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UV dosimeters based on neotetrazolium chloride

Andrew Mills*, Pauline Grosshans, Michael McFarlane

WestCHEM, University of Strathclyde, Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

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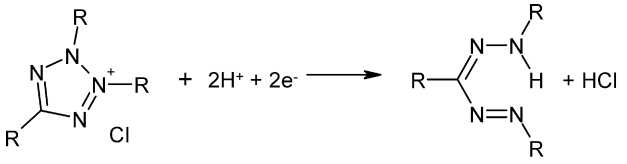
ABSTRACT

A novel UV dosimeter is described comprising a tetrazolium dye, neotetrazolium chloride (NTC), dissolved in a film of polymer, polyvinyl alcohol (PVA). The dosimeter is pale yellow/colourless in the absence of UV light, and turns red upon exposure to UV light. The spectral characteristics of a typical UV dosimeter film and the mechanism through which the colour change occurs are detailed. The NTC UV dosimeter films exhibit a response to UV light that is related to the intensity and duration of UV exposure, the level of dye present in the films and the thickness of the films themselves. The response of the dosimeter is temperature independent over the range 20–40 °C and, like most UV dosimeters, exhibits a cosine-like response dependence upon irradiance angle. The introduction of a layer of a UV-screening compound which slows the rate at which the dosimeter responds to UVR enables the dosimeter response to be tailored to different UV doses. The possible use of these novel dosimeters to measure solar UV exposure dose is discussed.

1. Introduction

Tetrazolium salts are water soluble organic heterocycles that can be readily reduced to form partially soluble and insoluble formazans. Tetrazoliums are generally colourless or pale yellow in solution while formazans are highly coloured species typically red, blue and purple. A general tetrazolium reduction reaction is as follows:



colourless **coloured** (1)

This colour changing reaction has made tetrazolium salts a popular choice of indicator for the evaluation of bacterial metabolic activity [1] as well as the detection of diseases such as tuberculosis [2]. The literature has numerous references to the "Tetrazolium Test" or the "Nitro Blue Test" [3–7] in which the tetrazolium dyes provide a quick visual indication of cell activity *via* its addition to a cell culture.

As well as occurring *via* electron transfer in biological environments, the reduction of tetrazoliums can also be induced by γ-radiation, which enables tetrazoliums to be used as dosimeters for measuring absorbed dose of γ-rays. Much work in this area has been carried out using triphenyl tetrazolium chloride (TTC) [8–11] the structure of which is illustrated in Fig. 1, along with some other cited compounds.

TTC based dosimeters for γ-radiation monitoring have been proposed in the form of aqueous [8,9] and alcoholic [10] solutions but also as agar gels [8]. Less well studied has been the use of tetrazolium dyes in films for UV dosimetry.

Ultraviolet radiation (UVR) plays an important role in maintaining the human body. The main benefit of UVR is generally ascribed to its role in the synthesis of vitamin D3 [12], which is required in many important functions within the human body, such as aiding the absorption of dietary calcium in the gut required to sustain healthy bones [12,13]. Individuals suffering from skin conditions such as psoriasis can also benefit from UV phototherapy [14]. Overexposure to UVR can, however, be hazardous to human health [15] with the severity of the damage caused depending on the type of UV, the intensity and length of the exposure and the sensitivity of the individual. Acute effects arising from short-term exposure to the skin and eyes include erythema i.e. the reddening of the skin more commonly known as sunburn, photokeratitis and photoconjunctivitus, the reversible sunburn of the cornea and conjunctiva, respectively [15,16]. Long-term exposure can lead to chronic conditions such as photoaging [12,17] and skin cancer [12–21] and cause clouding of the lens of the eye, i.e. cataracts [22]. There is also evidence that the human immune system is suppressed due to

* Corresponding author. Tel.: +44 141 548 2458; fax: +44 141 548 4822.
E-mail address: a.mills@strath.ac.uk (A. Mills).

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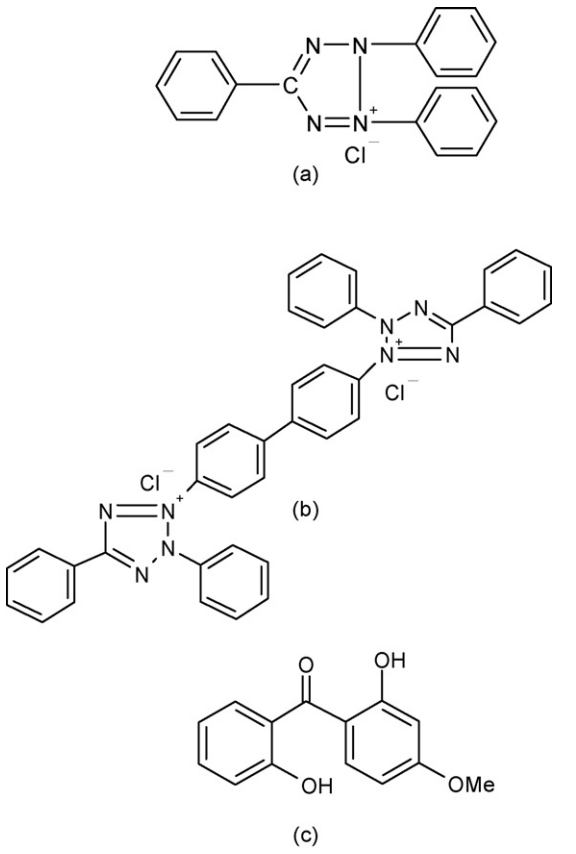

Fig. 1. The chemical structures for (a) triphenyl tetrazolium chloride (TTC), and (b) neotetrazolium chloride (NTC) and 2,2 dihydroxy-4-,metnoxy benzopohenone (DMB).

acute UVR exposure [16]. Incident UV levels are measured using a UV Index system, which on a typical summer's day in the UK will peak at 5 (Glasgow) or 6 (London) (≡125–150 mW m^{-2}) at around mid-day [23].

The amount of solar UV radiation absorbed by the skin at any time is known as the erythemal dose. In quantifying an individual's personal exposure to UVR, the term the '*minimum erythemal dose*' (MED) is useful, where the MED is defined as the minimum amount of radiation likely to cause erythema. The MED for an individual is largely dependent on skin type, of which there are six [24], I–VI. For example, for individuals with skin phototype II, which is typical for many Caucasians, the MED is equal to 250 J m^{-2} i.e. 69.4 mW m^{-2} per hour. Since a UV Index value of 1 is 25 mW m^{-2} it follows that even under mild UV solar conditions such as a UVI value of 3 (≡75 mW m^{-2}) as may be observed in the UK and much of Europe in April or September [23] most Caucasians will sunburn within 1 h if not properly protected.

The measurement of effective UV dosage experienced by an individual is essential if they are to avoid exceeding their MED, i.e. avoid sunburn. With the rise in number of people suffering from UVR-related health problems there is a growing need for a real-time, inexpensive, disposable, personal solar UV dosimeter to provide the user with a current measure of the cumulative dose of UV they have been exposed to during the day.

Since erythema is a consequence of DNA damage, it follows that the best UV dosimeters are ones that utilize biological material, such as, spores, bacterial cells or bacteriophages [25]. Work on spores, most noticeably *Bacillus subtilus*, has been particularly successful in generating an effective biofilm for use as a UV dosimeter, since, with an appropriate filter, the spectral responsivity of this system is very close to the responsivity curve attributed to human skin erythema [25,26]. The latter feature renders the UV dosimeter an effective indicator of erythema regardless of UV source and UV emission profile. The only downside to such biological dosimetry is the need to develop the films, which can take typically up to a day.

Of the many non-biological UV dosimeters, the most notable is that based on thin films of polysulphone [27,28]; a polymer which, upon exposure to UV, increases in its absorbance in the UV. This film is particularly successful because the polymer has an initial spectral profile not too dissimilar to that of the spectral responsivity of human skin with respect to erythema—although not as close at the *B. subtilus* UV dosimeter. The main practical drawback to this dosimeter is the need for a UV absorbance spectrophotometer to measure the change in film absorbance, since it is not assessable by eye.

In contrast to the above, effective, but non-real-time UV dosimeters, a number of colour-based, real-time dosimeters have been reported. The advantage of such devices is that they provide a real-time measure of the UV dosage an individual receives via a clearly perceivable colour change. However, their main disadvantage is that they utilize UV absorbing dyes that usually provide a poor match with the spectral sensitivity of human skin. As a result, such UV dosimeters are only appropriate when calibrated for use with a light source which has a fairly constant spectral profile. Thus, they are usually designed to work best on a clear day from mid-morning to mid-afternoon, using the sun as the source of UV, i.e. as sunburn warning indicators, since the shape of the solar spectrum changes, with the relative level of UVA with respect to UVB increasing, only in the early and late hours of the day when sunburn is 'practically impossible' [29].

Most of the latter systems to date are based on irreversible photochromic dyes [30] and photo-induced pH changing reactions [31]. Few are based on UV-induced electron transfer reactions, the focus of this work, which describes a simple colouration indicator based on the dye, neotetrazolium chloride (NTC) that can be used to indicate UV exposure dose and to warn of possible erythema. The structure of NTC is illustrated in Fig. 1.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemicals unless specified. The water used to produce inks was double distilled and deionised while the polymer used to produce the NTC films was 98–99% hydrolysed polyvinyl alcohol (PVA), with an average mol. wt. 124,000–186,000. The polymer used to produce the UV-screening ink was poly(vinyl butryal-*co*-vinyl-alcohol-*co*-vinyl acetate) (PVB), with an average mol. wt. 70,000–100,000.

2.2. Methods

UV/visible spectra for sample films were recorded using a Lambda 35 UV/visible spectrophotometer (PerkinElmer, UK). The NTC UV dosimeter films under test were typically irradiated for a total of 30 min, with spectra being recorded at 5 min intervals.

UV irradiation of samples was carried out using either UVA (λ_{max}(emission) = 365 nm) or UVB (λ_{max}(emission) = 315 nm) lights, both of which comprise two, 8 W fluorescence tubes (Vilber Lourmat). The irradiance (i.e. radiant power per unit area) for each of the UV sources was measured as 4 mW cm^{-2} using a Multi-Sense 100 UV light meter fitted with the appropriate UVA or UVB sensor.

The UV solar simulator used in this work comprised a 180 W xenon arc lamp (Speirs Robertson), with UG5 and the WG20 fil-

ters placed in the light path as described previously by Diffey [32]. The former allows transmission at UV wavelengths and absorbs in the visible region, while the latter absorbs in the short wavelength UVC region. The combination of these two filters with the emission spectrum of the Xe lamp provides a good match with the noonday UV spectrum of the sun [32]. Unless stated otherwise, the UV dosimeter films under test were placed square on to the UV light beam emitted by the Xe lamp placed 45 cm away. In this system the UVI of the UV solar simulated light was measure using a SafeSun^{TM} solar meter and was typically a UVI of 5 [33]. The UV induced change in the absorbance of the dosimeter film under test was measured at 532 nm, i.e. ΔAbs_{532}, at regular intervals with the UV/Vis spectrophotometer.

2.3. UV ink and dosimeter preparation

A typical NTC/PVA solution was prepared by dissolving 10 g PVA in 90 ml of water at 90 °C, which was then cooled to room temperature and stirred overnight. 20 mg of the NTC dye were then dissolved in 4 g of the PVA solution at room temperature with stirring. The casting ink was pale yellow in appearance and contained 5 phr of NTC i.e. 5 parts per hundred resin (or 5 g of dye to 100 g polymer). Films of the ink were cast on to 25 mm diameter, 1 mm thick, quartz discs using a spin coater. Thus, a few drops of polymer solution were deposited on the surface of the disc, which was then spun at 1200 rpm for 15 s. The final product was then dried for 2 min in oven at 70 °C, and allowed to cool to room temperature (5–10 min) and stored in the dark until used. The final product was a clear, colourless ca. 2.3 μm thick film on a quartz disc which will be referred to as a typical NTC film. Work carried out using the solar simulator used films produced from a standard formulation ink but cast at 300 rpm to make the films thicker (ca. 8 μm) and so ensure a more striking colour change, since the absorbance changes were as a consequence ca. four times larger, upon exposure to UV light. Such films will be referred to as typical solar NTC films.

3. Results and discussion

3.1. Optical characteristics of a NTC film

A typical NTC film was produced and the spectral fraction of light, f_A, it absorbs calculated from its absorption spectrum; the results are shown in Fig. 2, along with the known spectral sensitivity of human skin with respect to erythema, $S(\lambda)$ [34]. The film has an absorption maximum at 252 nm with a shoulder peak at 353 nm. From the data in Fig. 2 it is clear that the NTC dosimeter, like most dye-based chemical dosimeters, has a very poor overlap with $S(\lambda)$. This renders it only appropriate as a UV dosimeter for skin erythema when calibrated using the relevant UV light source, assuming the latter's profile does not change with time. Fortunately, as noted earlier, the solar spectrum does not change significantly in shape from mid-morning to mid-afternoon, the most likely time sunburn will take place.

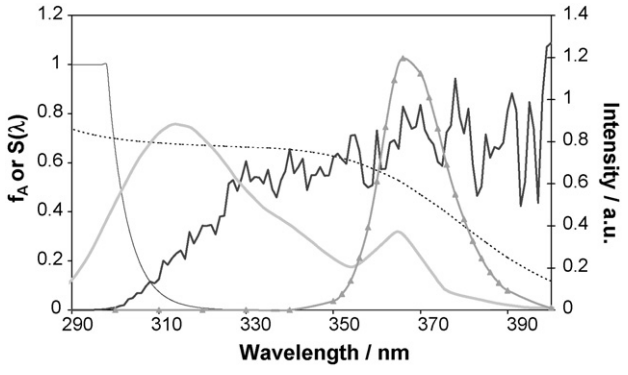

Fig. 2. A plot of the fraction of light (f_A) (- - - -) absorbed by the NTC film and human skin eythemal sensitivity, $S(\lambda)$ (—), vs. wavelength with overlays of the emission spectra of the: solar simulator (▬), UVA (–▲–) and UVB lamps (▬) used in this work.

The emission spectra of the UVA and UVB light sources and the UV solar simulator are also illustrated to highlight their overlap with the NTC film. Note from the data in Fig. 2 that the typical NTC film dosimeter absorbs a greater proportion of UVB than UVA. The latter is a useful feature in any UV dosimeter as it is UVB in particular that is responsible for sunburn. For example on a typical summer's day approximately 6% of terrestrial light is in the UVB wavelength range (i.e. 290–320 nm) and contributes 80% towards the harmful effects associated with the sun, while the remaining 94% UVA component in sunlight (320–400 nm) contributes to the remaining 20% [32].

3.2. UV irradiation of NTC film

When irradiated with either UVA or UVB light a typical NTC film develops a striking pink/red colour with time as seen in Fig. 3, which shows photographs of such a film before and after 30 min irradiation with UVB light (4 mW cm^{-2}). This feature is further illustrated in Fig. 4 which shows the UV/visible absorption spectral changes, exhibited by this film as a function of irradiation time. The insert diagram in Fig. 4 shows that the photocolouration process, as measured by the increase in absorbance at 532 nm i.e. ΔAbs_{532}, as a function of irradiation time, occurs at a greater rate under UVB radiation than UVA radiation of the same intensity. This difference in UV responsivity is expected given that the NTC dye absorbs a greater total fraction of UVB light (f_{UVB} ca. 0.60) than UVA light (f_{UVA} ca. 0.49), as is apparent from the spectral data in Figs. 2 and 4.

The colour change observed arises as a result of the partial reduction of NTC to give the stable monoformazan which proceeds by means of the step-wise addition of electrons and occurs *via* a transient state consisting of one tetrazolinyl radical centre and one tetrazolium centre as detailed in Fig. 5 [35]. Further reduction of the monoformazan, λ_{max} (532 nm) can yield the diformazan form of the dye, a purple species that absorbs at longer wavelength λ_{max} (550 nm) [36,37].

3.3. Kinetics of colouration of an NTC film

In one set of experiments a set of typical NTC films were exposed to different UVA and UVB irradiances for the same length of time. Specifically 1, 2 and 3 mW cm^{-2} from the UVA source and 0.5, 1, 2 and 3 mW cm^{-2} from the UVB source, with a total exposure time of 30 min for each film. The absorbances of the NTC films under test were measured spectrophotometrically and the initial rate, r_i, of colouration for each film was determined from a plot of ΔAbs_{532} vs. irradiation time. The plot of r_i as a function of UV irradiance arising from this work is illustrated in Fig. 6 and shows that r_i is directly related to irradiance, as might be expected for such a simple, direct photochemical process. From the gradient in Fig. 6 the UVB irradiation experiment, i.e. 1×10^{-4} (Abs unit s^{-1}/mW cm^{-2}), and given that the reduced NTC has a molar absorptivity of 22,000 M^{-1} cm^{-1} and a typical film is 2.3 μm thick, a formal quantum efficiency for the photoreduction of NTC in the PVA film was calculated as $(2.8 \pm 0.3) \times 10^{-3}$ molecules/photons of UVB. Similarly a value of $(1.7 \pm 0.2) \times 10^{-3}$ molecules/photons of UVA was calculated using the UVA irradiation data in Fig. 6.

The sensitivity of the NTC UV dosimeter towards UV light can be readily varied by changing the amount of dye in the film formula-

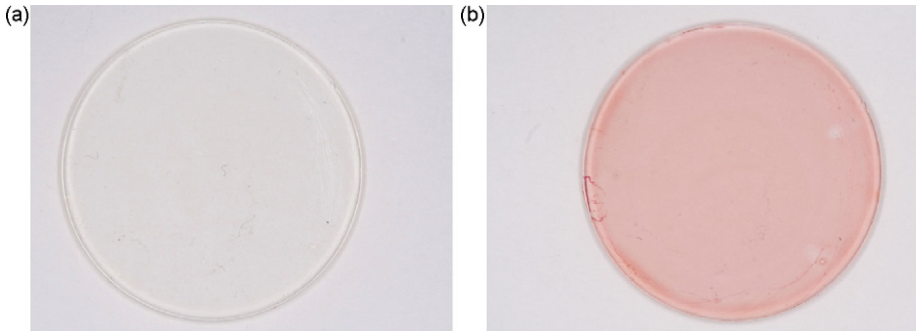

Fig. 3. Photographs of standard films taken before (a) and after (b) irradiation with UVB light.

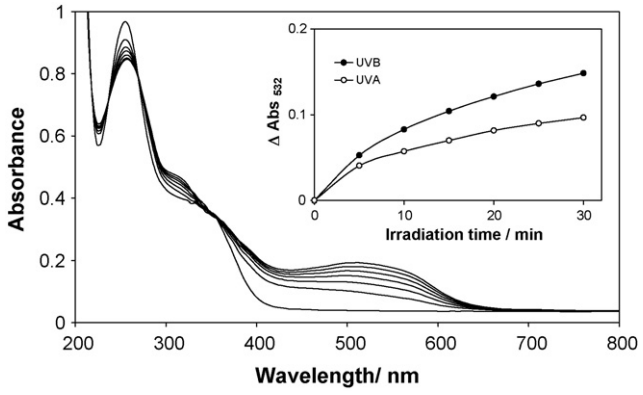

Fig. 4. Absorption spectra of a standard NTC films, after irradiation with 4 mW cm^{-2} UVB. Insert diagram is a comparison of the response of films to 4 mW cm^{-2} UVA.

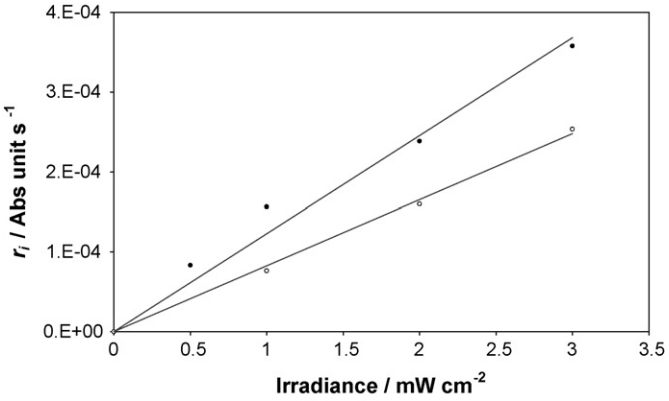

Fig. 6. A plot of initial rate of colouration, r_i as a function of UV irradiance for typical NTC films irradiated with different intensities of UVA (bottom) and UVB (top) light.

tions. Thus, a series of NTC casting inks were prepared containing 10–80 mg NTC, which were then cast on to quartz discs to produce films with NTC levels ranging from 2.5 to 20 phr, respectively. Using these films a series of ΔAbs_{532} vs. irradiation time profiles were generated with a 4 mW cm^{-2} UVB light source and the results are illustrated in Fig. 7. These show that the initial rate increases with increasing levels of NTC, i.e. [NTC]. The initial rate of colouration, r_i, was plotted against the fraction of UVB light absorbed f_{UVB}, by the NTC dye in each film and is shown in the inset diagram in Fig. 7, revealing r_i is directly proportional to f_{UVB}, as expected for a simple, direct photochemical process for which the rate of the photoreduction process is directly proportional to the absorbed irradiance.

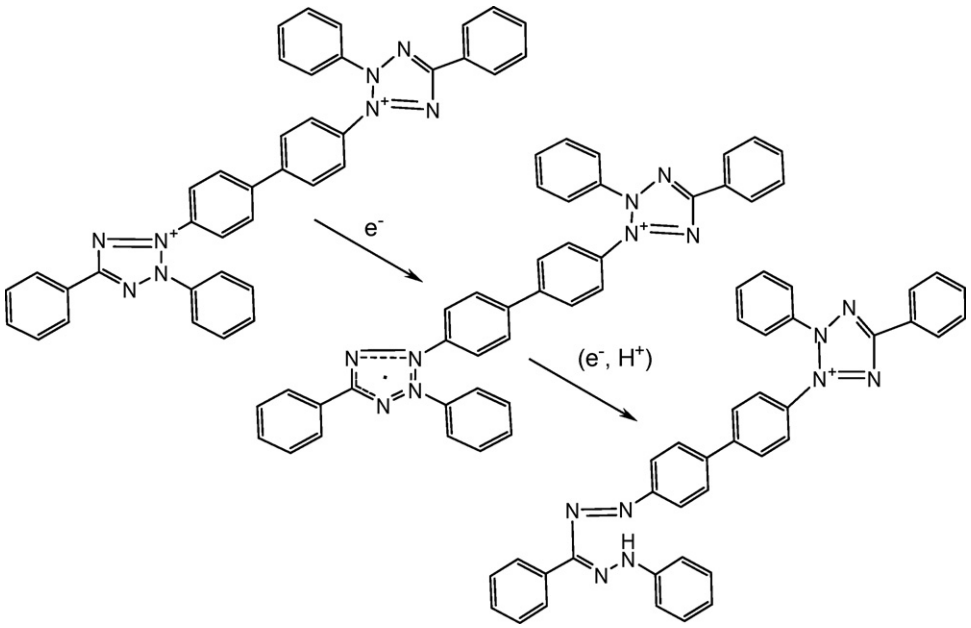

Fig. 5. Mechanism for the reduction of neotetrazolium dye (yellow) to its monoformazan (red).

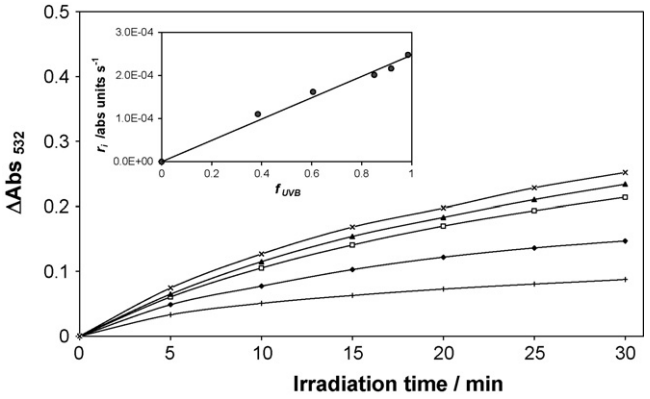

Fig. 7. A plot of ΔAbs_{532} against irradiation time for films containing different [NTC] after irradiation with 4 mW cm^{-2} UVB light. From top to bottom concentrations are 20, 15, 10, 5 and 2.5 phr. Insert diagram is a plot of the r_i against f_{UVB} for each film.

3.4. Enhancement of photocolouration of an NTC film

The NTC UV dosimeter reported here functions *via* a UV-induced photoreduction process, in which the dye converts to its formazan form (see Fig. 5). Since this process occurs in a polymer encapsulation medium (PVA in this case), it is presumed that the photoreduction of the NTC is accompanied by the oxidation of the polymer. It would appear likely, therefore, that the UV-induced photoreduction of NTC may be more easily effected if a more readily oxidised reagent, such as triethanolamine (TEOA) or glycerol, were present. In order to test this idea, casting solutions were prepared following the standard procedure, but with the addition of either 100 mg glycerol or triethanolamine. Films of these inks were cast on quartz discs in the usual way and irradiated with 4 mW cm^{-2} UVB light for 30 min. The variation in the parameter ΔAbs_{532} for these films was monitored spectrophotometrically as a function of irradiation time and the results are shown in Fig. 8. This plot compares the response of the typical film with those films containing glycerol or TEOA, and shows that the addition of an easily oxidisable electron donor, such as TEOA or glycerol increases the initial rate at which the NTC is photoreduced by UV light. Interestingly, the film containing the glycerol develops a purple colour when irradiated with UVB light, with an absorbance peak at 550 nm, rather than that of 532 nm found for the usual red coloured formazan generated using a typical NTC film. These results indicate that, in the presence of glycerol some of the monoformazan produced is further photoreduced to give the diformazan product, which is known to exist as an insoluble purple coloured solid [36,37].

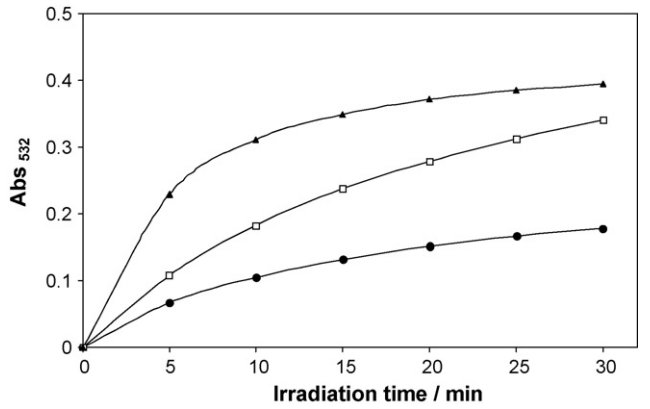

Fig. 8. A plot showing, from top to bottom, the responses of PVA films containing 5 phr NTC with the addition of glycerol or TEOA compared to the standard film after irradiation with 4 mW cm^{-2} UVB light.

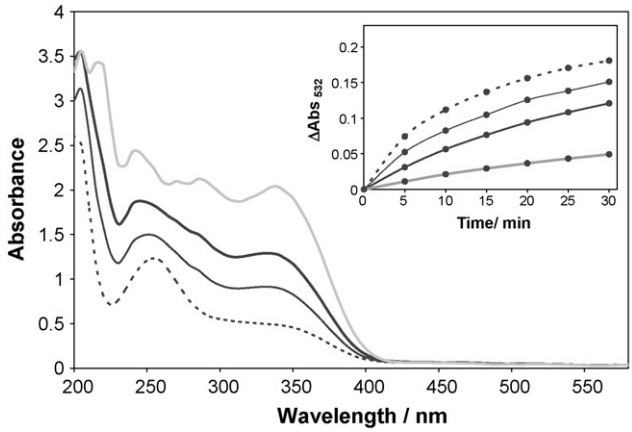

Fig. 9. A plot showing, from top to bottom, the absorption spectrum of a NTC film coated with 100 phr DMB/PVB layer, NTC film coated with 40 phr DMB/PVB layer, NTC films coated with 20 phr DMB/PVB layer and a standard NTC film with no blocker layer. The inset diagram is a plot of ΔAbs_{532} vs. irradiation time for the above-mentioned films generated under 4 mW cm^{-2} conditions.

3.5. Effect of UV blockers on the photocolouration of an NTC film

In order to effect the screening process a coating of a UV-screening solvent based ink (DMB in PVB) was cast on top of a typical NTC film. In this experiment a series of UV-screening solutions comprising of a 5% (w/w) PVB in *n*-butanol polymer solution were prepared containing different levels of DMB ranging from 40 to 100 phr. A set of standard NTC films were then each coated with a layer of one of the solvent based UV-screening inks, by spin coating them on top of the standard films at 1200 rpm, and drying the final product in the oven at 70 °C. The UV/visible spectra for these NTC/UV-screened films are shown in Fig. 9. The films were then irradiated with 4 mW cm^{-2} UVB light for 30 min and their UV/Vis absorption spectra recorded at regular intervals. From this data a series of ΔAbs_{532} vs. irradiation time profiles were generated and are illustrated in the inset diagram of Fig. 9. In order to show that the addition of the sun screen layer merely reduces the amount of UV light reaching the sample and thus reduces the rate of reaction, without interfering with the photochemistry of the tetrazolium two films, namely an NTC film and a 20 phr/UV screen/NTC film were irradiated with 4 mW cm^{-2} until their red colour was fully developed. The former took 120 min, where as the latter took 320 min to achieve the same maximum absorbance (0.28) at 532 nm. The use of a UV screen top layer to reduce the UV sensitivity of a typical NTC film dosimeter suggests that such an approach could be used to adapt the NTC film to provide an indication of impending erythema for any skin type.

3.6. Solar UV work using an NTC film

In a final set of experiments, UV solar simulated light at four different UVI levels spanning the range: UVI 1–8 were each used to irradiate a typical solar NTC film produced at 300 rpm. The data arising from this work allowed the UV dose for each film to be calculated in terms of MED for skin type II and plotted in the form of ΔAbs_{532} as a function of UV dose as illustrated in Fig. 10. The results reveal that all the data points for films exposed to UVI 1, 3, 5 and 8 lie on a common line indicating that a typical NTC film can be used as a quantitative method for assessing the solar UV dosage received.

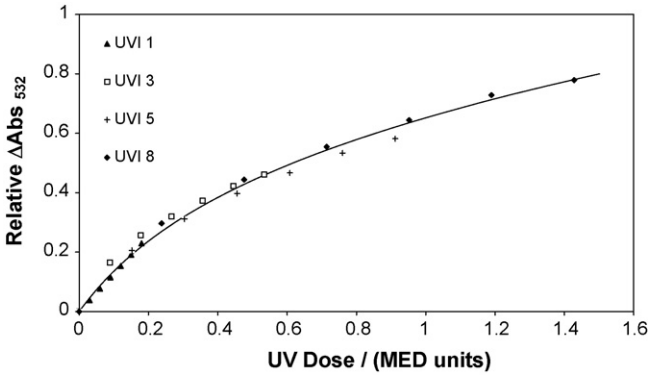

Fig. 10. A plot of ΔAbs_{532} vs. UV dose for skin phototype II received (where 1 = MED for skin type II i.e. 250 J m^{-2} h^{-1}) for standard formulation ink NTC films spun at 300 rpm. The solid line was calculated using Eq. (2).

For example, if upon exposure of a typical solar NTC film a ΔAbs_{532} value of approx. 0.67 is reached this will signify an MED value of 1 has been reached for skin type II and so erythema is likely to occur. In Fig. 10 the line of best fit to the data is given by the expression:

$$\text{UV dose (MED)} = (0.63 \pm 0.03)(\Delta Abs_{532} + \Delta Abs_{532}^2 + (1.85 \pm 0.29)\Delta Abs_{532}^3) \quad (2)$$

Which has the same form as that reported by Diffey [28] for the polysulphone UV dosimeter. Similar ΔAbs_{532} vs. MED curves were generated using solar UV. An error analysis of the data in Fig. 10 reveals that it is ca. 5% up to MED values of 0.3, but then increases with increasing MED, reaching 7% at MED = 1. As an alternative to reading off the measured value of ΔAbs_{532} as a method of determining the MED received, a colour match card could be used to enable the user to determine when they have been exposed to 1 MED, or more, for skin type II, although this is likely to increase significantly the likely error. If an additional polymer/sunscreen layer is introduced to the system, the indicator film could be used to show when erythema is likely to occur for other (higher) skin types. Further solar simulator work showed that the response of the dosimeter is temperature independent over the range 20–40 °C and, like most UV dosimeters, exhibits a cosine-like response dependence upon irradiance angle [25].

4. Conclusions

PVA films containing the dye NTC undergo reduction to the monoformazan form of NTC when exposed to UVA or UVB light. The rate at which the colouration of the films occurs is dependent on properties of the film, such as [NTC] and film thickness, and increases with increasing UV irradiance. The film response is temperature independent over the range 20–40 °C and exhibits a cosine-like response dependence upon irradiance angle. The rate of photocolouration can be reduced by the introduction of a UV-screening layer on top of the standard NTC dosimeter and the dosimeter films give a consistent response to solar simulated light of different irradiances. Using this light source the NTC film dosimeter can be used to identify the point when an MED = 1 has been reached and erythema is likely to occur upon further exposure to solar UV. Although a real-time UV dosimeter, like most dye-based UV dosimeters, the NTC film has a poor match with the erythemal spectral sensitivity of skin and so can only be used as an erythemal indicator when calibrated using the UV source of interest, which in most cases is the sun. The lack of overlap is in striking contrast to several biological UV dosimeters, such as that based on *B. subtilus*, and the polysulphone UV dosimeter, although the former requires extensive processing (taking about 1 day) and the latter requires access to a UV spectrophotometer. Clearly, dye-based UV dosimeters, such as the NTC films reported here, have a long way to go before they can challenge the more established biological and chemical UV dosimeters. However, they can play a useful role in warning of sunburn when used from the middle morning to middle afternoon.

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