢ, where A₀ and Aᵢ are values of absorbance at 472 nm for un-irradiated and irradiated films respectively). Each point on the dose response curve represents the mean optical density measurement of three dosimeter films irradiated at the same dose (I have taken the mean average of three films irradiated at the same dose. I would like to put error bar but I have two papers include it to avoid repeating process). The above data are represented in Fig. 3, where it is clear that dose saturation changes from 90 to 120 kGy with increasing dye concentration.

Effect of MgCl₂:

The absorption spectra of 4PNPAN/PVB containing 0.21phr azo dye and 1.33phr MgCl₂ irradiated at different doses are represented in Fig. 4. Increasing the applied dose reduces the amplitude of the peak at 472nm. It was noticed that degradation process is affected by MgCl₂, where 4PNPAN acts as Magnesium absorber. So, the dose range was reduced from 100 to 80 kGy for the same dye concentration.

Response Curves

Fig. 5 represents the response curves of 4PNPAN/MgCl₂/PVB films combining 0.21 phr 4PNPAN and various MgCl₂ concentrations. The results show that all the curves have the same trend but differ in the slope value. The sensitivity is directly proportional to MgCl₂ concentration. As mentioned before 4PNPAN azo dye acts as magnesium absorber, so dye concentration decreases in the medium. Subsequently, the degradation process becomes faster. As a result the dose range is reduced from 100 to 70 kGy with increasing MgCl₂ concentration.

Fig. 3: Variation of ΔA.mm⁻¹ against absorbed dose of 4PNPAN/PVB films containing different dye concentrations.

Fig. 4: The absorption spectra of 4PNPAN/MgCl₂/PVB films before and after irradiation at different absorbed doses. [4PNPAN]= 0.21 phr, [MgCl₂]=1.33 phr.
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 following relation determines the G-value [11].

\[
G(\text{-Dye}) = \frac{\Delta A}{D \cdot \epsilon \cdot b} \left( \frac{\text{mol}}{\text{J}} \right)
\]  

(5)

where \( \Delta A \) is the change in absorbance at \( \lambda_{\text{max}} \), \( b \) is the optical path length (cm), \( \epsilon \) is the molar extinction coefficient at \( \lambda_{\text{max}} \) (L mol\(^{-1}\) cm\(^{-1}\)), \( \rho \) is the density of the dosimeter (g cm\(^{-3}\)) and \( D \) is the absorbed dose (Gy). The molar extinction coefficient is calculated from the slope of \( \Delta A/b \) against concentration in mol/l to be 1342.37 Lmol\(^{-1}\)cm\(^{-1}\), where the density is 1.25 g cm\(^{-3}\) for PVB.

Table 1 represents the G (value) for 4PNPAN/PVB containing different dye concentrations.

<table>
<thead>
<tr>
<th>Dye concentration (phr)</th>
<th>G-value (μ mol .J(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.105</td>
<td>0.046</td>
</tr>
<tr>
<td>0.210</td>
<td>0.067</td>
</tr>
<tr>
<td>0.315</td>
<td>0.130</td>
</tr>
</tbody>
</table>

Table 2 G-values of 4PNPAN/MgCl\(_2\)/PVB films containing 0.21 phr of 4PNPAN and different concentrations of MgCl\(_2\).

<table>
<thead>
<tr>
<th>MgCl(_2) concentration (phr)</th>
<th>G-value (μ mol .J(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.067</td>
</tr>
<tr>
<td>0.66</td>
<td>0.095</td>
</tr>
<tr>
<td>1.33</td>
<td>0.136</td>
</tr>
<tr>
<td>2.66</td>
<td>0.172</td>
</tr>
</tbody>
</table>

The G-value of (4PNPAN/PVB) films increase by the increase of dye concentration and is directly proportional to MgCl\(_2\) concentrations.

Effect of humidity during irradiation

The influence of relative humidity (RH) during irradiation on the response of 4PNPAN/PVB films were inquired by irradiating the films containing 0.21 phr 4PNPAN to a dose of 30 kGy at various relative humidities (0, 23, 54, 76, 92 and 100% RH). The different relative humidities were maintained by using different saturated salt solutions [12]. The films were stored before irradiation for a period of three days under the same relative humidity conditions as when irradiated, so that the equilibrium moisture content in dosimeter was kept constant during irradiation.

Fig. 7 expresses the variation in \( \Delta A.\text{mm}^{-1} \) at 472nm with the change in relative humidity during irradiation, relative to the response value at 33% relative humidity. It can be seen that the response of 4PNPAN/PVB films exhibits a slight increase of ~1% till 40% relative humidity then there is a slight
decrease of ~ 1% till 75% and finally from 80 to 90% relative humidity there is a gradual increase of ~4%.

Fig. 7: Change of response of (4PNPAN/PVB) films against relative humidity during irradiation, λmax 472 nm, irradiation dose 30 kGy.

**Optical Energy gap**

The optical energy gap is defined as the gap energy between the minimum of the conduction band and the maximum of the valance band. We can calculate its value from the following relation [13, 14].

\[
\alpha (h\nu) = B (h\nu - E_g)^r
\]

where \(E_g\) is the optical energy gap; \(\alpha\) 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, 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 transition. 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\(^{-1}\)[15]. The absorption coefficient \(\alpha\) can be calculated according to Urbach rule as follows: [13].

\[
\alpha = \frac{1}{L} \ln \frac{I_o}{I_t}
\]

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

The present results were found to obey equation (2) applying the value of \(r = 2\) for all films, which indicate that the mode of transition is indirect allowed transition. Values of absorption coefficient were taken between 10 to \(10^3\) cm\(^{-1}\). The \((\alpha h\nu)^{1/2}\) yielded a linear dependence which describes the allowed indirect transition [13, 16, 17].

Fig. 8 represents the variation \((\alpha h\nu)^{1/2}\) against \(h\nu\) for 4PNPAN/PVB films containing 0.21 phr of 4PNPAN. The films were unirradiated and irradiated at different doses. The optical band gap can be determined from the extrapolation of these plots to the point at which they cross the abscissa to give the indirect allowed optical band gap. The plots show \(E_g\) is inversely proportional to the absorbed dose. Fig. 9 shows the value of \(E_g\) for indirect transition for 4PNPAN/PVB containing 0.21 phr 4PNAN. It shows that \(E_g\) decreases with the increase of absorbed dose.

We can conclude that the decrease in the band gap energy with the increase of dose may be attributed to an increase in structural disorder of the irradiated dye films. Irradiation of the dyed poly(PVB) induces 4PNPAN causing detachment of ions and unsaturated groups (−C = C−). These contributed to the structural defects, which reduce the band gap with increasing dose [16, 17].
Pre-irradiation stability

The effect of storage condition before irradiation was carried out by storing both (4PNPAN/PVB) and 4PNPAN/MgCl₂/PVB films in dark and light at 25 °C. In addition reading the films spectrophotometrically at different interval times during the pre-irradiation storage period of 45 days. Fig. 10 represents the stability of (4PNPAN/PVB) containing [4PNPAN] = 0.21 phr and the stability of (4PNPAN/MgCl₂/PVB) containing [4PNPAN] = 0.21phr and [MgCl₂] = 1.33 phr. It can be noticed that (4PNPAN/PVB) films stability before irradiation for 45 days in both light and dark is about 1%, while (4PNPAN/MgCl₂/PVB) films stability is 3% and 8% in dark and light, respectively.

![Graph showing stability of 4PNPAN/PVB and 4PNPAN/MgCl₂/PVB films before irradiation.](image-url)
Post irradiation stability

4PNPAN/PVB and 4PNPAN/MgCl\textsubscript{2}/PVB films irradiated to 45 kGy were stored in dark and light at a temperature of 25°C. The absorbance of these films at 472nm was measured at different time intervals during the post irradiation storage period of 45 days.

Fig. 11 shows the stability of (4PNPAN/PVB) containing \([4PNPAN]= 0.21\text{phr}\). The response increase gradually by ~3 % in dark and 5% in light at the first 10 days then the response tends to be stable to the end of the storage period. Fig. 11 also shows the stability of (4PNPAN/MgCl\textsubscript{2}/PVB) containing \([4PNPAN]= 0.21\text{phr}\) and \([\text{MgCl}_2] = 1.33\text{phr}\). It indicates that immediately after irradiation the response gradually decreases by ~ 3% in dark and ~6.4% in light through the first 10 days, the response curve keeps decreasing by about 7% and 10% in dark and light respectively up to 30 days then it remains nearly stable till the end of the storage period (45 days).

Fig. 11: Stability after irradiation of 4PNPAN/PVB films \([4PNPAN]= 0.21\text{phr}\) and 4PNPAN/MgCl\textsubscript{2}/PVB films stored in dark and light at room temperature.
Conclusion

Radiation-induced decoloration of 4PNPAN/PVB film dosimeters with variable concentration of 4PNPAN dye (0.105, 0.210, 0.315 phr) was investigated. The degradation of color of 4PNPAN/PVB film dosimeter is directly proportional to the absorbed dose in the dose range (5-80 kGy) for the lowest dye concentration. The dose sensitivity increases significantly with increase of dye concentration. Addition of MgCl₂ with different concentrations increases the bleaching reaction of the dye. The response of 4PNPAN/PVB film was slightly affected by relative humidity. The (G-value) was calculated for the 4PNPAN/PVB films and its value is directly proportional to MgCl₂ concentrations. Optical energy gap was determined and its value is inversely proportional to the absorbed dose. These results show that 4PNPAN/PVB films can be used as a dosimeter in high dose applications.

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References