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Atmospheric Chemistry and Physics Discussions

Utilising polyphenylene oxide for high exposure solar UVA dosimetry

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Abstract

Researchers at the University of Southern Queensland have developed a personal UV dosimeter that can quantitatively assess high exposure solar UVA exposures. The chemical polyphenylene oxide has been previously reported on its ability to measure high UVB exposures. This current research has found that polyphenylene oxide, cast in thin film form, is responsive to both the UVA and UVB parts of the solar spectrum. Further to this, the UVB wavelengths were filtered out with the use of mylar. This combined system responded to the UVA wavelengths only and underwent a change in optical absorbance as a result of UVA exposure. Preliminary results indicate that this UVA dosimeter saturates steadily when exposed to sunlight and can measure exposures of more than 20 MJ/m^2 of solar UVA radiation with an uncertainty level of no more than ± 5%.

1 Introduction

Exposure to UV radiation is known to be a causative factor in the induction of skin cancers and other sun-related disorders. Most acute responses of humans to UV exposure occur as a result of UVB (280 to 315 nm) exposures, as these wavelengths are highly effective in creating a human biological response. However, this does not mean that UVA radiation has no impact on human UV exposures and health. UVA can cause erythema in human skin, yet, the exposures required to create such a response is much larger than UVB radiation. UVA radiation penetrates much deeper into human skin tissue than UVB, resulting in impacts that are not as acute, taking many years to manifest. Past research has shown that UVA (315 to 400 nm) plays a significant role in human skin carcinogenesis, immune suppression, DNA damage, photoageing and wrinkling (Agar et al., 2004; Moan et al., 1999; Garland et al., 2003). Skin cancer is considered the most common malignant neoplasm in Australia and the USA (Kricker and Armstrong, 1996; Glanz and Mayer, 2005; NCI, 2006). Over 1,600 Australians

die from skin cancer each year and a further 380,000 Australians are treated for skin cancer each year (NCCI, 2003; AIHW, 2004; AIHW, 2005). Estimates put direct health care costs of all types of skin cancer in Australia in the region of $734.9 million per year, with the indirect costs in the form of sick leave and foregone earnings in the region of $1.395 billion per year (Armstrong, 1995). As a result, it is essential to decrease the amount of exposure to damaging solar UV radiation that the population experiences. This requires methods to understand the solar UV radiation environment that humans live in. Quantification of the individual level of solar UV radiation exposure requires personal dosimetry due to changes in the position of people compared to the radiation source.

Commonly used UV chemical dosimeters are polysulphone and phenothiazine. Phenothiazine has been used for measuring UVA wavelengths in various environments (Parisi et al., 2005). However, phenothiazine only has the capability to record a cumulative exposure over a small time period, usually three to four hours. This small dynamic range greatly reduces the amount of time over which a UVA exposure can be measured in the field. Therefore, a chemical dosimeter that is capable of measuring large amounts of UVA radiation over a long time period would be very useful. Research conducted by Davis et al. (1976) showed that Poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) film could be employed to measure high levels of UV exposure. Further research found PPO to be ideal for this purpose as it would allow for unattended measurements to be made at various locations over extensive amounts of time with high levels of accuracy when compared against radiometric measurements (Davis et al., 1981; Berre and Lala, 1989; Lester et al., 2003). Schouten et al. (2007) found that PPO has a progressively increasing response to UVA wavelengths over time. PPO dosimeters have been utilised in the measurement of global UV exposures, however, they have not been used to measure high exposure solar UVA exposures. The aim of this paper was to extend the previous research that has employed PPO dosimeters for the measurement of solar UVB and erythemal exposures to investigate the suitability of PPO for the measurement of high exposure solar UVA irradiances.

2 Materials and methods

2.1 PPO

PPO film of approximately 40 μm thickness was attached with adhesive tape to a plastic holder. The holders for the dosimeters were 3×3 cm in size and fabricated from thin polyvinylchloride with an aperture of approximately 1.2×1.6 cm (Fig. 1). A UV/visible spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) was used to measure the pre and post exposure absorbance of the dosimeter. The uncertainty range for optical absorbance measurements in the spectrophotometer has been stated as ± 0.002 by the manufacturer. PPO is responsive to both the UVA and UVB part of the solar spectrum, therefore the UVB wavelengths were filtered by placing 120 μm thick mylar film (Cadillac Plastics, Australia) on top of the PPO film. For each dosimeter, the change in optical absorbance (ΔA_{320}) due to UV exposure was measured at 320 nm (with mylar removed) at four different sites over the dosimeter in order to minimise any errors due to any possible minor variations in the PPO film over the size of the dosimeter. The change in optical absorbance was measured at 320 nm as previous studies have shown that this is the wavelength where the greatest overall UV energy induced change occurs (Lester et al., 2003; Schouten et al., 2007). The post exposure absorbance was measured at a standardized time following exposure to minimize any error associated with the post exposure "dark reaction" of the PPO (Lester et al., 2003; Schouten et al., 2007). Lester et al. (2003) has shown previously that the PPO dosimeter is not a temperature dependent system, so fluctuations in temperature over the exposure time period will not have any influence upon the subsequent measurement error.

2.2 Calibration

The dosimeters were calibrated for UVA exposures by exposing a series of dosimeters on a horizontal plane, to relatively clear sky solar UV from approximately 0800 to 1600 h

Australian Eastern Standard Time (EST) for a total of 22 days. These calibrations ran over the months of April and May at a subtropical Southern Hemisphere site at the University of Southern Queensland, Toowoomba, Australia (27.6° S, 151.9° E, altitude 693 m). The solar zenith angle (SZA) ranged from 30° to 75°. The PPO dosimeters were calibrated on a horizontal plane with a UVA meter (501 Biometer, Solar Light Co., Philadelphia, USA). The UVA meter was calibrated against a scanning spectroradiometer (Bentham Instruments, Ltd, Reading, UK). The spectroradiometer is based on a double grating monochromator, a UV sensitive detector and amplifier with software variable gain provided by a programmable high voltage power supply. The interior of the spectroradiometer enclosure is temperature stabilised to 23.0± 0.5° C, using a Peltier heater/cooler unit. The input optics of the spectroradiometer are provided by a PTFE (polytetrafluoro ethylene) diffuser and connected by an optical fibre to the input slit of the monochromator. The spectroradiometer is programmed to start scanning the global UV spectrum in 0.5 nm increments from dawn, and thereafter every 10 min till dusk. The instrument is wavelength calibrated to the UV spectral lines of a mercury lamp and irradiance calibrated to a 150 Watt quartz tungsten halogen lamp with calibration traceable to the National Physical Laboratory, UK standard.

To produce the calibration curve, the UVA exposure (MJ/m^2) was measured over specific intervals with the UVA meter. This measurement was then calibrated to the scanning spectroradiometer by employing a transfer equation with a calculated R^2 value of no less than 0.99. After each interval, the ΔA_{320} for a single PPO dosimeter was measured by the spectrophotometer to provide a single data point, where ΔA_{320} was calculated by the following

$$\Delta A_{320} = A_{320}^{\mathrm{FINAL}} - A_{320}^{\mathrm{INITIAL}}$$

where A_{320}^{FINAL} is the final optical absorbance measurement after exposure taken at 320 nm and $A_{320}^{\mathrm{INITIAL}}$ is the initial absorbance measurement before exposure taken at 320 nm. After the absorbency was measured, the dosimeter was then removed from the batch.

2.3 Reproducibility

To test the reproducibility of the dosimeters for the measurement of solar UVA, ten dosimeters (with mylar filter) were exposed simultaneously to solar UV over a three hour period on a horizontal plane. These exposures were conducted on an unshaded sports oval in spring for clear sky conditions.

3 Results

3.1 Filtered exposures

The spectral transmission of the mylar film was measured pre-exposure and post-exposure to solar UV to test for any significant changes. The change in spectral transmission of the mylar film is provided in Fig. 2. The maximum change was approximately 13% from 331 to 337 nm. The change in absorbency of the PPO film pre- and post-exposure is provided in Fig. 3.

3.2 Calibration

The calibration of the PPO dosimeters for solar UVA exposure is shown in Fig. 4. The data points are the averages of the four ΔA's measured for each dosimeter and the error bars on the x-axis values are the standard deviation of the four measurements. A power law was fitted to the calibration data with the form of:

$\mathrm{UVA}=11.7(x^{0.51})\mathrm{MJ/m^2}$ where x is the change in absorbency. The resulting R^2 for the calibration was greater than 0.99.

3.3 Reproducibility

For reproducibility tests, ten dosimeters were placed on a horizontal plane and exposed to solar UV. All dosimeters received the same exposure of solar UV producing a mean

ΔA_{320} of 0.598 with a standard deviation of no more than 3% and a coefficient of variation equal to approximately 5%. This variation may be due minor variations over the surface of the sheet of PPO film from which the dosimeters were fabricated and the influence of dust particles that accumulated on the surface of the dosimeters during the exposure period.

4 Discussion

Preliminary results indicate that this UVA dosimeter saturates reasonably slowly when exposed to sunlight and can measure exposures of more than 20 MJ/m^2 of solar UVA radiation with an uncertainty level of no more than ±5%. The size and lightweight properties of the dosimeter means that it can be attached to any anatomical site on the human body in different environments such as underneath shade or in a vehicle in order to measure the solar UVA exposures with a level of ease, simplicity and cost-effectiveness not associated with counterpart radiometric measurements. The usage of the dosimeter requires the calibration against a calibrated UVA meter. The profile of the calibration curve will vary with the season and this can be overcome by calibrating the dosimeter in the season that it will be employed to measure the solar UVA exposures.

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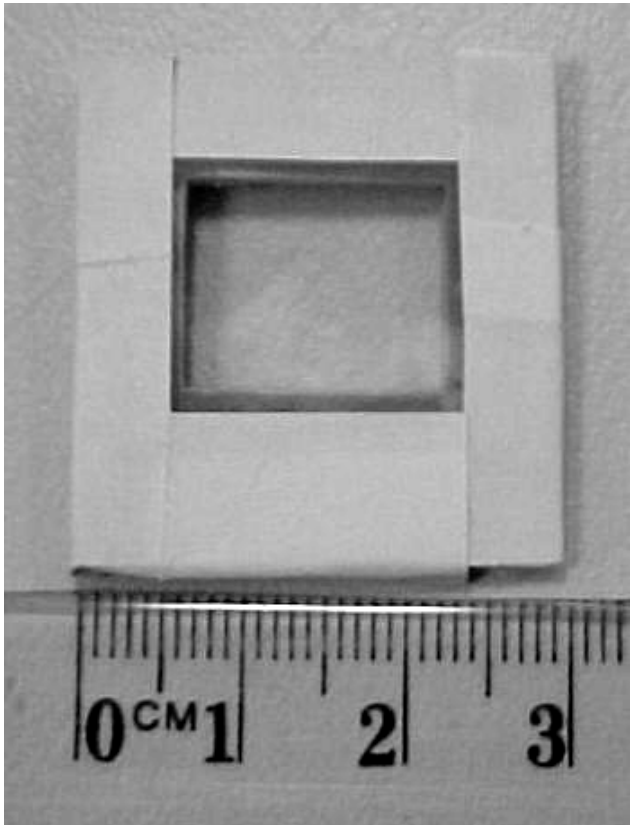

Fig. 1. A sample PPO dosimeter with the mylar film attachment.

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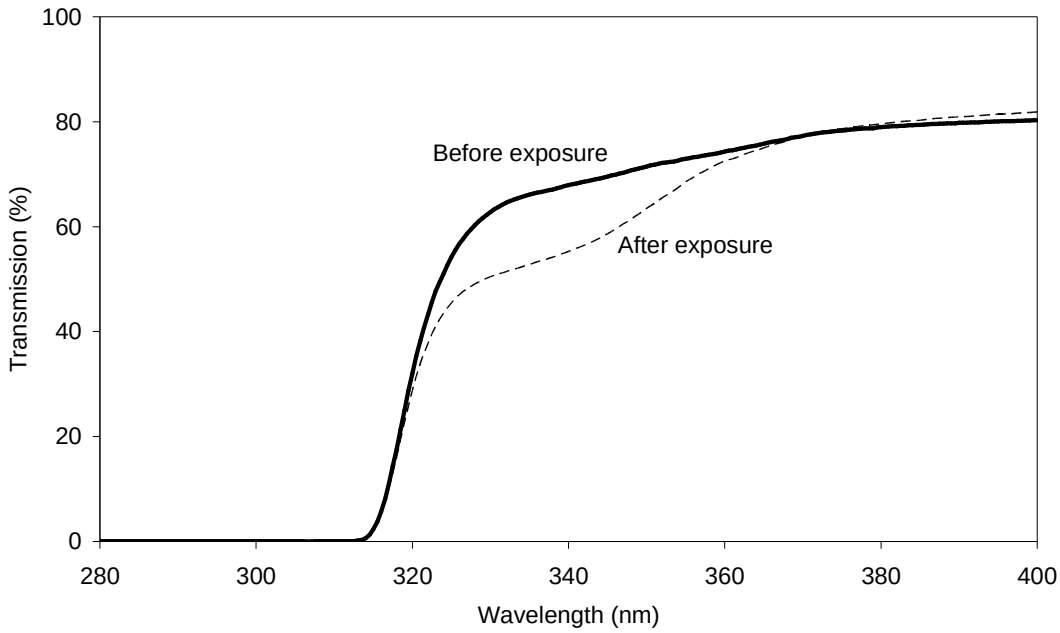

Fig. 2. The spectral transmission of mylar film before and after a total solar UVA exposure of 20 MJ/m^2.

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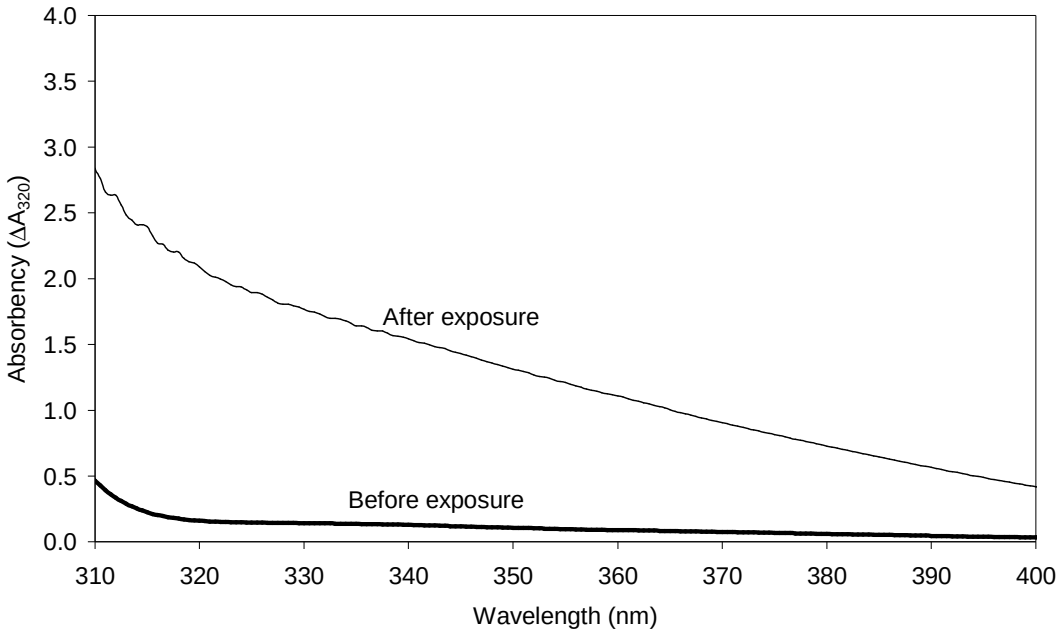

Fig. 3. The absorption spectrum of PPO before and after a total solar UVA exposure of 20 MJ/m^2.

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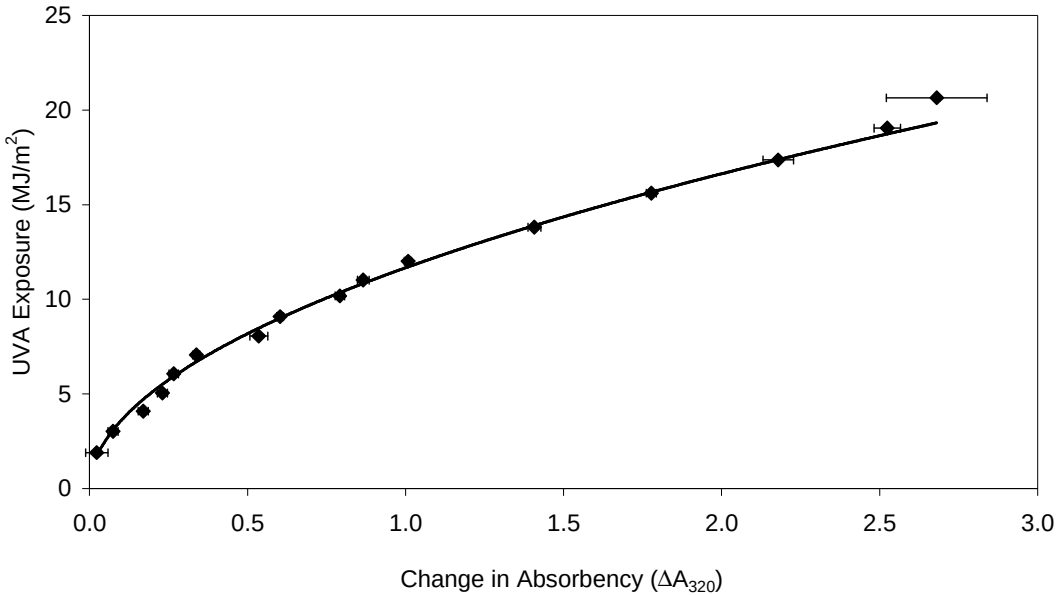

Fig. 4. Calibration curve of PPO for UVA exposures. The error bars represent the standard deviation in each series of absorbency measurements.

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