



Effect of gamma irradiation dose on phthalate free PVC dyed thin film dosimeter

P. Oberoi^{1*}, C. Maurya² and P. Mahanwar³

¹ Department of Chemistry, Guru Nanak Khalsa College, Nathalal Parekh Marg, Matunga, Mumbai- 400019, India.

² KLE College of Science & Commerce, Plot no. 29, Sector 01, Kalamboli, Navi Mumbai- 410218, India.

³ Department of Polymer & Surface Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai- 400019, India.

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oberoi.priyanka20@gmail.com

Phone: +91-9819710283

Abstract

The effect of irradiation on optical properties of the film dosimeter made up of polyvinyl chloride based dimethyl yellow using a phthalate free plasticizer. The comparative results at different dye concentration have been studied. The film samples subjected to gamma irradiation at various doses (1-5, 10, 15, 20, 25 and 30 kGy) in a controlled manner using ⁶⁰ Cobalt gamma source at 12.5 kGy/hour. The color change from yellow to red has been observed after gamma irradiation which have been differentiated by color spectroscopy and measuring the absorbance. UV-Vis spectrophotometer shows an increase in absorbance with the increase in absorbed dose. The radiation chemical yield shows the g-values for dye concentrations of 0.2, 0.4 and 0.6 phr. The FT-IR analysis reveals the change in structural groups. The use of phthalate free plasticizer shows the stability of the films analyzed for 180 days.

1. Introduction

Ionizing radiation exposure have widespread applications in the arena of industries, medical sectors, educational, research institutes and nuclear provisions [1]. The use of x-rays, gamma and electron beam in the field of radiations have become essential. Efficient choice of radiation detector depends on the interest along with the type of radiations, its suitability, efficiency and applications [2,3]. A very essential role has been played by the dosimeter in order to measure the dose of ionizing radiations exposed. Dosimeters absorb the dose prompting a visual response in the form of coloration in the visible region bringing a physical change there within [4]. The change measured for low or high dosimetry is because the “absorbed dose is proportional to intensity of the color and also proportional to the character of the color”[5]. The pertinent phenomena of any dosimeter is to attain sustainability, stability, simple, economic, ease in handling. Indicators and dyes sensitive towards radiation induce change in color after irradiation have been used commercially in the area of medicines, radiation sterilization and food irradiation, water and other mineral purification, crosslinking of polymers [1,6–9]. The film dosimeter’s high response towards the change in temperature, dose rate of radiation, atmosphere, surrounding oxygen and humidity [9–13] have brought in the response for newly modified forms of dosimeter in order to fulfil the need and norms of dosimetry systems and for the applications in radiation processing technology [14,15].

Sterilization has evolved with a remarkable progress in the field of medical industry over the last two decades. The primary methods for medical device sterilization are electromagnetic radiation (e.g. gamma rays, electron beam and UV light) and particulate radiation [16]. Production of free radicals by such radiations causes high energy excitation of electrons which are remarkably noted with the use of dosimeter [17–19]. Various polymer materials like vinyl acetate[20], polyvinyl chloride [21,22], polystyrene [8], cellulose acetate[23], polyvinyl butyral [24] are used as dosimeters where change induced in polymeric matrix is dependable on the type or composition of dye incorporated.

Reported work on polyvinyl chloride (PVC) dyed films had been manufactured for the application of UV dosimeter which contains either phthalate containing compounds or tetrahydrofuran solutions [25,26]. Various dyes such as malachite green, methyl red, copper chloride have also been reported along with PVC matrix for the application of high dose dosimeter. Results from Artandi and Stonehill [5] and McLaughling et. al [27] indicates color change in rigid vinyl films on ionizing radiation (from green to yellowish-brown to reddish brown) but at a high absorbed doses of 10⁵-10⁸ rads. The phenomena of the reaction between the halogen containing compound

and the polymer due to gamma irradiation brings a change in the coloration of the film with some physical and chemical changes is well known [28]. The effect of the stabilizer on the enhancement of ionizing radiation is highly influenced by the choice of stabilizers being used and thus determines the stability of the polyvinyl chloride films. Non-hazardous varied metals and metal soaps tends to perform at low levels. In order to avoid such stabilizers, use of Cadmium-Barium-Zinc stabilizer have been used here. The improvement of the polyvinyl chloride films mainly depends on the loading and type of plasticizer. The use of phthalate free plasticizer makes it much feasible and harmless. It also helps in softening of the material and reduces the effect of yellowness before and after its exposure to gamma irradiation. [27], [29], [30].

The effect of gamma irradiation on di-methyl yellow blended PVC dyed films have been studied to observe the color change. The use of additive in the form of liquid plasticizer helps in softening the PVC material. It also improves the durability and flexibility making it suitable to cast a uniform film. PVC film has a tendency of releasing chlorine while processing the films so; there is a possibility of generation of hydrogen chloride. Addition of Cadmium-Barium-Zinc stabilizer helps in achieving the temperature stability in the sample while processing the PVC films in twin roll mill, further preventing the initial elimination of chain reaction of hydrogen chloride from the polymer before irradiating the films to gamma rays. The influence of gamma irradiation on the use of phthalate free plasticizer at 0.2, 0.4 and 0.6 phr concentrations of dye being further characterized for visual color appearance, CIE L*A*B* values, UV-Vis spectrometry, radiation, FT-IR, reproducibility and post-irradiation stability studies.

2. Material and Methods

2.1. Material

Polyvinyl chloride (PVC) powder procured from Finolex Industries Ltd. with the following physical characteristics: powder, Kw value: 68 ± 1 units; bulk density 0.47 g/ml. Di-butyl Maleate (DBM) as a plasticizer, obtained from Sigma Aldrich with a molecular weight of 228 g.mol, boiling temperature of 281°C and density of 0.988 g/cm³. Di-Methyl yellow (DMY) having CI No. 11020 purchased from Loba Chemie Pvt. Ltd whereas Cadmium-Barium-Zinc (Cd-Ba-Zn) complex obtained from a local supplier. The reagents of analytical grade have been used without any additional purification.

2.2. Method

To the pure 100 phr of PVC powder, 30 phr di-butyl maleate have been added on the basis of weight by weight ratio of PVC, kept well stirred and soaked overnight. After 24 hours, Cadmium-Barium-Zinc complex added to the mixture at a fixed concentration of 0.1 phr and the mixture have been divided into three parts. Prepared stock solution of di-methyl yellow at three concentrations (0.2, 0.4 and 0.6 phr) have been incorporated in to the respective beakers and stirred till a uniform yellow color has been obtained. Compounding of PVC with plasticizer, heat stabilizer and dye have been carried out in Two-roll mill at 150°C for compounding. Thereafter every compounded material have been measured for its uniformity and thickness being measured by thickness gauge (Mitutoyo) and found to be 40µm.

3. Characterization

3.1.1. Gamma irradiation

All the prepared PVC samples have been irradiated at 0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 40 and 50 kGy. The irradiation of has been carried out at RTDD Section of BARC, Mumbai, India by using γ -chamber with a ⁶⁰Co source at delivery dose rate of 12.5 kGy/hr..

3.1.2. Color spectrometric analysis (CIE L*a*b*)

The major advantage in performing the 1976 CIE L* a* b* color space being visually comparing and discriminating the relation as well as the difference between the two or more color and its uniformity of the color space which ideally cannot be categorized with a naked eye[31]. The three different coordinates represented as L*, a* and b* coordinates signifying lightness and darkness, green and red, blue and yellow from negative to positive axis respectively [28], [32]. Color dissimilarity of the polymeric dyed films characterized using Gretag Macbeth's color-Eye 7000A for CIE L*a*b values at an angle of 2° using illuminant C, in the spectral range of 360 nm to 750 nm with a reflectance mode. The calibration have been performed using a black and a white calibration tile. The samples being tested in triplets followed by calibration after each set of different concentrations. The measurement of un-irradiated and irradiated colored samples have been carried out on CIE L*a*b* color space [31], [33] and the overall difference of ΔL^* Δa^* Δb^* calculated using the formula as follow:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad \text{----- } l$$

3.1.3. UV-Vis spectrophotometric analysis

Optical absorbance measurements made spectrophotometrically using a film holder fitted to a UV/Vis-Spectrophotometer, Evolution 300 UV-Vis (Thermo Fisher Scientific) in the range of 200 to 700 nm. The absorbance of each sample has been measured post-irradiation. The response curve being calculated using Eq. 2.

$$\Delta A = (A_0 - A_i) \text{ ----- } 2$$

Where, ΔA is the change in the optical density, and A_0 and A_i are the values of optical density for unirradiated and irradiated films respectively[3], [34].

3.1.4. FT-IR spectrometer

The chemical structure of PVC/DBM/DMY at 0.2, 0.4 and 0.6 phr concentration of dye being analyzed on Bruker –Alpha FT-IR. The spectra of the films (un-irradiated and irradiated samples) have been recorded by attenuated total reflection (ATR) model. The resolution and the scan numbers being set to 4 cm^{-1} and 25 seconds respectively. The spectra recorded have been in the range of 4000 cm^{-1} to 400 cm^{-1} at room temperature. The characterization of the gel using FTIR symbolizes the existence of specific groups.

3.1.5. Post-irradiation stability

The post-irradiation stability have been studied by storing the irradiated films at room temperature for a duration of 180 days (six months) and further characterized using UV-Visible spectrophotometry.

4. Results and discussion

4.1. Effect of gamma irradiation

The exposure of phthalate free PVC based dyed films samples irradiation in the dose range of 0, 1, 2, 3, 4, 5, 10, 15, 20, 25 and 30 kGy. The effect of gamma irradiation have been resulted into darkening of the film as a function of absorbed dose. The change in color from yellow to red has been studied.

4.2. The visual color difference in the gel dosimeter

Figure 1 represents the visual color difference between the unirradiated and the irradiated film samples. The yellow colored control sample being compared to that of the irradiated samples showed changes from yellow to orange to red as a function of increasing doses of gamma rays. Gamma irradiation plays the utmost and essential role in the change in the films by liberation of HCL from PVC further altering the color of the dye. This phenomenon has been further studied by various characterization techniques which helps in finding the main reason behind the change in color for the application of a dosimeter for the sterilization process.



Figure 1 Colored PVC films (a) Control sample and gamma irradiated at (b) 5 kGy, (c) 30 kGy (concentration of 0.2 phr dye)

4.3. Color Measurements

On analysing the irradiated film samples, the effect of gamma irradiation has been observed on the change in the color index. Figure 2 (a), (c) and (e) showing a gradual decrease in the values of L^* , b^* and yellowness index resembling a shift in the color space from yellow to red alternatively. Fig 2 (b) shows a significant increase in concentration of 0.2 phr but a decreasing pattern for 0.4 and 0.6 phr approaching to a red shade in the color space. Figure 2 (d) shows a rise in a slope indicating a difference in the color change which appears due to the gamma ray photons excite the electrons shifting from one state to another[35]. The change in the color represents the shifting is the result of the trapped free radicals initiated by ionization[36], [37]. The change in color thus also represents the change in the color indices as well as in yellowness index.

When the values of the fig. 2 have been compared with the above mention coordinates, it has been observed that the L index shows a gradual dropdown due to the increase in the darkness of the films on irradiating the films with gamma ray doses. Whereas, an increase in the values of the index graph which shows the shift towards the red color space. The color space shift away from yellow being inspected in the b index which further confirmed with the values of yellowness index. Total deviation (ΔE) of samples increased with increased in dosage

from control to 30 kGy. This analysis concludes the physical change held which sometimes cannot be differentiated with the naked eye.

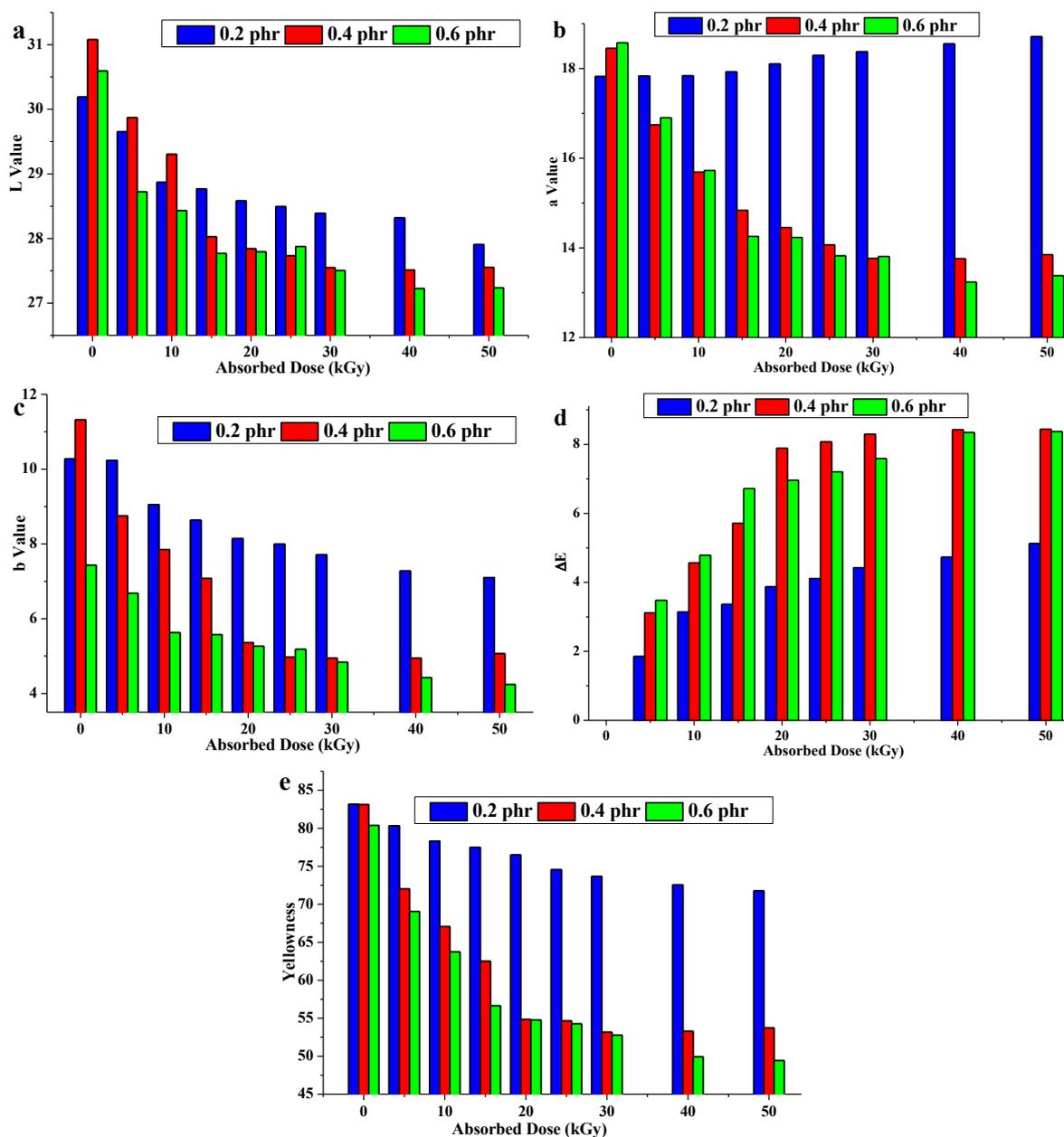


Figure 2 Color index values of (a) L^* , (b) a^* , (c) b^* , (d) ΔE and (e) Yellowness dyed PVC films at 0, 5, 10, 15, 20, 25, 30, 40 and 50 kGy.

4.4. UV-Visible spectroscopic studies

Figure 3 illustrates the UV-Visible absorption spectra of both the unirradiated and for the irradiated films at various doses. The spectra reveal three bands in the visible regime in all the three graphs in fig 3 (a), 3 (b) and 3 (c) representing data at concentrations 0.2 phr, 0.4 phr and 0.6 phr respectively. Absorption band 1 observed to have a constant wavelength at 237 nm for all the doses. This could be considered the polymer peak in this case polyvinyl chloride, which is steady without any major change in the shift. There is a change in the absorption band 2 and 3 with respect to the exposure of the dose absorbed. It can be seen that the absorbance of the band 2 at 460 nm becomes weaker with the increase in dose from 5 kGy to 30 kGy. The absorption peak band at wavelength 545 nm dominates the spectra. By visualizing the UV spectra it is observed that band 3 is more distinct and red-shifted relative to the analogous peaks for 1 and 2, whereas band 1 is in the blue shift. The absorption features, however, are not altered upon gamma irradiation which is a further proof that it is the HCl derived from PVC, upon irradiation causes this simple phthalate free acid±base chemistry crucial for the optical changes[27]. It can also be observed that absorbance rising in all the irradiated samples from 5 kGy to 30 kGy but the same band is missing in the control sample which also confirms that the formation of the new band due to the effect of

gamma irradiation on the PVC dyed films. The acid environment estimates the alteration of the anions to the protonated uncharged form forming HCl in the PVC matrix [38]. The usual cause of de-hydro chlorination as reported by Luther and Linsky, 1996 due to gamma radiation in a dose-dependent fashion [29], [31], [39], [40]. As the absorbed dose increases, there has been generation of release of HCl and breakage of bonds, significantly affecting the structure of the dye molecule resulting in blue shift to red shift (color change from yellow to red). The modification in the chromophore of azo dyes induced by ionizing radiation is believed to be irreversible as it is attributed to a cleavage of the azo group[38], [41].

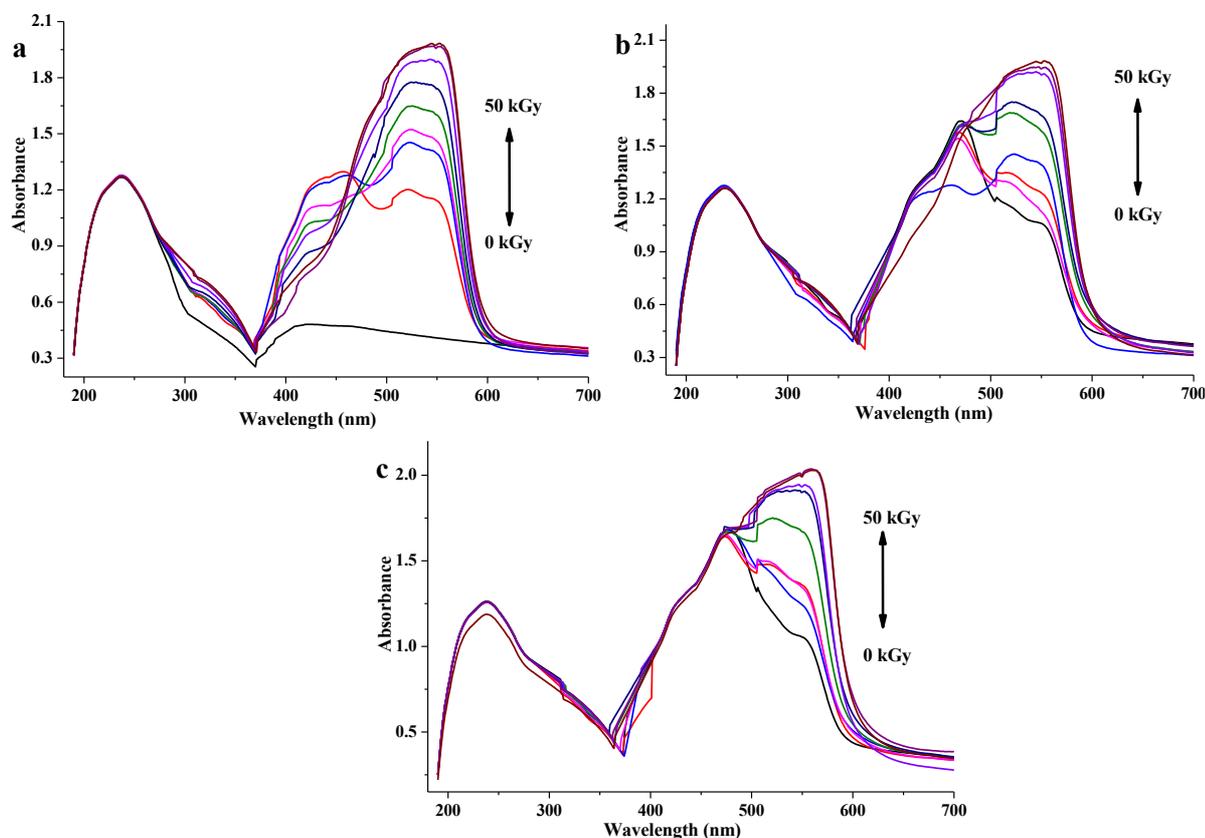


Figure 3 UV spectra of DMY dyed PVC films at 0 to 50 kGy. Absorption spectra of DMY dyed PVC films at 0 to 50 kGy. (a) 0.2 phr, (b) 0.4 phr, (c) 0.6 phr.

4.5. Response curve

The dose-response curve graph in the Fig. 4 (a), (b) and (c) shows 3 different slopes representing absorbance and an overall view of change in absorbance versus the absorbed dose at a specific absorbance of 545 nm. The values have been calculated using the formula Eq. 2. The dose response of the film appears to have a linear regression ($R^2 = 0.974$) between the change in the intensity and the dose absorbed up to 50 kGy which can be observed in the individual relative absorbance dose curves. This indicates that the response is highly dependable on the dose.

Absolute and relative standard deviations of the responses of repeated samples at 545 nm to various doses. The dose response of the film appeared to be in a linear relation between the change in the intensity and the dose absorbed up to 30 kGy which can be observed in the individual relative absorbance dose curves. This indicates that the response is highly dependable on the dose. As the absorbed dose increases, there is generation of free radicals and electrons in this case de-chlorination and breakage of bonds modifying the structure of the resulting into the change of color from yellow to red. This can be correlated with the *section 4.8* with the spectra related to FTIR. Also another cause of the change is the presence of azo dye which on irradiation initiates the change which further on reaction with the chlorinated atoms liberated from PVC polymer changes the color of the film.

Discoloration of PVC upon UV exposure (yellowing) and irradiation with high-energy radiation have long been studied for imaging and for electron beam dosimetry. Even incorporation of acid-sensitive dyes into PVC for dosimetric purposes had been reported [42]. Figure 4a, 4b and 4c shows the same micro-scale pattern in terms of absorbance change with respect to the change in absorbed dose at 545 nm respectively. The color change is linear with absorbed dose and it can be easily evaluated by a UV spectrophotometer which corresponds a bath-

o-chromic shift from the blue region to red region. It is observed from absorbance graph that the prepared PVC films showed increased in absorbance from control up to 30 kGy followed by a flat plateau for 40 and 50 kGy. The cause of the optical and/or chemical changes can easily be stated as the dehydrochlorination of PVC itself [43].

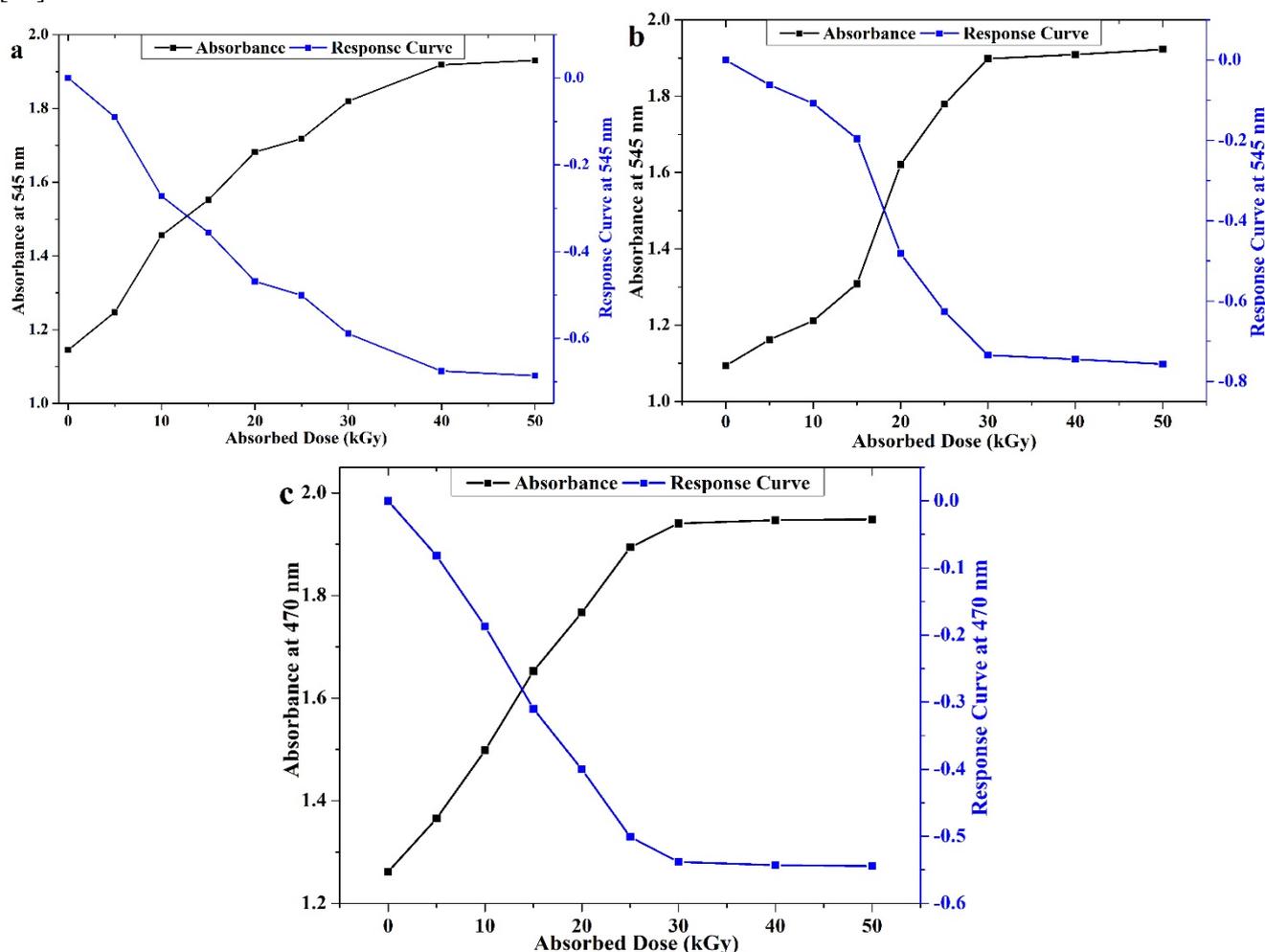


Figure 4 a) Absorbance and Response curve at (a) 0.2 phr (b) 0.4 phr and (c) 0.6 phr of dye at λ_{\max} 545 nm.

4.6. Dechlorination

The effect of dechlorination can be observed in the visual representation of the film samples and from the discussion in section 4.5. Conjugated bond formation on the exposure of gamma irradiation on to the polyvinyl chloride chains happens due to a special type of mechanism known as zipper elimination. The involvement of phthalate free plasticizer acts as a catalyst to help preventing the degradation of PVC films by elimination of HCL at room temperature. The liberation of HCL by the elimination of the free radicals of chlorine on irradiation attracts to a hydrogen from the adjacent methylene group producing double bonds, additionally reacting with the dye present in the film. This reaction mechanism has been the foremost source of changing the color of film from yellow to orange to red [30]

4.7. Reproducibility

Absolute and relative standard deviations of the responses of repeated samples at 545 nm to various doses are tabulated in table 1.

4.8. Fourier Transmission Infra-red Spectroscopic Analysis

From the Fig. 5, structural changes in the dyed film have been determined. Analysis reveals the variation in the intensity of absorbance in samples as there have been an increase in dose of gamma radiations. Due to stretching and bending on irradiation, different bands at particular wave numbers have been observed, indicating changes in the structure of the films. The peak at 2917.20 cm^{-1} and 2851.32 cm^{-1} indicates the presence of aliphatic C-H stretch bonds. Acid group has been observed at a characteristic peak of 1728.88 cm^{-1} with an increasing intensity thus indicating the release of acid from the polymer. Band at 1647.48 cm^{-1} indicates for C=O stretching possibility

of opening of double bond from the polymer chain for further reaction with the dye. The peaks at 1420.35 cm^{-1} and 1251.04 cm^{-1} are due to stretching bonds of $\text{CH}_2=\text{CH}_2$ groups respectively and shows an increase in intensity. The intensity of peaks have been increased with the increase in the irradiation dose. Peak at 957.56 cm^{-1} shows aliphatic stretching and C-Cl groups have been observed at 690.42 cm^{-1} and 617.38 cm^{-1} in increasing order due to darkening shade on being irradiated by gamma ray photons. The new emerging peak observed has been enlarged in inset at 513.91 cm^{-1} indicating reaction between the acid generating polymer and the dye. Thus, from all the analysis done, it can be confirmed that there have been a visual as well as structural change in the films as it have been irradiated with different doses of gamma radiation.

Table 1 Reproducibility of the response to various doses.

Absorbed Dose (kGy)	Standard Deviation (545 nm)			Relative Standard Deviation (%) (545 nm)		
	0.2 phr	0.4 phr	0.6 phr	0.2 phr	0.4 phr	0.6 phr
0	0.004	0.001	0.054	0.429	0.123	4.320
5	0.007	0.002	0.049	0.602	0.164	3.573
10	0.004	0.013	0.042	0.292	1.050	2.784
15	0.007	0.029	0.045	0.478	2.216	2.738
20	0.004	0.035	0.127	0.218	2.181	0.720
25	0.007	0.034	0.003	0.387	1.908	0.150
30	0.007	0.032	0.005	0.381	1.676	0.259
40	0.009	0.017	0.003	0.469	0.889	0.145
50	0.006	0.014	0.004	0.32	0.713	0.178

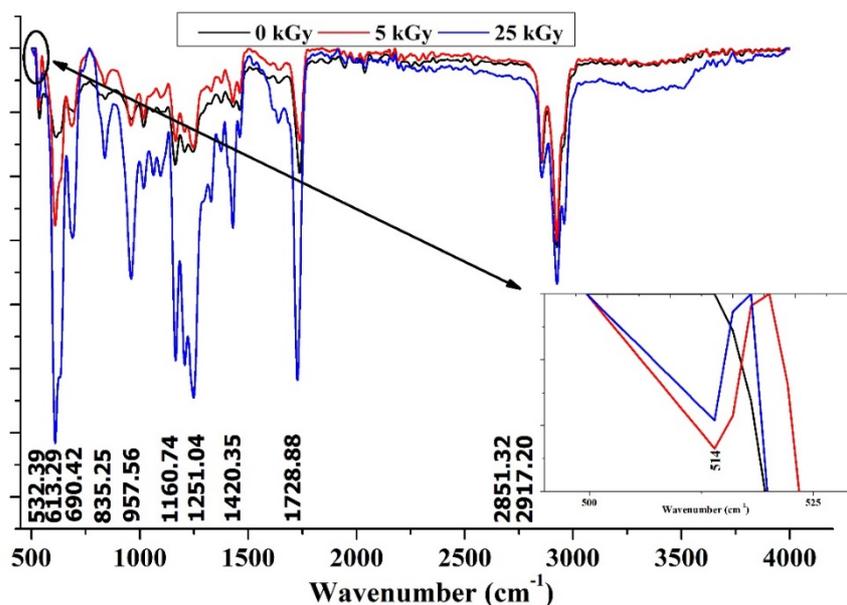


Figure 5 FT-IR spectrum of un-irradiated and irradiated film samples (inset: new band at 514 cm^{-1})

4.9. Self-life and Post-irradiation Studies

The post-irradiation studies of the stored samples when compared to the control samples revealed no drastic change with respect to the absorbed doses. Samples irradiated at an ascending doses kept at room temperature for a period of 180 days. Further comparison of the stored samples against the control samples have been measured

using UV-Vis spectrophotometer at a fixed wavelength of 545 nm. Figure 6 shows the change in absorbance as a function of storage time relative to that before storage at various concentrations of dye. All the three concentrations follows the same trend without any drastic change. The study reveals that the films have a stable nature exhibiting a good stability before and after irradiation over a period of 6 months.

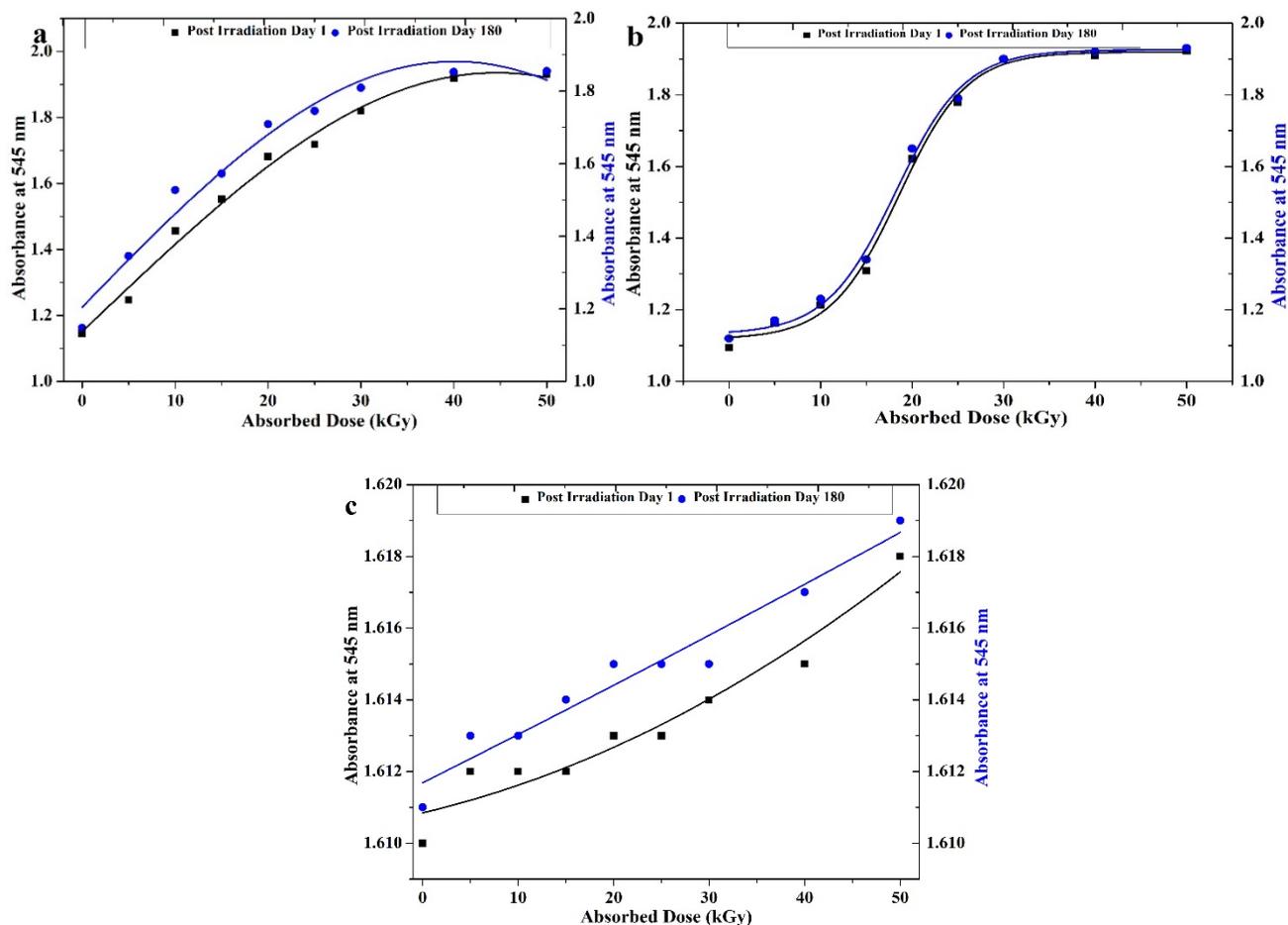


Figure 6 Post irradiation stability graph showing absorbance on day 1 and day 180 for (a) 0.2 phr dye, (b) 0.4 phr dye and (c) 0.6 phr dye at 545 nm.

5. Conclusion

It is concluded that phthalate free PVC dyed films can be used as dosimeter as it gives a gradient in the color followed by the change in absorbance with respect to gamma dose. It has been also found that color index value ($I^* a^* b^*$), total deviation (ΔE) of samples increased with an increase in dosage from control 0 to 50 kGy. The color change is linear with absorbed dose and it can be easily accessed by UV spectrophotometer at a wavelength of 460 nm and 545 nm. The relative change in absorbance has been found to depend linearly on the absorbed radiation dose up to 50 kGy. FT-IR revealed the change in the functional groups with respect to de-chlorination altering the dye molecule. The relative standard deviations of signals of replicate dosimeters have been within the range at all the studied doses and it showed a good stability for a period of six months.

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