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Comparison of the photochromic behaviour of dyes in solution and on polyester fabric applied by supercritical carbon dioxide

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Abstract. Photochromic textiles are of considerable interest for smart and functional textile applications due to their remarkable dynamic colour changing effect when irradiated with light of a certain wavelength. The use of resource efficient processes, such as digital inkjet printing and supercritical carbon dioxide (scCO₂) dyeing techniques enables an economic production of those high-end functional products with high material costs. In this study, photochromic polyester fabric has been prepared by applying two commercially important photochromic dyes from spirooxazine (SO) and naphthopyran (NP) dye classes using scCO₂-dyeing technique. The properties of scCO₂ dyed photochromic fabrics were compared with the properties of the same dyes in a non-polar solvent, hexane. UV-Vis spectroscopy and a specially designed online colour measurement system capable of simultaneous UV irradiation and colour measurement were used to evaluate the photochromic colour behaviour. Both photochromic dye types embedded in textile as well as in solution showed significant reversible colour changing properties when exposed to UV light and revert to their original non-coloured form when the UV light is removed. The scCO₂ dyed polyester fabrics exhibited similar trends of colour build-up as in solution, while contrasting behaviour was observed in terms of colour changing rates compared to their behaviour in solution.

Keywords: supercritical CO₂ (scCO₂), dyeing, polyester, photochromic, spirooxazine, naphthopyran

1. Introduction

Photochromism is a phenomenon, in which the absorption spectrum of a molecule or a crystal changes reversibly when the sample is irradiated by light of a certain wavelength. Photochromic materials undergo a colour change when irradiated with UV light, most commonly from colourless to coloured, which can be reversed either by the influence of temperature or wavelengths of visible light [1]. The ability of photochromic compounds to switch between different molecular states makes them interesting and feasible for many commercial applications as ophthalmic lenses, optical data recording



and storage, memories, light control filters, sensors and displays. In recent years, there has been a growing interest in the development of photochromic textiles for smart and functional textile applications such as brand protection, responsive camouflage and as UV sensors [2, 3]. Several methods have been used to apply photochromic dyes to various textile substrates such as exhaust dyeing [4-6], screen and digital inkjet printing [7-11], sol-gel coating [12], pad-dry method [13, 14], electro spinning [15, 16] and mass colouration [17, 18]. However, due to technical and performance limitations, it appears that the search for an appropriate production technique that meets the necessary commercial requirements is still underway.

In this investigation, we studied the potential application of photochromic dyes to polyester fabric using $scCO_2$ dyeing technique and compared the photochromic behaviour in solution and on polyester fabric. The use of a resource efficient technique as $scCO_2$ dyeing to develop photochromic fabrics is an attractive alternative to other methods, which use both water and organic solvents, as $scCO_2$ dyeing offers significant environmental and economic benefits. CO_2 is inexpensive, non-toxic, non-flammable, and inert with easily accessible critical conditions ($T_c=31\text{ }^\circ\text{C}$ and $P_c=7.38\text{ MPa}$). The process completely avoids the use of water and the associated wastewater pollution, simpler dye formulation without auxiliary chemicals, shorter dyeing times, and drying is not required with 50 % lower cost [19].

The kinetics of photo-colouration and bleaching were analysed by using UV-Vis spectroscopy for photochromic dyes in solution and a specially designed online colour measurement system, which is capable of simultaneous UV irradiation and colour measurement for photochromic fabrics. Both photochromic dye types in textile and in solution showed significant reversible colour changing properties when exposed to UV light and revert to their original non-coloured form when the UV light is removed. The $scCO_2$ dyed polyester fabrics exhibited similar trends of colour build-up as in solution, while contrasting behaviour was observed in terms of colour changing rates compared to their behaviour in solution. Ruby red (RR) from naphthopyran dye class displayed fast colouration and decolouration in solution but its speed of colour conversion become slower when incorporated to polyester fabric. For Sea green (SG) from the spirooxazine family, opposite trends with slower kinetics in solution and faster photochromic conversion on the fabric were observed. This study provides important information for the application of photochromic materials in solid state embedded within a crystalline polymer matrix.

2. Experimental

2.1. Dyeing process in $scCO_2$

Two commercial photochromic dyes namely ruby red (RR) and sea green (SG) from Vivimed labs, UK were used to dye a plain-woven polyester fabric of 147 gsm (FOV fabrics, Sweden) in $scCO_2$ medium. The dyeing was performed using a batch type $scCO_2$ dyeing apparatus equipped with a high-temperature oil (glycerine) bath, a rotary wheel where the vessels are mounted, a motor, temperature and time controller, a heater, and cooling element. The polyester fabric (21×30 cm, ca. 9 g) was wrapped around a Teflon mesh, suspended inside the dyeing vessel (internal volume of 290 mL) and a small amount of photochromic dye (0.027 % owf ~ 2.56 mg) was placed below the fabric at the bottom of the vessel. Dyeing was carried out at 120 °C temperature and 25 MPa pressure for one hour, which is the optimum dyeing condition selected based on our preliminary study. After dyeing, the vessels were removed from the oil bath and the CO_2 was vented slowly until the pressure reached atmospheric pressure and the samples were taken out from the vessels for further analysis without reduction cleaning procedure.

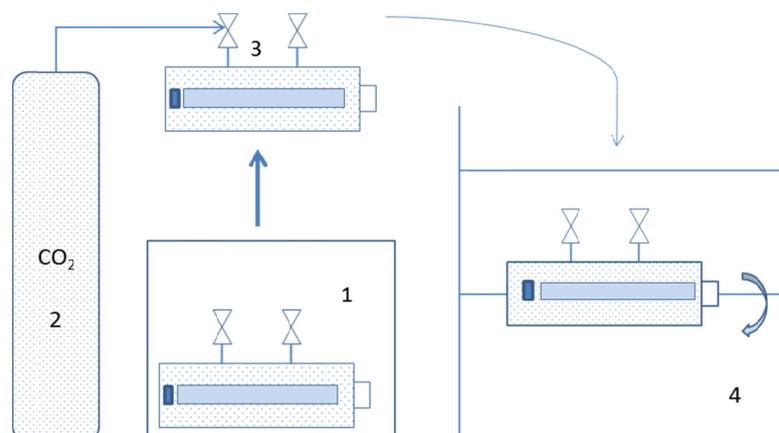


Figure 1. Schematic scCO₂ lab dyeing procedure, (1) freezer, (2) CO₂ tank (3) dyeing vessel, (4) high-temperature oil bath

2.2. Colour measurement

UV-Vis spectra of the photochromic dyes in solution were measured at their specific dominant wavelength (absorbance maximum), defined by a wavelength scan between 400 and 800 nm after UV activation using an Evolution 200 (Thermo scientific) UV-visible spectrophotometer at 21°C. The performance of each dye to undergo reversible photo-isomerization under the influence of UV and visible light was studied at their absorbance maximum wavelength using six different exposure times (30, 60, 120, 180, 210, and 300 s). The dye solutions (0.05mg/ml) were irradiated using a UVA light torch with maximum emission wavelengths at 395-400 nm. Upon UV-irradiation the torch was placed on top of the PMMA cuvettes containing the dye solutions in the UV-Vis measurement cell with open lid. After exposure time, the lid of the measurement cell was closed and the measurement started with a short delay (ca. < 2 s) between exposure and measurement. The absorbance was recorded after each exposure time and the fading performance was estimated qualitatively by observing the time required to revert into their original uncoloured state and comparing each other. The colouration and decolouration properties of the photochromic textiles were measured using an LCAM Photochrome 3 spectrophotometer (Technical University of Liberec, Czech Republic), which is capable of measuring the colour development and fading performance continuously over various cycles of UV exposure and relaxation. The measured reflectance values (R) are recorded in 2-second intervals of continuous UV irradiation and the K/S values are calculated from the reflectance data using the Kubelka-Munk function using equation (1)

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (1)$$

where: R is the reflectance percentage at the maximum absorption wavelength, K is the absorption coefficient, and S is the scattering coefficient of the dyed samples.

Table 1. Activation and deactivation intervals (in seconds) of UV light during continuous colour measurement

Measurement settings	Samples	
	Sea green (SG)	Ruby red (RR)
Activation	300	500
Deactivation	400	1000

The colouration and fading kinetics, determined from the K/S-time data sets, were fitted to an extension of the first-order kinetic model, equation (2).

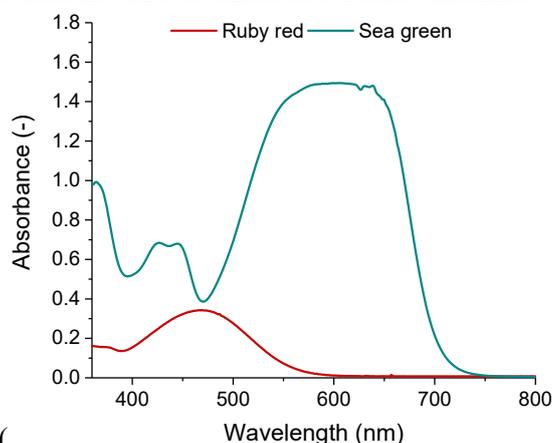
$$\frac{K}{S} = \left(\frac{K}{S_0} - \frac{K}{S_\infty} \right) \times e^{-kt} + \frac{K}{S_\infty} \tag{2}$$

where: K/S_0 and K/S_∞ are the initial and final (equilibrium) colour intensity values respectively attained upon exposure or relaxation of UV light, k is the rate constant and t is the time of exposure.

The photochromic performance of $scCO_2$ dyed photochromic polyester fabrics were evaluated in terms of the average colour yield ($\Delta K/S$) upon activation with UV-light, rate constants of colour growth ($k_{\text{colouration}}$) to achieve maximum colouration (K/S_∞), and rate constant of colour decay ($k_{\text{decolouration}}$) to revert to the ring-closed colourless state (K/S_0).

3. Results and discussion

The absorbance maxima of the dyes were defined by a wavelength scan between 400 and 800 nm after UV activation of the dye solutions. The obtained absorbance maxima were 472 and 600 nm for SG



and RR dyes, respectively (

Figure 2) and these wavelengths were used in our investigations.

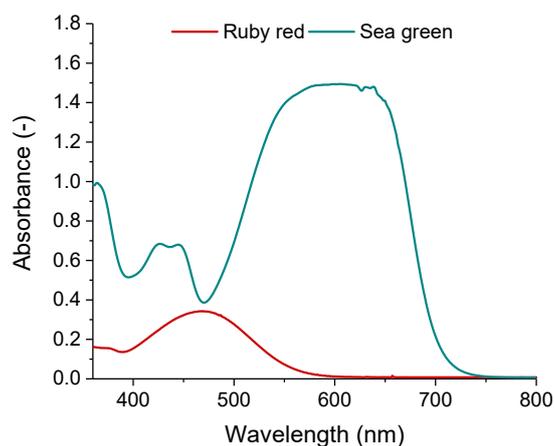


Figure 2. UV-Vis spectra of sea green and ruby red in hexane (0.05mg/ml)

The photochromic behaviour of the dyes in solution and on polyester fabric has been compared. A non-polar solvent, hexane, was selected as a solvent due to its similar polarity to CO_2 [20] to minimize the solvent effect for comparison purposes. The photochromic compounds in both media, in solution as well as in textile, showed reversible colour changing properties when exposed to UV light, and revert to their original colourless state when UV light is removed. SG exhibited higher colour intensity than RR in both mediums with $\Delta K/S$ of 0.096 in textile and an absorbance of 1.89 in solution while

RR has $\Delta K/S$ of 0.088 in textile and lower absorbance of 0.27 in solution. A direct and quantitative comparison of $\Delta K/S$ and absorbance values is not possible also due to different UV-sources and powers for sample activation. However, the data gives sufficient information on trends of maximum colour yields. In terms of rate kinetics, RR showed faster photo-colouration and fading rates in solution and slower colour conversion rates in textile and the opposite is true for SG (Figure 3 and Figure 4). In solution, the plateau of maximum absorbance of RR was already reached after 30 s of UV activation (linear fit), SG reached saturation of maximum absorbance after 60 s (exponential fit) (figure 3 A). Whereas, when applied in textile, SG achieved maximum colouration at a rate of 0.141 s^{-1} , while fabrics dyed with RR are remarkably slower with $k_{\text{colouration}}$ of 0.020 s^{-1} .

Figure 3 B shows the reversion to uncoloured state of the dyes in a nonpolar solvent, hexane. As illustrated in the picture, all dye solutions before UV irradiation were colourless and upon exposure to UV at their wavelength maxima, SG becomes deep blue and RR becomes light orange. It can be clearly seen that, all cuvettes with SG dye solution still show a colour (top) while for RR dye solution (bottom), only the cuvette used for the last activation was coloured, which confirms slow decolouration for SG and fast fading rate for RR in solution. However, opposite fading rates were observed when incorporated into the fabric (Figure 4 b) compared with their decolouration speed in solution. For SG dyed samples it took less than 20 s to revert to its uncoloured state while for RR dyed samples it needs more than 200 s to fade back to their original colour, which is significantly slower.

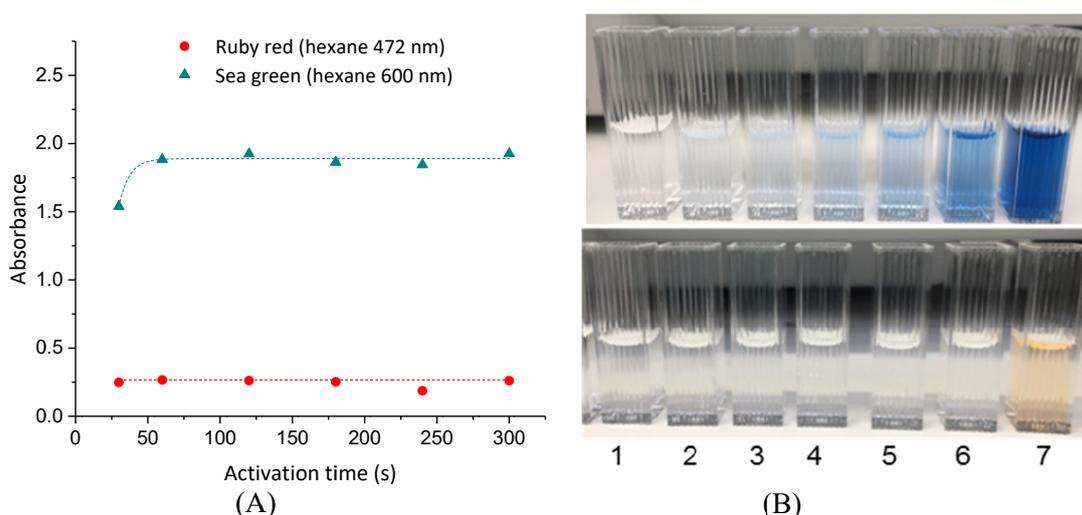


Figure 3. (A) Absorption spectra of Ruby red and Sea green in hexane at different UV activation times, (B) Colour reversion of the dye solutions directly after removal of the 300 s activation; Top is Sea green and the bottom is Ruby red, both in hexane. Cuvettes from left: (1) reference cuvette with solvent only, (2) 30 s, (3) 60 s, (4) 120 s, (5) 180 s, (6) 240 s and (7) 300 s activation.

According to previous studies, dyed photochromic fabrics generally tend to give slow colour switching speed, because the dye molecules incorporated into rigid polymer matrices are physically restricted, which slows down the photochromic transformations [2, 21]. Naphthopyran dyes printed on textiles generally are more durable and slower switching compared to spirooxazines, which are fast-switching, but more temperature-sensitive [22]. This agrees with our observation of photochromic dyed polyester fabrics, but opposite behaviour was observed when the dyes are dissolved in hexane as presented above. In solution, one explanation for the slow switching speed for Sea green may be related to the structural differences between the two dye classes. The spirooxazines are inherently rigid in their structure because of the indoline ring, whereas the naphthopyrans are relatively flexible [22, 23]. Thus, spirooxazines are more restricted during the photochromic conversion due to their rigid nature, which makes the conversion speed relatively slower. While in textile, SG from the spirooxazine family, are believed to be located close to the fabric surface due to the non-planarity and

bulky molecular characteristics of some spirooxazine derivatives, which could limit efficient penetration of the dye molecules into the tightly packed crystalline structure of polyester fiber [6]. This provides relatively more free space for SG dye molecules, which facilitated faster photochromic conversion. However, for NP dyed samples, due to their flexible structure, the dye molecules have a higher chance to penetrate inside the fiber structure, which limits the configuration change of photochromic molecules resulting in a slower speed of photo-isomerization. Generally, differences in kinetic behaviour of photochromic dyes in solution compared to in solid state and applied in matrices are reported. Whereas photo-colouration and thermal reversion of spirooxazines and naphthopyrans in solution follow mono-exponential kinetics, more complex, multi-exponential behaviour of the dyes can be expected in polymer matrices[24]. At this point, however, conclusions on the specific effect of the polyester matrix on the multiplicity of the rate constants involved in the photo-colouration process of SG and RR dyes are impossible.

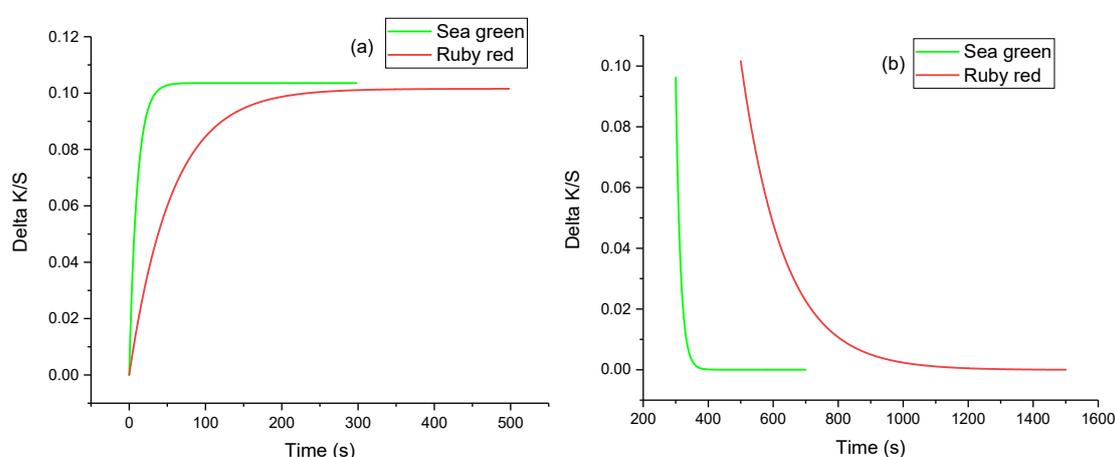


Figure 4. Colouration (a) and decolouration (b) behaviour of photochromic polyester fabrics dyed in $scCO_2$. Experimental data is fitted to first order kinetic model (Equation (2)) and normalized to have the same initial value.

4. Conclusions

Two photochromic dyes belonging to the spirooxazine and naphthopyran dye classes were successfully applied to polyester fabric using $scCO_2$ dyeing technique. Both photochromic dyes in textile and in solution showed significant reversible colour changing behaviour. The dyed polyester fabric exhibited similar level of colour strength to that of the photochromic dyes in solution while opposite photochromic behaviour was observed in terms of rate kinetics. The rate of colour conversion for both dyes to undergo photo-isomerization depends on the media (in solution or textile) as well as their inherent structural differences. The effect of the Polyester matrix on the multiplicity of the rate constants needs further investigations which will be dealt in our future study.

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