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Effect of Gamma Radiation on Bromophenol Blue Dyed Films as Dosimeter

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***Abstract*—**Ionizing radiation can cause a drastic change in the physical and chemical properties of the material exposed. Numerous medical devices are sterilized by ionizing radiation. In the current research paper, an attempt was made to develop precise and inexpensive polymeric film dosimeter which can be used for controlling radiation dosage. Polymeric film containing (pH sensitive dye) indicator dye Bromophenol blue (BPB) was casted to check the effect of Gamma radiation on its optical and physical properties. The film was exposed to gamma radiation at 4 kGy/hr in the range of 0 to 300 kGy at an interval of 50 kGy. Release of vinyl acetate from an emulsion on high radiation reacts with the BPB fading the color of the film from blue to light blue and then finally colorless, indicating a change in pH from basic to acidic form. The change was characterized by using CIE l*a*b*, ultra-violet spectroscopy and FT-IR respectively.

***Keywords*—**Bromophenol blue, dosimeter, gamma radiation, polymer.

I. Introduction

ONE of the latest technology transpired in the field of nuclear and other radiation sources is radiation processing technology [1]–[3]. Interaction of radiation photons pioneered the creation of dosimeter in determining this absorbed dose which linearly corresponds to the radiation [4], [5]. It actuates the change in either physical and/or chemical [6]. Accuracy in the detection of these radiations is of utmost important for the health and safety of the human beings [4]. Indicators which are distinctly sensitive to radiation are utilized to demonstrate that products have been exposed to radiation source [7]. Many polymers are used in preparation of dosimetric films because of their flexibility, high stability and moreover their ease of availability. A regime is being followed in determining the absorbed doses as well as dose rate of the films irradiated using ionizing radiation [8]–[11].Variety of polymers namely polyvinyl chloride, polyvinyl acetate, polystyrene, cellulose acetate etc. along with different dyes and pigments were used for routine dosimetry [12]–[15].

The selection of dyes based on their nature (acid, basic, inorganic or organic) has a very predominant impact on the dosimeter films, caused by the influence of varied chemical groups incorporated [10], [16], [17]. In addition, an effect of gamma radiation was also observed on the chemical groups of the polymers as well as the chromophore groups of the dye present in the films [18]. Chemical changes caused by the irradiation include change in pH [3] and optical properties of the dosimetry film [19]. So far, UV-spectroscopical studies have established the impact of gamma radiation. But a minimal focus was rendered on assessing the impact using the colour indices. The current work discusses the effect of gamma irradiation on the change in colour value of the films measured by CIE L*a*b spectroscopy (color). In here, dosimetry films were made of vinyl acetate emulsion containing pH indicator and acid sensitive BPB dye [3], [11], [20], [21]. The color change was measured after irradiating the films using gamma ray photons and established as a function of the irradiation dose. A gradual change detection was also confirmed by Ultraviolet spectroscopy and Fourier transform spectroscopy.

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II. Experimental

A. Materials

Water based emulsion containing vinyl acetate used as a matrix in the study was obtained from Pidilite Industries Ltd. Dye BPB procured from Merck Ltd. India, Biaxially oriented polypropylene (BOPP) sheet was procured from Paper N Films International, India. All the chemicals were used as it is.

B. Preparation of films

To 50 ml of emulsion, 5 parts per hundred (PHR) of BPB dye was added and kept under agitation using a magnetic stirrer at room temperature to attain a homogeneous solution. The dyed solution was casted onto BOPP sheet using a 100 µm bar applicator and dried at room temperature. Films were then peeled off from the sheet and cut to the dimensions of 5 × 5 cm before storing in a desiccator for further investigations. The dry film thickness was found to be 80 measured using Baker Mercer thickness gauge (within an accuracy of ±1 µm).

III. Characterization

The irradiation of was carried out at Board of Radiation and Isotope Technology Section of BARC, Navi Mumbai, India by using γ –chamber with a source and delivery dose of 0.45 kGy/hr. The samples were irradiated with dose range of 0-300 kGy with an interval of 5 to 50 kGy. The measurement of un-irradiated and irradiated colored samples were obtained using CIE L*a*b* values to sensitize a visual variation in the color change. Further detection was characterized by UV-vis spectrophotometer +3000 by Lab India to measure the absorbed dose rate before and after radiation and Bruker FTIR

System to confirm the change in the structure and reaction in spectra from 4000 to 400 cm^{-1}.

IV. Results and Discussion

In the current work, we have studied the effect of ionizing radiation on the dyed polymer films. The film specimens were subjected to gamma ray photons at 50kGy, 100kGy, 150kGy, 200kGy, 250kGy and 300kGy. As a result, the fading of blue color to light blue to colorless was observed and the difference in the absorbance dose and the structural change was analysed by Ultra-violet spectroscopy and FT-IR. Comparison of both un-irradiated and irradiated films were carried out to determine the corresponding changes.

A. Color Spectroscopy

Evaluating the color quantitatively as well as qualitatively gives a better and clear difference and thus has a great advantage with respect to the sensitivity, repeatability and clear perception. The use of CIE L* a* b* (1976) color space was explored in the field of plastic and paint industries. This color space functions in displaying the color difference in the specimens focusing on the characteristic features of lightness, change in the scale of grey, green, blue, yellow and red chromes. This helps in correlating between the visual and instrumental judgment. The visual change of the films was remarkably diminishing from a shade of blue to colorless. The analysis was performed according the norms of ASTM E308-01 [22] and ASTM E313 [23] for the CIELAB color scales and yellowness index [24] respectively.

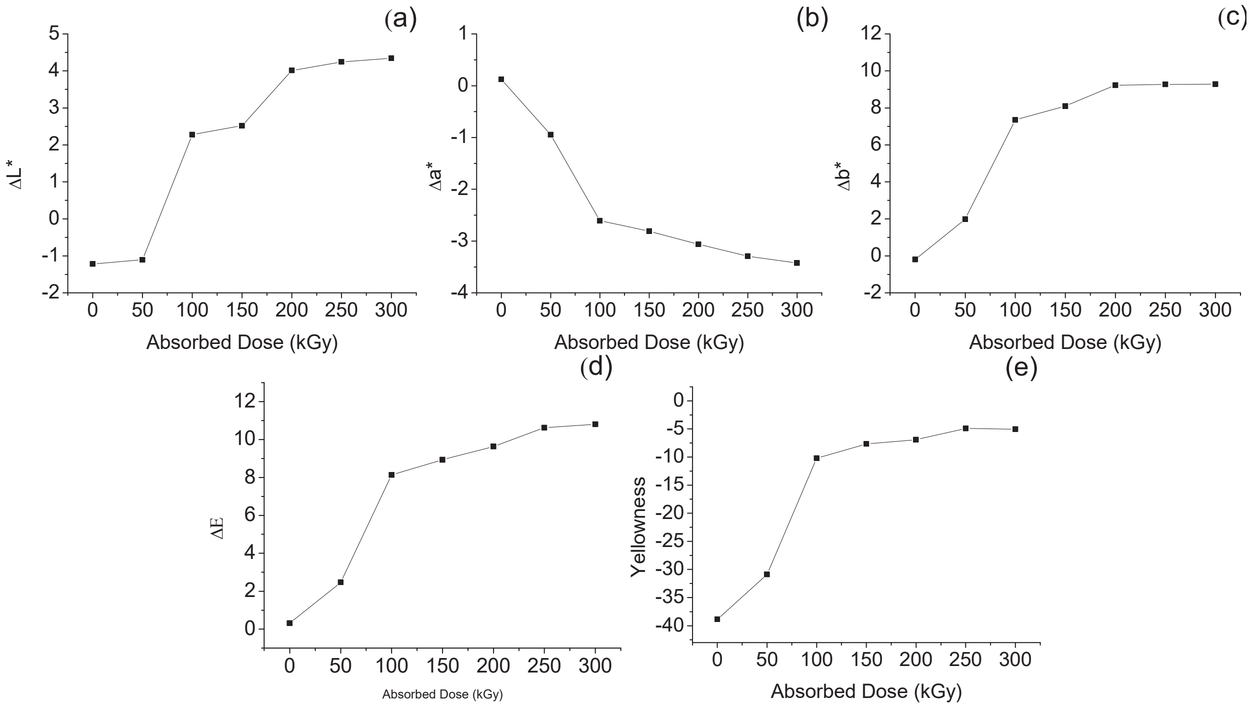

Fig. 1 (a) ΔL*, (b) Δ a*, (c) Δ b*, (d) ΔE and (e) Yellowness values of the samples with varying Gamma dosage

With the reference of the CIELAB parameters, 2° observer and illuminant as C was set for the analysis. The values of a* describes a correlative amount of redness and greenness with positive and negative respectively. Framework b* reports amounts of yellow and blue color with positive indicating yellowness and negative values indicating blueness whereas L* values describes the darkness to lightness shift from negative to positive scale in the color difference graph. From Fig. 1 (a), ΔL* shows a sigmoid (S shape) graph denoting an increase in the values of L* from negative to positive. The change signifies that there was an alteration in the irradiated films from a dark to lighter shade of blue. Fig. 1 (b) inferred that there was a shift from positive to negative values indicating a change towards green regime. Whereas Fig. 1 (c) shows an increasing slope stipulating a shift from blue to yellow which was also approved from the yellowness index graph in Fig. 1 (e) showing an upward slope. The overall difference of L*a*b* when combined in Fig. 1 (d) shows an increase in the 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. This shift fades the films [25].

B. Ultraviolet Visible Spectroscopy

The measurement of optical absorption spectra of all the unirradiated as well as irradiated films were analysed in the wavelength range extending from 400 nm to 700 nm using UV/Vis spectrophotometer to confirm the visual changes and also the change in the intensity through absorbance. In the graphical presentation of absorption spectra of Fig. 2 (a), the main absorption band of BPB in the film was detected in the visible region crowning at 600 nm [3], [11], [20]. Films after subjecting to radiation were visually faded and appeared completely colorless after the irradiation dose of 150 kGy as seen in Fig. 2 where there was disappearance of the absorption band at 600nm from the dose rate of 150 kGy to 300 kGy. The main focus of this analysis was to observe the intensity of the films. Distinguishingly decreasing intensity of the films were noted as there was increase in the dose of gamma radiation. The highest intensity was observed in the film sample which was not subjected to gamma radiation.

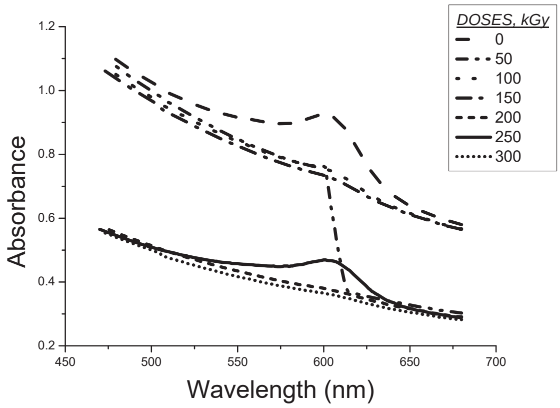

Fig. 2 Absorption spectra of films before and after irradiating from 50 to 300 kGy doses

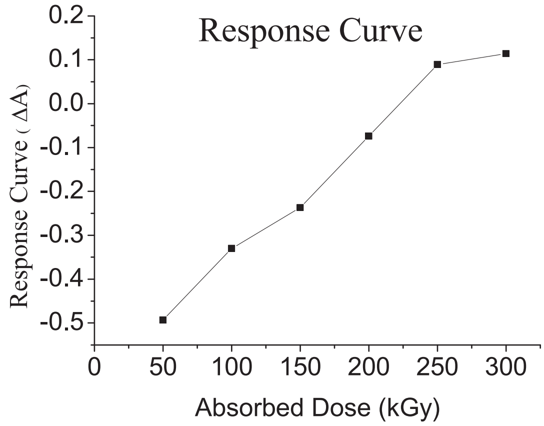

Fig. 3 Response curve of irradiated films in terms of change in absorption at different doses of gamma rays

C. Response Curve

The response curve graph in Fig. 3 gives an overall view of modification in optical density at a specific absorbance which was calculated using the formula, $\Delta A=A_0 - A_i$ where, ΔA is the change in the optical density, and A_0 and A_i are the values of optical density of unirradiated and irradiated films respectively [3], [20]. There appeared a linear relationship between the change in the intensity and the dose absorbed. This indicates that the response is highly dependable on the dose.

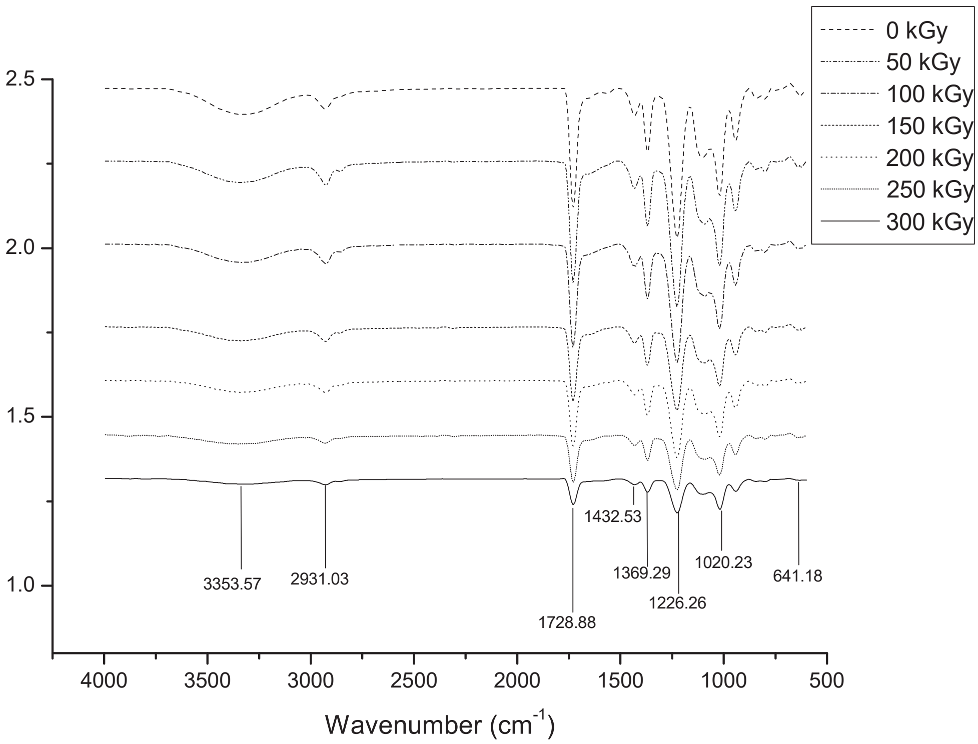

Fig. 4 FT-IR spectrum of unirradiated and irradiated film samples

D.FT-IR Analysis

Fig. 3 shows FTIR spectra of film samples containing films irradiated at different doses from 0 kGy to 300 kGy in the range of 4000-500 cm^{-1}. Analysis reveals the variation in the intensity of absorbance in samples as there was an increase in dose rate of gamma radiations Due to stretching and bending on irradiation, different bands at particular wavenumbers were observed, indicating changes in the structure of the films. The band at 3353.57 cm^{-1} shows scission of the main bonds and change in –OH groups, aromatic C-H stretching and water which was used as solvent. The peak at 2931.03 cm^{-1} indicates the presence of aliphatic C-H stretch bonds. Acid group was observed at a characteristic peak of 1728.88 cm^{-1} with a decreasing intensity thus indicating the release of acid from the polymer. The peaks at 1432.53 cm^{-1}, 1369.29 cm^{-1} and 1226.26cm^{-1} are due to stretching bonds of CH_2=CH_2, C=N, C=H and also sulfur groups which are present in BPB. Peak at 1020.23 cm^{-1} shows C=O stretching and C-Br groups was observed at 641.18 cm^{-1} but was on the verge of disappearance due to bleaching effect of the films after they were irradiated by gamma ray photons. Thus, from all the analysis done, it can be confirmed that there was a visual as well as structural change in the films as it was irradiated with different doses of gamma radiation. This change was due to the reaction between the dye and the polymer used. The modification of acid from the polymer bonds with the halogen (Bromine) in the dye brings a color change.

V. CONCLUSION

In the current research work, polymeric film containing an acid sensitive dye. BPB belongs to triarylmethane group of dyes, acts as a halo chromic chemical. It helps in indicating the color change by the degree of acidity or basicity levels with a change in the pH. The effect of gamma radiation the film displayed a visual change analyzed using CIE L*A*B* color scale where it showed a significant rise in the graph values of ΔL*, Δb*, ΔE* values and decreasing Δa* values. The yellowness index also denoted the change from blue to colorless. The structural change confirmation was characterized by techniques like, UV-Vis spectroscopy and Infra-red spectroscopy.

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