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A new developed radiochromic film for high-dose dosimetry applications

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ABSTRACT

A colorless polyvinyl butyral film (PVB) based on a radiochromic leuco brilliant blue cyanide dye (LBB), was investigated as a high-dose dosimeter for gamma radiation processing applications in the dose range of 3–165 kGy. The useful applications for such dose range are food irradiation treatment, medical devices sterilization, and polymer modification. Upon γ-ray exposure, the prepared film undergoes visual color change to deep blue color characterized with an absorption band peaking at 638 nm. The variation in response of irradiated film stored in the dark and under laboratory light illumination was less than 5% during the first week of storage. The effect of temperature and relative humidity on the performance of film during irradiation and the overall uncertainty associated with absorbed dose monitoring were investigated in the present study.

1. Introduction

Radiochromic thin film dosimeters have wide-spread application in radiation processing for installation and process qualification and routine dose control for both gamma and electron irradiation [1–3]. Many colorless derivatives of triphenylmethane dyes can be made radiochromic upon exposure to ionizing radiation, that some of radiochromic films were prepared using the colorless triphenylmethane leuco dyes [4]. Polyvinyl chloride (PVC) film dyed with malachite green (MG) was studied for high-dose radiation dosimetry using visible spectrophotometry [5]. In which, MG dye is degraded by ionizing radiation, which is characterized by a decrease in the absorbance value at 628 nm. Another thin film dosimeter (GIC-79) incorporating a radiochromic dye of malachite green methoxide (MGMO) was investigated in the high-dose range of 1–80 kGy [6]. Coloration detectors (material that turns color upon being irradiated) have a rich and interesting history in the field of ionizing radiation dosimetry [7]. The coloration and the absorption bands formed in these radiochromicfilms are due to the radiolytic scission of the −CN or −OCH3 groups of the colorless leuco dye molecule, resulting in isomerization to the highly colored polar carbonium cation of the dye [8]. A film dosimeter based on radiochromic nitro-blue tetrazolium (NBT) and PVB polymer for routine dosimetry applications in the dose range of 5–55 kGy was developed by Ref. [9]. A radiochromic dye of pararosaniline cyanide (PRC) mixed with thin PVB film was investigated using spectrofluorimetry based on emission properties for high-dose range of 5–120 kGy [10] that Upon irradiation, the colorless film turns into red color due to the radiolytic scission of PRC dye and the red color increases proportionally with increasing absorbed dose. The uncertainty associated with the dosimeter response of this film was monitored as 6.04% at 2σ without taking in their consideration the effects of temperature and humidity levels on dose response of the film as well as the stability of response.

The objective of the present work is to develop a PVB film based on a BB cyanide radiochromic dye and study all of dosimetric characteristics of the film for possible use in routine dose control in the high-dose range of 1–165 kGy. The dose–response function, the chemical yield of LBB dye, the color stability (before and after irradiation) and the environmental effects (temperature and humidity levels) during irradiation on the dosimeter performance were evaluated.

2. Materials and methods

2.1. Preparation and synthesis of brilliant blue cyanide dye

Ten grams of brilliant blue dye (product of Aldrich), is dissolved in 100 ml of methanol and 10 ml of triethyl amine is added. The

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color fades as the dye base is formed. The solution is filtered from any insoluble inorganic salts present in the dye. Two grams of hydrogen cyanide is distilled into the solution, and then the flask is cooled in a bath of ice and water to a solution temperature of between 5° and 10 °C. This is placed in a sealed bottle and allowed to stand in the dark at room temperature until a small sample diluted and acidified with 5% aqueous acetic acid does not develop a blue color. A number of days may be required for complete reaction. Evaporation of the methanol, triethyl amine, an excess hydrogen cyanide yields solid dye cyanide as a pale blue color (or leuco brilliant blue cyanide dye) (prepared and synthetic method according to international patents no. US4507226 A; patents/US4918317; US4057563A and US4257944, http://www.google.co.in/patents/US4057563).

2.2. Preparation of the film dosimeter

Three different polymeric solutions of 20% PVB (average molecular weight of about 36,000 g/M, product of Wacker Co., USA) were prepared by a solvent mixture of butanol/acetone (1/3 v/v). Suitable amounts of LBB dye were mixed with the polymeric solutions to prepare PVB films incorporating 1, 2, and 3 phr (part per hundred parts of resin) from the LBB dye. All solutions were-well stirred magnetically at room temperature (RT) for a period of 24 h and then coated on transparent polyester sheets (A4 size). The coated layers were dried at RT in a dark place for 72 h, stripped from transparent sheets and cut into 1 × 1 cm^2 before storing at RT for subsequent investigations. The thickness of the obtained dry films was found to be 0.037 ± 0.003 mm (2σ). All solvents were supplied by Sigma–Aldrich Corporation, of analytical grade and were used without any further purification.

2.3. Equipment and irradiation

The LBB-PVB radiochromic films were irradiated at various in radiation doses using a ^{60}Co Gamma Cell GC-220 Excel (manufactured by MDS Nordion, Canada) with absorbed dose rate of 6.7 kGy/h. Gamma irradiation was carried out in the dose range of 0–165 kGy using a specially designed holder made from polymethylmethacrylate (PMMA thickness, 3 mm) to ensure an electronic equilibrium during irradiation. The temperature during irradiation was set with an air chiller system (Turbo-Jet, Kinetics, USA). The dose rate of the gamma source was measured using a ferrous sulfate (Fricke) dosimeter [11]. UV–Vis spectrophotometer (UVIKON 860 spectrophotometer product of Unicam Co. Ltd, England) was used to measure the optical spectra of unirradiated and irradiated films. The film thickness was measured using a Digitrix-Mark II thickness gauge (precision ± 1 μm, 1σ).

3. Results and discussion

3.1. Absorption spectra

To study the effect of γ-radiation on LBB-PVB colorless films, the optical absorption spectra was inspected for films irradiated at a series of absorbed doses (3–165 kGy) in the spectral range of 400–900 nm as shown in Fig. 1 upon gamma irradiation, the colorless film turns blue color and the color intensifies proportionally with the increase of absorbed dose. As shown from Fig. 2, the unirradiated film has no absorption peak in the visible spectrum range, however the irradiated film has a main absorption band at 638 nm, characteristic of the blue color of brilliant blue (ionized form BB+) [5,4]. The intensity of this band increases proportionally with the increase of absorbed dose without any shift in spectral band positions. The main absorbance band at 638 nm

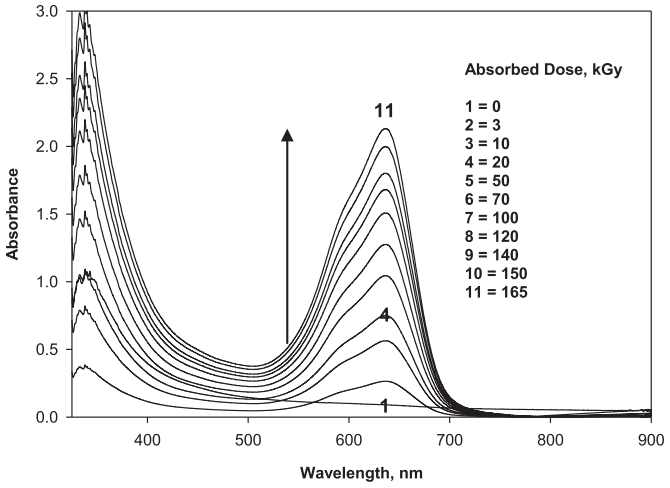

Fig. 1. The absorption spectra of LBB-PVB films (3 phr) unirradiated and irradiated to different absorbed doses.

arises from the excitation of an electron from the non-bonding molecular (NBMO) to the lowest anti-bonding ($n \rightarrow \pi^*$ transition) [12]. This is in agreement with the finding of [13] for copolymer of polyvinyl alcohol containing malachite green cyanide (MGCN) moiety (PVAMG), where it was stated that PVAMG undergoes photoionization upon exposure to UV light producing a main band of MG^+ at 625 nm. The original molecular structure of the colorless LBB is shown in Scheme 1 together with that of BBCN. The mechanism of radiation-induced blue color in LBB dye can be explained by that γ-irradiation induced scission of ≡C–H bond (similar to ≡C–CN). Upon irradiation ≡C–CN bond is broken, and one of the triarylmethane groups becomes the highly colored quinoid chromofore as a part of resonant carbonium cation or other aryl groups (BB^+) [14,15,4].

3.2. Dose response curves

The dose–response functions of LBB-PVB films were investigated at the main peak of 633 nm in the dose range of 3–165 kGy as shown in Fig. 2. The response functions were established in terms

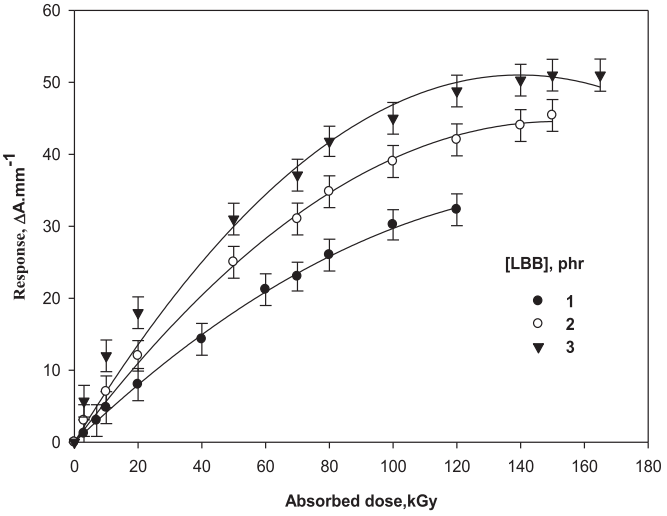

Fig. 2. Dose response of the LBB/PVB films at 638 nm in the full dose range of 3–165 kGy. $\Delta A = (A_i - A_o)/f$, where A_i and A_o are absorbances of the irradiated and unirradiated films, respectively, and f is the film thickness.