

**Spectral response of solvent-cast polyvinyl chloride (PVC) thin
film used as a long-term UV dosimeter.**

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Abstract

The spectral response of solvent-cast polyvinyl chloride (PVC) thin film suitable for use as a long-term UV dosimeter has been determined by measuring the UV induced change in the 1064 cm^{-1} peak intensity of the PVC's infrared (IR) spectra as a function of the wavelength of the incident radiation. Measurements using cut-off filters, narrow band-pass filters and monochromatic radiation showed that the $16\text{ }\mu\text{m}$ PVC film responds mainly to the UVB band. The maximum response was at 290 nm and decreasing exponentially with wavelength up to about 340 nm independent of temperature and exposure dose. The most suitable concentration (W/V%) of PVC/Tetrahydrofuran solution was found to be 10% and the best thickness for the dosimeter was determined as $16\text{ }\mu\text{m}$.

Keywords: Dosimetry; UV; Erythema; Exposure

1. Introduction

The dual effects of exposure to solar ultraviolet (UV) radiation (280– 400 nm) on human health have long been an important subject of research. Moderate exposures to UV radiation are essential for cutaneous synthesis of vitamin D [1,2] which plays a key role in skeletal health [3-5]. The daily exposure time required for an exposure dose that produces sufficient vitamin D levels, defined as a blood level of 25-hydroxyvitamin D of at least 20 ng/ml (50 nmol/litre) [5], varies mainly depending on the environmental conditions and individual genetic factors [5-7]. Exceeding the doses required for vitamin D production may cause sunburn, which takes hours to days to develop following the exposure [1,8]. Furthermore, and more dangerous, large doses accumulated through prolonged exposures or excess of intermittent exposures have been shown to cause harmful effects including photoageing, immunosuppression, eye damage, DNA mutations and skin cancers [1,8-13] which may develop after years to decades of exposure to UV [1]. The assessment of safe personal UV exposure limits is, therefore, a vital requirement, as is the development of personal UV exposure measuring devices that monitor short and prolonged exposures [14].

Three main categories of personal UV dosimeters are used to quantify personal UV exposure. The first of these is the electronic UV dosimeters. They are miniature electronic devices with a spectral response that matches the erythral action spectrum defined by the International Commission on Illumination (CIE) [15], and have been successfully used to record the cumulative exposure at specific anatomical sites within predefined intervals [16,17]. Although electronic dosimeters are reusable, accurate and suitable for prolonged exposures, the cost and availability may restrict their use for simultaneous large scale anatomical measurements. Secondly, the biological dosimeters, reviewed in detail by Berces, et al. [18] and Yagura, et al. [19], have also been successfully applied for assessing the UV exposure of individuals. Rettberg and Cockell [20] state that the DLR-biofilm can measure up to two

months of continuous exposure to solar UV radiation. However, the dosimeter preparation and readout process require specialised expertise and equipment. The third category is the chemical UV dosimeters which have been intensively employed in measuring the anatomical distribution of personal UV exposures during normal daily activities [21-27]. The most widely used chemical UV dosimeters are polysulphone and polyphenylene oxide, but they are limited to measuring solar UV over periods of approximately half a day and five days of exposure at subtropical latitudes, respectively [28-30]. For longer periods, the dosimeters have to be frequently replaced, increasing not only the cost and effort, but also the margin of error.

Estimating prolonged solar UV exposure, which is a risk factor of skin cancers, using existing chemical UV dosimeters is done by circulating (multiplying) the dose measured in a short period over a longer period. Lengthening the measuring period will take into account the daily variations of solar spectrum and hence improve the accuracy and reliability of evaluated doses.

Previous research has demonstrated the proportionality between the UV induced absorbance decrease in the 1064 cm^{-1} peak intensity of unstabilised solvent-cast polyvinyl chloride (PVC) thin film and the absorbed UV exposure [31]. The measured dose-response curves indicate that the PVC can measure about three weeks of continuous exposure to solar UV radiation which is a great advantage compared to polysulphone and polyphenylene oxide dosimeters. However, the reliable use of any UV dosimeter requires the determination of its spectral response (wavelength sensitivity) to identify the waveband of UV radiation that the dosimeter can measure.

The pure (virgin) PVC is transparent to ambient UV radiation (280-400 nm) and any absorption in this region is dependent upon the processing conditions or added ingredients. Therefore, the spectral response of PVC varies according to the type of photodegradation process, which in turn depends on the nature and concentration of existing impurities, and the criterion employed to evaluate this degradation. Furthermore, studies on the widely used polysulphone UV dosimeter have shown the dependency of the spectral response and dose-response curves on the dosimeter film thickness [32,33].

Change in the carbonyl absorbance at 1730 cm^{-1} of melt-pressed $160\text{ }\mu\text{m}$ PVC films as a function of the wavelength of irradiation has been reported [34] and the wavelength region 355-385 nm was identified as the most active region in inducing photo-oxidation within the polymer. Different findings were reported by Hirt et al. [35] who found that 320 nm was the wavelength with the greatest effect on photodegradation of PVC as detected by means of the change in UV absorbance spectra, but neither the film preparation method nor its thickness were given. Reinisch et al. [36] also used the UV absorbance spectra to measure UV induced changes in solvent-cast PVC films of thickness 14-30 μm irradiated in a vacuum to investigate the potential of PVC for use in extraterrestrial space. The resulting response was to wavelengths between 238 and 332 nm with a maximum response at 254 nm. Andrady et al. [37] used the yellowness index (YI) as a measure of photodegradation of UV irradiated PVC thin films and found that the maximum change in YI for extruded rigid 1 mm thick PVC films is due to wavelengths between 300 and 320 nm while, under similar exposure conditions, the solvent-cast 5 μm thick films did not show any change in YI.

This paper reports on the determination of the spectral response of solvent-cast PVC thin film by measuring the change in the 1064 cm^{-1} peak intensity as a function of the wavelength of

incident radiation. The best concentration of PVC/Tetrahydrofuran solution employed to prepare PVC thin films for use as a UV dosimeter was determined as well as the most suitable film thickness. Three different techniques were employed in this research to investigate the PVC spectral response. These were: cut-off filters with a UV fluorescent lamp as a source of radiation, narrow band-pass filters with a solar simulator and an irradiation monochromator.

2. Materials and Methods

2.1 Mixing Ratio

Different concentrations (W/V%) of PVC solution were prepared by dissolving between 2 and 15 grams of PVC powder (Aldrich Chemical Company, Inc., catalogue number 34675-6) in 100 ml of tetrahydrofuran (THF) solvent under vigorous stirring at 25 ± 2 °C. Each solution was cast in a thin layer over a highly polished glass plate using a stainless steel casting blade adjusted to be 100 μm above the plate. The solvent was allowed to evaporate at 25 ± 2 °C for at least two hours and the dry thin film was then removed. The thickness was measured at five different sites on the film using a manual thickness gauge (Logtech, UK) which was previously calibrated against feeler gauge leaves; its accuracy was found to be within $\pm 2\%$ of the measured thickness. Five PVC dosimeters were then fabricated from each film by cutting the PVC film into $2 \text{ cm} \times 2 \text{ cm}$ pieces, each attached by a tape to cover the $1.8 \text{ cm} \times 1.2 \text{ cm}$ aperture of a $3 \text{ cm} \times 3 \text{ cm}$ plastic holder. The infrared (IR) absorption spectra of the dosimeters within the range $400 - 4000 \text{ cm}^{-1}$ (IR region) were recorded using a Fourier Transform Infrared (FTIR) spectrophotometer (IRPrestige-21/FTIR-8400S, Shimadzu Co., Kyoto) at a resolution of 4 cm^{-1} in the absorption mode and corrected baseline.

2.2 Film Thickness

PVC thin films of different thicknesses were prepared, as described above, using 10% PVC/THF solution and changing the distance between the casting blade and the glass plate from 60 μm to 480 μm in 30 μm steps. After measuring their thicknesses, the films were utilised to fabricate PVC dosimeters whose IR absorption spectra were measured using the FTIR spectrophotometer. The dosimeters' quality was evaluated and four thicknesses were selected to examine the relationship between the PVC's sensitivity to UV radiation and film thickness. Three dosimeters of each of the four thicknesses were irradiated (after measuring their pre exposure IR absorption spectra) at 28 ± 2 °C for about 650 hours ($\sim 20 \text{ MJ/m}^2$ of UV) using a UV fluorescent lamp (model Philips TL40/12, supplier Lawrence and Hansen, Toowoomba). The distance between the lamp and the dosimeters was adjusted to be 7 cm and the spectral irradiance of the lamp was measured regularly with a calibrated scanning spectroradiometer (model DMc150, Bentham Instruments Ltd, Reading UK). The average integrated UV irradiance, average deviation of the lamp output and irradiance uniformity at the dosimeters' site were 9.1 W/m^2 , 3% and 3% respectively. The dosimeters were removed from exposure for measurement of the IR absorption spectra at various exposure time intervals. The decrease in the absorption intensity of the dosimeters at the 1064 cm^{-1} peak after a period t of exposure $(\Delta A)_t$ was calculated by:

$$(\Delta A)_t = A^{initial} - A_t^{final} \quad (1)$$

where $A^{initial}$ is the initial absorbance of the dosimeters at 1064 cm^{-1} and A_t^{final} is the absorbance after a period t of exposure. The dose response curves were constructed by relating the change in the absorbance to the corresponding unweighted UV radiant exposure (H) over 280-400 nm which was calculated from the relation:

$$H = \left(\sum_{\lambda=280}^{\lambda=400} E(\lambda) \times \Delta\lambda \right) \times t \quad (2)$$

where $E(\lambda)$ is the spectral irradiance, $\Delta\lambda$ is the wavelength increment and t is the exposure time. The dose response curves were then compared to determine the most suitable thickness for the PVC dosimeter.

2.3 Determination of the spectral response

2.3.1 Cut-off filter technique

A set of nine glass cut-off filters (Schott AG, Mainz, Germany) for the wavelength range 285-377 nm (10% transmission) was used to investigate the relative ability of the UV sub-bands to induce changes in 16 μm thick PVC dosimeters. Figure 1 shows the transmittance spectra $T(\lambda)$ of the nine filters measured using a spectrophotometer (model UV-1601, Shimadzu Co., Kyoto, Japan). Nine pairs of PVC dosimeters were simultaneously exposed behind the filters to the Philips UV fluorescent lamp for 135 hours at 28 ± 2 °C along with an unfiltered pair, a pair covered with a UV cut-off filter (Llumar, Scotchline, Australia) to block wavelengths below 400 nm from reaching the dosimeters and a pair covered with an opaque cardboard that obscured the dosimeters from any radiation. The spectral irradiance of the source $E(\lambda)$ over the UV band (280 nm-400 nm) at the dosimeters exposure plane was periodically measured with the Bentham spectroradiometer; and the spectral irradiance behind each filter $E_n(\lambda)$ was then calculated by:

$$E_n(\lambda) = E(\lambda)T_n(\lambda) \quad (3)$$

where $T_n(\lambda)$ is the spectral transmission of the n^{th} filter. The IR absorbance of the dosimeters was measured before the exposure A_n^{initial} and immediately after the exposure A_n^{final} ; and then the absorbance change $(\Delta A)_n$ was calculated by:

$$(\Delta A)_n = A_n^{\text{initial}} - A_n^{\text{final}} \quad (4)$$

2.3.2 Narrow band-pass filter technique

Four narrow band-pass filters (model 03 FIU, Melles Griot Optics) with wavelengths of maximum transmittance 300 nm, 324 nm, 343 nm and 361 nm as measured using the Shimadzu spectrophotometer were used to irradiate four PVC dosimeters using different narrow UV sub bands. The irradiation source was a 300 W UV solar simulator (19160-1000, Newport Co., California, USA) combined with an exposure controller (model 68945, Newport Co., California, USA) to minimise variations in the lamp output. The dosimeters were placed at 1 cm behind the filters and continuously exposed at 32 ± 2 °C for 31 hours to the collimated UV beam. The UV spectral irradiance at the dosimeters' site $E(\lambda)$ was measured by the Bentham spectroradiometer and then utilised with the transmission spectra of the filters to calculate the spectral irradiance behind each filter. Pre and post exposure FTIR absorbance was measured to compare the resulting change with the received exposure.

2.3.3 Monochromatic radiation

Six PVC dosimeters were sequentially exposed to a fixed dose of 0.5 MJ/m^2 at 25 ± 2 °C using different UV wavelengths obtained by setting a 1600 W irradiation monochromator (model 66870, Oriel Instruments, USA) at the selected wavelength from 290 to 340 nm in 10 nm increments. For the maximum output irradiance, the monochromator input and output slits were set to a width of 4.5 mm and 4 mm respectively and the resulting irradiances at the dosimeters' surface (measured by the Bentham spectroradiometer) were very narrow wavebands of nearly the same full width at the half maximum (FWHM) (5.6 ± 0.1 nm) (Figure 2). The integrated irradiance of the selected wavelengths was between 14.0 and 21.5 W/m^2 and the exposure time ranged between 6.5 and 9.9 hours. The exposure related IR absorbance change of the dosimeters was measured with wavelength and the wavelength responsible for the maximum change was determined (290 nm) and used to normalise the

results to unity. The exposure was repeated for a dose of 0.1 MJ/m^2 at $25 \pm 2 \text{ }^\circ\text{C}$ and $40 \pm 2 \text{ }^\circ\text{C}$ to investigate the dependency of the spectral response on exposure dose and temperature. The exposure time in this case ranged between about 1.3 and 2 hours.

3. Results

3.1 *Mixing Ratio*

PVC films prepared via solutions of concentrations less than 7% tended to wrinkle and tear; while solutions of concentrations greater than 12% were difficult to spread on the glass plate and resulted in brittle films that showed a pronounced surface unevenness. Smooth films with an acceptable quality could be cast using concentrations between 7% and 12% with a dissolution time up to 7 hours at $25 \pm 2 \text{ }^\circ\text{C}$. However, for a fixed casting blade height, the greater the concentration the thicker the resulting film. Comparison of the PVC powder dissolving time and the physical properties of the films showed that a 10% concentration is the most suitable concentration for preparing PVC dosimeters.

3.2 *Film Thickness*

PVC films prepared from a 10% PVC/Tetrahydrofuran solution were of thicknesses between $4 \text{ }\mu\text{m}$ and $58 \text{ }\mu\text{m}$. The relationship between the dosimeters' initial absorbance (A_i) at 1064 cm^{-1} and their thickness (l) (Figure 3) was:

$$A_i = 0.0155 \times l \quad (5)$$

This is in agreement with the Beer-Lambert law. The error bars shown on the curve are the standard error in the measured thickness and IR absorbance on five PVC dosimeters fabricated from each film. Some of the error bars are shorter than the dimensions of the associated averaged point and do not appear clearly on the graph. Thicknesses between 8.4

μm and $20\ \mu\text{m}$ were of a better quality in terms of the absence of surface blemishes and defects and hence they were employed to investigate the dose response of PVC as a function of film thickness.

Figure 4 shows the dose response curves of PVC dosimeters fabricated from films of thicknesses $8.4\ \mu\text{m}$, $14\ \mu\text{m}$, $16\ \mu\text{m}$ and $20\ \mu\text{m}$. The x error bars represent the standard error in the measured absorbance of the three irradiated dosimeters of each thickness while the y error bars represent a variation of 3% in the lamp output. The short error bars reflect the high reproducibility of the dosimeters. It can be noticed that the curves for the thicker films, which have higher initial absorbance, have a higher change to the same exposure as well as a higher gradient. However, the curve linearity decreases with increasing thickness. The $16\ \mu\text{m}$ thickness seems to be the best compromise between physical quality, sensitivity to UV and linearity of dose response curve. Consequently, the $16\ \mu\text{m}$ thick PVC film cast using 10% (W/V %) concentration and obtained by altering the plate height to $240\ \mu\text{m}$ was determined as the most suitable thickness for the PVC dosimeters.

3.3 Determination of the spectral response

3.3.1 Cut-off filter technique

After 135 hrs of exposure, the cumulative UV dose received by the dosimeters ranged between $4.9\ \text{MJ/m}^2$ for the unfiltered pair and $12.6\ \text{KJ/m}^2$ for the pair exposed behind filter number 9. All the dosimeters underwent a measureable change at the $1064\ \text{cm}^{-1}$ peak. The largest change was for the unfiltered pair (16%), while those pairs exposed behind filters 5–9 experienced approximately the same change as the pairs covered with the cardboard and the UV cut-off filter (3.2%), indicating that this change may be due only to thermal degradation and that wavelengths longer than about $345\ \text{nm}$ do not contribute to the photo degradation

process. Each pair (n) of dosimeters was subjected to an integrated irradiance of ΔE more than the next pair ($n+1$), where:

$$\begin{aligned}\Delta E &= \sum [E_n(\lambda) - E_{n+1}(\lambda)] \times \Delta\lambda \\ &= \sum E(\lambda) [T_n(\lambda) - T_{n+1}(\lambda)] \times \Delta\lambda\end{aligned}\quad (6)$$

which leads to a difference (δA) between the absorbance change of the two pairs, where:

$$\delta A = [(\Delta A)_n - (\Delta A)_{n+1}] \quad (7)$$

The overlap between spectral bands encumbers the correlation between the spectral irradiance and the difference in the absorbance change. As a result, just three bands that had minimum overlap and covered the active part of the UV region were chosen for comparison (Figure 5). Assuming the validity of the reciprocity law and the linearity between the exposure dose and absorbance change, the difference in the absorbance change per exposure dose unit $(\delta A)_u$ was calculated for the consecutive pairs by:

$$(\delta A)_u = \frac{\delta A}{\Delta E \times t} \quad (8)$$

where t is the total exposure time.

$(\delta A)_u$ is then normalised to obtain the relative sensitivity of each of the spectral bands. Figure 6 presents the three bands, using the FWHM, and their relative ability in inducing change in the PVC dosimeter. The maximum sensitivity was for the shorter wavelengths investigated to approximately 312 nm.

3.3.2 Narrow band-pass filter technique

Figure 7 shows the calculated spectral irradiance behind the four narrow band-pass filters. After 31 hours of exposure, the four dosimeters exposed behind the filters with wavelengths of maximum transmittance 300 nm, 324 nm, 343 nm and 361 nm received about 2.1 KJ/m², 138.2 KJ/m², 2.1 MJ/m² and 1.2 MJ/m², respectively. The absorbance change per exposure

dose unit for each dosimeter was calculated, normalised and presented in Figure 6 which shows that the maximum effectiveness in inducing change within the PVC dosimeter was again at the shorter wavelengths.

3.3.3 Monochromatic radiation

The PVC spectral response measured using the irradiation monochromator by exposing the dosimeters to 0.5 MJ/m^2 at $25 \pm 2 \text{ }^\circ\text{C}$, 0.1 MJ/m^2 at $25 \pm 2 \text{ }^\circ\text{C}$ and 0.1 MJ/m^2 at $40 \pm 2 \text{ }^\circ\text{C}$ is presented in Figure 8. The error bars indicate the 5.6 nm FWHM of each exposure waveband. The maximum response of the dosimeter occurred at 290 nm and decreased with increasing wavelength up to 340 nm independently of temperature and exposure dose. The averaged spectral response measured by the irradiation monochromator is shown in Figure 6.

4. Discussion and Conclusion

This study found that concentrations of between 7 and 12% of PVC/Tetrahydrofuran solution and thicknesses between 9 and 20 μm are suitable for preparing good quality PVC thin films for use as a UV dosimeter. This evidence was used to prepare a 16 μm PVC film from 10% solution which employed in this study for measuring the PVC spectral response.

Spectral response curves of PVC measured using cut-off filters, narrow band-pass filters and an irradiation monochromator showed close qualitative agreement. The greatest response of solvent-cast 16 μm PVC thin films based on the UV induced change in the 1064 cm^{-1} peak intensity was in the UVB band and decreasing with wavelength up to about 340 nm in the UVA. The cut-off filter technique shows no response of PVC to wavelengths longer than 345 nm. The maximum response was due to wavelengths between 292 and 312 nm and dropped to about one half and one quarter of this value for the 315-332 nm and 324-346 nm bands respectively. Almost the same band is dominant in the spectral curve determined by narrow band-pass filters (Figure 6), where longer bands showed less response than that measured by

cut-off filters. This might be because the bands with the cut-off filters are wider and interfere with each other with more chance for a synergistic effect. Although filter techniques provide reliable estimation for band effectiveness, individual wavelengths from the irradiation monochromator produce a more precise spectral response curve. The maximum in the response curve achieved using monochromatic radiation was at 290 nm and the response is exponentially decreasing with wavelength independently of temperature and exposure dose. Figure 9 compares the PVC spectral response curve with the polysulphone [38], polyphenylene oxide [39] spectral response curves and the erythemal action spectrum [15]. It can be noticed that none of the three spectral responses match exactly the erythemal response. The PVC response coincides with the erythemal response at 304 nm. The difference between the two curves is less than 37% at the shorter wavelengths while at longer wavelengths the PVC response is considerably higher than that of the erythemal response. However, in a similar manner as the polysulphone and polyphenylene oxide are used for measuring erythemal exposures provided that the dosimeters are calibrated for the season and conditions of the field measurements, it is expected that the PVC dosimeter can be calibrated for the appropriate seasonal and field conditions to measure long term erythemal UV exposures.

5. References

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6. Figures

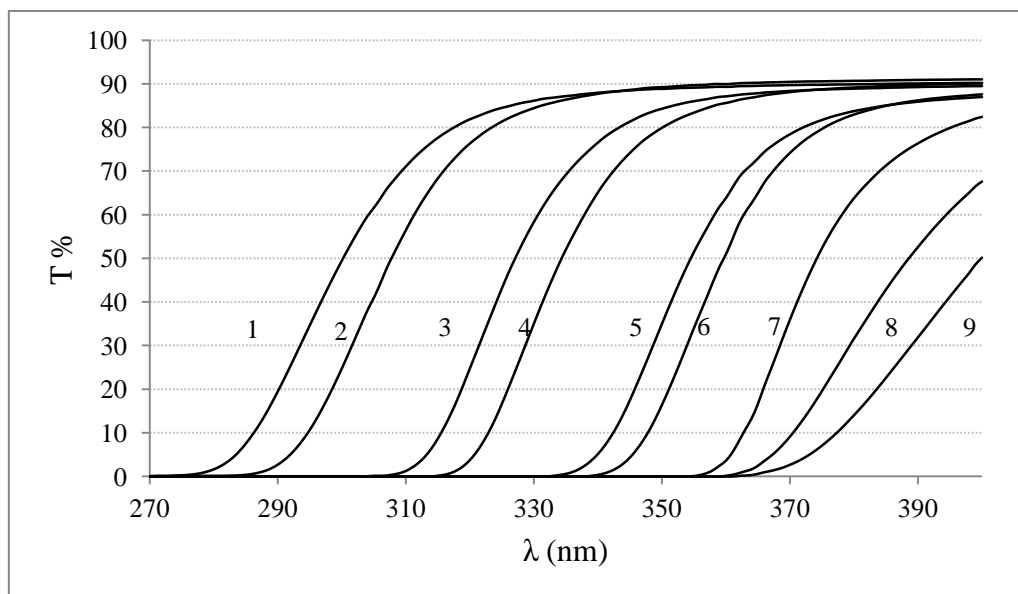


Figure 1: Transmittance spectra of the nine cut-off filters.

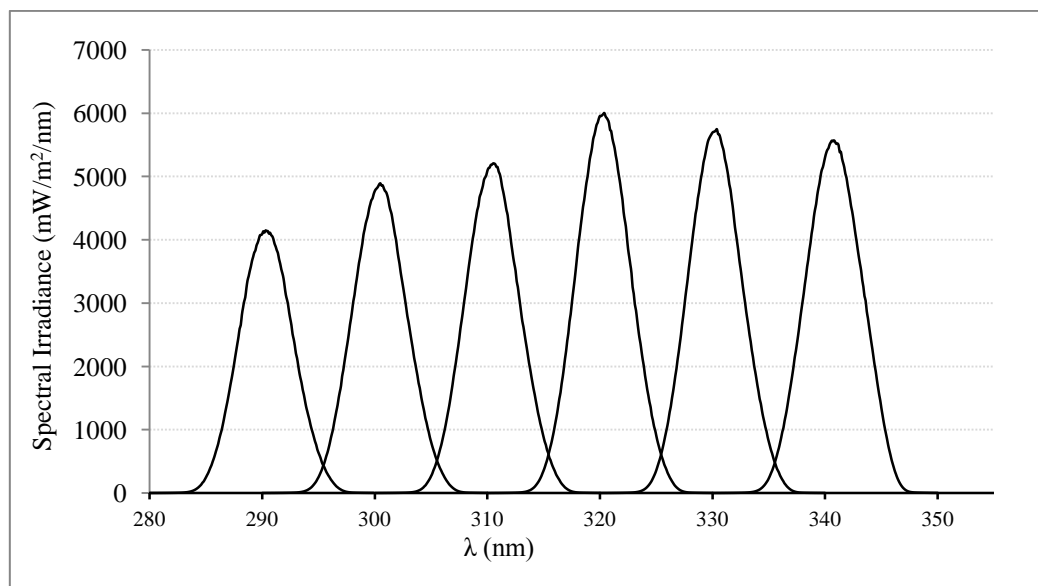


Figure 2: Spectral irradiance of the narrow wavebands supplied by irradiation monochromator.

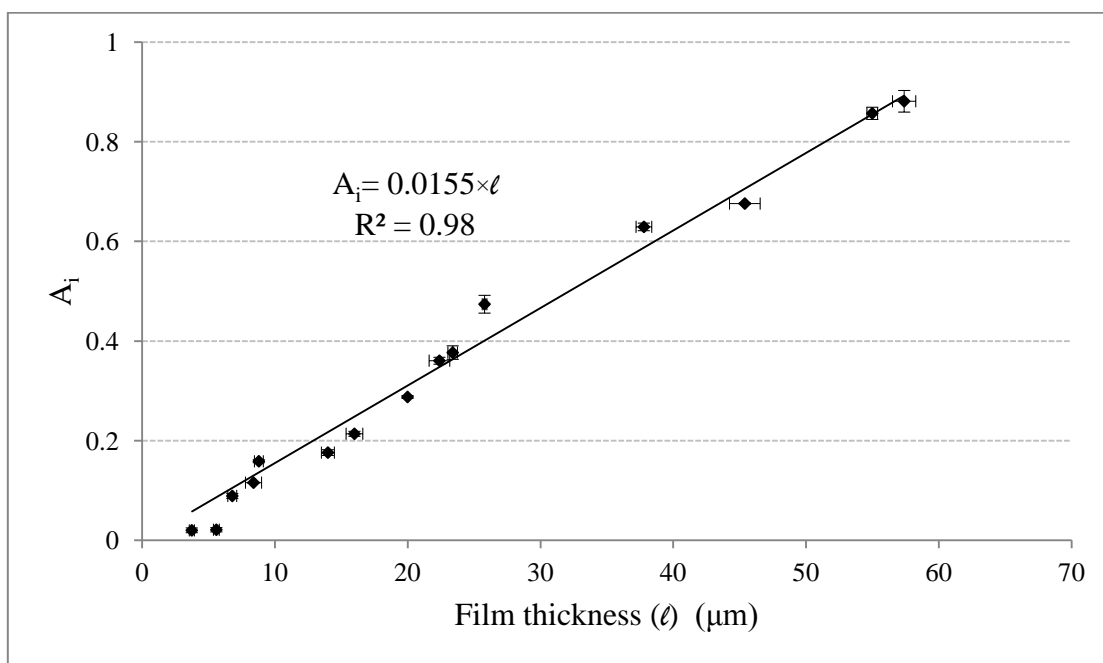


Figure 3: The absorbance of PVC thin films at 1064 cm^{-1} as a function of film thickness.

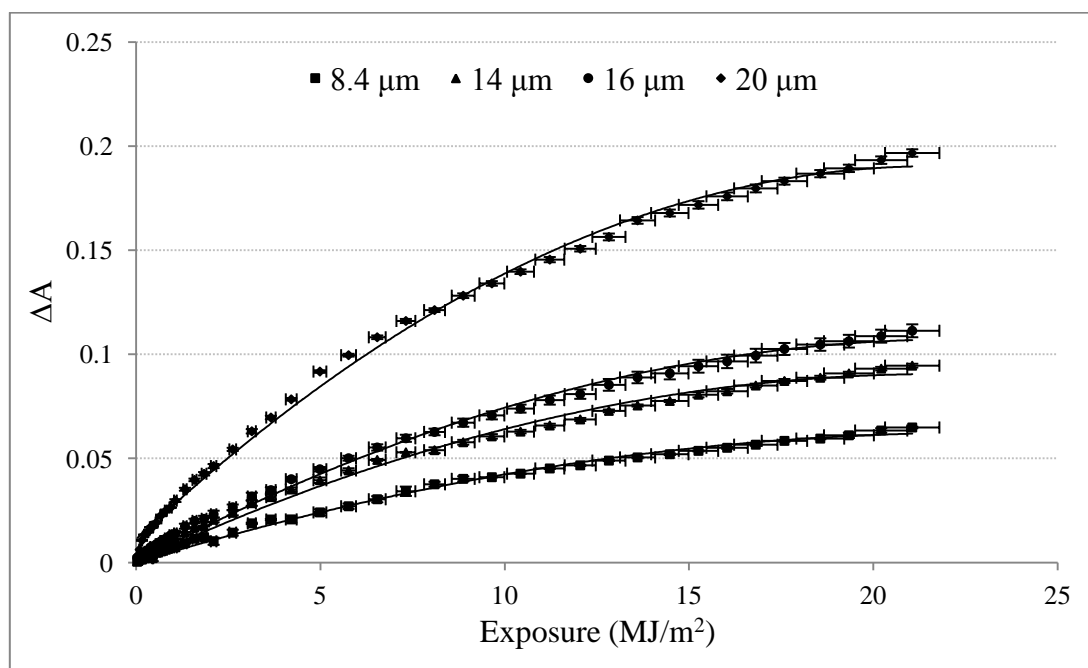


Figure 4: Dose-response curves of PVC thin films of different thicknesses.

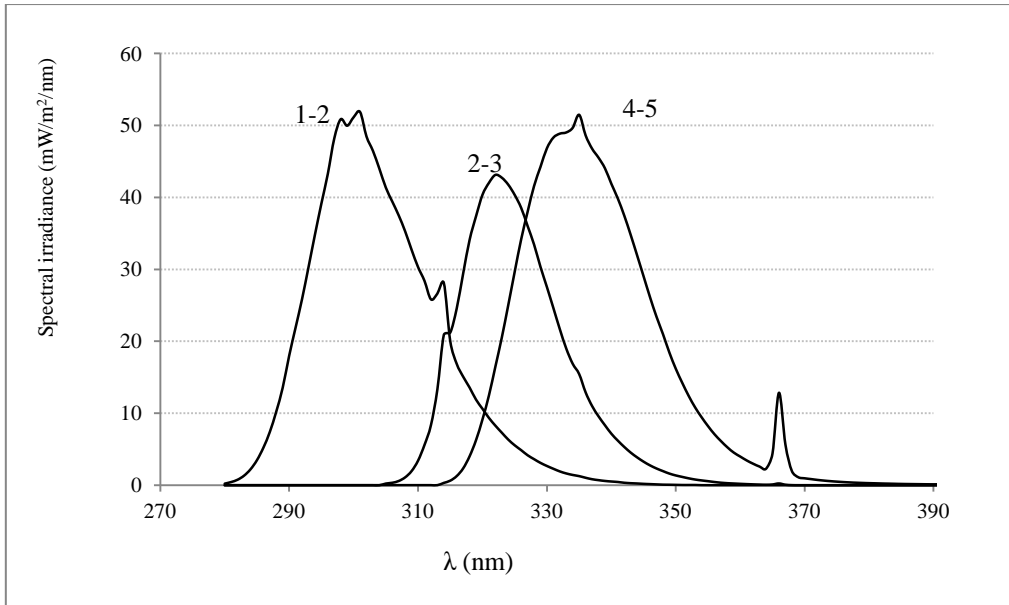


Figure 5: The irradiance difference received by the consecutive pairs irradiated behind the filters 1-2, 2-3, and 4-5.

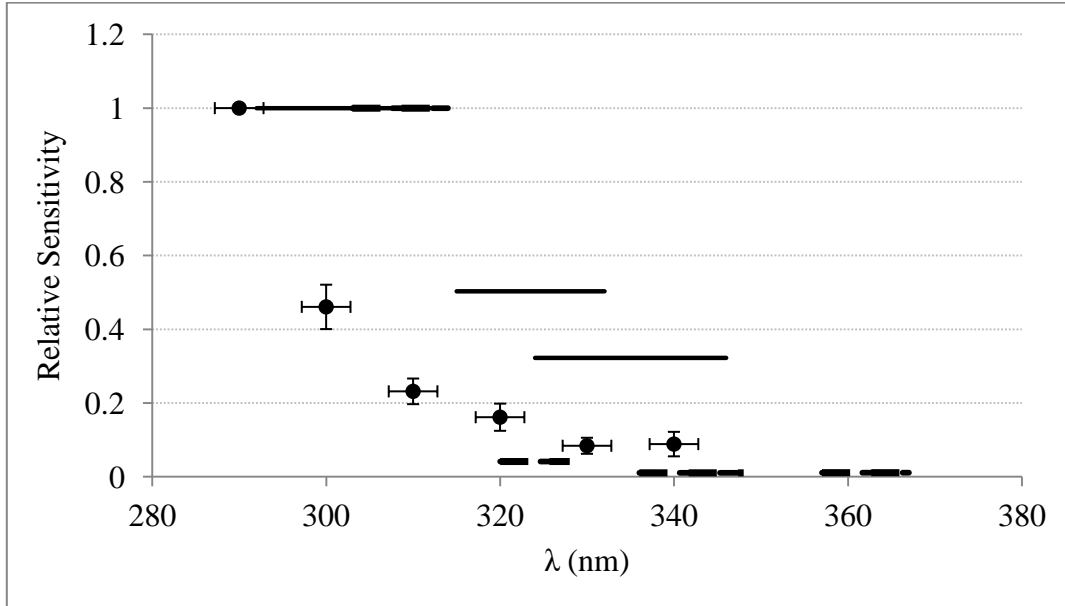


Figure 6: Spectral response of the PVC dosimeter obtained using cut-off filter technique (line), narrow band-pass filter technique (dashed line) and irradiation monochromator (circle).

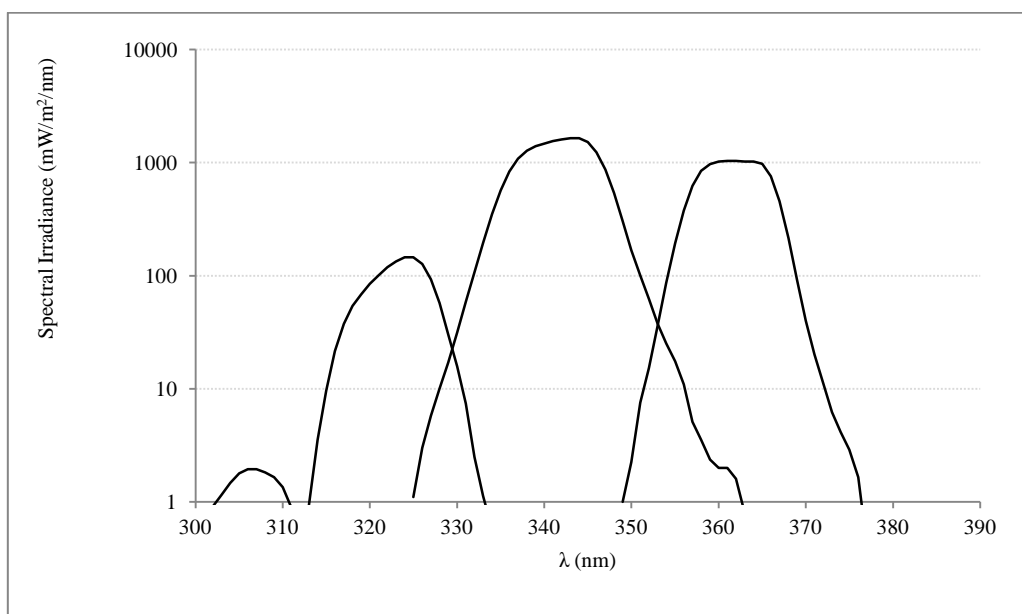


Figure 7: Spectral irradiance as calculated behind each of the four narrow band-pass filters.

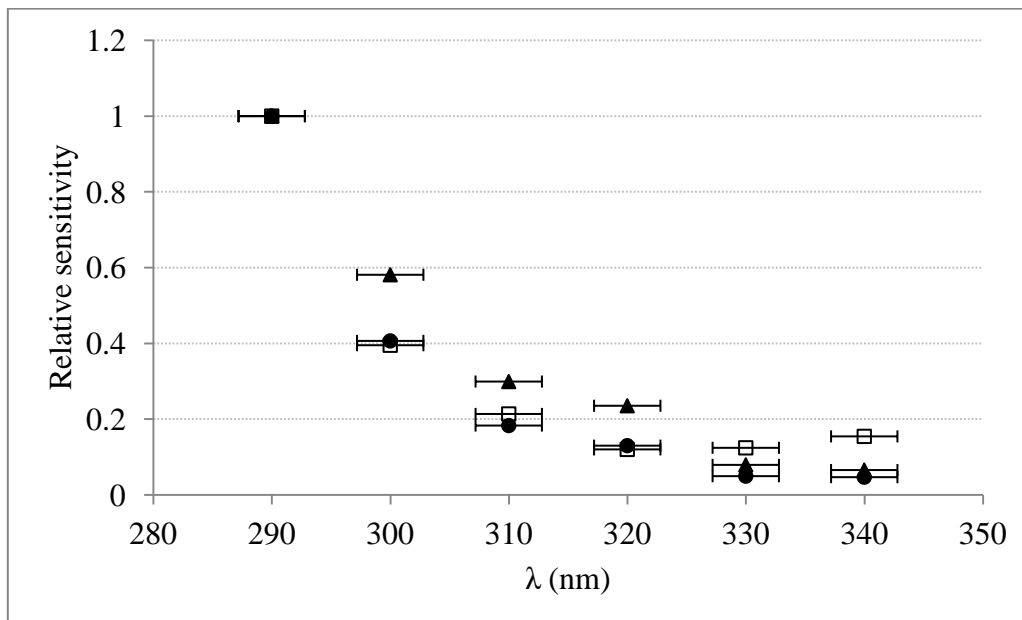


Figure 8: Spectral response of the PVC dosimeter obtained using irradiation monochromator where the dosimeters exposed to 0.5 MJ/m^2 at $25 \pm 2 \text{ }^\circ\text{C}$ (circle), 0.1 MJ/m^2 at $25 \pm 2 \text{ }^\circ\text{C}$ (square) and 0.1 MJ/m^2 at $40 \pm 2 \text{ }^\circ\text{C}$ (triangle).

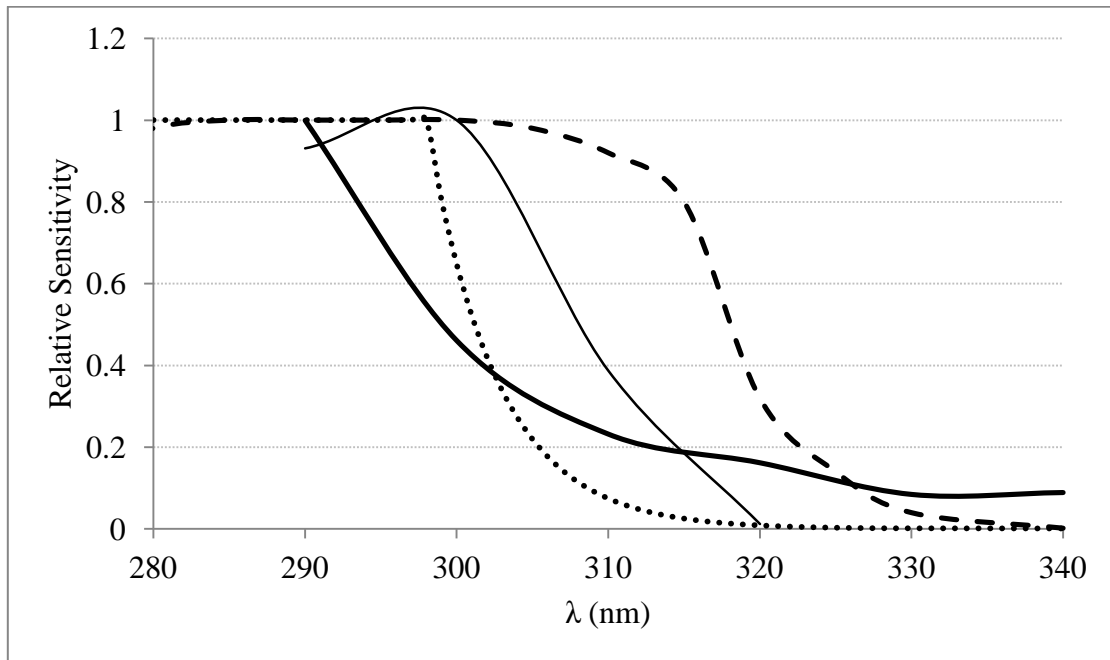


Figure 9: Spectral response of 16 μm PVC dosimeter (thick line) compared to erythemal action spectrum [15] (dotted line), polysulphone spectral response [38] (dashed line) and the polyphenylene oxide spectral response [39] (thin line).