

Photochromic Print's Distinct Photo-Fading Characteristics under Continuous UV Irradiation Measurement Modes

Utkarshsinh B Solanki^{1*}, Martina Viková¹, Michal Vik¹

¹ Department of Material Engineering (KMI), Technical University of Liberec, Studentska 1402/2, Liberec, Czech Republic

* Corresponding author. E-mail: utkarshsinh.solanki@tul.cz

Abstract

When studying photochromic materials, photostability and endurance are crucial considerations. These characteristics can benefit UV sensors, optical rewritable storage devices, and anti-counterfeiting techniques, as well as the ophthalmic industry. When light irradiates a photochromic system, chromophoric dye molecules, the chromophoric part of the dye, and fatigue resistance refer to how well they hold up against photodegradation, photobleaching, and photooxidation. In our experiment, we examined the photo-fading tendency of a photochromic dye with photochromic textiles. We used the screen-printing technique to create photochromic prints with different dye concentrations. We then continuously exposed the prints to UV light using a spectrophotometer. UV light caused the photochromic dye molecules in these prints to fade and photodegrade. We used three distinct ways to assess UV irradiation over many cycles. We proposed three hypotheses: When photodegraded using various techniques, the UV dosage exhibits additive behaviour during recorded UV irradiance cycles. In addition, a visible light source is more likely to cause photodegradation entirely or partially when the reversion process repeats over several cycles. Next, the prints exhibit photofading when subjected to one UV cycle and multiple irradiance cycles within a single measurement block and numerous irradiance cycles within a single measurement period. The plateau of each measured photochromic cycle adheres to the one-phase dissociation feature for photo-fading behaviour. In contrast, the colour span values for the photochromic system, measured during the development phase of each UV irradiation cycle, fit the one-phase association model.

Keywords

photochromic dye, UV irradiance cycles, colour span values, photo-fading, photochromic prints.

1. Introduction

Photochromic compounds exhibit a structural change when exposed to external stimuli, such as UV light. Chromophores present inside the photochromic dye change from colourless to coloured when they are exposed to UVB (280–315 nm) and UVA (315–400 nm) ultraviolet light, which are used for irradiance ($h\nu_1$). This change cannot be undone at the molecular level. Energy from the visible range ($h\nu_2$) typically restores the isomeric form of a substance to its bleached state when the activation source (400–700 nm) is no longer present.

Photochromism is when electromagnetic light changes the state of a chemical species so that it can absorb light in two different ways (Figure 1). The incident light's frequency corresponds to the energy levels, and the interaction of radiation from molecules can cause an irreversible transformation in the electron density distribution. As a result, molecules become energized, reducing the strength of radiation. Both states exhibit coherence in the internal

conversion direction and the frequency with which they transition from a colored to a colourless state, justifying several photochromic cycles. It is during these interstate conversions that partial or complete photodegradation takes place. The absorption of ultraviolet (UV) radiation and the prevailing wavelength in various media substrates, including paper, fabric, films, and glass, influence the transition between unexcited and excited states. The process entails the excitation of a molecule's electronic state by UV irradiation [1, 2].

When they encounter light, the spiroxazine-based photochromic dye undergoes a photodegradation of dye molecules inside a photochromic system. This leads to thermal cis-trans isomerisation into zwitterionic or quinonoid merocyanine structures. These transitions, influenced by the quantity of chromophore molecules and the intensity of UV light, cause the electromagnetic spectrum's red and blue shifts. The process is essential for comprehending the molecular structure's reactivity, stability,

and physical transition in its pure state. However, we enclose the photochromic dye in tiny capsules with additives and process it by adding other substances for screen printing. These systems' photo-fatigue characteristics depend on their reactivity to UV light, UV radiation duration, photostability, and ability to return to a colourless state. This can occur when exposed to visible light sources [1, 2]. Cotton-based photochromic fabrics use various technological techniques

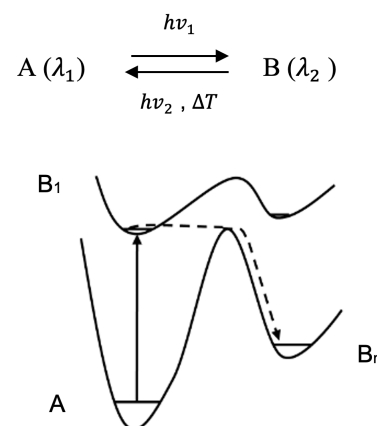


Fig. 1. Unimolecular photochromic systems and a class of diabatic photoreactions

to create a photo-responsive system, including printing, coating, padding, sol-gel, and exhaust [3]. The production of photochromic systems involves several techniques, such as mass dyeing, melt spinning, screen printing, inkjet printing, pad drying, exhaustion dyeing, and electrospinning. Every technical method possesses distinct advantages and disadvantages. Little et al. fabricated photochromic fabric by employing screen printing and dispersing photochromic colourants as dyes [4,5]. Víková et al. and their research group fabricated the chromic system using a variety of textiles and the screen-printing technique, as well as photochromic dyes and other production methodologies, like electrospinning and mass dyeing, to produce photochromic nonwovens and studied their photo-fading behaviour, designing the measurement protocols [6-9].

The photo-fatigue test involves shining UV light on a photochromic system to make it change colour and lose its colour intensity, then letting it return to its original state using the standard photochromic cycle curve (Figure 2). This approach investigates the photodynamics of photochromic compounds, specifically examining thermal stabilisation, the growth phase, and decay phase, as previously mentioned [7-9]. Figure 2 depicts the photochromic cycle, including thermal stabilisation, kinetic profile development, and decay phases. This enables us to observe photochromic phenomena during the forward and reverse processes. The experimental measurements were conducted in a laboratory under controlled conditions at room temperature, specifically at $20 \pm 2^\circ\text{C}$, once the FOTOCHROM3 spectrophotometer was stabilised. Solanki et al. proposed a novel approach for analysing data and investigating the photo-fatigue behaviour of photochromic prints and photochromic nonwoven-based photochromic systems [7-9]. We evaluated the photodegradation of the prints during the measured growth phase of UV irradiance cycles using identical prints [7,8]. Moreover, we investigated the photochromic system's photo colouration and decolouration phases, photo failure behaviour, and photodegradation. In

addition, we assessed the system's growth phase behaviour over a specific number of UV irradiation cycles using various measurement modalities. The process begins with thermal stabilisation (VIS+), followed by the growth phase (UV+), and finally, the decay phase (VIS+), as shown below.

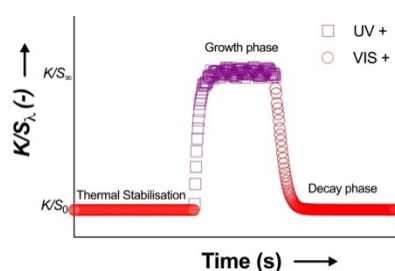


Fig. 2. General kinetic profile curve of a photochromic cycle

Seipel et al. introduced an extended kinetic model that defines rate constants for colouration, decay, and decolouration, allowing for predicting colour performance in photochromic textiles. This model offers a thorough comprehension of how specific fabrication parameters, like inkjet printing and UV-curing processes, can modify the kinetics of the photochromic reaction [3,10,11]. Previously, scientists only looked at the observed cycles, and raw data plots containing many irradiance cycle plots can be seen in their work; but there was no deep data analysis to understand the photo-fading characteristics' profile curve for its repeatability cycles, considering their rewritable devices and usage repeatability. These plots show the colouration (K/S) values during the growth and decay phases as a function of the cycles of the experiment and how resistant photochromic materials are to fatigue in solid substrates. The number of flashes used determines the colour value of a liquid substrate. We collected several measurements during the experiment to account for any equipment-related inaccuracies. The main question being investigated is what the pattern of photo-fading observed throughout the growth phase of each photochromic cycle is, as observed throughout the experiment across all the UV irradiation cycles used. The amount of UV light used during each growth phase cycle

for photodegradation and during the reversion process helps the chromic dye break down through photodegradation. The specific spectrophotometer or the measuring equipment provides the cyclic, continuous, and flash types of measurement for studying photochromic dyes and their degradation behaviour following the photochromic profile curve as one irradiance cycle. In photochromic textiles, like photochromic prints based on spiroxazines, the photofading of photochromic dye occurs throughout the photocoloration process, which also results in the colour reversibility and reproducibility of colour intensity values over the irradiance cycles measured and their mode of measurements. When analysing the colour intensity values using the Kubelka-Munk values and fitting the raw data using first-order kinetics, the conventional photochromic cycle curve is adhered to. The photo-fatigueness of photochromic dye in its coloured form upon excitation has its own limitations regarding reproducibility and repeatability, which are more significant to study and investigate for its applications based on its resultant photo-fatigue characteristics. First, for practical application in real time, the fatigue test that considers the photochromic cycle and its kinetics should be monitored and evaluated for several hundred cycles instead of a few dozen photochromic cycles. The colour change that takes place with every cycle causes the kinetic parameter to fluctuate and not remain constant, even if we assume that it remains constant for a single cycle. Finally, there is no standard testing protocol for assessing and monitoring photochromic textiles in real-world, everyday environments. The photo-fatigue resistance and repeatability of the measurements and their results directly affect the long-term photostability of the photochromic system. Because of this, it is challenging to predict the photo-fatigue behaviour of photochromic fabrics using existing measuring methods and the first-order kinetic model [12-19].

The study employed specifically designed photo-fading tests. The main objective was to examine photochromic devices' degrading and fading characteristics under

different UV irradiation conditions. Using a FOTOCHROM3 spectrophotometer, we obtained spectroscopic reflectance factor values under constant UV light for all three measurement modes. Based on the data, we proposed three hypotheses. One idea is that the intensity of UV light exposure at each stage of the photochromic system's development accelerates the photodegradation of photochromic molecules and causes their behaviour to accumulate. We can witness this phenomenon by observing multiple short cycles. The UV energy used throughout the experiment for the UV irradiance cycles behaves in an additive manner. The second concept and its associated experiment focus on photochromic compound reversion. More precisely, they investigate the impact of the relaxation phase on the processes of photodegradation and photofading. During the relaxation process, the photocoloration's strength weakens, which causes chromophore molecules to break down slowly through photodegradation. These molecules can either remain intact for future cycles or completely disintegrate. In photochromic processes, photodegradation occurs through a series of UV cycles corresponding to an equivalent number of UV irradiance cycles. The visible light source exhibits an inverse effect and also causes the degradation of a photochromic system. The third idea states that the upper plateau (K/S_{∞} values) is made by fitting the raw data to the first-order kinetic model for each UV irradiance cycle recorded during the growth phase. The data curve constantly exhibits a fading tendency, indicating adherence to the one-phase dissociation model.

2. Material and Methodology

2.1. Photochromic print preparation

We used two different concentrations of photochromic dye in printing paste to form photochromic systems. We applied the printing paste to a cloth of a polyester and cotton blend (65:35). The photochromic prints underwent drying and curing at temperatures of 120°C and 150°C for

two and three minutes, respectively. The following concentrations of the photochromic dye: 100 g.kg⁻¹ and 200 g.kg⁻¹, were used for the study. We used a photochromic dye [7]: 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3-(3H) naphth[2,1-b](1,4) oxazine. This dye changes colour when exposed to UV light, undergoing the chromic phenomenon.

2.2. Photo-fatigue measurements using FOTOCHROM3

The FOTOCHROM3 spectrophotometer enables the measurement of UV+ and VIS+ modes, including sequential cycles of short and long continuous irradiance. Furthermore, it allows for measurement, specifically in the UV+ mode, without requiring a relaxation phase by tracking the dynamic profile curve of a single photochromic cycle. The system consists of two light sources: an excitation light source that emits light at a wavelength of 360 nm (UV+) and a visible light source (VIS+). This arrangement facilitates the measurement of reflectance data from the photochromic systems under investigation. Photo-fatigue measurements of photochromic prints were performed at a controlled temperature of 20±2°C using a FOTOCHROM3 spectrophotometer. We conducted the measurements during photochromic cycles using an asymmetrical configuration of UV+ and VIS+ timing. We configured the time for all three modes with the following photo-fatigue scenario: from 240 seconds for the exposure phase (E) to 360 seconds for the decay phase (D), considering the photochromic cycle curve. We quantified the duration of these phases in seconds. The spectral irradiance (UVA region) area remained consistent at 7.82 W.m⁻². We calculated the UV dosage by integrating the spectral irradiance with the duration of UV exposure.

Figure 3 in the proposed protocols used for investigating the photofading behaviour of a photochromic dye provides an in-depth characteristic profile of behaviour through the

measurement protocols designed. The development of measurement protocols includes Mode A, Mode B, and Mode C to investigate the photo-fading behaviour of dye's photodegradation, where the photodegradation of dye influences the measurements that are carried out. In Figure 3a, the cyclic blocks measure six photochromic cycles using five repeating measurements as an intermittent mode of measurement (Mode A). A time-length break and a gap between successive observations separate these measurements. In the results and discussion section, Figures 5a, 6a, and 6b show the gap with a dashed line (in vertical dashes) following each measurement block for each photochromic system. At the same time, the growth phase's fading pattern specifies the time interval between the measurements. We measured it with the defined protocols in a repetitive manner to use statistical tools; however, the photofading behaviour follows a continuous profile of characteristics rather than a discontinuous one. We conducted the measurements in an extended continuous mode (Mode B), measuring 30 cycles in a single block (Figure 3b). We conducted a study to determine the number of UV-irradiation photochromic cycles required for the molecules to recover or irreversibly deteriorate the photochromic system during the decay phase. In this study, we used the fatigue scenario for the cyclic mode. The photochromic prints achieve their stable equilibrium condition more rapidly, namely, the colour span value (the upper plateau) obtained from the data fitting. Furthermore, Figure 3c shows that when using the UV exposure mode without a decay (relaxation) phase, the system applies the equivalent number of UV cycles to the other two modes, without the relaxation of a photochromic system, as if it were one long continuous measurement. Without the relaxation phase, the photochromic system repeatedly breaks down the photochromic dye molecules of a photochromic sample under UV irradiance.

The UV irradiance dose was measured as UV dose (mW.s.cm⁻²) = UV energy received (mW.cm⁻²) * UV irradiance time (s) used for UV exposure under

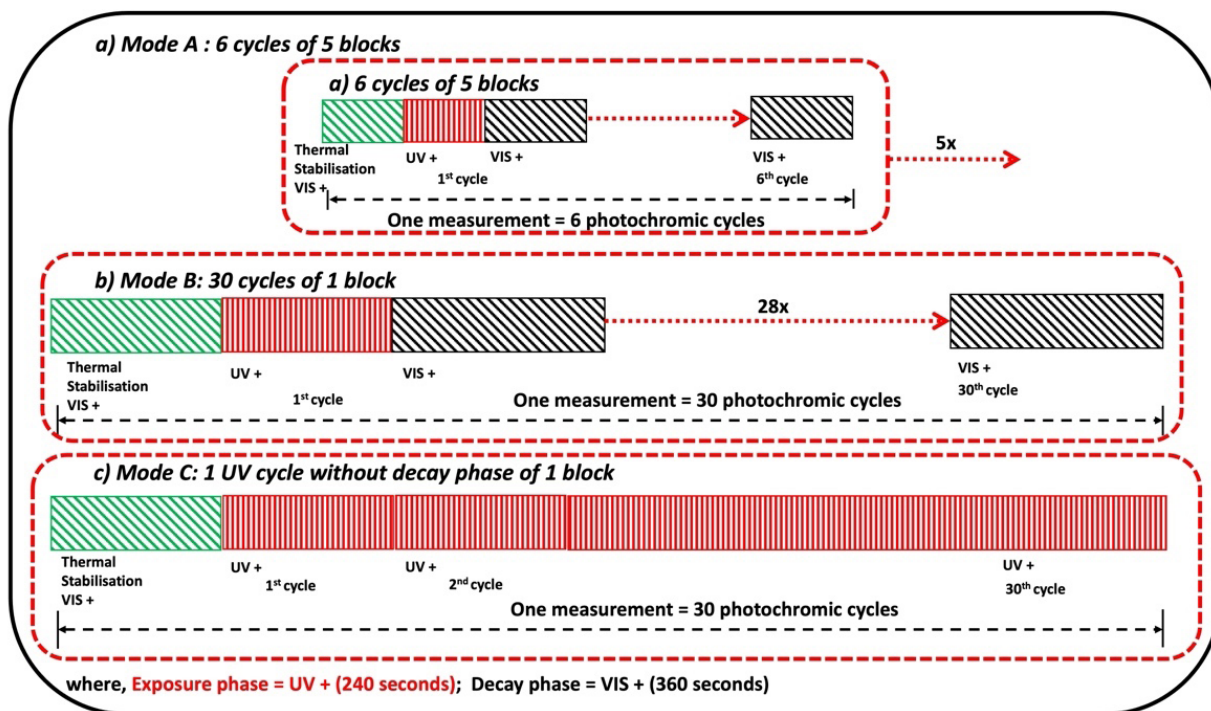


Fig. 3. Schematic representation of photofatigue experiment under continual irradiance: a) Mode A: 6 cycles of 5 blocks, b) Mode B: 30 cycles of 1 block, and c) Mode C: 1 UV cycle without decay phase of 1 block

continuous UV irradiance using a FOTOCHROM 3 device. Mathematically, the dose can be measured as, $H \text{ (W.h.m}^{-2}\text{)} = E \text{ (W.m}^{-2}\text{)} * t \text{ (s)} / 3600$. The Y-axis represents the degree of photocoloration and photodegradation that occurs during each measurement mode: Mode A, Mode B, and Mode C. The X-axis represents the applied fluence (UV dose) in an additive manner as per Equation 2. This can be observed in the resultant plots of the photocoloration values that undergo the photo-induced degradation of dye in photochromic prints in the results and discussion section.

2.3. Data treatment

The photochromic system undergoing the photochromic phenomena can be described by the first-order kinetic association and dissociation model, which explains the photo coloration and decoloration processes. This model accurately represents the profile of the photochromic cycle. We transformed the raw data using the Kubelka-Munk (K/S) function, and when it enters the photoexcitation state and transitions into the thermal relaxation state, it conforms

to the first-order kinetic model. When exposed to a constant and particular wavelength of the light source, the photochromic system can attain a state of photo-steady equilibrium. The upper plateau curve of the growth phase represents this state, characterising the system as open and coloured. Under continuous UV irradiation, the photochromic prints prepared exhibit a photo-fading characteristic. As detailed in previous work, we transformed and treated the colour values using the Solanki et al. [7,8] methodology for the data treatment of such photochromic systems and to obtain kinetic parameters.

The photo-kinetic behaviour of the photochromic system is analysed using the first-order kinetic model, as described in earlier works that investigated the kinetic behaviour utilising various photochromic dyes [8,10,11]. The photofading characteristic can be described by Equation 1, where the photochromic dye undergoes photo-fading at a certain dose for a chosen UV irradiance time used for the experiment. Equation 1 resembles the first-order kinetic model, which looks at how photochromic systems fade in UV light during recorded

photochromic cycles with the UV dose used. We apply this model to fit raw data for both the growth and decay phases. We documented the rate-constant behaviour of each development phase during photodegradation under the measured UV irradiation cycles. Nevertheless, this study specifically assesses the photofading characteristics of development phases across multiple cycles of UV irradiation using various modes.

$$\frac{K/S_{(H)}}{\exp(-kH) + K/S_{(\infty)}} = \left(\frac{K/S_{(0)}}{K/S_{(\infty)}} - 1 \right) \quad (1)$$

$$H = (E_1 * t_1 + E_2 * t_2 + \dots + E_n * t_n) * n \quad (2)$$

Where, $K/S_{(0)}$ – initial upper plateau obtained after fitting the raw data (first UV irradiance cycle), $K/S_{(\infty)}$ – the upper plateau obtained after fitting the raw data of each growth phase cycles, n – is the total number of growth phases of each photochromic cycle curve, the subscript (H) – UV irradiance dose at certain UV light intensity and the UV irradiance time used: $H = E * t$, H is UV dose (fluence in W.h.m^{-2}), E – UV irradiance of the UV light source used (mW.cm^{-2}),

t – UV irradiance time used in (s) during the growth phase for each photochromic cycles (n), k – rate constant (s^{-1})

[Note: E and t for this research work have been used the same for each UV irradiance (n^{th}) cycle]

When subjected to several UV irradiation cycles during consecutive measured growth stages, the photochromic system exhibits deterioration behaviour. Therefore, we denote the number of UV radiation cycles as the converted UV dosage necessary for photo-fading photochromic dye molecules. The first step in processing the data is using the *Kubelka-Munk* (K/S) function, as per the data treatment using the first-order association model, after transforming the reflectance data into colour intensity values at its dominant wavelength, which makes them stand out the most, and their interconversion through colour transformation. Subsequently, the data undergo additional analysis using a one-phase association model. The photochromic system's dominant wavelength ($\lambda_{\text{max}} = 570 \text{ nm}$) experiences a transition in colour, shifting from a colourless state to a rich and strong purple hue over n^{th} UV exposure time duration. We used the colour span data to fit a one-phase association model at its dominant wavelength, which allowed us to calculate the kinetic parameters: rate constant k (s^{-1}), half-life $t_{1/2}$ (s), and maximum colour span value (K/S) for the photocolouration phase. Equation 2 reflects our initial hypothesis, which suggests that the dose employed for each recorded UV irradiance cycle has a cumulative additive effect on the photodegradation behaviour and occurs during consecutive UV irradiance cycles. The UV irradiance cycles and the upper plateau behaviour were observed during the extended continuous mode. The photodegradation behaviour conforms to a one-phase decay model for all the cycles measured. Furthermore, we note that the photodegradation behaviour is consistent in the UV mode without a relaxation phase, wherein the photochromic system is just exposed to UV light. The $\Delta K/S$ (%) as a percentage of photodegradation of a photochromic system was determined

by calculating the difference in colour intensity (K/S_{∞} values) between the first and last UV irradiation cycles after treating the raw data using Equation 1 (the fitted K/S_{∞} values – the upper plateau) and the growth phase of a photochromic cycle, which results in the photo-fading characteristic curve. The study explored chromic dye's photo-fading and photodegradation behaviour under continuous UV irradiance. It also examined three distinct measurement treatments for the growth phase of a photochromic cycle to study the photo-fading characteristic under continuous UV irradiance. We performed the raw data fitting and data analysis using *GraphPad Prism 10 (10.3.0)* statistical software on the *MacOS* platform.

3. Results and Discussion

The molecules undergo electronic transitions in the visible range, changing colour. This colour change can be classified based on the type of molecules or the specific transition, ultimately forming intermediate products with low energy and a lower half-life to last longer in the photo-fading process. Exposure to ultraviolet (UV) light causes the photochromic print to change colour, with a chromophore group within the dye's structure contributing to its visibility. To understand its composition, it must consist of two components: the chromophore and the auxochrome. The chromophore, a component of a substance's chemical structure, determines its colour.

On the other hand, auxochrome enhances the substance's colour. The chromophore is subjected to photo-induced UV irradiation, resulting in a chromic phenomenon that causes a colour change. It entails the transfer of electronic energy between the ground and excited states. The chromophore contains an electron-accepting group, whereas the auxochrome has an electron-donating group that can function as a conjugated system. Electronic energy transitions occur between the ground state and the excited state of an energy conversion system due to the presence of acceptor and donor groups.

Using specially designed measurement modes, we systematically exposed the photochromic systems to UV irradiation. Figure 3 illustrates the three continuous irradiance modes specifically designed for the experiment, as outlined in the previously mentioned hypothesis in the introduction. We selected the growth phase's duration, assuming it had reached a photo-steady equilibrium state. During the preliminary measurements, we observed the growth phase peak and the decay phase trough while the system was in the relaxation mode. For photoexcitation, we used ultraviolet (UV) energy converted into a specific dosage for a specific area to irradiate the photochromic prints. This energy transforms one state into another. However, the fatigue exhibited by the photosensitive material throughout a specific number of photochromic cycles, the response of the excited state under various conditions, and the resulting deterioration from exposure all vary. Photochromic compounds are exposed to light because the dye's molecules go back and forth between their open and closed forms. After repeated exposure to UV light, photochromic systems experience a depletion of their photochromic molecules. The process described is known as photodegradation of the photochromic species, also referred to as fatigue. Oxidation is the primary source of degradation in photochromic materials. This process occurs when the chromic system shifts from a colourless to a coloured state. The amount of energy absorbed by the chromophoric dye molecules determines how the compound's molecules change shape from a *cis-trans* configuration to a *trans-cis* configuration during these events. This allows for the acquisition of the intermediate by-products. The cyclic continuous measuring mode makes it easier to observe these by-products. Exposure of the photochromic system to UV radiation causes the compound to transition from a colourless to a colourful state. The human retina detects colour and transmits information about its appearance to the brain.

Figure 4 shows the absorbance curves in the visible range, where colour

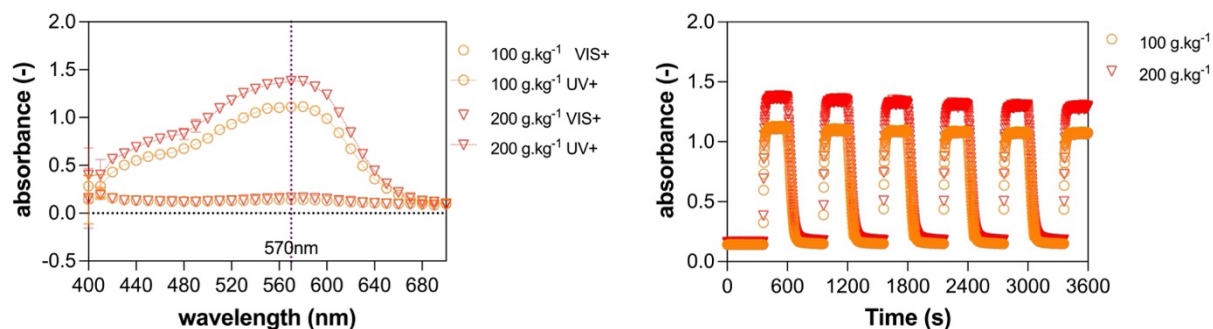
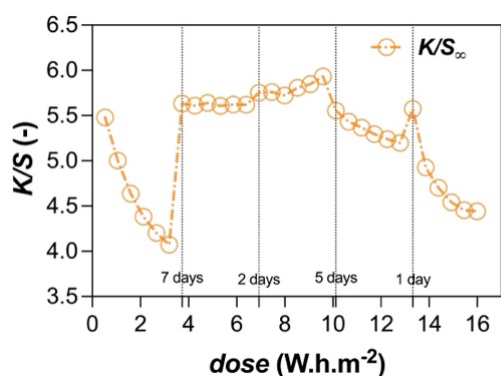
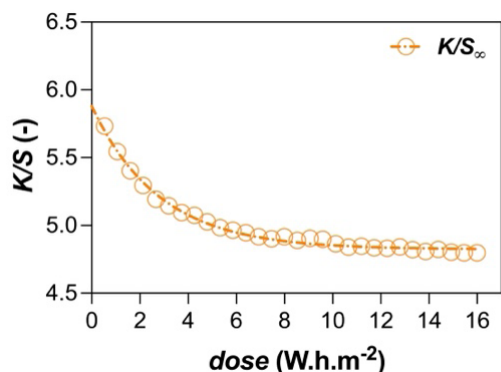


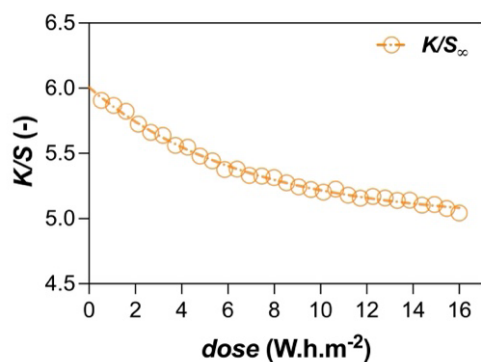
Fig. 4. Absorbance curves of photochromic prints and their characteristics of photochromic cycle measurements under continuous UV irradiance



a) Mode A



b) Mode B



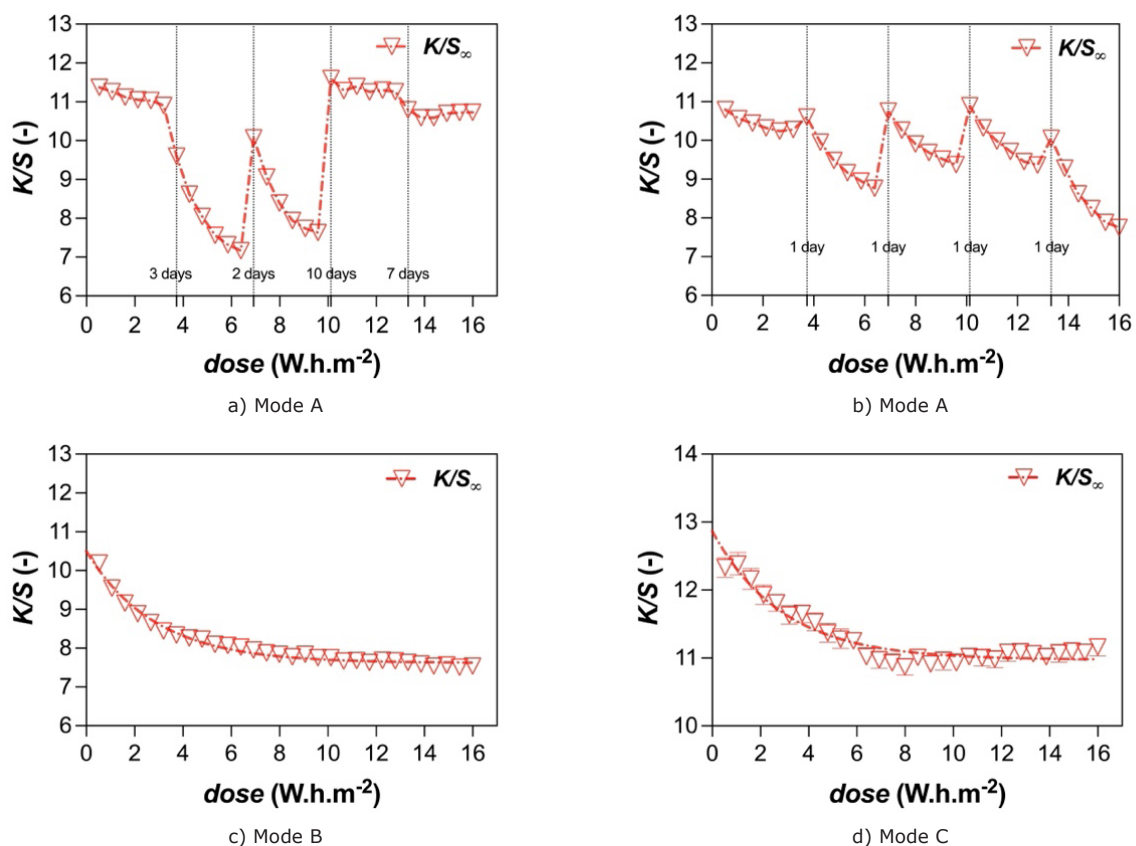
c) Mode C

Fig. 5. Photo-fading behaviour vs. dose of photochromic dye with 100g.kg⁻¹: a) Mode A: 6 cycles of 5 blocks, b) Mode B: 30 cycles of 1 block, c) Mode C: 1 UV cycle without decay phase of 1 block

transformation occurs. The curves also illustrate the photochromic kinetics at their most prominent wavelength. We analysed the photo-fading behaviour of the photochromic systems using these recorded curves of the growth phase cycle. We converted the spectrokinetic parameters and reflectance values into coloured intensity values as (K/S) using the *Kubelka-Munk* function at its dominant wavelength. We tested how the photochromic prints would break down in light by keeping the same photo-fatigue and spectral irradiance levels throughout the experiment, while keeping the same measurement conditions. This made sure that the data analysis would be consistent. We positioned the photochromic prints below the instrument's aperture to conduct the measurements for all experiments. In this study, we observed a decline in the coloured (K/S) values and documented their photofading behaviour under various continuous UV irradiance modes.

Figures 5 and 6 illustrate the photo-fading characteristics of the photochromic systems when subjected to cyclic continuous UV irradiation under different modes. We conducted the measurements for six irradiance cycles, dividing them into five blocks. In this mode, we conducted random measurements for each photochromic system, taking three or five measurements and using their average. Nevertheless, the properties of photocolouration and photofading exhibit wave-like behaviour. Furthermore, the hypothesis regarding using UV doses to assess photodegradation behaviour is cumulative.

Mode B: 30 cycles of 1 block			Mode C: 1 UV cycle without decay phase of 1 block		
	100g.kg ⁻¹	200g.kg ⁻¹		100g.kg ⁻¹	200g.kg ⁻¹
K/S_{∞}	5.880	10.50	K/S_{∞}	6.007	12.87
K/S_0	4.823	7.615	K/S_0	4.990	10.97
k	0.3564	0.3525	k	0.1498	0.3425
H	1.945	1.967	H	4.627	2.024
$R\ squared$	0.9920	0.9856	$R\ squared$	0.9949	0.9309
$RMSE$	0.0208	0.0772	$RMSE$	0.0178	0.1152
AIC_c	-223.7	-145.1	AIC_c	-232.8	-121.1
$\Delta K/S$	16.30 %	26.01 %	$\Delta K/S$		9.48 %

Table 1. Best-fit values for 100 g.kg⁻¹ and 200 g.kg⁻¹Fig. 6. Photo-fading behaviour vs. dose of photochromic dye with 200g.kg⁻¹: a) Mode A: 6 cycles of 5 blocks, b) Mode A: 6 cycles of 5 blocks, c) Mode B: 30 cycles of 1 block, d) Mode C: 1 UV cycle without decay phase of 1 block

However, we saw a simultaneous increase in colouration and photodegradation in the photochromic system. The assumptions for the cyclic mode say that the UV dosage energy used to break down photochromic devices after each cycle of UV irradiance acts in a way that adds up. Using a smaller number of photochromic cycles in a block mode measurement is not advisable for researching photo-fading behaviour, as it is both intermediate and random. The photochromic system tends

to restore molecules that have undergone degradation due to exposure to ultraviolet radiation. The photochromic system with a concentration of 100 g.kg⁻¹ was utilised for three different UV irradiance modes (Figure 3). The photo-fading behaviour of the system after data treatment is depicted in Figures 5 and 6, which show the characteristics of their behaviour over the UV irradiance cycles measured for the three modes. The photochromic system was utilised with a concentration

of 200 g.kg⁻¹ for two different UV irradiance modes (Figure 3). We took the measurements 24 hours after each set of UV irradiation cycles to evaluate the photodegradation behaviour. The study included six cycles in five blocks, as shown in Figures 6a) and 6b), with random intermittent measurements and after 24-hour gap measurements (one day gap between consecutive measurements), respectively. The measuring conditions for the other two modes remained

unchanged from those stated for 100 g.kg⁻¹ and 200 g.kg⁻¹, as well as their photofading characteristics. The K/S_{∞} (upper plateau) values for each UV irradiance cycle were determined by fitting the one-phase association model to the raw data at their dominant wavelength. The percentage of photodegradation $\Delta K/S$ (%) of the photochromic system is determined by calculating the difference between the initial (K/S_{∞}) and final (K/S_{∞}) measurements after a series of UV irradiation cycles.

The photodegradation of the photochromic system with dye concentrations of 100 g.kg⁻¹ and 200 g.kg⁻¹ results in varied $\Delta K/S$ values due to variations in the exposure area content and the homogeneity of the photochromic system during its production. The best-fit values from Equation 1, corresponding to Figures 5 and 6 and Table 1, show that these modes behaviour demonstrates their best-fit values for the following modes: 30 cycles of 1 block and 1 UV cycle without the decay phase of 1 block. This analysis employs the one-phase dissociation model, processing the raw data from each UV irradiance cycle with the appropriate UV modes to obtain the plateau values. This model uses the one-phase dissociation model to show how the photochromic dye molecules in the textile substrate fade in response to UV light. We obtained these plateau values by analysing and deriving them after treating the raw data. The $\Delta K/S$ (%) for 30 cycles in 1 block is 16.30%, while for 1 UV cycle without the decay phase of 1 block, it is 14.61% for the 100 g.kg⁻¹ photochromic system. The $\Delta K/S$ (%) for 6 cycles in 5 blocks is 28.12%; for 30 cycles in 1 block, it is 26.01%; and for 1 UV cycle without the decay phase of 1 block, it is 9.48% for the photochromic system with a concentration of 200 g.kg⁻¹.

A one-phase dissociation model describes the photodegradation of a photochromic system, where the system undergoes degradation in two modes: a long continuous mode with a relaxation phase and a UV mode without a relaxation phase. Without the relaxation phase, the photochromic system does not return to its initial phase before each

subsequent cycle of UV irradiation. Only the photodegradation process happens constantly during the recurrent cycles of UV irradiation. However, analysis of photodegradation behaviour also depends on the density of photochromic dye molecules in the exposed area. The reverse photochromic phenomenon, which occurs more rapidly during the relaxation phase in the presence of visible light, primarily impacts the fading of a photochromic system. In larger measurement blocks, the repeated UV irradiation cycles observed lower the colour intensity values. This is because the chromic dye's molecules in the photochromic prints break down partially or completely. The photochromic system breaks down less when exposed to a UV light source without a relaxation phase in one UV cycle mode compared to when it is exposed to long block UV irradiance cycles.

However, the UV mode without the decay phase consistently follows the one-phase dissociation model throughout the UV dose used for the photochromic systems. To investigate photo-fading behaviour, we used the characteristics of the upper plateau. We found a positive variance in the measurements from the device and the duration of each data measurement. We employed first-order kinetics to analyse the data and examine the photo-fatigue behaviour of the samples while exposed to continuous UV light. To investigate a substance's photodegradation capabilities and photo-fading characteristics, the study results recommend using a precise number of cycles within a single measurement block rather than a short cycle within a block. Furthermore, it is recommended to use the continuous UV irradiance measuring modes and a UV light source with a distinct spectrum power distribution (SPD).

4. Conclusion

Chromic phenomena cause the photochromic dye on the base substrate to change colour when exposed to light. These changes depend on the dye's chemical structure, content, and uniformity during its preparation for

a photochromic system. The photo-fading behaviour checks how much the colour fades and degrades during cycles of UV light (the growth phase) in photochromic systems in correlation to the dye's photo-fading behaviour. The measurement protocols that impact the resulting characteristic curve when using three continuous UV irradiance modes are substantial. The duration of UV exposure and the UV light source's strength significantly impact colour alteration and fading. We measured the photodegradation characteristic curve through designed measurement protocols. The cumulative UV dosage in continuous irradiance does not conform to the one-phase dissociation model for photodegradation behaviour (Mode A). Using the small cyclic block mode, the photofading behaviour features a waviness curve with increasing and decreasing colour span values. We can measure many cyclic block modes and one UV cycle without a decay phase for an extended period. Each photochromic cycle's growth phase has an upper plateau that follows the one-phase dissociation model over the UV irradiance cycles measured. For this reason, it is better to do a long measurement in a single block without stopping than to use a few cyclic block modes or a single UV cycle without a decay phase when studying how photochromic materials break down when mixed with any solid substrate. Therefore, we recommend using Mode B and Mode C experimental designs to study the photo-induced degradation behaviour of photochromic dyes for their repeatability, irradiance cycles, and recovery after excitation of a photochromic system for its applications in the ophthalmic industries.

Acknowledgements

This work was supported by the Student Grant Competition of the Technical University of Liberec, Czech Republic [grant number SGS-2022-6039, 2022].

I would like to thank Marcela Pechová for preparing the samples and for her feedback during this study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the research work reported in this paper.

References

- Bamfield P, Hutchings MG. Chromic phenomena: technological applications of colour chemistry. Royal Society of Chemistry; 2010. <https://doi.org/10.1039/9781788012843>
- Vik M, Periyasamy AP. Chromic materials: fundamentals, measurements, and applications. CRC Press; 2018 Aug 6. <https://doi.org/10.1201/9781351171007>
- Seipel S, Yu J, Periyasamy AP, Viková M, Vik M, Nierstrasz VA. Inkjet printing and UV-LED curing of photochromic dyes for functional and smart textile applications. RSC advances. 2018;8(50):28395-28404. <https://doi.org/10.1039/c8ra05856c>
- Little AF, Christie RM. Textile applications of photochromic dyes. Part 2: factors affecting the photocoloration of textiles screen-printed with commercial photochromic dyes. Coloration Technology. 2010 Jun;126(3):164-70. <https://doi.org/10.1111/j.1478-4408.2010.00242.x>
- Little AF, Christie RM. Textile applications of photochromic dyes. Part 3: factors affecting the technical performance of textiles screen-printed with commercial photochromic dyes. Coloration Technology. 2011 Oct;127(5):275-281. <https://doi.org/10.1111/j.1478-4408.2011.00307.x>
- Vikova M, Vik M. Alternative UV sensors based on color-changeable pigments. Advances in Chemical Engineering and Science. 2011 Oct 26;1(04):224. <http://dx.doi.org/10.4236/aces.2011.14032>
- Solanki U, Viková M, Vik M. New Method for Prediction of Photochromic Textiles Fatigue Behavior. In Materials Science Forum 2022 Jul 11 (Vol. 1063, pp. 163-172). Trans Tech Publications Ltd. <https://doi.org/10.4028/p-ld65c6>
- Solanki UB, Viková M, Vik M. Spectrokinetic Investigation of the Photochromic system under continuous UV irradiance using reflectance vs. time curves. Fibres and Textiles 31(2), 2024, 35-41. <https://doi.org/10.15240/tul/008/2024-2-005>
- Solanki UB, Viková M, Holec P, Erben J, Vik M. Characterisation and photo-fatigue behaviour of UV-sensitive photochromic systems produced using electrospinning. Journal of Industrial Textiles. 2024 May 31;54:15280837241260068. <https://doi.org/10.1177/15280837241260068>
- Seipel S, Yu J, Viková M, Vik M, Koldinská M, Havelka A, Nierstrasz VA. Color performance, durability and handle of inkjet-printed and UV-cured photochromic textiles for multi-colored applications. Fibers and Polymers. 2019 Jul;20:1424-1435. <https://doi.org/10.1007/s12221-019-1039-6>
- Seipel S, Yu J, Periyasamy AP, Viková M, Vik M, Nierstrasz VA. Resource-efficient production of a smart textile UV sensor using photochromic dyes: Characterization and optimization. In: Kyosev, Y., Mahltig, B., Schwarz-Pfeiffer, A. (eds) Narrow and Smart Textiles. Springer, Cham. 2018:251-257. https://doi.org/10.1007/978-3-319-69050-6_22
- Salemi C, Giusti G, Guglielmetti R. DABCO effect on the photodegradation of photochromic compounds in spiro [indoline-pyran] and spiro [indoline-oxazine] series. Journal of Photochemistry and Photobiology A: Chemistry. 1995 Feb 15;86(1-3):247-252. [https://doi.org/10.1016/1010-6030\(94\)03926-L](https://doi.org/10.1016/1010-6030(94)03926-L)
- Baillet G, Giusti G, Guglielmetti R. Study of the Fatigue Process and Yellowing of Polymeric Films Containing Spirooxazine Photochromic Compounds. Bulletin of the Chemical Society of Japan. 1995;68(4):1220-1225. <https://doi.org/10.1246/bcsj.68.1220>
- Christie RM, Agyako CK, Mitchell K. An investigation of the electronic spectral properties of the merocyanines derived from photochromic spiroindolinonaphth [2,1-b][1,4] oxazines. Dyes and Pigments. 1995 Jan 1;29(3):241-250. [https://doi.org/10.1016/0143-7208\(95\)00049-L](https://doi.org/10.1016/0143-7208(95)00049-L)
- Kellmann A, Tfibel F, Dubest R, Levoir P, Aubard J, Pottier E, Guglielmetti R. Photo-physics and kinetics of two photochromic indolinospirooxazines and one indolino-spiro-naphthopyran. Journal of Photochemistry and Photobiology A: Chemistry. 1989 Sep 1;49(1-2):63-73. [https://doi.org/10.1016/1010-6030\(89\)87106-0](https://doi.org/10.1016/1010-6030(89)87106-0)
- Pimienta V, Micheau JC. Kinetic analysis of photoreversible photochromic systems under continuous monochromatic irradiation from Abs. vs time curves. Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals. 2000 Jun 1;344(1):157-62. <https://doi.org/10.1080/10587250008023830>
- Deniel MH, Lavabre D, Micheau JC 2002. Photokinetics under Continuous Irradiation. In: Crano, J.C., Guglielmetti, R.J. (eds) Organic Photochromic and Thermochromic Compounds. Topics in Applied Chemistry. Springer, Boston, MA. https://doi.org/10.1007/0-306-46912-X_4
- Ortica F. The role of temperature in the photochromic behaviour. Dyes and Pigments. 2012 Feb 1;92(2):807-16. <https://doi.org/10.1016/j.dyepig.2011.04.002>
- Gaeva EB, Pimienta V, Delbaere S, Metelitsa AV, Voloshin NA, Minkin VI, Vermeersch G, Micheau JC. Spectral and kinetic properties of a red-blue pH-sensitive photochromic spirooxazine. Journal of Photochemistry and Photobiology A: Chemistry. 2007 Sep 25;191(2-3):114-21. <https://doi.org/10.1016/j.jphotochem.2007.04.011>