Color Performance, Durability and Handle of Inkjet-Printed and UV-Cured Photochromic Textiles for Multi-Colored Applications

Sina Seipel^{1*}, Junchun Yu¹, Martina Viková², Michal Vik², Marie Koldinská³,
Antonín Havelka³, and Vincent A. Nierstrasz¹

¹*Textile Materials Technology, Department of Textile Technology, Faculty of Textiles, Engineering and Business, University of Borås, Borås 50190, Sweden*

²*Department of Material Engineering, Faculty of Textile Engineering, Technical University of Liberec, Liberec 461 17, Czech Republic*

³*Department of Clothing Technology, Faculty of Textile Engineering, Technical University of Liberec, Liberec 461 17, Czech Republic*

(Received October 31, 2018; Revised January 14, 2019; Accepted March 9, 2019)

This article is published with open access at Springerlink.com

Abstract: The development and design of novel functional and smart textile materials such as textile sensors and multi-colored systems based on photochromic dyes necessitate controls of color intensities, switching speeds, and material durability. Precise control and synchronization of dye kinetics are important for multi-colored photochromic applications especially. However, durability towards abrasion and washing should not be compromised on if we aim to design reliable future textile products. In this study, two different commercial photochromic dyes – a naphthopyran and a spirooxazine-based dye – have been applied on PET fabric by inkjet printing and UV-LED curing. The photochromic textiles' color behavior, fastness to abrasion and washing, and handle are evaluated using spectrophotometry, scanning electron microscopy, and Kawabata evaluation system. Despite a decrease in color performance after washing, the photochromic inkjet print is effective and barely influences the textile structure. Reduced rigidity of the host matrix promoted higher color yields and faster dye kinetics, but also improved durability towards abrasion and washing. In order to synchronize kinetics of the different dye types for multi-colored applications, distinct curing conditions are preferable, which, however, result in varying print durability. In the design of multi-colored photochromic textiles, dye kinetics, and durability have to be balanced.

Keywords: Inkjet printing, UV curing, Textile sensor, Photochromic, Durability

©The Author(s) 2019, corrected publication 2019

Introduction

Although a limited number of products have reached the market, smart and functional textile high-end products have been an important topic for many years. In recent years, there has been an increasing interest in developing wearable, highly integrated technologies using resource-efficient processes [1]. Resource-efficiency, flexibility, and cost-effectiveness play a key role in triggering innovation and promoting the production of smart and functional niche products like photochromic textiles among others. Combining inkjet printing and curing with UV-LED light facilitates a sustainable, flexible, and economic textile production and avoids the use of water, unnecessary amounts of chemicals, and energy while producing less waste. However, to the best of our knowledge, few studies on the resource-efficient production of photochromic textiles have been done. Aldib [2] explored inkjet printing of solvent-based photochromic inks and Fu *et al.* [3] investigated photonic curing.

What often is neglected is that the usage of novel technologies in the application of smart materials presents new challenges in the general behavior, durability and

handle of functional textile materials. In general, inkjet printing and UV-curing are ideal technologies for functional multi-colored patterns because of their flexibility, cost-effectiveness, and technical precision. Still, when combining different photochromic dyes in one product, it is important to synchronize coloration effects and fastness properties in order to provide consistent product quality. Therefore, we investigate the color behavior, fastness, and handle of multi-colored photochromic textiles as seen in Figure 1(b), which are used in the design towards smart textile UV-sensors. A naphthopyran dye, Reversacol Ruby Red (RR), and a spirooxazine dye, Reversacol Sea Green (SG) are representatives of a more durable, but slow switching dye and a faster switching, but more temperature-dependent dye, respectively [4,5]. Both dyes are T-type photochromic compounds, which can reversibly switch color as a result of the absorption of electromagnetic radiation and thermally triggered reversion.

A common challenge in the application of photochromic dyes is their endurance in use, which is known as fatigue behavior. As a result of long-term UV-exposure and the influence of the predominant environmental factor oxygen, the color switching effect of photochromic compounds is weakened. Fatigue, which can also be referred to as photo-

*Corresponding author: sina.seipel@hb.se

Figure 1. (a) Inkjet printing and UV-curing in a continuous production process using combined conveyor belt speeds (i) and lamp intensities (ii) of 50 mm/s and 80 % and 300 mm/s and 1 % and (b) partially activated multi-colored photochromic print on PET with RR and SG.

degradation, causes an irreversible chemical transformation where an undesired by-product is formed [6]. The formation of the fatigue product prevents the photochromic dye to revert to its original form, which prohibits further photo-switching [7]. Depending on the dye class and specific molecular modifications, photochromic dyes show varying photo-stability. Therefore, it is important to distinguish between fatigue of the dye and durability of the photochromic print as in its adhesion to the textile surface.

This study focuses on the durability of the photochromic prints produced and its implication on the design of a textile UV-sensor. The photochromic prints have been printed in single-pass mode and cured under strong and weak curing conditions, which means at a conveyor belt speed of 50 mm/s combined with 80 % of the maximum lamp intensity and 300 mm/s combined with 1 % of the maximum lamp intensity in a continuous pilot-scale inkjet printing system (Figure 1(a)). Seipel *et al.* [8] studied the interaction of a photochromic dye and ink matrix on molecular level to tune the kinetics of the photochromic reaction based on chosen fabrication parameters using inkjet printing and UV-curing. In that study, photochromic prints based on a naphthopyran dye, which are produced with a belt speed of 300 mm/s and 1 % lamp intensity, as well as 50 mm/s combined with 80 %, indicated good wash fastness. Altering the viscosity and free volume of polymeric matrices to influence kinetics of photochromic dyes is an up-to-date topic. Dye kinetics in a host matrix can be influenced through different ways of polymer architecture by varying the type, dye placement, or T_g of soft polymers [9–14], by the use of block copolymers [15], through the control of photo-polymerization [8,16] and through pore dimensions in sol-gels [17]. In this study, however, we explore the effect of matrix rigidity on the durability of a spirooxazine and a naphthopyran-based print on textile via fastness tests, which generate mechanical action through abrasion and mechanical-chemical action at elevated temperature through washing. As textile sensors in use will be exposed to abrasion and washing, this investigation is necessary in regards to feasibility and design

of future products for wearable or other textile sensor applications. Furthermore, the textile character and handle of the photochromic textiles are evaluated after intensive washing using a Kawabata evaluation system (KES) to determine the impact of the photochromic inkjet print on the textile structure.

We conclude that the choice of fabrication parameters of an industrially applicable process can modify dye kinetics, but also increase the durability of photochromic textiles via tuning the rigidity of the host matrix. The photochromic surface functionalization is effective without influencing the textile character. For multi-colored photochromic textiles, synchronization of dye kinetics and durability towards abrasion and washing have to be weighed against each other.

Experimental

Materials

Two types of photochromic dye were used in the formulation of UV-curable inkjet inks to produce UV-sensing textiles. The commercial heterocyclic spiro-compounds Reversacol Ruby Red and Reversacol Sea Green from Vivimed Labs, UK represent dyes of two different dye classes, naphthopyran and spirooxazine, respectively. The dye concentration in the designed inkjet inks was 4 g/l. The UV-curable resin consists of dipropylene glycole diacrylate monomers (DPGDA), amine modified polyetheracrylate oligomers (Ebecryl 81) supplied by Allnex SA/NV, Belgium, and a UV-LED photo-initiator (Genocure TPO-L) supplied by Rahn AG, Switzerland. Solvents were used to disperse the photochromic dyes in the UV-curable resin, which were removed after stirring by vacuum pumping. For Ruby Red, ethyl acetate, 99.9 % (Chromasolv Plus) and for Sea Green, hexane, ≥ 97 % (Chromasolv HPLC), both purchased from Sigma-Aldrich were used. The textile substrate for inkjet printing was a plain-woven polyester (PET) fabric with a weight of 147 g/m² and 20 and 23 threads/cm in warp and weft direction, respectively, received from FOV Fabrics, Sweden.

Production of Photochromic Prints

UV-responsive smart textiles were produced by inkjet printing and UV-curing in a continuous process using a pilot-scale inkjet printing system with a conveyor belt for substrate transportation. Printing was carried out with a Starfire SA print head from Fujifilm Dimatix, USA at a resolution of 400 dpi in single-pass mode. The Starfire SA print head is able to print 4 different color scales, i.e. ink amounts. In this study, the darkest shade, i.e. the highest amount of a single pass with an effective ink amount of 16 g/m^2 was used. The print head temperature was set to 35°C to facilitate ink flow upon printing. For curing, a UV-LED lamp FireJet from Phoseon Technology, USA with emission wavelength of 380 to 420 nm and a maximum emission power of 6 W/cm^2 was used. The photochromic prints were cured at two distinct conditions, which represent a high and low crosslinking density of the ink on the textile. Printing and curing was carried out at conveyor belt speeds of 50 mm/s and 80 % of the maximum lamp intensity (50_80) and at 300 mm/s and 1 % of the maximum lamp power (300_1).

Fastness Testing of Photochromic Prints

The fastness of the photochromic prints in terms of mechanical and chemical action was evaluated as a result of abrasion and washing. The photochromic prints were abraded using a Martindale tester according to ISO 12947:2006 with a weight of 9 kPa during abrasion cycles of 5000, 10000, 15000, and 20000 rubs. To determine the effect of washing on the print durability, samples were washed once and ten times after printing and curing. Washing was conducted according to ISO 6330:2012 using procedure 4N and reference detergent 3. The samples were dried using drip flat drying.

Color Analysis

To evaluate the color behavior upon excitation (coloration) and relaxation (decoloration) of the photochromic prints an LCAM Photochrom 3 spectrophotometer was used. The specially designed device allows continuous color measurement

Figure 2. Scheme of color measurement cycle with 300 s of UV-exposure for coloration and 800 s of relaxation for decoloration.

upon cycles of UV-exposure and relaxation [18] (Figure 2).

As described previously, two distinct light sources were used for substrate activation and for color measurement [8]. An Edixon UV-LED lamp (EDEV-3LA1) with a radiometric power Φ_V of 350 mW and an emission peak with wavelengths between 395 nm and 410 nm was used for activation. For measurement a dual light source system of combined high power white LEDs with CCTs of 4000, 5000, and 7000 K with sample illuminance of 60 klx was used. Measured reflectance values R are calculated to color values K/S using the Kubelka-Munk equation.

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

The kinetic model shown in equation (2) follows first-order kinetics and is generally used to describe photochromic color behavior for both the coloration and decoloration reaction as seen in Figure 2 [19].

$$\Delta\left(\frac{K}{S}\right) = \left[\left(\frac{K}{S}\right)_0 - \left(\frac{K}{S}\right)_\infty\right] \cdot e^{-kt} + \left(\frac{K}{S}\right)_\infty \quad (2)$$

In the case of UV-curable materials, equation (2) is used for prints with a high degree of polymer crosslinking. For prints with lower polymer crosslinking density, equation (3) is used, which defines the kinetics of a decay mechanism as a result of continuous curing while color measurement and reconstructs the actual coloration curve [8].

$$\Delta\left(\frac{K}{S}\right)_{col} = \left(\frac{K}{S}\right)_{\infty col} \cdot (1 - e^{-k_{col} \cdot t}) - \left(\frac{K}{S}\right)_{\infty dec} \cdot (1 - e^{-k_{dec} \cdot t}) \quad (3)$$

where, under the boundary condition that the processes of coloration and decay start simultaneously and at $\Delta K/S=0$, $K/S_{\infty col}$ is the maximum coloration value and $K/S_{\infty dec}$ is the final value of the decay reaction for each activation cycle. Kinetic rate constants for the coloration reaction and decay are defined as k_{col} and k_{dec} , respectively.

Based on the kinetic models, the performance of the textile UV-sensors was specified by its achieved color intensity $\Delta K/S$ upon activation with UV-light, its rate constant of color increase k_{col} to achieve maximum coloration K/S_∞ , and its rate constant of color decrease k_{decol} to revert to the initial colorless state K/S_0 . The color performance of the photochromic prints was analyzed at each dye's reflectance minima. For prints containing naphthopyran dye Ruby red this refers to a wavelength of 500 nm and for those containing spirooxazine dye Sea green analysis was made at 620 nm.

Kawabata Evaluation System

The change in handle of the plain-woven PET compared to after printing with Ruby red ink and after washing for 10 cycles was objectively analyzed using a Kawabata evaluation system (KES). The samples with dimensions of 200×200 mm were printed and cured as three parallel stripes and measured both in warp and weft direction using a KES. KES measures

properties of textile fabrics and predicts the aesthetic quantities perceived by human touch. The primary hand value (HV) and the total hand value (THV) were calculated based on tensile, shear, bending, compression, and surface properties of the fabrics. To categorize the non-skin contact, wearable textile UV-sensor, a men's summer suit was chosen as reference application for the KES-test. Here, the HV of the samples is based on evaluated stiffness (koshi), crispness (shari), fullness and softness (fukurami), and anti-drape stiffness (hari) of the fabrics on a scale between 1-10, where 1 stands for weak and 10 for strong properties. THV is evaluated using a scaling system between 0-5, where 0 stands for out of use and 5 for an excellent fit of the measured material for the application.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using a JEOL JSM-6301F instrument. Images were taken at an acceleration voltage of 6 kV and a working distance of 39 mm. To improve sample conductivity prior to SEM analysis the substrates were sputtered with a 3 nm thick layer of gold.

Results and Discussion

Fitting of the Color Data of Prints Produced at 300 mm/s and 1 %

The extended model according to equation (3) is a mathematical approach to fit the color data of UV-curable photochromic materials with a low polymer crosslinking

density. Based on the measured K/S values of a photochromic dye, the coloration curve is fitted while taking a decay mechanism upon color measurement during UV-exposure and resulting activation into account. Equation (3) is a valid model for printed and abraded samples, which exhibit decay during color measurement. The fitted coloration curve of printed RR (Figure 3(a)) reaches a $\Delta K/S$ of 0.27, whereas after abrasion with 20000 rubs (Figure 3(b)), $\Delta K/S$ is lowered to 0.2. However, when fitting the color data of SG prints, $\Delta K/S$ of the printed sample (Figure 3(c)) with a value of 0.06 is lower than after abrasion with $\Delta K/S$ of 0.1 (Figure 3(d)). This repeated observation for all SG prints, which are cured at 300 mm/s belt speed and 1 % lamp intensity, shows that abrasion provides a loosening effect in the matrix and therewith less rigidity and more space for the dye molecule to undergo isomerization. A factor of influence on the distinct dye-matrix interaction of SG prints could be that spirooxazines have a large dipole moment [20]. A large dipole moment increases interactions of the dye molecule with the surrounding matrix and hence affects dye kinetics. Larkowska *et al.* [21] observed that the relaxation reaction appeared to be slower when the dipolar interactions were more pronounced. Therefore, the large dipole moment of the spirooxazine dye molecules and their consequent higher polarity during isomerization may influence their behavior in relation to the matrix more compared to RR prints.

Factors of Influence on the Durability of Photochromic Prints

Statistical analysis via a three-way ANOVA at a confidence

Figure 3. Fitting of K/S data of prints cured at 300 mm/s + 1 % (a) RR printed, (b) RR abraded with 20000 rubs, (c) SG printed, and (d) SG abraded with 20000 rubs.

Figure 4. Effects of the factors curing intensity (■), dye (●), and treatment (▲) on (a) $\Delta K/S$, (b) k_{col} , and (c) k_{decol} with connecting lines to guide the eyes.

interval of 95 % showed that the factors, curing intensity, dye, and treatment have significant effects on the color performance of photochromic prints in terms of the color yield $\Delta K/S$ and the reaction rates k_{col} and k_{decol} . Curing intensity refers to a combined belt speed and lamp intensity of 50 mm/s and 80 % (50_80) and 300 mm/s and 1 % (300_1), which represent a high and a low curing intensity, respectively. Dye refers to naphthopyran dye Ruby red (RR) and spirooxazine dye Sea green (SG). Treatment includes printed, abraded with 20000 cycles, 1× washed, and 10× washed samples. As seen in Figure 4(a), prints cured with a low intensity (300_1) result in higher $\Delta K/S$ compared to curing with a high intensity (50_80) and red prints result in higher $\Delta K/S$ than green prints. Abrasion with 20000 cycles and 1 washing cycle have a similar effect, whereas 10 washing cycles reduce $\Delta K/S$ values by 50 %. The kinetics of the coloration reaction as seen in k_{col} (Figure 4(b)) is higher for a low curing intensity (300_1), as well as for RR compared to SG.

Samples treated by abrasion, 1 wash, and 10 washes exhibit gradually decreasing k_{col} as compared to printed samples. The same trend in regards to the effect of curing intensity, dye, and treatment is seen for k_{decol} (Figure 4(c)). Higher k_{decol} is achieved with higher belt speed and lower lamp power (300_1) and for RR dye. A gradual decrease in the decoloration kinetics is seen for abraded, 1× washed, and 10× washed prints.

Kinetics of photochromic dyes is affected by various properties of the surrounding media. Among these are the viscosity of the media, chain lengths of polymers, and specific placement of the dye molecules in the matrix [9,11-13,15]. Seipel *et al.* [8] showed that adjusting the curing intensity of photochromic prints in an industrially applicable process changes the polymer crosslinking density of the UV-resin. As a result of changed matrix rigidity, the dye-matrix interaction can be influenced and the kinetics of a photochromic textile controlled. Usually, spirooxazines are faster switching dyes than naphthopyrans [4]. Spirooxazines are more rigid with a higher molecular weight and more non-planar in structure in their colorless state [22]. However, upon isomerization spirooxazines become more or less planar and polar [23-25]. As can be seen in Figure 4 for the factor dye, RR disposes of stronger $\Delta K/S$ and higher switching rates k_{col} and k_{decol} . Consequently, the integration of photochromic dyes in a UV-cured, cross-linked matrix largely affects their kinetics upon isomerization between the non-colored ring-closed and colored ring-opened states. The UV-cured, cross-linked matrix disturbs the isomerization of photochromic dyes between the non-planar and relatively non-polar form, i.e. the colorless state, and more or less planar and polar form, i.e. the colored state. In general, the factors polarity, free volume, rigidity, and direct interactions influence the photochromic response of materials [26,27].

Dye-matrix interactions are most pronounced for the

colored form of photochromic dyes as the dyes change structure and polarity upon isomerization. The different treatments, which are differentiated in mechanical and chemical-mechanical action, affect the color performance of both dyes in different extent. Generally, in the factor analysis it is observed that mechanical action as in abrasion influences the color behavior less than chemical-mechanical action as in washing. In a study of Kert and Gorjanc [28], where cotton, PET, and a blend fabric was functionalized with commercial photochromic microcapsules in a pad-dry-cure process, fastness to washing, wet and dry cleaning, and wet and dry rubbing were tested among others. According to their study, dry rubbing (crock fastness) affected the color difference value ΔE of the samples less than washing. They conclude fastness properties to be a measure of adhesion of the binder to the fiber, in which the photochromic microcapsules are entrapped. Hence, compared to dry rubbing, washing has a harsher effect on the padded samples due to elevated temperature and combined mechanical and chemical action.

Color Performance as a Result of Abrasion

Via abrasion tests using a Martindale instrument photochromic prints undergo mechanical wear. As observed after consequent color analysis, mechanical action by

various rubbing cycles (5000 to 20000 in 5000 steps) influences the photochromic prints on the textile surface compared to printed, i.e. non-abraded substrates. As seen in Figure 5(a) and (b), $\Delta K/S$ of SG prints is lower than for RR prints. However, the difference between a high and low crosslinking density of the ink resin on $\Delta K/S$ plays less role for SG, the spirooxazine dye than for naphthopyran dye RR. SG prints with a low crosslinking density decrease in color yield from $\Delta K/S$ of 0.117 to 0.110 compared to the dye in a more rigid resin from $\Delta K/S$ of 0.085 to 0.063. SG as the generically more rigid dye molecule might not have enough space to switch between its different isomers in neither the low nor highly cross-linked structure of the UV-resin. RR, however, is more flexible and therewith, larger differences in color yield can be observed. The difference in color kinetics observed in k_{col} between the curing intensities 300_1 and 50_80 is larger for SG (5:1) than for RR (2:1) as seen in average values for 5000 to 20000 rubs in Tables 1 and 2. As a result, it can be concluded that the rigidity of the UV-resin as a result of the curing intensity affects SG more than RR.

As previously mentioned, spirooxazines are generically faster switching dyes than naphthopyrans, but they also are more rigid in structure with a higher molecular weight and non-planarity in the colorless state than naphthopyrans [4,22,29]. If a dye that is generally fast-switching, but rigid

Figure 5. Effect of abrasion cycles 5000, 10000, 15000, and 20000 on $\Delta K/S$ of RR (a) and SG (b) prints cured at 50 mm/s and 80 % (50_80) and 300 mm/s and 1 % (300_1) on and on k_{col} of RR (c) and SG (d) prints cured at 50 mm/s and 80 % (50_80) and 300 mm/s and 1 % (300_1).

Table 1. Color yields $\Delta K/S$ and rate constants k_{col} and k_{decol} of RR prints printed, 1× and 10× washed and abraded with 5000, 10000, 15000, and 20000 cycles

	50 mm/s+80 %			300 mm/s+1 %		
	$\Delta K/S$	k_{col}	k_{decol}	$\Delta K/S$	k_{col}	k_{decol}
Printed	0.103±0.009	0.089±0.007	0.011±0.000	0.235±0.068	0.114±0.027	0.014±0.002
1× washed	0.062±0.002	0.059±0.008	0.009±0.000	0.154±0.044	0.102±0.007	0.012±0.001
10× washed	0.039±0.003	0.048±0.009	0.008±0.001	0.136±0.005	0.101±0.005	0.013±0.001
5000 rubs	0.086±0.008	0.060±0.000	0.010±0.000	0.266	0.120	0.012
10000 rubs	0.077±0.013	0.056±0.002	0.010±0.000	0.262	0.123	0.013
15000 rubs	0.079±0.002	0.056±0.002	0.010±0.001	0.242	0.108	0.013
20000 rubs	0.075±0.004	0.053±0.001	0.009±0.000	0.225±0.012	0.113±0.006	0.014±0.001

Table 2. Color yields $\Delta K/S$ and rate constants k_{col} and k_{decol} of SG prints printed, 1× and 10× washed and abraded with 5000, 10000, 15000, and 20000 cycles

	50 mm/s+80 %			300 mm/s+1 %		
	$\Delta K/S$	k_{col}	k_{decol}	$\Delta K/S$	k_{col}	k_{decol}
Printed	0.107±0.002	0.020±0.002	0.008±0.001	0.079±0.040	0.080±0.033	0.013±0.003
1× washed	0.086±0.025	0.017±0.004	0.007±0.004	0.153±0.011	0.045±0.007	0.014±0.001
10× washed	0.050±0.006	0.012±0.001	0.005±0.000	0.102±0.005	0.030±0.002	0.010±0.001
5000 rubs	0.085±0.006	0.016±0.000	0.007±0.000	0.117±0.008	0.072±0.012	0.019±0.010
10000 rubs	0.085±0.003	0.016±0.000	0.007±0.000	0.104	0.071	0.012±0.000
15000 rubs	0.073±0.003	0.014±0.000	0.006±0.000	0.115	0.069	0.013±0.002
20000 rubs	0.063±0.000	0.013±0.000	0.007±0.004	0.110±0.007	0.071±0.005	0.013±0.001

in structure is entrapped in a matrix with high rigidity, its degree of freedom is limited and slow kinetic rates can be expected. However, when the rigidity of the matrix is decreased, a larger effect of relative increase in k_{col} can be observed for a fast-switching dye as a result of loosened dye-matrix interaction. This can explain why the difference in photo-switching speed of SG prints is a 5-fold larger for 300_1 than for 50_80. The same change in matrix rigidity only affects RR prints with a 2-fold faster k_{col} for 300_1 compared to 50_80. k_{col} of RR prints are decreased by 50 % in a more rigid resin. For SG, an increased polymer crosslinking density of the matrix results in 20 % of the initial k_{col} compared to a softer matrix. SG prints seem to have a better abrasion resistance both observed in the color yield $\Delta K/S$ and the coloration rate k_{col} . Compared to RR prints, which show a steady decrease in $\Delta K/S$ and k_{col} as function of abrasion cycles, SG prints are more stable. What can also be seen in $\Delta K/S$ values, which are presented in Tables 1 and 2, is that the fastness properties are improved with increased matrix softness.

Whereas $\Delta K/S$ of 300_1 RR prints are superior against abrasion compared to washing (Table 1), $\Delta K/S$ of 300_1 SG prints show generally stable values for washed and abraded samples compared to in a more rigid matrix (Table 2). UV-curable coatings are in general known for their good durability and abrasion resistance [30-32]. Guan *et al.* [33] observed

superior rubbing, wash, and color fastness of a UV-curable pigment ink compared to a commercial pigment ink, while the print softness was improved.

After 20000 abrasion cycles, RR prints 50_80 and 300_1 dispose of similar remaining color yield $\Delta K/S$ with 70 % and 67 %, respectively. However, the speed of the coloration reaction is influenced more pronounced for 50_80 prints in regard to k_{col} with remaining 55 % of the initial rate constant compared to 300_1 prints with 76 % of the non-abraded value. SG prints, which have been abraded with 20000 rubs dispose of 58 % of the initial $\Delta K/S$ for a rigid ink resin (50_80) and of 140 % for a softer ink resin (300_1). After abrasion, the coloration rate k_{col} of 50_80 SG prints accounts for 70 % of the initial rate and 88 % for 300_1 SG prints. As previously mentioned, the increase in color yield $\Delta K/S$ for 300_1 SG prints is believed to result from a loosened matrix effect, which increases the mobility of the spirooxazine molecules and therewith the color intensity of the print.

Color Performance as a Result of Washing

The effect of washing on the photochromic prints is determined both after a single washing cycle and after extended washing of 10 cycles. Washing cycles have a significant effect on the color performance of RR and SG prints. The color yield $\Delta K/S$ of RR prints decreases gradually as a result of washing cycles. Decreasing $\Delta K/S$ of

the naphthopyran dye is observed both when integrated in a matrix with high rigidity (50_80) and in low rigidity (300_1). However, the absolute $\Delta K/S$ with 0.103 (50_80) is lower for prints with high polymer crosslinking density compared to prints with low crosslinking density with $\Delta K/S=0.235$ (300_1) as seen in Table 1. Lower $\Delta K/S$ of prints with high matrix rigidity can be explained as a result of reduced space in the host matrix and hence limited degree of freedom for the dye upon isomerization.

In terms of durability, 300_1 RR prints dispose of 58 % after 10 washing cycles compared to 50_80 RR prints, which only have 38 % remaining of the initial $\Delta K/S$. Although the fastness to washing for 300_1 RR prints is better than for 50_80 RR prints, it should be noted that washing significantly affects the color yield of 300_1 prints as compared to abrasion. Abrasion after 20000 revolutions barely shows an effect with $\Delta K/S=0.225$ compared to initial 0.235. Washing after 10 cycles, however, results in a significantly lower $\Delta K/S=0.136$. Rate constants of the coloration reaction k_{col} differ between 300_1 and 50_80 RR prints. Prints with a low degree of polymer crosslinking (300_1) show higher switching speeds with $k_{col}=0.114$ 1/s

compared to prints with high matrix rigidity (50_80) with a $k_{col}=0.089$ 1/s of printed samples. After washing, rate constants are lowered for all RR prints. Whereas washing with different cycles gradually reduces the rate of photo-switching of 50_80 prints from 0.089 to 0.054 to 0.048 1/s, 300_1 prints barely show a change between 1 and 10 washing cycles with k_{col} of 0.102 and 0.101 1/s (Figure 6(a)). Compared to the rate constant of printed samples, prints with low crosslinking density show superior fastness against washing with remaining 89 % of the printed k_{col} . 50_80 RR prints dispose of 54 % the initial k_{col} . The speed of the decoloration reaction is approximately one order of magnitude slower than k_{col} with $k_{decol}=0.011$ 1/s and 0.014 1/s of printed RR 50_80 and 300_1 samples, respectively. The same trend as function of washing cycles as for k_{col} can be seen for rate constants under color reversion. Whereas k_{decol} of 50_80 prints decreases continuously after 1 to 10 washing cycles from 0.011 to 0.009 to 0.008 1/s, k_{decol} of 300_1 prints is stable after a single washing (Figure 6(a)). With $k_{decol}=0.013$ 1/s after 10 washing cycles compared to the initial k_{decol} of 0.014 1/s RR prints still dispose of 93 % of the reversion rate. RR prints with high rigidity show remaining 73 % after extensive washing. The degree of crosslinking of the UV-resin has a significant effect on the kinetics of the naphthopyran dye RR, but also its durability as a result of washing. It can be concluded that a softer and more flexible host matrix, which gives more space for the dye upon isomerization, also promotes the fastness properties as a result of chemical-mechanical action.

The color performance of SG prints as a function of washing cycles differs from RR prints. In particular, color yield and kinetics of printed 300_1 samples deviate. As seen in Figure 6(b), $\Delta K/S$ of 300_1 printed, i.e. 0 washing cycles, with 0.079 is lower than after 1 washing cycle with 0.153 and also after 10 washing cycles with 0.102. Washing gradually decreases color yields of SG prints with a high degree of polymer crosslinking from $\Delta K/S=0.107$ to 0.086 after 1 wash to 0.050 after 10 washes (Table 2). Whereas 50_80 prints show remaining 47 % of the initial color yield after extensive washing, 300_1 prints dispose of 129 % of the initial $\Delta K/S$.

Little and Christie [4] have observed that an initial washing process increased coloration for spirooxazine in screen-prints, but then decreased coloration for further washing cycles. For naphthopyran dye in screen-prints the coloration was decreased directly for initial washing, as we also observe in RR prints. The initial color increase for spirooxazine was argued to be a consequence of a loosened binder matrix and hence facilitated isomerization. Since, spirooxazines are more rigid in structure than naphthopyrans, a change in rigidity of the host matrix has a large effect. Little and Christie [4] concluded that much of the behavior they observed was due to binder, not dye effects. Similarly, Billah *et al.* [22] found that a mild washing with an aqueous

Figure 6. Effect of 0, 1, and 10 washing cycles on $\Delta K/S$, k_{col} , and k_{decol} of (a) RR prints cured at 50 mm/s and 80% (■, ■, □) and 300 mm/s and 1% (■, ▲, △) and of (b) SG prints cured at 50 mm/s and 80% (■, ■, □) and 300 mm/s and 1% (■, ▲, △).

alkaline surfactant treatment facilitated the formation of the merocyanine form of a spirooxazine and thereby increased photochromic intensity.

Rate constants of the coloration reaction of prints with the spirooxazine dye differ depending on the curing intensity, i.e. the crosslinking density of the UV-resin. Same as for RR, 300_1 prints show faster photo-switching of printed SG with $k_{col}=0.080$ 1/s than 50_80 prints with $k_{col}=0.020$ 1/s. Washing affects the dye kinetics for both prints with high and low matrix rigidity. However, prints with low crosslinking density (300_1) are more affected with a loss in coloration rate of 62 % after 10 washing cycles. Prints with high crosslinking density affect k_{col} of SG with a 40 % decrease. The decoloration reaction, which has approx. 3 times slower k_{decol} compared k_{col} , is also significantly affected by washing. A continuous decrease in k_{decol} is seen for 50_80 SG prints from 0.008 1/s after printing to 0.007 1/s after 1 wash and to 0.005 1/s after 10 washes. Decoloration kinetics of SG in prints with low matrix rigidity (300_1) are unchanged after 1 washing cycle, but then decrease from 0.014 to 0.010 1/s after 10 washing cycles. This effect can also be a result of a loosened structure of the UV-resin upon initial washing, but then decreases due to extensive chemical-mechanical action after 10 washing cycles. In terms of fastness to washing, SG 50_80 prints with 63 % remaining k_{decol} are inferior compared to 300_1 prints with 77 %.

Maintenance and Repeatability of the Color Performance of Photochromic Prints

Repeatability of the photochromic color switching is an essential characteristic toward the design of a textile UV-sensor in use. Hence, the color performance of 1× and 10× washed prints is assessed throughout several cycles of color activation and deactivation. Color measurement of RR prints with an applied ink amount of 19 g/m² cured at a belt speed of 300 mm/s and 1 % lamp intensity, show distinct behavior after 1 and 10 washing cycles. After a single washing process a continuous decrease in $\Delta K/S$ as function of activation and deactivation cycles is observed. However, prints after 10 washing cycles show stable and insignificantly different color yields $\Delta K/S$ and coloration, as well as decoloration rates over five and four activation cycles, respectively, compared to prints, which have been washed once (Figure 7). Periyasamy *et al.* [29] concluded that photo-degradation usually is higher during the initial cycles of UV-exposure due to a superficial layer of photochromic material, which degrades faster than material, which has penetrated further into fibers and fabrics. Our observation that more stable color performance is achieved after intensive washing, confirms the behavior. Therefore, we suggest that intensive washing should be considered as reduction process for UV-curable photochromic prints with low crosslinking density. Given that prerequisite, stable

Figure 7. Comparison of $\Delta K/S_{col}$ (a), reaction rates k_{col} (b), and k_{decol} (c) of prints with 19 g/m² of Ruby red ink cured at 300 mm/s and 1 % after 1 and 10 washes during 5 cycles of coloration and 4 cycles of decoloration.

color behavior is expected for long-term use.

Effect of the Photochromic Print on the Fabric Structure and Handle

KES analysis is made to objectively evaluate the handle of

Table 3. HV including the single components and THV of the reference PET, printed and washed samples are tabulated. The functionalized samples were printed with 16 g/m² of ink, cured at a belt speed of 300 mm/s and lamp intensity of 1 %, and then washed for 10 cycles

	HV				THV
	Koshi (stiffness)	Shari (crispness)	Fukurami (fullness and softness)	Hari (anti-drape stiffness)	
PET reference	8.14	4.45	3.68	10.27	1.60
Printed	8.37	5.73	3.22	10.55	1.84
10× washed	7.95	5.75	3.49	10.35	2.01

the inkjet-printed PET fabric via measurement of mechanical properties. The results of the objective evaluation of the fabric handle show that the chosen application for the fabric was not ideal with a THV of 1.60, which expresses a poor to below average fit. However, what can be seen is that after printing and washing the THV increases and therewith indicates a slightly better fit for the application. Important is the relative change of the fabric properties after printing and again after washing.

According to the stiffness values (koshi) in Table 3, it can be seen that the stiffness of the fabric increases after printing from 8.14 to 8.37 and decreases to 7.95 after 10 washing cycles. This shows that the stiffness of the fabric is in general high and increases due to the application of an ink layer. 10 washing cycles smoothen the printed fabric. The fabric crispness (shari) also increases after printing, but does

not change after washing. The fabrics' fullness and softness, however, decreases slightly after functionalization with the photochromic ink, which is almost reversed again by 10 washing cycles. All measured samples show high anti-drape stiffness (hari) with values above 10. The highest value with 10.55 is observed for the printed fabric and which is also slightly decreased again after washing.

Another essential property of a fabric, which is related to fabric comfort (softness and rigidity), is the bending moment. It quantifies the feeling by hand when bending the product. When bending the fabric under low-stress mechanical action, the comfort of the finished fabrics is assessed. The printed fabric has a bending moment $B=0.249$ g·cm²/cm. After 10 washing cycles B is reduced to 0.221 g·cm²/cm. The larger the value of B is, the harder is the object. Therefore according to the definition the printed

Figure 8. Printed PET samples with 19 g/m² of Ruby red ink after printing and curing at 100 mm/s belt speed and 25 % lamp intensity compared to reference PET; (a) printed weft multi-filament, (b) unprinted weft multi-filament, (c) printed warp multi-filament, and (d) unprinted warp multi-filament.

photochromic textile is less comfortable and the washed photochromic textile is more comfortable than the non-printed reference PET with $B=0.231 \text{ g}\cdot\text{cm}^2/\text{cm}$. In summary, it can be said that KES-measurements confirm a stiffening effect of the fabric after printing, which is more or less revoked after 10 washing cycles despite preserved photochromic activity, which is seen in color measurements.

Also, observed changes of the fabric properties are low, which is attributed to the small amount of applied ink. In a research study of Karim *et al.* [32], where a UV-curable inkjet layer was applied on PLA fabric, the abrasion resistance of the fabric was improved while KES measurements showed that the ink layer did not significantly influence the handle of the fabric. Our study asserts their observation and hence that the photochromic surface functionalization of PET barely influences the textile handle of the plain-woven fabric. KES results are in line with the subjective handle when touching the fabrics, and are also supported by SEM analysis. As can be seen in Figure 8, the functional inkjet-printed material does not affect the fabric structure in terms of that the space between the fibers is not blocked. After printing with Ruby red ink (Figure 8(a) and (c)), the PET fabric does not show a difference compared to the reference fabric (Figure 8(b) and (d)). Therefore it can be expected that fabric properties like porosity and breathability are not affected. The pico-liter sized droplets, which are applied by ink jetting on the PET surface, are not detectable using SEM. Screen-printed fabrics typically show a change in surface structure, where the printing paste can clearly be detected on the fiber surface and pores between fibers are covered by the paste [4,5]. However, as is seen from the color data, inkjet-printed samples dispose of a photochromic color effect and hence prove that the ink adheres to the PET substrate without affecting the textile structure.

Conclusion

This study investigates important performance, durability and textile properties towards the production of a textile UV-sensor using inkjet printing and UV-curing. With the aim to develop reliable textile sensors and multi-colored systems based on photochromic dyes, the controls of color intensities, switching speeds, and material durability in use are critical characteristics. In both cases, defined or even synchronized properties of different dyes are the pre-requisite for reliable future products. In this study, we showed that when combining the photochromic dyes Reversacol Ruby red and Sea green in one UV-cured smart textile, differences in kinetics and fastness towards abrasion and washing are to be expected. For spirooxazine-based UV-cured prints, color build-up will be slower and color yields lower than for naphthopyran-based dyes if prints are cured with the same intensity. Therefore, to synchronize dye kinetics with similar k_{col} between 0.05 and 0.08 1/s RR should preferably be cured

with a strong intensity and SG with a weak intensity. However, synchronization of dye kinetics brings about compromises in terms of weakened durability of RR prints towards washing and abrasion. If synchronization of dye kinetics can be compromised on, the choice of suitable fabrication parameters of an industrially applicable process can increase the durability of photochromic textiles exceeding the control of kinetics. Reduced rigidity of the host matrix promotes higher color yields and faster dye kinetics, but also improved fastness towards abrasion and washing. Mechanical action through abrasion has less impact on the color performance of the photochromic prints than mechanical-chemical action at elevated temperature through washing. Although washing affects the material on the textile, the photochromic activity of the inkjet print is preserved and barely influences the textile character. KES analysis shows that the textile handle is stiffer as a result of ink jetting and curing of the photochromic ink on the fabric surface, which, however, after 10 washing cycles is revoked. SEM analysis also indicates that the inkjet layer does not affect the textile structure in terms of its porosity and resulting breathability.

Acknowledgements

The authors are grateful for the support from Borås stad, TEKO (The Swedish Textile and Clothing Industries Association), Myfab and Sparbanksstiftelsen Sjuhärad for enabling this research.

Open Access: This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. C. Lang-Koetz, N. Pastewski, and H. Rohn, *Chem. Eng. Technol.*, **33**, 559 (2010).
2. M. Aldib, *Color. Technol.*, **131**, 172 (2015).
3. R. Fu, J. Shi, E. Forsythe, and M. Srou, *Opt. Eng.*, **55**, 124105 (2016).
4. A. F. Little and R. M. Christie, *Color. Technol.*, **127**, 275 (2011).
5. M. Víková, "Photochromic Textiles", Heriot-Watt University, Edinburgh, 2011.
6. J. C. Crano and R. J. Guglielmetti, "Organic Photochromic and Thermochromic Compounds", Springer, New York, 2006.
7. R. Pardo, M. Zayat, and D. Levy, *J. Sol-Gel Sci. Technol.*,

- 63, 400 (2012).
8. S. Seipel, J. Yu, A. P. Periyasamy, M. Viková, M. Vik, and V. A. Nierstrasz, *RSC Adv.*, **8**, 28395 (2018).
9. F. Ercole, N. Malic, S. Harrisson, T. P. Davis, and R. A. Evans, *Macromolecules*, **43**, 249 (2010).
10. N. Malic, I. J. Dagley, and R. A. Evans, *Dyes Pigment.*, **97**, 162 (2013).
11. N. Malic, J. A. Campbell, and R. A. Evans, *Macromolecules*, **41**, 1206 (2008).
12. G. Such, R. A. Evans, L. H. Yee, and T. P. Davis, *J. Macromol. Sci., Polym. Rev.*, **43**, 547 (2003).
13. R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball, and D. A. Lewis, *Nat. Mater.*, **4**, 249 (2005).
14. F. Ercole, T. P. Davis, and R. A. Evans, *Macromolecules*, **42**, 1500 (2009).
15. K. Mutoh, Y. Kobayashi, and J. Abe, *Dyes Pigments*, **137**, 307 (2017).
16. J. H. Kim, S. Y. Ban, Q. Zhang, G. W. Kim, M. J. Cho, and D. H. Choi, *Mol. Cryst. Liq. Cryst.*, **445**, 307/[597] (2006).
17. M. Parhizkar, Y. Zhao, Z. Xu, A. Gestos, Z. Xie, Z. Liu, and T. Lin, *Fiber. Polym.*, **16**, 2318 (2015).
18. M. Vik and M. Viková, "A Method and Device for Fatigue Testing of Photochromic, Fluorescent or Phosphorescent Dyes", Technicka Univerzita V Liberci, 2016.
19. M. Viková and M. Vik, *Adv. Chem. Eng. Sci.*, **1**, 224 (2011).
20. A. Ranjkesh, M.-K. Park, H. D. Park, J.-S. Park, J.-C. Choi, S.-H. Kim, and H.-R. Kim, *Sensors*, **16**, 38 (2016).
21. M. Larkowska, M. Wuebbenhorst, and S. Kucharski, *Int. J. Polym. Sci.*, **2011**, 6 (2011).
22. S. M. R. Billah, R. M. Christie, and R. Shamey, *Color. Technol.*, **124**, 223 (2008).
23. M. Natali and S. Giordani, *Chem. Soc. Rev.*, **41**, 4010 (2012).
24. H. Xia, K. Xie, and G. Zou, *Molecules*, **22**, 2236 (2017).
25. J. Zhou, Y. Li, Y. Tang, F. Zhao, X. Song, and E. Li, *J. Photochem. Photobiol. A: Chem.*, **90**, 117 (1995).
26. G. K. Such, R. A. Evans, and T. P. Davis, *Macromolecules*, **37**, 9664 (2004).
27. X. Zhao, G. Wang, and K. Zhang, *J. Appl. Polym. Sci.*, **124**, 4157 (2011).
28. M. Kert and M. Gorjanc, *Color. Technol.*, **133**, 491 (2017).
29. A. P. Periyasamy, M. Vikova, and M. Vik, *Text. Prog.*, **49**, 53 (2017).
30. M. B. V. Shukla, D. K. Singh, and R. Shukla, *Pigm. Resin Technol.*, **33**, 272 (2004).
31. O. A. Hakeim, A. A. Arafa, M. K. Zahran, and L. A. W. Abdou, *Colloids Surf. Physicochem. Eng. Aspects*, **447**, 172 (2014).
32. M. N. Karim, S. Afroj, M. Rigout, S. G. Yeates, and C. Carr, *J. Mater. Sci.*, **50**, 4576 (2015).
33. Y. Guan, B. Tawiah, L. Zhang, C. Du, and S. Fu, *Colloids Surf. Physicochem. Eng. Aspects*, **462**, 90 (2014).