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TOWARDS A NEW THICKNESS-INDEPENDENT GAMMA RADIATION PLASTIC FILM DOSIMETER

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ABSTRACT

A 100% national single-use gamma radiation plastic film dosimeter is presented in this work. A new approach for the development of this material allowed a step forward in the performance of poly(methyl metacrylate) films (PMMA) colored with bromothymol blue (BTB) acid-base indicator. We manage to improve dosimeter performance by introducing a gamma radiation insensitive dye to compensate film thickness variations. By doing so, we were able to obtain consistent dose-response correlations within a set of samples presenting 46 to 110 micrometers in thickness. Hence, our PMMA/BTB-P film dosimeter is suitable to measure absorbed dose in the 2-100kGy range even when film thickness undergoes more than 100% of variation. In addition, dose-response data remain practically unaltered for four months after the exposure, when dosimeter films are kept in dark conditions and under refrigeration. The radiation effects on the optical properties were evaluated for Ultraviolet-Visible (UV-Vis) spectrophotometric analysis. Data of characteristic dose-response correlation in terms of changes in the maximum UV-Vis absorption due to radiation, and stability in time are also described. This potential new product is a promising tool for industrial radiation facilities, especially in gamma sterilization of medical supplies.

1. INTRODUCTION

Chemical plastic film dosimeters are inexpensive, lightweight, practical devices to measure absorbed dose in a number of irradiation processes. In general, they consist of a polymer matrix, blends of matrices or even layered matrices dyed with a radiation-sensitive colored substance, which is somehow altered by the absorption of energy from gamma-rays, electron beams, or other types of radiation. Thus, radiation imparts a change in the optical absorbance of the film for specific wavelengths of light. This technology may be used to measure high doses applied in industrial irradiators and accelerators [1-3] or lower doses associated with medical applications [3] or food irradiation processing [4]. Many types of plastic dosimeters have been reported worldwide, as for example, alanine-polyethylene dosimeter system [5], pararosaniline cyanide-polyvinyl butyral dosimeter system [6] or hexa(hydroxyethyl)pararosaniline nitrile and an undisclosed dye dispersed in nylon matrix [7]. In 2008, we reported the first national radiochromic plastic film for gamma dosimetry, made of polymethylmethacrylate (PMMA) as the matrix and 3',3'' – dibromothymol sulfonephthalein, commonly designed as bromothymol blue (BTB), as the radiation-sensitive component [8]. PMMA is a thermoplastic, linear and amorphous polymer. It has excellent transparence and resistance to atmospheric agents. BTB, in its turn, is a commercial acid-base indicator with approximate pH range for color change of 6.0-7.6. This dye is yellow in its acid form and blue in its base form. Thus, PMMA/BTB radiochromic film has a light yellow color, which intensity fades under irradiation, and is efficient in the 5-100kGy dose range.

One of the setbacks of thin radiochromic films is their thickness-dependent response. As radiation promotes physicochemical changes in the sensitive dye, which are proportional to the dose, a lengthier optical pathway will contain a larger number of molecules to be altered. Thus, the same dose will result in different fading on the final light absorption capacity in a given spot of the film. As a result, small variations in thickness within a single film batch bring uncertainties to the measurement. In addition, the film response to the absorbed radiation energy will vary depending on the exact point on the film the light beam might pass through. To minimize such effects, variations under 10% in thickness are recommended [2]. Other alternative is to include corrections for thickness variation by dividing absorbance for film average thickness [2]. A different approach was presented by Miller and Colleagues, in 1988 [6]. These authors suggested the addition of a radiation-insensitive dye, in order to automatically correct thickness variations, as the measurement of the absorbance of the radiation-insensitive dye is solely proportional to the film thickness. The same approach was taken by Rickey and Humpherys [9] to improve the commercial dosimeter FWT-60-00, preventing the users to mechanically measure dosimeter films thickness in order to correct radiation dose determinations, which could be done up to 50kGy for that dosimeter system.

In the present work, we improve our PMMA/BTB film dosimeter, by introducing a background radiation-insensitive dye. Our PMMA/BTB-P is able to endure over 100% thickness variation without significant precision loss. In addition, our dosimeter is able to retain dose information for over seven weeks, if kept under refrigeration in dark conditions. The dose range presented by PMMA/BTB-P is from as low as 2kGy up to 100kGy, which allows a number of applications, including food processing, industrial sterilization or industrial material modifications.

2. MATERIALS AND METHODS

PMMA (UNIGEL S. A., Mn = 100 kg.mol^{-1}) was purified by re-precipitation with hexane from butanone solutions. Butanone (Cinética®, Brazil), hexane and chloroform (Dinâmica®, Brazil) were dried over $NaSO_4$ and distilled before use. BTB was used as received.
UV-Vis Spectrophotometer (Jenway 6400, 320-900nm range), was used to absorbance readouts. Film thickness was taken as the average of three measurements in different areas with a digital paquimeter (Mitutoyo 500-144b, 10 micrometers precision). Films were irradiated in a Co-60 Gamma Cell irradiator, in air, at room temperature, dose rate 5.993 KGy/h.

2.1. Dosimeter Film Preparation

PMMA matrix was dissolved in distilled butanone at room temperature. BTB (0.65% w/w) and the background dye P were added to the solution and the resulting mixture was stirred for 24h. Orange translucid films, with thickness between 46 and 156 micrometers were obtained by casting the solution onto Petri dishes and evaporation in solvent-saturated atmosphere.

2.2. Film Irradiation

Films were irradiated in a Co-60 Gamma Cell irradiator, in air, at room temperature, dose rate 5.993 KGy/h.

For irradiation process, films were cut in 2x1cm pieces and irradiated at 2, 5, 15, 30, 45, 50, 80 and 100kGy. Films were kept under refrigeration (around 8.0 ^{0}C) and protected from light before and up to 4 months after irradiation.

3. RESULTS AND DISCUSSION

Irradiated and unirradiated films presented two main UV-Vis absorbance peeks at 403 and 530 nm, associated with BTB and background dye P, respectively, and two additional minor peaks at 495nm (shoulder peak) and 574nm, also attributed to background dye P. Figure 1 shows typical UV-vis spectra for the PMMA/BTB-P films with average thickness between 70 and 76 micrometers (72 micrometers ± 3%). Note how 403nm band fades in a well-behaved manner with irradiation dose, while 530nm background dye P band remains unchanged.

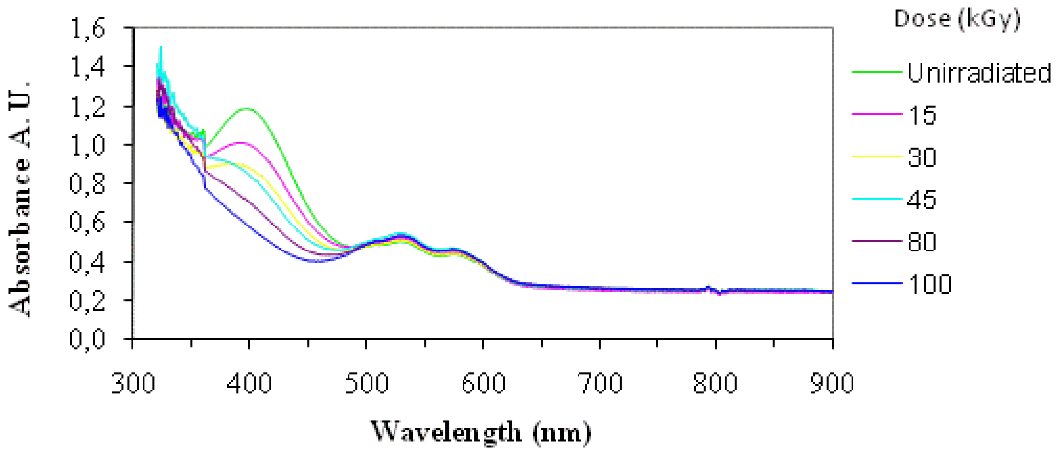

Figure 1. UV-Vis spectra of PMMA films dyed with bromothymol blue and background dye P, with thickness ranging from 70 to 76 micrometers, unirradiated or irradiated at several doses.

Problems with proportionality between dose and 403nm band absorption appears when film thickness presents variations higher than 10%, as can be seen in Figure 2. Films with average thickness ranging from 80 to 100 micrometers (0.094 micrometers ±15%) present different baselines, and absorbance at 403nm with intensities influenced by dose and optical pathway, as expected. Thus, any measurement of absorbance at 403nm has to be made taking film thickness as a parameter.

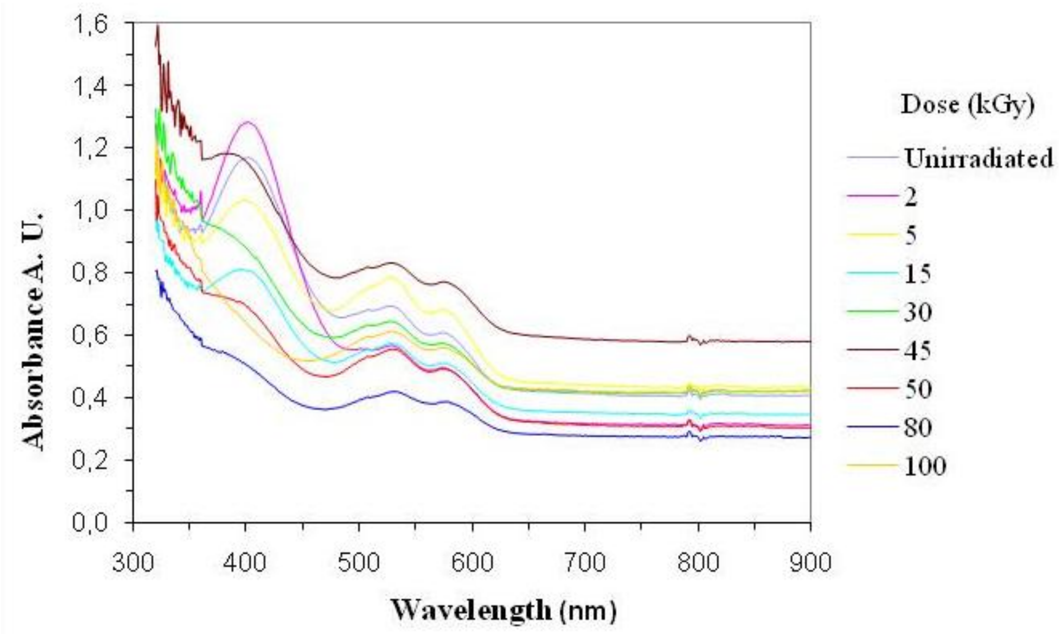

Figure 2. UV-Vis spectra of PMMA films dyed with bromothymol blue and background dye P, with average thickness of 0.094 micrometers±15%, unirradiated or irradiated at several doses.

Correlation between absorbance at 530nm (background dye P peak) and film thickness becomes clear when the two variables are plotted against each other (Figure 3). For films with thickness ranging from 46 to 156 micrometers, irradiated at 2 to 100kGy doses, the following linear correlation equation was calculated for the two variables:

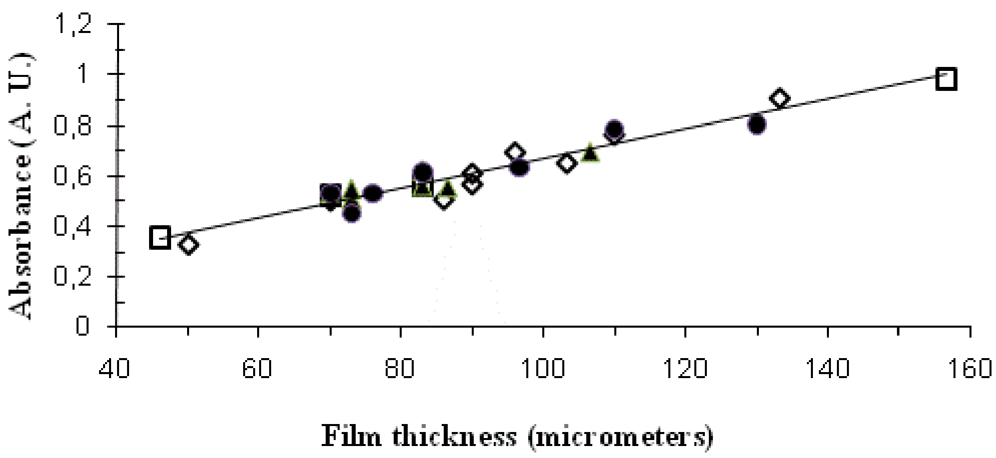

Figure 3. Linear correlation between PMMA/Bromothymol Blue-P film dosimeter absorbance at 530nm and film thickness. Legend: ◊, non-irradiated or 2kGy; □, 5 or 15kGy; ▲, 30, 45 or 50kGy; ●, 80 or 100kGy

$$A_{(530nm)} = (0.057 \times thickness) + 0.10 \quad (1)$$

where,

$A_{(403nm)}$ = Absorbance peak of BTB and correlation coefficient $R^2 = 0.92$.

These results evidenced the good performance of background dye P as a tool for precise estimation of thickness of unirradiated or irradiated films without any tedious mechanical measurement.

In order to determine the best way of correlating background P dye and BTB absorbance behavior with dose and film thickness, we combine available data in many different ways, starting from the Equation (2) suggested by Rickey and Humpherys [9], which shows an ratio of absorbance (RA) between sensitive and insensitive components of the gamma dosimeter.

$$RA = (A_{(403nm)} - R_{(403nm)})/(A_{(530nm)} - R_{(530nm)}) \quad (2)$$

Where:

$A_{(403nm)}$ = Absorbance peak of BTB, $R_{(403nm)}$ = absorbance loss due to reflection at 403nm, $A_{(530nm)}$ = Absorbance peak of background dye P, $R_{(530nm)}$ = absorbance loss due to reflection at 530nm.

$R_{(530nm)}$ can be satisfactory obtained from the linear coefficient of Equation (1), which is 0.10. This value represents the loss of incident light due to non-absorptive phenomena, that are mostly reflections at the surfaces of the film.

Similarly, $R_{(403nm)}$ is obtained from the linear coefficient of Equation (3), obtained from the linear correlation of absorbance at 403nm with thickness. In this case, as absorbance is not dose-independent, thus, the linear coefficient was estimated for non-irradiated, and irradiated at 30 and 100kGy, respectively.

$$A_{(403nm)} = (a \times thickness) + b \quad (3)$$

Dose (kGy)	a	b	R^2
Non-irradiated	0.010	0.377	0.92
30	0.007	0.380	0.98
100	0.003	0.322	0.93

Hence, $R_{(403nm)}$ was estimated to have the average value of the three linear coefficient (b) values, or, 0.36.

Figure 4 shows the linear correlation presented when the absorbance at 403nm of non-irradiated or irradiated PMMA/BTB-P films are plotted against thickness. Note that the slop (a) decreases with the increase of the dose, as expected, since BTB color fades during irradiation.

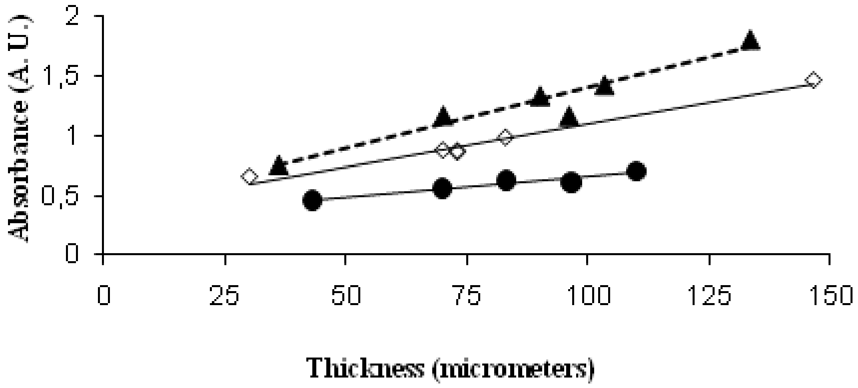

Figure 4. Linear correlation between PMMA/Bromothymol Blue-P film dosimeter absorbance at 403nm and film thickness. ◊, non-irradiated 0; ▲, 30kGy. ; ●, 100kGy

Now, it is possible to compute RA values from Equation (2), and plot these values against dose, to obtain the curve shown in Figure 5, with linear correlation coefficient $R^2 = 0.90$

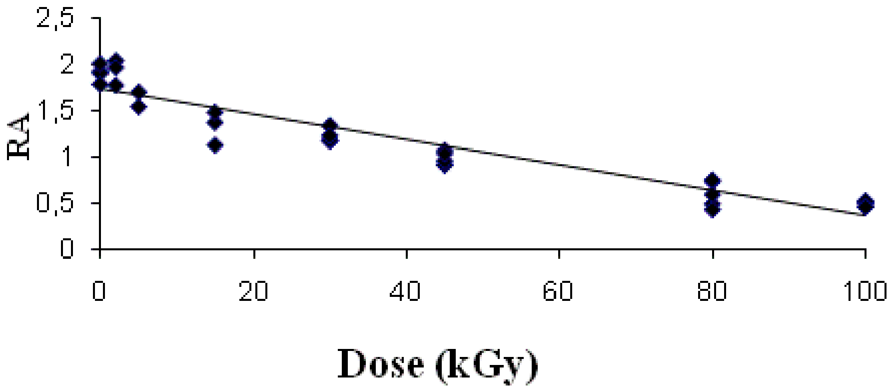

Figure 5. Linear correlation between PMMA/Bromothymol Blue-P film dosimeter Ratio of Absorbance (RA) with dose. Thickness of films ranged from 36 to 156 micrometers.

Another correlation of PMMA/BTB-P dosimeter film UV absorptions and dose was also tested, considering the difference between absorptions at $A_{(403nm)}$ and $A_{(530nm)}$ (Eq. 4), in order to verify if BTB absorption above background dye P absorption would allow sufficient response sensitivity at the same range of thickness.

$$DA = A_{(403nm)} - A_{(530nm)} \quad (4)$$

Using DA calculations, we only could reach linear correlation coefficient similar to RA calculations if film thickness range were kept between 46 and 110 micrometers. Thus DA can also be considered as a good variable to be correlated do dose as it precludes correction for absorbance loss due to reflections.

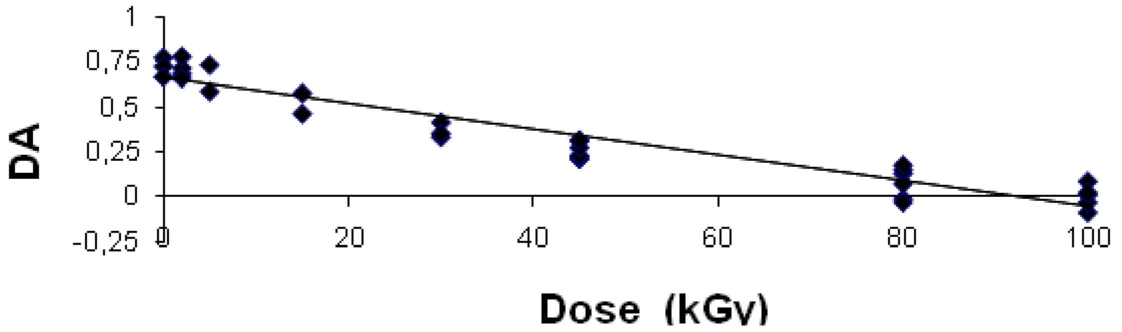

Figure 6. Linear correlation between the difference of absorption at 403 nm (bromothymol blue band) and absorption at 530nm (background dye - P band) (DA = $A_{(403nm)} - A_{(530nm)}$) with dose. Film thickness ranged from 46 to 110 micrometers. Linear correlation coefficient R^2 = 0.91.

Dosimeter film response stability with time was assessed in films kept under refrigeration and protected from light. Under these conditions, absorbance at 403nm unaltered for more than 4 months (Figure 7). Absorbance at 503nm exhibited similar behavior (data not shown).

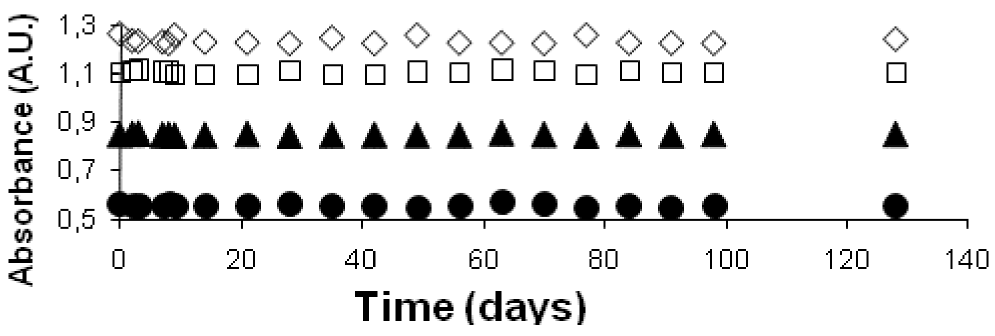

Figure 7. Stability of PMMA/Bromothymol Blue-P film absorbance at 403nm in time. ◊, non-irradiated; □, 5kGy; ▲, 30kGy; ●, 100kGy.

4. CONCLUSIONS

Background dye P allowed good film thickness indirect measurement, as its absorbance peak at 530nm is linearly correlated to film thickness ranging between 36 and 156 micrometers, In addition, film irradiation did not altered this correlation in doses up to 100kGy, showing that background dye P is highly resistant to gamma rays damage. PMMA/BTB-P dosimeter film presented good sensibility and linear response in doses up to 100kGy and is suitable as a thickness-independent gamma radiation plastic film dosimeter when film thickness ranged from 36 to 156 micrometers, when RA is plotted against irradiation dose. Alternatively, DA can be used when film thickness presented a less broader range of 46 – 110 micrometers.

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