UV-sensitive indicators based on bromophenol blue and chloral hydrate dyed poly(vinyl butyral)

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Abstract

UV-sensitive indicators based on dyed poly(vinyl butyral) (PVB) containing acid-sensitive dye (bromophenol blue, BPB) and chloral hydrate have been developed and used successfully to measure the integrated UV irradiance. This flexible film changes colour from blue to green and finally to yellow on exposure to UV irradiation. The radiation-induced change in colour was analysed spectrophotometrically at the absorption band maxima of 421 and 601 nm. The film responds faithfully to UVA, UVB and UVC radiation, showing a maximum sensitivity at 200 nm. Correlations were established between the incident energy of UV radiation and the change in absorbance of BPB/PVB films at 421 and 601 nm using irradiation wavelengths of 248.5, 298.8 and 366 nm. The assessment of the uncertainties, the effect of the irradiation wavelength and chloral hydrate concentration on the performance of BPB/PVB films and the post-irradiation stability in different storage conditions were investigated. © 1997 Elsevier Science S.A.

Keywords: Bromophenol blue; Chloral hydrate; Poly(vinyl butyral); UV-sensitive indicator

1. Introduction

UV radiation is being increasingly employed for beneficial large-scale applications in medicine and industry, e.g. bactericidal action, treatment of skin diseases and curing processes [1–3]. However, UV radiation has adverse effects on human health, specifically for workers professionally exposed to UV radiation and generally for the total population. Therefore the measurement of UV irradiance is not only a periodic necessity, but also ensures that work with UV radiation can be carried out safely.

The biological effects of UV radiation in humans are limited to the skin and the eye because of its low penetrating properties in human tissues [4–7]. The normal responses of the skin to UV radiation may be classified as acute, e.g. erythema, melanin pigmentation and vitamin D production, or chronic, e.g. skin aging and skin cancer [8]. Erythema (the reddening of the skin in sunburn) is a photochemical response of the skin normally resulting from overexposure to wavelengths in the UVC and UVB regions (180–315 nm). Erythema induced by the longer UVB wavelengths (280–315 nm) is more severe and persists for a longer period than

that induced by shorter wavelengths [9]. The UVC region has a high penetrating power, and so causes most of the significant adverse health effects, such as skin aging, skin cancer and eye photokeratitis [6].

Increasing awareness of the causative role of UV radiation in the development of many skin and eye disorders has prompted researchers to develop convenient methods for UV dose assessment. Many substances in the form of dyed and undyed plastic films, which exhibit a measurable change in their properties on exposure to UV radiation, have been investigated in the search for a UV badge dosimeter, e.g. polysulphone films [10,11], diazo films [12,13] and polyvinyl chloride (PVC) films incorporating photosensitizing drugs [14–16]. Recently, we have developed several thin plastic films for UV radiation dosimetry [17–20]. As a continuation of this work, we decided to study several photoactive chemicals incorporated into a polymeric matrix with a view to developing UV dosimeters.

In this work, thin plastic films were prepared by casting poly(vinyl butyral) (PVB) solutions containing bromophenol blue (BPB) and chloral hydrate; these were evaluated as UV-sensitive indicators. The assessment of the uncertainties, the effect of the irradiation wavelength and chloral hydrate concentration on the performance of BPB/PVB films

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and the post-irradiation stability in different storage conditions were investigated.

2. Experimental procedures

2.1. Preparation of stock solution of indicator

The stock solution of the sodium salt of the indicator was prepared by dissolving 0.08 g of BPB indicator (product of CHEMAPOL, Czech Republic) in 1.7 ml of an aqueous solution of NaOH ([NaOH] = 0.1 mol l^{-1}), followed by the addition of ethanol in a 25 ml volumetric flask.

2.2. Preparation of the films

PVB (7.5 g) (Pioloform BM18; product of Wacker Co., USA) was dissolved in 150 cm^3 of n-butanol at about 50 °C. The solution was well stirred at the same temperature for about 24 h; it was then left to cool. The BPB indicator stock solution (1 ml) was added and well stirred at room temperature for about 3 h in order to obtain a uniformly dyed solution. To each 30 cm^3 aliquot of the well-mixed solution, 0.3, 0.5 or 1.0 g of chloral hydrate (CCl$_3$CH(OH)$_2$, 2,2,2-trichloroethan-1,1-diol; product of Merck, Germany) was added, stirred, poured on a 15 cm × 15 cm horizontal glass plate and dried at room temperature for about 48 h. After drying, the films were stripped from the glass plate, cut into 1 cm × 1 cm pieces and stored for different investigations. The thickness of the films obtained was 0.065 ± 0.005 mm (1σ).

2.3. Irradiation procedure and apparatus

For calibration purposes and irradiation of the samples, a standard 180 W mercury lamp (type EMITA VP-60; made in Poland) was used. Monochromatic filters (bandwidth, 5 nm) at 200, 248.5, 298.8 and 366 nm (Oriel Corporation, Stratford, CT, USA) were used to provide the required irradiation wavelength. Intensity meters for short- and long-wave UV (models J-225 and J-221, Ultraviolet Products, Inc., San Gabriel, CA, USA) were used to measure the intensity of UV light from the mercury lamp. The sample was covered by a filter and then fixed at a certain distance within the path of the UV lamp radiation.

A Unicam UV4 spectrophotometer (product of Unicam Co. Ltd., UK) was used to measure the absorption spectra of the unirradiated and irradiated films.

3. Results and discussion

3.1. Radiation-induced absorption spectra

The absorption spectra of BPB/PVB films (containing 33.3 phr[1] chloral hydrate), unirradiated or irradiated to dif-

ferent doses at irradiation wavelengths of 248.5 ± 5, 298.8 ± 5 and 366 ± 5 nm, are shown in Figs. 1–3, respectively. Similar absorption spectra of BPB/PVB films containing 20 and 66.7 phr chloral hydrate at the same irradiation wavelengths were obtained.

On UV irradiation, the blue BPB/PVB film shows a significant colour change to yellow, indicating the transformation of BPB to its acidic form. The absorption spectrum of the unirradiated blue BPB/PVB film (curve 1, Figs. 1–3)
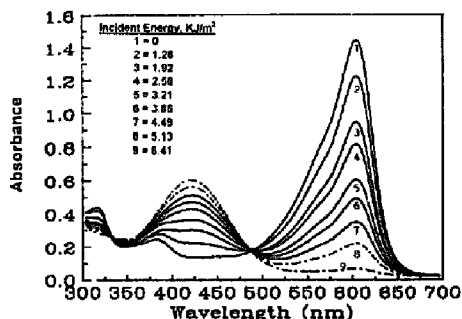

Fig. 1. Variation in the absorption spectrum of BPB/PVB films ([chloral hydrate] = 33.3 phr) with incident UV dose at an irradiation wavelength of 248.5 ± 5 nm.
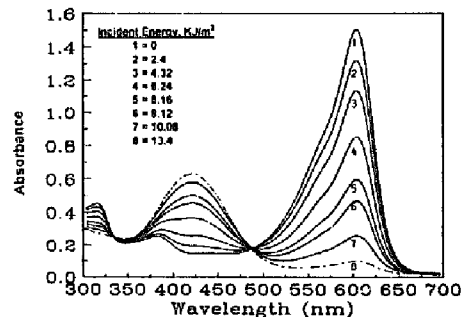

Fig. 2. Variation in the absorption spectrum of BPB/PVB films ([chloral hydrate] = 33.3 phr) with incident UV dose at an irradiation wavelength of 298.8 ± 5 nm.
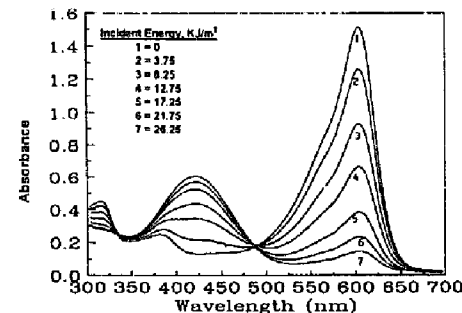

Fig. 3. Variation in the absorption spectrum of BPB/PVB films ([chloral hydrate] = 33.3 phr) with incident UV dose at an irradiation wavelength of 366 ± 5 nm.

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[1] Part per hundred parts by weight of resin.

shows a maximum absorbance at 601 nm. The amplitude of this absorption band at 601 nm (characteristic of the blue colour) decreases gradually with increasing UV radiation dose. At the same time, a yellow colour (represented by an absorption band at 421 nm) begins to develop and increases with increasing incident UV radiation. It can be seen that the radiation-induced change in colour from blue to yellow takes place through an isosbestic point at about 490 nm.

It has been found experimentally that films of PVB alone and films of BPB/PVB without chloral hydrate do not undergo a change in colour or absorbance on UV irradiation within the dose range studied. Therefore it can be concluded that chloral hydrate is responsible for the change in colour of BPB/PVB films. In other words, UV irradiation of BPB/PVB films containing chloral hydrate probably produces H^+, which reduces the pH of the film, leading to a change in colour of the BPB indicator [21].

An examination of the change in absorbance ΔA ($\Delta A = |A_0 - A_i|$, where A_0 and A_i are the absorbances before and after irradiation respectively) as a function of the UV incident energy indicates that the largest changes occur at 421 and 601 nm. Therefore these spectrophotometric wavelengths were used to quantify the UV-induced changes in BPB/PVB films at different irradiation wavelengths.

3.2. Dose and wavelength responses

In order to establish the dose response curves of BPB/PVB films containing different concentrations of chloral hydrate (20, 33.3 and 66.7 phr) to UV radiation, the changes in absorbance (ΔA) at 421 and 601 nm were investigated as a function of the incident UV dose (three films at each dose) for different irradiation wavelengths (248.5 ± 5, 298.8 ± 5 and 366 ± 5 nm). Fig. 4 shows the results obtained for BPB/PVB films containing 33.3 phr chloral hydrate at 248.5, 298.8 and 366 nm. Similar response curves for BPB/PVB films containing 20 and 66.7 phr chloral hydrate at the same irradiation wavelengths were obtained. The results show that the sensitivity of the films to UV radiation decreases with increasing irradiation wavelength. In addition, the response at all three irradiation wavelengths is non-linear (S shape) and tends to saturate at high UV exposure doses. It may be observed from the data illustrated in Fig. 4 that the initial part of the curve depends on the UV irradiation wavelength. The flattening of this portion of the curve decreases with decreasing wavelength. Accordingly, this behaviour may be attributed to the [H⁺] formed on irradiation, as its concentration is expected to increase with decreasing UV irradiation wavelength. Therefore a certain [H⁺] level is required, corresponding to a certain pH value, in order for the indicator BPB to start to change colour. The final non-linear section of the curve may be ascribed to the complete transformation of the indicator from the basic to acidic form.

Statistical analysis of the results obtained for the BPB/PVB film containing 33.3 phr chloral hydrate, irradiated at 298.8 nm, indicates that the radiation-induced colour changes
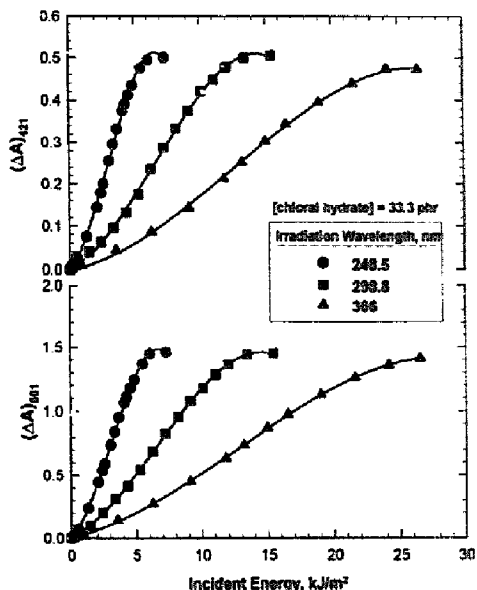

Fig. 4. Variation in ΔA (at 421 and 601 nm) of BPB/PVB films ([chloral hydrate] = 33.3 phr) with UV dose at different irradiation wavelengths.

at 421 and 601 nm can be expressed by the following empirical relationships

$$D = 44.8a - 112a^2 + 150.2a^3 \tag{1}$$

and

$$D = 14b - 10.75b^2 + 5.15b^3 \tag{2}$$

where D is the UV incident energy (kJ m^{-2}), $a = \Delta A_{n,421}(D, \lambda)$ (the change in absorbance measured at 421 nm for a UV exposure energy D (kJ m^{-2}) at an irradiation wavelength λ) and $b = \Delta A_{601}(D, \lambda)$ (the change in absorbance measured at 601 nm for a UV exposure energy D (kJ m^{-2}) at an irradiation wavelength λ).

Eqs. (1) and (2) were derived on the basis of the data obtained at 298.8 nm. As the sensitivity of the film towards UV radiation depends on the irradiation wavelength, it is expected that the constant values of these two equations will vary in magnitude with varying irradiation wavelength. Hence it is necessary to determine the correction factor related to the sensitivity of the BPB/PVB films towards the irradiation wavelength. This correction factor, which is a function of the irradiation wavelength, is referred to as the relative irradiation wavelength response, $K(\lambda)$, normalized to unity at 298.8 nm. Accordingly, Eqs. (1) and (2) can be rewritten in a general form for the assessment of the UV exposure dose at any irradiation wavelength as follows

$$K(\lambda)D = 44.8a - 112a^2 + 150.2a^3 \tag{3}$$

and

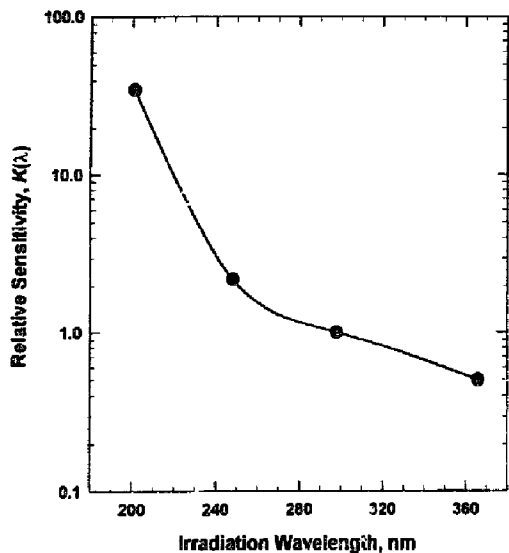$$K(\lambda)D = 14b - 10.75b^2 + 5.15b^3 \tag{4}$$

Fig. 5. Relative spectral sensitivity of BPB/PVB films ([chloral hydrate] = 33.3 phr).

The irradiation wavelength response $K(\lambda)$ of the BPB/PVB film containing 33.3 phr chloral hydrate was studied by applying a dose of 5 kJ m^{-2} to the films at different irradiation wavelengths in the range 200–400 nm (three films at each irradiation wavelength) and observing A_{421} and A_{601}. The relative responses $K(\lambda)$ were evaluated at each irradiation wavelength by employing Eqs. (3) and (4) and setting D equal to 5 kJ m^{-2}. The resulting $K(\lambda)$ values were plotted as a function of the irradiation wavelength (Fig. 5). It can be seen that the sensitivity of the film increases gradually with decreasing irradiation wavelength in the range studied, and reaches a maximum at 200 nm. On the basis of the values obtained for $K(\lambda)$ at different irradiation wavelengths, it was found that the curves given in Fig. 4, which represent the expressions given in Eqs. (3) and (4), agree fairly well with the experimental data points, with most of the points within 3%.

3.3. Effect of chloral hydrate concentration on dose response

The effect of a change in the concentration of chloral hydrate on the dose response of the BPB/PVB films was studied using films containing 20, 33.3 and 66.7 phr of chloral hydrate. Fig. 6 shows the response curves of BPB/PVB films containing different concentrations of chloral hydrate using an irradiation wavelength of 298.8 nm. All curves show the same behaviour, namely they have an S shape and reach saturation at higher doses, but they differ in the initial response value (slope). It can be seen that the suitable range of UV dose depends solely on the concentration of chloral hydrate in the film.

A plot of the maximum range of response, i.e. the dose at which the film changes colour completely from blue to yellow, vs. the concentration of chloral hydrate gives a straight line as illustrated in Fig. 7. It can be seen that the useful range decreases with increasing concentration of chloral hydrate. From this figure, we can predict the suitable concentration of chloral hydrate in the film for any desired range of UV dose
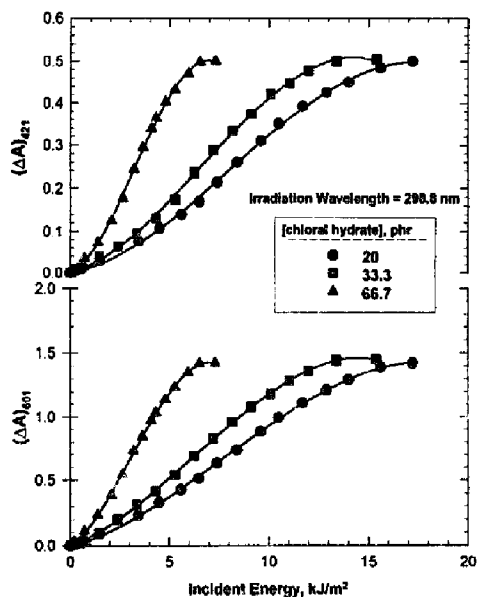

Fig. 6. Variation in ΔA (at 421 and 601 nm) of BPB/PVB films with concentration of chloral hydrate at an irradiation wavelength of 298.8 nm.
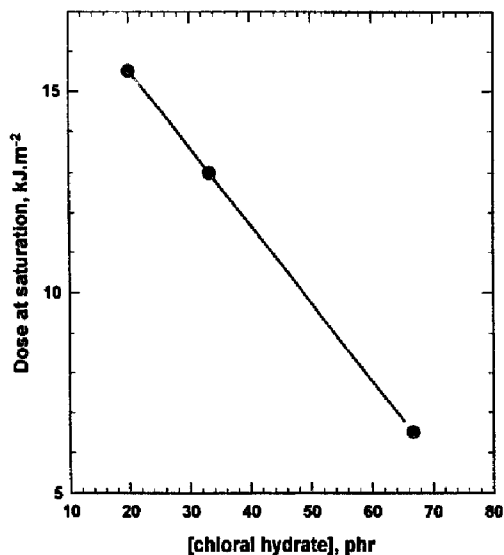

Fig. 7. Dose at saturation as a function of the concentration of chloral hydrate. Irradiation wavelength, 298.8 nm.

and the dose at which the film will change colour from blue to yellow.

3.4. Combined effect of concentration of chloral hydrate and irradiation wavelength

From the above results on the influence of the chloral hydrate concentration and irradiation wavelength on the dose response of the film, it was found that the dose response depends on both of these factors. Therefore the two parameters must be considered together. The study of the combined effect on the dose response of BPB/PVB films was performed using different films containing 20, 33.3 and 66.7 phr of chloral hydrate and different irradiation wavelengths of 248.5, 298.8 and 366 nm. This effect is presented in a three-dimensional (3-D) diagram (3-D plot) showing the variation of the response (ΔA_{421} or ΔA_{601} at a dose $D = 3$ kJ m^{-2}) as a function of the concentration of chloral hydrate as well as the irradiation wavelength (Fig. 8). From this diagram, it can be seen that the response points, represented as a surface, continuously increase as the concentration of chloral hydrate increases and decrease with increasing irradiation wavelength.

3.5. Assessment of uncertainty

To be meaningful, a measurement of the UV incident energy must be accompanied by an estimate of the uncertainty in the measured value. Factors contributing to the total uncertainty may include the film response, measurement equipment, irradiation time and intensity measurement. The type A uncertainty (at one standard deviation, i.e. 1σ) arising during calibration of the BPB/PVB film ([chloral hydrate] = 33.3 phr) using an irradiation wavelength of 298.8 nm at each measurement wavelength (i.e. 421 and 601 nm) was calculated using the following equation [22]

$$CV\% = \sqrt{\frac{\sum_i (n_i - 1)(\sigma_{i-1}/\overline{X}_i)^2}{\sum_i (n_i - 1)}} \times 100 \quad (5)$$

where CV% is the percentage of the coefficient of variation, σ_{i-1} is the sample standard deviation of a spectrophotometric quantity for the ith set of data, $(n_i - 1)$ is the number of degrees of freedom for the ith set of data, $\overline{X}_i$ is the average value of a spectrophotometric quantity (e.g. ΔA) for the ith set of data and n_i is the number of replicate measurements for the ith set of data.

Three replicate measurements of absorbance were made at each value of the incident energy and 15 incident energies were applied in the range 0.5–15 kJ m^{-2}, i.e. 45 replicates were performed. The type A uncertainties (1σ) associated with the measurement of the dose responses at 421 and 601 nm are 2.5% and 2% respectively.

The reproducibility of the spectrophotometer (UV4) used in the measurements was determined by reading the absorb-
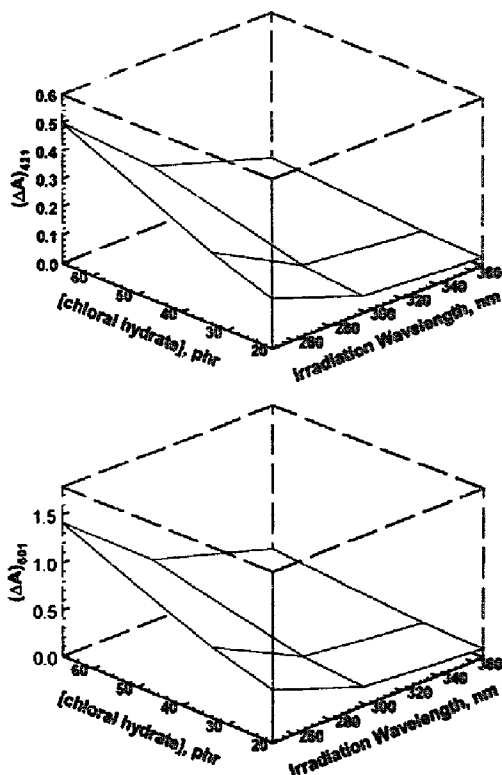

Fig. 8. Variation of the response as a function of the concentration of chloral hydrate and irradiation wavelength.

ance of an irradiated film (100 readings per film) at 421 and 601 nm. The coefficient of variation (1σ) at the two wavelengths is 0.4%. On the other hand, the standard errors determined by the Egyptian Bureau of Standards of the timer and intensity meter (1σ) are 0.2% and 1% respectively.

The combined uncertainty (U_c) is calculated by combining all the components in quadrature at one standard deviation (1σ) as follows

$$U_c \text{ (at 421 nm)} = \sqrt{(2.4)^2 + (0.4)^2 + (0.2)^2 + (1)^2} = 2.6\% \quad (6)$$

and

$$U_c \text{ (at 601 nm)} = \sqrt{(2)^2 + (0.4)^2 + (0.2)^2 + (1)^2} = 2.3\% \quad (7)$$

The combined uncertainty (at two standard deviations, i.e. 2σ, approximately equal to a 95% confidence level) is found by multiplication of U_c (at 1σ) by two. Hence the combined uncertainty using the measurement wavelength of 421 nm is 5.2% and that using the measurement wavelength of 601 nm is 4.6%. In other words, the error associated with the determination of an incident energy D (at a confidence level of 95%) using the BPB/PVB films under our experimental conditions does not exceed 5%.

The standard deviation dD of the estimated exposure dose D for a change in absorbance at 421 or 601 nm is given by differentiating Eqs. (3) and (4) as follows

$$dD = \frac{1}{K(\lambda)} \frac{\delta D}{\delta a} da \qquad (8)$$

and

$$dD = \frac{1}{K(\lambda)} \frac{\delta D}{\delta b} db \qquad (9)$$

where da is the standard deviation of a and equals $0.052a$ and db is the standard deviation of b and equals $0.046b$.

As an example, it is assumed that a BPB/PVB film containing 33.3 phr chloral hydrate is exposed to a dose D at an irradiation wavelength of 248.5 nm inducing a change in absorbance $\Delta A_{601} = 0.8$; the value of the dose D can be calculated using Eq. (4) to be 3.16 kJ m^{-2}. The standard deviation of dD in turn can be calculated using Eq. (9) to be 0.079. Accordingly, the estimated dose inducing a change in absorbance of the BPB/PVB film of 0.8 at 601 nm is 3.16 ± 0.079. The standard error of the dose determination in this example at a confidence level of 95% is $\pm 2.5\%$.

3.6. Post-irradiation stability

Two irradiated BPB/PVB films with [chloral hydrate] = 33.3 phr and an exposure dose of 8 kJ m^{-2} at 298.8 nm were stored at room temperature immediately after irradiation, one in the dark and the other in indirect daylight.

Fig. 9. Post-irradiation stability of BPB/PVB films stored in the dark and indirect daylight. Exposure dose of 8 kJ m^{-2} at 298.8 nm.

The films were measured spectrophotometrically at 421 and 601 nm at different intervals of time during the post-irradiation storage period of 35 days. Fig. 9 shows the change in ΔA_{421} and ΔA_{601} relative to the value at zero time as a function of the storage time. It can be seen that ΔA_{601} of the film stored in light decreases sharply to about 90% during the first few hours after irradiation, and then decreases gradually during the first 12 days to about 85% before reaching stability; ΔA_{421} of the same film increases gradually by about 5% during the first 12 days of storage and is then stable up to the end of the storage period. The film stored in the dark shows a change in ΔA_{601} of about -3% and in ΔA_{421} of about $+4\%$ over the 35 day storage period.

4. Conclusions

BPB/PVB films in the presence of chloral hydrate as the photosensitive element were investigated for monitoring UV radiation. The films change colour from blue to green and finally to yellow on irradiation. The dose at which the film changes colour, i.e. the useful range, depends on the concentration of chloral hydrate and the irradiation wavelength. The sensitivity of the film towards the irradiation wavelength increases exponentially with decreasing irradiation wavelength. The standard error in estimating the energy incident on the film dosimeter at 421 and 601 nm does not exceed 5%. The film dosimeters show good post-irradiation stability when stored in the dark and measured at 421 or 601 nm or when stored in indirect daylight and measured only at 421 nm. This dosimeter, if suitably filtered, may provide the basis for a UV badge with many medical and industrial applications in the UVA, UVB and UVC regions of the spectrum.

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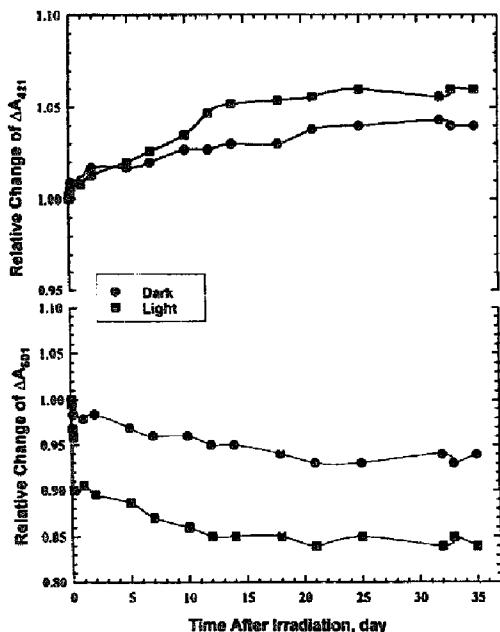[13] J.B. Ali, R.E. Jackobson, J. Photogr. Sci. 28 (1980) 172–176.

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