Ink Jetting of Photochromic Ink
Towards the Design of a Smart Textile Sensor

Sina Seipel
Abstract

Smart textiles have been a hot topic in research for several decades; however, comparatively few products can be found on the market. Resource-efficient processes can boost the breakthrough of smart and functional textiles, which often necessitate high-cost materials and only require small batches. This thesis provides a technology-driven approach with resource-efficient solutions for the production of UV-sensing textiles, while pointing out the challenges of the new materials, which are created when novel production processes are used. The performance of UV-sensing textiles produced by ink jetting and UV curing of ink with commercial photochromic dyes is primarily explored. Several steps in the development of a UV-sensing textile are covered in thesis; development and jetting performance of the photochromic UV-curable inkjet ink, optimization of the color performance of photochromic prints using production process parameters by tuning color kinetics, and evaluation of the durability and textile character of photochromic textiles. Other focuses included in the thesis are dyeing of photochromic textiles with supercritical carbon dioxide (scCO₂), novel ways of stabilizing photochromic prints and ink jetting of functional ink for sports and work wear.

It was shown that physical properties of the ink and temperature affected the jetting behavior of the ink. A discrepancy between the drop formation of UV-curable photochromic ink and existing models for jetting of inkjet ink was highlighted. Reversibly color-changing textiles can be produced with inkjet printing and UV curing of photochromic inks. The combination of the resource-efficient processes with the photochromic material required the introduction of an extended kinetic model to describe the coloration reaction of prints. An essential finding was that the kinetics of photochromic dyes in UV-curable ink applied on polyester fabric could be tuned using fabrication parameters during printing and curing in a continuous resource-efficient production process. By changing fabrication parameters during production, the prints’ crosslinking density is influenced and hence dye kinetics can be modified as a result of matrix rigidity of the UV ink. Furthermore, fabrication parameters influence and can be used to improve print durability as of abrasion and washing. Also, printing with photochromic UV-curable ink did not affect the fabric properties significantly in regards to flexibility and surface morphology. With the results obtained, photochromic textiles can be produced resource-efficiently using inkjet printing and UV curing, as well as scCO₂ dyeing to boost the cost-effective and flexible production of smart textile UV sensors.

Keywords: Inkjet printing, UV curing, photochromic, UV-sensing, smart textile, resource-efficient, scCO₂ dyeing, jetting, dye kinetics, color performance, durability, stabilization
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Paper II

Paper III

Paper IV/Book chapter

Paper V

Paper VI

Contribution to Appended Papers

Paper I
Sina Seipel planned the experiments with the co-authors, conducted all experiments and wrote the main part of the article, finalizing it with the co-authors.

Paper II
Sina Seipel planned the experiments with the co-authors, conducted all experiments and wrote the main part of the article, finalizing it with the co-authors.

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Sina Seipel took part in planning of the experiments, discussion of results, proofread and improved the article.

Paper VI
Sina Seipel took part in planning of the experiments, analysis and discussion of results, co-wrote, proofread and improved the article.
Nomenclature

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<td>E</td>
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<td>ν</td>
<td>Frequency of absorbed light</td>
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<td>Velocity of light</td>
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<tr>
<td>Z</td>
<td>Inverse of Ohnesorge number</td>
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<tr>
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<td>Bending moment</td>
<td>kg·m&lt;sup&gt;2&lt;/sup&gt; m&lt;sup&gt;-1&lt;/sup&gt;</td>
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1. Introduction

Research on smart and functional textiles has been on-going for decades with an exponentially growing research output since the 1990s, however the share of smart textile products on the market is limited until today \(^1\). Most research to develop smart textile materials and products has been made using conventional production processes such as dyeing and screen-printing. However, these production processes require large amounts of resources such as water and chemicals, they consume large amounts of energy and produce much waste. This hinders a sustainable, flexible and cost-efficient production, which is especially important for niche products, which require a small batch production. Replacing conventional technologies by novel and more resource-efficient processes increases the capability to innovate and economically boost the manufacturing of future trend products.\(^2,3\)

This thesis presents a technology-driven approach to facilitate the production of smart and functional textiles. Photochromic dyes are used as smart material to develop UV-sensing textiles with the vision to produce a smart textile UV sensor. While smart textiles shall help the user to sense and respond to external stimuli and ideally adapt to them \(^4\), the products are likewise expected to be lightweight with highly integrated functions that do not influence comfort and the visual experience negatively. In this respect, novel, digital and resource-efficient production techniques like digital inkjet printing for pattern and functional printing combined with UV-curable materials\(^5\) and dyeing with supercritical carbon dioxide have large potential for the production of smart materials. Next to the environmental benefits, resource-efficient techniques make a cost-effective, fast and flexible production of small batch products possible. For the textile industry the given circumstances open up new opportunities for innovation and niche products, enabling Western industrial countries to sustain their role in the textile industry within functional textiles.

In recent years, the development of UV-sensing textiles with photochromic dyes has been explored with several production techniques such as exhaust dyeing \(^7,13\), sol-gel coating \(^14,15\), pad-drying \(^16,16\), electro-spinning \(^17,19\), mass coloration \(^20,21\), screen printing \(^22,23\) and digital printing \(^27\). Applications ranging from everyday clothing to high-tech smart and functional clothing like intelligent design, decorative and fun applications, security and brand protection, camouflage, active protective clothing and UV sensors \(^28\) are aimed at. The driving force behind establishing a textile UV sensor with photochromic dyes is health concerns as a result of harmful UV rays, which are well known: overexposure to UV radiation causes DNA damages and genetic mutations, which can lead to skin cancer \(^29,30\). The severity of the individual effects is influenced by skin fairness and general sensitivity to UV light. Also environmental conditions like ozone depletion, altitude and weather changes determine how intense the exposure to UV rays on the earth’s surface is \(^31\). To limit the harmful effects of UV radiation a wearable UV sensor can create awareness and warn the user in everyday situations where UV light is not an obvious threat. For this purpose, photochromic compounds provide suitable properties to function as switchable sensing material for smart textile applications.

The main part of this thesis focuses on the development of UV-sensing textiles by printing and UV curing of photochromic inkjet ink, which is discussed in detail in papers I, II, III and IV. Additional results from a preliminary study about the light stabilization of UV-curable photochromic prints are elaborated in chapter 7. Furthermore, the exploration of textile dyeing with supercritical carbon dioxide of photochromic dyes, paper V, and the development and application of water-repellent ink for sports and work wear, paper VI, widen the scientific scope of the thesis in regards to resource-efficient dyeing of photochromic textiles and inkjet printing with functional ink, respectively.

1.1 Motivation and State-of-the-Art

The application of chormic materials in textiles has received increased attention in recent years, with photochromic \(^7,13,16,18,20-25,27,28,32-40\), thermochromic \(^32,33,41\) and halochromic \(^42-44\) textiles being the largest research scope in this domain. The choice to focus on the resource-efficient application of photochromic dyes and neglect thermo- and halochromatic materials for the time being, is motivated by several reasons. Whereas, the active range of thermochromatic materials is not sensitive enough for wearable applications and the research field of halochromic materials is claimed and well explored, photochromic materials are commercially available, well researched on but still exhibit several challenges in research before wearable UV sensors can be commercialized successfully. The choice to use UV-curable ink as carrier for ink jetting of the photochromic material was motivated by the aim to establish an as dry process as possible with minimized use of water, chemicals and energy in the production process.

1.2 Aim

The aim of this thesis is to explore the application of photochromic dyes by novel and resource-efficient production processes to foster a flexible and economic production of functional and smart textiles. In depth, the high-energy electromagnetic radiation of UV rays is exploited in the development towards smart textile UV sensors in two ways: i) make use of electromagnetic radiation to cure photochromic ink on a textile surface and ii) display the presence of electromagnetic radiation once the inkjet-printed sensor material is in use, i.e. the photochromic material is activated.
2. Smart Textile Sensors

In the last decades innovation has been triggered through the synergetic effect of historically distinct technologies, continuously opening new opportunities for further development. The advancement of textile applications from traditional clothing and home textiles to technical textiles in the automotive, aerospace, medical, civil engineering, sportswear and protection wear sector has been the first step. An additional step is taken through the commercialization of smart textiles, where the gained knowledge in technical textiles is combined more intimately with engineering, science and design. Smart textiles are textiles that can sense stimuli from the environment react to them and adapt to them by integration of functionalities in the textile structure. Stimuli like temperature, electricity, moisture, pH, pressure and light are some examples, which can trigger smart behavior.

One goal of research and innovation is to reduce the various components being used to a higher degree of integration and self-sufficiency. Instead of manufacturing smart textile applications with different materials and separate objects, a homogenous and highly integrated sensor is desired. Smart textile systems should be stand-alone units, not requiring any wired connections for communication and energy supply, as well as having the ability to withstand normal conditions of use (deformation, laundry etc.)

This thesis focuses on the characterization of the properties of a UV-sensing textile, which functions autonomously based on smart materials, i.e. photochromic dyes, where the presence of UV light is indicated by a visual effect of a color change of a fabric. The indication of a color results from a change in absorption spectra of the molecule. Upon photo-isomerization other molecular properties such as emissive behaviors, refractive index, electronic properties, magnetic responses etc. also change.

As per definition, a sensor is a device that can react to light, heat, pressure, etc. in order to make a machine etc. do or show something. A sensor detects or measures a physical property and records, indicates, or otherwise responds to it. According to Cao et al., smart materials are used to construct smart structures, which can perform both sensing and actuation functions. Photochromic materials have the ability to undergo light-induced isomerization. The resulting color yield of photochromic dyes upon excitation is in linear relation to the activation energy of the UV light source. As Qin et al. state in their work, except for light-induced reactions, isomerization of photochromic sensors can also be tuned by temperature, pH values, ion species, electric fields, etc. By analysis of the changes of signal outputs, multiple external stimulations can be monitored and detected.

With the aim to realize the production of an integrated smart textile sensor produced by inkjet printing and curing with UV-LED light of photochromic dyes several necessary development steps are explored. Specifically, the jettability of photochromic ink, the optimization of the color performance in terms of color yield and kinetic rate constants...
and the durability of textile prints are examined with the desired use for sensor applications.

3. What is Chromism?

Chromism is a natural phenomenon present all around us, as Timothy L. Dawson describes in his article. Plants detect light using a photochromic receptor molecule called a cytochrome, which operates in the far red/near infrared wavelengths, and regulates the time of flowering (according to the length of day) and controls the germination of seeds and leaf numbers and shape. Some land animals and a variety of sea creatures have evolved with an ability to change their skin colors rapidly in complex and multi-hued patterns, either for camouflage to escape predation, as a mood indicator or even as a means of controlling their body temperature.

The phenomenon results from external stimuli on compounds resulting in a change of molecular arrangement and absorption spectra. The word chromism, as a suffix, means “reversible change of color.” There are various types of chromism, which are specified with an according prefix to indicate the external color-changing stimulus. The stimuli range from UV light, change in temperature, a certain gas, an electronic charge, pH-value etc. The following table lists the most common types of chromism and their corresponding stimulus.

Table 1: Common types of chromism

<table>
<thead>
<tr>
<th>Stimulus</th>
<th>Chromic effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun/UV light</td>
<td>Photochromism</td>
</tr>
<tr>
<td>Change in temperature</td>
<td>Thermochromism</td>
</tr>
<tr>
<td>pH value</td>
<td>Halochromism</td>
</tr>
<tr>
<td>Electrical charge</td>
<td>Electrochromic</td>
</tr>
<tr>
<td>Moisture</td>
<td>Hygrochromism</td>
</tr>
<tr>
<td>Pressure</td>
<td>Piezochromism</td>
</tr>
<tr>
<td>Polarity of the solvent</td>
<td>Solvatochromism</td>
</tr>
<tr>
<td>Specific chemical agents</td>
<td>Chemochromism</td>
</tr>
<tr>
<td>Ions</td>
<td>Ionochromism</td>
</tr>
<tr>
<td>Acids</td>
<td>Acidochromism</td>
</tr>
<tr>
<td>Deformation</td>
<td>Mechnochromism</td>
</tr>
</tbody>
</table>
3.1 Photochromism

The term *photochromism* (Greek: *phos* = light, *chroma* = color) was first introduced in 1950 by Hirshberg. At that time photochromic materials experienced a sudden increase of scientific interest, along with the development of physical methods (IR, NMR, X-ray, UV, time-resolved and flash spectroscopy) and organic synthesis. However, it was not until the 1980s where the development of more fatigue-resistant compounds have made applications such as ophthalmic lenses possible. Photochromism is a reversible transformation of a chemical species between two isomers upon photoirradiation. The activation occurs through high-energy photons $h\nu_1$ from the near UV range. Due to the changes in the electron density, material B is able to absorb low-energy photons $h\nu_2$ from the visible part of the electromagnetic spectrum giving the coloration. When the excited molecule B absorbs visible light with the frequency close to the absorption maximum, reverse reaction to state A takes place.

![Absorbance spectra of photochromic compounds A and B](Figure 1: Change of absorbance spectra upon isomerization between colorless form A and colored form B)

The photochromic effect, i.e. a visible color change of organic photochromic compounds results through the stimulation of UV light. UV light activates the compounds from their thermodynamically stable form A to form B; isomerization occurs. There are various forms of isomerization, which determine the photochromic process depending on the photochromic compound. The categories of isomerization imply heterolytic cleavage, homolytic cleavage, triplet-triplet isomerization, trans-cis isomerization, tautomerism and photo-dimerization. The photochromic reaction of pyrans follows heterolytic cleavage, where breakage of the covalent bond of the excited molecule results in conformations with quinoidal or zwitterionic structures. For homolytic cleavage, which takes place for azo-compounds for example, bond

breakage results in two or more parts. Trans-cis ($E/Z$) isomerization plays an important role in many photochemical processes, which also results for azobenzenes and which is mostly reversible. Chromophores, which both quickly absorb radiation to reach the excited state and reverse with a fast bleaching rate to the ground state, follow triplet-triplet photochromism as pentacene and dibenzanthene. Tautomerism is based on the interconversion of hydrogen atom transfer, which determines the photochromism of ketones and fulgides.

The absorption spectrum changes the appearance of compounds showing unimolecular reactions from colorless (A) to a color (B), i.e. positive photochromism. Depending on the compound class and specific characteristics the appeared color varies. If the compound changes from color to colorless, we speak of negative or inverse photochromism. This phenomenon occurs with bimolecular systems.

The reverse reaction of the photochromic phenomenon can be subdivided in two types; T-type and P-type photochromism. While T-type photochromism is thermally driven, P-type compounds return to their original state when induced with light of another range of wavelengths, i.e. photochemical back reaction. The type of photochromism thus depends on the compound class.

Photochromic materials can typically be applied in ophthalmic lenses, prints for smart and fashionable or for security purposes, cosmetics, optical data storage, memories and switches and sensors.

3.1.1 Basic Theories and Mechanisms

3.1.1.1 Photoelectric Excitation

Absorption of light is the process where radiant energy is utilized to raise molecules to higher energy states. The difference of energy $\Delta E$ between the ground state and the excited state of a molecule is given by Planck’s relationship,

$$\Delta E = h\nu$$

where $h$ is a constant (Planck’s constant) and $\nu$ is the frequency of absorbed light. The equation can also be expressed as,

$$\Delta E = \frac{hc_{\text{light}}}{\lambda}$$

where $c_{\text{light}}$ is the velocity of light (constant) and $\lambda$ is the wavelength of absorbed light.

If a shift in absorption spectra due to structural change of a molecule occurs, the shift can result as bathochromic or hypsochromic, depending on the hue direction. A change from yellow – orange – red – violet – blue – green is termed bathochromic and hypsochromic vice versa.
Upon excitation and relaxation, a molecule transitions between various vibrational levels, which is depicted in a Jablonski diagram (Figure 2). When excited by the absorption of radiant energy, the molecule takes on an excited state $S_i$ ($n = 1, 2, 3, \ldots$). Via internal conversion processes or vibrational relaxation, the molecule will remain in the lowest singlet excited state $S_1$. After excitation to a higher state the molecule will return to its ground state by various processes. In the case of non-radiative decay or fluorescence, the molecule can return to its ground state from there. In the case of photochromism, the molecule changes structure in the excited state and relaxes to a vibrational ground state with a different molecular structure.  

The photochromic reaction consists of (3.1) a photochemical reaction (excitation and change in absorption band) from state A to B and (3.2) an exothermic reversion (relaxation) from state B via a transition state X to A as follows,  

$$ A \left( S_0^A \right) \to A \left( S_0^B \right) \to B \left( S_0^B \right) \to X \to A \left( S_0^A \right) \quad (3.1) $$  

$$ B \left( S_0^B \right) \to X \to A \left( S_0^A \right) \quad (3.2) $$

Figure 2: Jablonski diagram illustrates the electronic states of a molecule and transitions between them.

### 3.1.1.2 Absorption spectroscopy

With the aim to measure photon absorption of a molecule, intensities of incident light $I_0$ and transmitted light $I$ can be measured when a sample is irradiated with light. The molar extinction coefficient $e$ at a colorant’s $\lambda_{\text{max}}$ is a useful measure for the intensity of color. The value can be obtained through absorption spectroscopy using the Beer-Lambert law,

$$ A \left( \lambda \right) = \log \frac{I_0}{I} = e(\lambda)cL $$  

where $A$ is the absorbance of the dye molecule, $e$ is the molar extinction coefficient, $c$ the concentration of the dye and $L$ the path length of the cell (commonly 1 cm in UV/Vis spectroscopy). Bright colors generally show a narrow absorption band and dove colors a wider one.

#### 3.1.1.3 Color

Color is the perception of the human eye of an object illuminated by a source of light. The human brain responds to the stimulation by light via the optic nerve in the eye. Light enters the eye through the cornea and passes through a transparent flexible lens, which acts to form an inverted image on the retina. The retina owes its photosensitivity to a mosaic of light sensitive cells known as rods and cones. Three separate types of cone cells (S, M and L cones) enable the human being to distinguish colors. The different cone types have their peak sensitivities in different ranges of wavelength — short, middle and long. Under ideal conditions, a normal observer can distinguish about 10 million individual colors. The human eye responds to light of the narrow wavelength range between 360 and 780 nm of the whole electromagnetic spectrum. Ultraviolet light (UV) has wavelengths below 360 nm and infrared light (IR) above 780 nm. Normal white light contains the entire range of wavelengths. The various perceived colors have their respective wavelength range of light within the visible spectrum. Table 2 lists the range of wavelength and the according color, as well as their complementary color, whose wavelengths are reflected or transmitted.

### Table 2: Wavelengths of light, respective perceived and complementary colors.

<table>
<thead>
<tr>
<th>Wavelength range (nm)</th>
<th>Color</th>
<th>Complementary color</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 – 435</td>
<td>Violet</td>
<td>Greenish-yellow</td>
</tr>
<tr>
<td>435 – 480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480 – 490</td>
<td>Greenish-blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490 – 500</td>
<td>Bluish-green</td>
<td>Red</td>
</tr>
<tr>
<td>500 – 560</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>560 – 580</td>
<td>Yellowish-green</td>
<td>Violet</td>
</tr>
<tr>
<td>580 – 595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>595 – 605</td>
<td>Orange</td>
<td>Greenish-blue</td>
</tr>
<tr>
<td>605 – 750</td>
<td>Red</td>
<td>Bluish-green</td>
</tr>
</tbody>
</table>
3.1.1.4 Color assessment

Coloration on textiles and other opaque surfaces is traditionally measured by reflectance spectrophotometry. Spectral reflectance $R$ is the reflection of light at an object boundary or an interface between two media and hence is the fraction of incident radiation reflected by a surface.

$$ R = \frac{I}{I_0} \quad (5) $$

where $I$ is the reflected light intensity and $I_0$ the incident light intensity. The concept of spectral reflectance holds for opaque, transparent and translucent materials.

The intention of color measurement is to objectively assess color performance, which is essential for quality control. In the case of chromic materials for smart textile use, color assessment exceeds the visual and aesthetic component, where color assessment evaluates the functionality of the sensor as follows:

- At which wavelength does a specific compound have the absorption peak/dominant wavelength (which color appears)?
- How strong/intense is the change in color, i.e. color yield $\Delta K/S$ or color difference $\Delta$?
- How long does it take to colorize and revert/fade, i.e. kinetic rate constants $k_{\text{cat}}$ and $k_{\text{decat}}$?
- How can different compounds showing different effects/color be compared in their performance?
- How is the color or optical yield related to the intensity of the UV light?

The last question has not been a matter of discussion in this thesis as it has been proven in prior research that the observed color yield is linearly related to the intensity of the UV light source. A linear increase in light intensity linearly increases the optical yield of the photochromic dyes $^{35,55}$.

3.1.2 Reaction Kinetics

The chemical reaction of photochromic dyes follows first-order kinetics and consists of a coloration reaction upon exposure to UV light, and a decoloration reaction upon relaxation triggered by visual light and/or temperature (Figure 3). The optical density of photochromic dyes increases under UV irradiation from $I_0$ at time $t_0$ to a saturated optical density $I_s$ at time $t_1$, which is reverted to $I_0$ at $t_2$ once the UV source is switched off. The accumulated optical yield $\Delta I$ at a kinetic rate constant $k$ can be calculated according to Equation 6.

$$ \Delta I = (I_0 - I_\infty) \cdot e^{(-k \cdot t)} + I_\infty \quad (6) $$

In order to measure the color intensity, which is also referred to as color yield of photochromic textiles, the color is measured based on spectral reflectance $R$ using the Kubelka-Munk function, which enables color measurement of translucent and opaque materials.

$$ \frac{K}{S} = \frac{(1-R)^2}{2R} \quad (7) $$

Hence, the optical density $I$ in Equation 5 can be replaced by $K/S$ values for photochromic textiles.

$$ \Delta \frac{K}{S} = \left( \frac{K}{S_0} - \frac{K}{S_\infty} \right) \cdot e^{(-k \cdot t)} + \frac{K}{S_\infty} \quad (8) $$

3.1.3 Fatigue Behavior

A challenge in the application of photochromic dyes is their fatigue resistance in use, which makes the material reliability and commercialization of products more difficult. Photochromic dyes exhibit fatigue, however, to different extent depending on the class and specific molecular modifications. Fatigue or also referred to as photo-degradation
determines the loss of performance over time as a result of chemical degradation. Chemical degradation is often caused by environmental factors as water and oxygen or free radical exposure, which limit the repeatability of the photochromic reaction and weaken the color switching effect over time. In such case, a reversible chemical transformation takes place with the result of an undesired by-product, which prevents the dye from reverting to its colorless form, inhibiting further photo-switching. In order to improve the fatigue behavior of photochromic dyes several means of light stabilization have been tried. The most common ways of light stabilization are through UV absorbers, i.e. blocking of UV light in a certain range of wavelength or through hindered amine light stabilizers (HALS) and antioxidants to chemically bind the free radicals and thereby limit oxygen inhibition. As for photochromic dyes, the use of UV absorbers competes with the intensity of the coloration reaction and hence is less successful. Light stabilization using HALS has so far shown best results in the use of photochromic dyes in textiles. Photochromism is a phenomenon portrayed by inorganic and organic substances. The inorganic substances are metal oxides, alkaline earth metal sulphides, titanates, copper compounds, mercury compounds, certain minerals etc. Photochromic organic substances are heterocyclic molecules, which are mostly biosynthesized by plants and animals and are biologically active. Several photochromic compound classes are commercially available of which a number of classes are listed as follows:

- Spiropyans
- Spirooxazines
- Azobenzenes
- Stilbenes
- Salicylidene Anilines
- Diarylethenes
- Fulgides
- Anthracenes
- Etc.

Another natural photochromic molecule is rhodopsin, a photosensitive compound present in the retina of the human eye. Through light activation rhodopsin nerve stimuli are induced and transmitted to the brain for visual perception. It has also been found in a bacterium, halobacterium halobium, which converts sunlight into energy for metabolism.

In the following paragraphs a selection of the most commonly used and studied organic compounds is given with a more detailed description of their characteristics. In general, the different heterocyclic molecules show similar reversible ring-opening mechanism when excited by UV light. Photo-irradiation changes the electronic and geometrical structure accompanied by an alteration of absorption spectrum. A covalent bond is broken creating new dipolar structures. While the open, excited structure (photo-merocyanine form) is colored the closed ring structure appears colorless in visible light.

3.1.4 T-Type Photochromism

The reverse reaction of the T-type photochromic compound classes is thermally driven. When the source of UV radiation is removed, the molecular ring-structure closes due to the impact of temperature.

Spiropyans

Spiropyans belong to the most extensively studied compound class, consisting of a pyran ring linked to another heterocyclic ring via a spiro group. They mainly show unimolecular reactions, although there are few molecules that portray inverse photochromic behavior, i.e. colored in the dark and bleached through UV light. In the colorless state spiropyans are non-planar, preventing the delocalization of \( \pi \) electrons. The influence of irradiation breaks the weak bond between carbon and oxygen, so that the pyran ring is opened. In the excited and instable merocyanine form, planar ring-opened molecular structures are formed (see Figure 4).

![Figure 4: Photochromic reaction of spiropyans (reprinted from Periyasamy et al. with the permission of Taylor and Francis Group).](image)

Electrons can be delocalized and coloration occurs. Depending on the desired application, the fast back reaction to the colorless form of spiropyans can be seen as a disadvantage. Therefore studies have been conducted to retard color reversion by creating a steric hindrance through photo-cycloaddition between the chalcone units. By using polar solvents the back reaction can be slowed down in solution, which stabilizes the merocyanine form.

Spirooxazines

Spirooxazines are nitrogen-containing analogues to spiropyans. They are neutral molecules with a balance of hydrophobic and hydrophilic character. Generally, the molecules are non-planar in their ring-closed form. The connecting spiro linkage causes
the molecules to be orthogonally aligned to one another \(^7\). This makes the dye uptake when applied on polyester by disperse dyeing, for example, more difficult. Molecular planarity facilitates the penetration into the crystalline polymer structure \(^34\).

![diagram](image_url)

Figure 5: Non-planar ring opening and closing of spirooxazine (reprinted from Periyasamy et al. with the permission of Taylor and Francis Group). \(^40\)

Spirooxazines containing a reactive dichloro-s-triazinyl group can be applied as reactive dye to polyamide fabric. The reactive groups of the photochromic molecules form a covalent bond with the amino groups of the polymer resulting in a good fixation\(^73\).

**Naphthopyran**

Naphthopyrans, also known as chromenes, show slower color build-up and reversion than spirooxazines, even leaving a residual color after back reaction \(^34\), but they are less sensitive in temperature dependency for the reverse reaction than oxazines \(^35\). Other properties such as a broad color spectrum, fine control over fading kinetics, and good resistance to photocatalytic fatigue make naphthopyrans an important class of photochromic dyes \(^34\).

![diagram](image_url)

Figure 6: Ring opening and closing of chromenes (reprinted from Nigel Corns et al. with the permission of John Wiley & Sons Publications). \(^75\)

**Azobenzene**

The azobenzene class shows a trans cis isomerizations upon UV irradiation. This implies that the excited and the stable form vary more than simply opening and closing the ring structure. They exhibit a color change between different colored forms, instead from colorless to a color \(^75\). Azobenzenes are used as optical switches in biological systems to drive functional changes in peptides, proteins, nucleic acids, lipids, and carbohydrates \(^36\).

**3.1.4.2 P-Type Photochromism**

These compound classes revert to their original molecular state on irradiation with a light of different wavelength. Compared to T-type compounds, research on P-type classes has begun more recently. Attention has increased in the last decade in order to develop new applications. Generally, P-type photochromic colorants are mainly used in textile application \(^33\).

**Diarylethenes**

The diarylethene molecule changes its shape in size upon irradiation. The ring-opened structure is smaller than the closed structure after reverse isomerization \(^59\). They are more resilient than fulgides \(^75\). Dihetarylethenes have been targeted for use in nanotechnology, for example, by exploiting the remarkable photo-induced shape change in dye crystals that certain members exhibit as the basis for light-driven actuators. They have also been investigated in connection with the control of polymer surface properties for water repellency through reversible dye-moderated microfibril formation. It is not clear which, if any, of these avenues will be successful in the long term \(^75\).

![diagram](image_url)

Figure 7: Photoisomerization of dithienylhexafluorocyclopentene (reprinted from Nigel Corns et al. with the permission of John Wiley & Sons Publications). \(^75\)

**Fulgides**

Fulgides can exist in two different forms – Z (colorless) and E (colored), which are produced by rotation around a double bond. The excited P-type isomer is usually intensively colored \(^58\). In the dark they are reluctant to bleaching and also photochrome in solid form \(^74\).
4. Resource-Efficient Production Processes

4.1 Digital Inkjet Printing

Research on digital inkjet printing is of great interest to the textile industry as it offers promising opportunities for textile finishing and the production of technical and smart textiles in the future. Although inkjet printing has already been used in the production of medical products by Siemens in the 1950s \(^2\) and has seen commercial success by introducing the drop-on-demand technology in the 1970s \(^3\), only in more recent years the technology and its potential industrial applications received increased attention in textile production. Despite its wider potential, the inkjet technology nowadays is applied on textiles almost exclusively for decorative purposes. Colorants are used for the decoration of fashionable and personalized garments, reel-to-reel textiles, flags, banners, awnings, home textiles etc. Functional finishes on textiles via inkjet printing, such as water and dirt repellency \(^7\), hydrophilicity for fog harvesting \(^8\), conductivity or fire retardancy etc. are still in the stage of research and development.

The main advantage of digital printing is that a sustainable and environmentally friendly production can be realized. Compared to conventional textile dyeing and finishing, inkjet printing reduces the use of resources to a minimum, where only necessary amounts of water, chemicals and energy are needed. Inkjet printing is considered an overall dry process, where picoliter-sized droplets are applied on the printable surface only \(^9\). In addition, inkjet technology favors the reduction of time and cost when introducing new designs or functions. Minimized use of materials and the fact that the digital technology bridges design and technology especially fosters the economic production of technical, smart and other specialty products with high material cost and short run lengths. Since the preparation of screens is superfluous, as opposed to rotary or flatbed screen-printing, costs and also the production time can be decreased from days to hours and the overall batch production time from design to post-treatment can be reduced from months to weeks. Another technological advantage of inkjet printing is the precise and controlled placement of ink droplets, which enables high-resolution prints and building of micro and macro structures \(^10\). In inkjet printing technology the subtractive colors cyan, magenta, yellow and black are used for color mixing (CMYK system).

4.1.1 Inkjet Printing Systems

The most common inkjet printing systems are the drop on demand (DOD) and continuous inkjet (CIJ) system. As the name continuous inkjet implies, droplets are created continuously with this method. Those droplets, which are not intended for placement on the substrate will be collected and re-used. With the CIJ single droplets can be created but is yet challenging to determine their exact fall on the surface. The DOD-mechanism, ensuring the printability of tiny droplets and controlled placement on the printable surface, generally is the most common method as well as the most
suitable for the research purposes in this thesis. With DOD a drop is formed when there is a demand for it according to the current setting of the printing software and the resolution of the printable image. This means that when the printer nozzle receives a signal for a pixel, a drop is placed on the textile appearing as a dot on the surface. Characteristic for the DOD-technique is a tail formation of the droplet. For the DOD-mechanism two major types of print heads can be distinguished – thermal and piezoelectric jet. While thermal jets are most used in consumer desktop printers, piezoelectric jets (short: piezo jets) are currently used for most existing and emerging industrial inkjet applications, as the piezo jet is preferred for functional molecules. Generally, the piezo jet has a good reliability and long life expectancy while allowing controlled printing of a very wide variety of liquids. A piezo jet features a piezoelectric crystal usually made of lead zirconium titanate. When an electrical field is applied, the crystal undergoes distortion creating a pressure pulse in the ink chamber. Consequently, a demand is generated and a drop is ejected from the nozzle onto the substrate. Today, the main suppliers of piezoelectric DOD-print heads are Fujifilm Dimatix, Kyocera, Konica Minolta and Ricoh.

![Figure 9: Interaction of ink, textile and the print head](image)

In textile inkjet printing there are three components affecting the quality of the printed image – an interaction between the textile, the print head and the ink (colorant or other chemicals) takes place. Through each component’s properties, the outcome of the print is influenced and the best combination possible for the corresponding end-use has to be found. Figure 9, referring to Provost et al., illustrates the correlation between the various components. The ink’s physical and chemical requirements and especially the stability of the fluid are of major importance for the printed result. The combination of that and the textile determine the products durability, fastness and the general quality. The print head contributes its part through the operability and compatibility with the ink.

### 4.1.2 Inkjet Inks

There are currently four main types of inkjet inks available: water-based, solvent-based, UV-curable and hot melt, also called phase-change inks. Whereas water- and solvent-based inks are dried and cured via evaporation, hot melt inks are solidified and UV-curable inks are polymerized. Aqueous and solvent inks represent the largest share of inks on the market. Solvent-based inks enjoy popularity due to generally good image quality, print durability and variety of substrates to print on. However, they are not environmentally friendly and require high maintenance of the print heads due to highly volatile solvents. Aqueous inks are inexpensive and environmentally friendly, but may require large amount of additives, such as surfactant and rheology modifiers. Hot melt inks, which are heated prior to printing and solidify via cooling down, dry fast, do not spread out and are of little concern environmentally wise, but adhesion to the printable substrate and durability are a concern. Color or function can be imparted in the carrier medium fully dissolved as dyes or dispersed as pigments.

### 4.1.3 Ink Jettability

The jettability of ink depends on its physical-chemical properties such as surface tension, viscosity and ink stability, which needs to fit the requirements of the specific print heads. The theory and models, which are well established, hold for the jetting of Newtonian fluids.

#### 4.1.3.1 Surface Tension

The surface tension of liquids is defined by the cohesive energy of molecules at the substance’s surface. It determines the shape and allows evaluating the wetting ability of liquids on another surface. Generally, the single molecules of a liquid attract each other. In the bulk of the substance the molecular forces are in equilibrium in all directions. However, at the interface of fluid and air an imbalance of forces can be observed, which makes the surface tension push the fluid inwards resulting in a pressure increase within the droplet.

As Young and Laplace have first formulated in 1806, the two energies of surface energy and pressure-volume energy occur owing to the opposing forces at the interface. Both the surface energy and volume-pressure energy are affected to the same extent once the drop radius changes, which is expressed in the Young-Laplace equation:

\[
\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

(9)
where \( r_1 \) and \( r_2 \) are the two radii of a drop and which are equal to one another if the drop is spherical in shape.

Eventually, a substance with strong cohesive bonds, resulting in a high surface tension, will tend to form a droplet when in contact with another material. A liquid with a low surface tension and the desire to create adhesive bonds has a good wetting ability.

### 4.1.3.2 Viscosity

Viscosity is the response measure of a fluid to shear. The viscosity \( \eta \) is the ratio of the shear stress \( \tau \) and the shear rate \( \dot{\gamma} \) and describes a fluid’s resistance against deformation (also flow) \(^{85}\)

\[
\eta = \frac{\tau}{\dot{\gamma}} \tag{10}
\]

In the simplest case of a Newtonian fluid, where the shear stress is proportional to the shear rate, the shear stress \( \tau \) is defined by the shear force \( F \) and the contact area \( A_{contact} \) between the liquid and a plate.

\[
\tau = \frac{F}{A_{contact}} \tag{11}
\]

The shear rate \( \dot{\gamma} \) is described as the ratio of the moving plate’s velocity \( v \) and its distance \( d \) to the static plate.

\[
\dot{\gamma} = \frac{v}{d} \tag{12}
\]

### 4.1.3.3 Drop formation

The way a drop of an ink is formed is influenced by a fluid’s properties – viscosity, surface tension, density – and by the velocity and size of the droplet \(^{86}\). In inkjet printing the ink reservoir is not pressurized, which prevents unwanted ink flow from the nozzles when in standby mode. Once printing is desired, an electric voltage and pulse shape (wave form) apply pressure and influence the drop formation related to the nozzle geometries \(^{86, 87}\). Pressure initiated by the piezoelectric signal helps to overcome a certain surface tension in order for a drop to be ejected from the orifice. The pressure difference, which has to be exceeded, is \(^{88}\),

\[
\Delta P = \frac{2\gamma}{r} \tag{13}
\]

where \( \gamma \) is the surface tension and \( r \) the radius of the nozzle.

The theoretical printability of ink has been widely discussed in literature \(^{90-93}\) and can be calculated by a combination of dimensionless numbers, which depend on physical properties of the printable fluid and dimensions of the printing orifice. The Reynolds number \( Re \) and the Weber number \( We \) specify the relative magnitude of the fluid’s interfacial, viscous and inertial forces \(^{86}\).

\[
Re = \frac{\nu r \rho}{\eta} \tag{14}
\]

\[
We = \frac{\nu^2 r \rho}{\gamma} \tag{15}
\]

where \( \nu \) is the velocity, \( \rho \) the density and \( \eta \) the viscosity of the fluid. The Reynolds number determines the fluid’s inertia to its viscosity, whereas the Weber number defines the ratio of inertia to its surface tension.

Based on the Navier-Stokes equations \(^{94}\) Fromm has developed a solution to express the limitations of drop ejection in regards to interfacial, viscous and inertial properties of a fluid, which is defined as dimensionless number \( Z \) \(^{86}\).

\[
Z = \left(\frac{\nu \rho r}{\eta}\right)^{1/2} \frac{1}{\nu \eta} \frac{Re}{We^{1/2}} \tag{16}
\]

\( Z \) is the inverse of the Ohnesorge number \( Oh \) and is specified as the ratio of the Reynolds number and the square root of the Weber number; also known as Laplace number \( La \).

The initial specification of ink printability by Fromm \(^{91}\) that \( Z > 2 \) is required for the ejection of stable drops was revised and updated by Derby \(^{95}\) to a range of \( 1 < Z < 10 \). Stable drop formation implies that single drops with a tail are formed (iii) as seen in Figure 10. If these conditions cannot be met, so-called satellite drops (ii) will be formed, which impede print quality.

![Figure 10: Drop formations with (a) continuous fluid flow, (b) satellite drops and (c) stable drop with tail](image-url)
4.2 UV Curing

Research on radiation curing for textile application has begun in the late 1970s and early 1980s, where the focus was mostly on coating and screen-printing. Soon with the upcoming of inkjet printing, a significant increase in interest in combining the technology with radiation curing was seen. The driver for UV-curable ink systems has been the need to cure fast and energy-saving, to enhance abrasion and chemical resistance, and to print on thick or irregular substrates. Applications are typically in the areas of packaging with flat sides and various types of cylindrical surfaces including bottles and cans. The advantages for UV curing over traditional drying techniques are that drying is instant, no volatile organic compounds (VOC) are emitted, curing is space and energy saving, cured films have good adhesion to substrates they are printed on and are durable, and the overall “environmental friendliness” increases. However, caution should be taken in the handling of uncured resins, where unreacted monomers can cause dermatological reactions.

4.2.1 Ways of Polymerization

In UV curing of adhesives three mechanisms can be differentiated; free radical curing, cationic curing and hybrid curing. With free radical and cationic curing being the predominant techniques (see Figure 11), free radical photo-initiation is a mature technique with high curing rates, and cationic curing is more suitable for deep-layer curing with strong wear resistance. Free radical systems have the disadvantage that oxygen can inhibit polymerization and that the bonding strength is lower. Cationic curing has higher bonding strength, though lower cure rates and higher costs, and the amount of selectable monomers is limited.

\[ \text{Free radical polymerization} \quad \text{PI} \xrightarrow{hv} R^* + \text{Monomer} \xrightarrow{O_2} \text{Polymerization} \]
\[ \text{Inhibition} \]

\[ \text{Cationic polymerization} \quad \text{PI} \xrightarrow{hv} H^+ + \text{Monomer} \xrightarrow{O_2} \text{Polymerization} \]
\[ \text{Polymerization (no inhibition)} \]

Figure 11: Free radical and cationic polymerization reactions.

4.2.2 Chemistry of UV-Curable Inkjet inks

The majority of commercial inks are of the free radical type. But both free radical and cationic inks are available as 100% solid or as solvent-diluted formulations. UV-curable inks are made of liquid components, which are solidified under the influence of UV light. Colorants (dyes or pigments) and additives (surfactants to promote wetting and inhibitors to reduce low light cure) are added to the formulation. In more detail, UV curing systems mostly consist of the following ingredients, while the first three substances (water-insoluble) are always apparent:

- Pre-polymer (or oligomer)
- Diluents (or monomers)
- Photo-initiator
- Co-initiator, including reducing agent, chain transfer agent and spectral sensitizer (for cationic curing)
- Light stabilizer
- Thermal stabilizer
- Colorants, plasticizer and additives

The technology has first been developed around acrylate monomers, as they polymerize very rapidly under the presence of free radicals. Free radicals are formed through the photo-initiator, which absorbs UV light and decomposes thereupon. The result of this reaction is a 3D polymer structure that binds with itself, the pigments and the substrate. The properties of the surface coating are determined by the characteristics of the starting materials. High molecular pre-polymers and oligomers or a low functionality (one or two reactive groups) will give more flexible and elastic films - which, however, have a lower strength. For textile applications these characteristics are mostly desired to preserve the textile flexibility. The disadvantage of a formulation with a low amount of reactive groups is a higher risk of oxygen inhibition. When developing UV-curable ink, it is important to choose a photo-initiating system, which is applicable under identical conditions irrespective of the used pigment.

4.2.3 Constraints and Challenges of the UV Curing Technology

UV curing technology for textile inkjet application faces various challenges in research. The flexibility and soft character of a textile compared to hard substrates like plastics, wood or ceramics, limits the combination of oligomers, diluents and photo-initiators to keep the textile properties. For a flexible film on top of the textile surface, ink formulation with low reactive components is required. This nevertheless increases the risk of oxygen inhibition, hinders curing or at least decreases the curing speed. Through higher UV lamp intensity, optimization of the photo-initiator system, curing in inert atmosphere or auxiliary additives it can be improved. The addition of tertiary amines...
and silicon diacrylate in a coating formulation can reduce the blocking of curing through oxygen without slowing down the polymerization process. The higher the porosity of a textile and the more hydrophilic it is, the more the ink can be absorbed by the textile. As a result, the ink’s surface layer would be cured, but the absorbed/migrated part would still be liquid and release an unpleasant odor. This can be controlled through respective surface treatments, lower curing speeds, and maybe double-sided curing. Skin and respiratory irritation caused by uncured monomer is a health concern, which needs to be paid attention to and to be controlled in the production process. Furthermore, UV-LED-curable photo-initiators have a tendency to yellowing which can be disturbing in the case of photochromic coloration of a sensor. The addition of pigments to the formulation reduces the curing ability. The right concentration of pigments has to be found to achieve an appropriate effect. A special case is the UV curing of a resin on 100% polyester fabric. As the benzene rings in the fiber absorb UV light, the light intensity for curing decreases. Therefore lower curing speeds and higher intensity is advised. UV curing inks can only be applied on transparent, translucent or white substrates. Dark surfaces are impossible to print on, as they absorb all light.

4.2.4 Oxygen Inhibition

There are several approaches to reducing oxygen inhibition in photo-polymerization reactions, which include physical means as nitrogen inerting, lamination and use of higher light intensity. Chemically, anti-oxygen inhibition in UV resins can be achieved by adding reducing agents, decomposing molecules or hydrogen donors (amines, thiols, ethers etc.) to scavenge oxygen.

4.3 Dyeing with Supercritical Carbon Dioxide

Dyeing is a preferred production technique when uniform through-coloration of the textile is desired compared to printing for surface pattern and one-sided applications. The use of the supercritical carbon dioxide (scCO₂) dyeing technique to develop photochromic fabrics is an attractive alternative with high potential compared to conventional dyeing due to its significant environmental and economic benefits. In this process the use of water as dyeing medium is completely avoided, which also means that no wastewater pollution is associated. Eventually, scCO₂ dyeing enables simpler dye formulations without auxiliary chemicals, shorter dyeing times and avoids drying, which leads to a 50% lower operating cost. The advantage to dissolve dyes in carbon dioxide in its supercritical state is that the dyes can penetrate into the fiber homogeneously and faster compared with water because of the low viscosity and high diffusivity of CO₂. Hence, uniform dyeing in a short time can be achieved. ScCO₂ dyeing is a yet uncommon but successful technique for disperse dyeing of PET and other synthetic fibers owing to the fluids’ high dissolving power and good swelling and plasticizing effect towards hydrophobic polymers. As photochromic dyes are similar in structure to conventional disperse dyes, their application with scCO₂ on PET is promising in the development of uniform-colored photochromic textiles. Paper VI presents a preliminary study on scCO₂ dyeing of photochromic dyes, which investigates the potential of the production technique and compares the color behavior of scCO₂-dyed photochromic textiles to conventional dyeing techniques and to inkjet-printed photochromic textiles.
5. Our Approach to Designing a Textile UV Sensor

The application of photochromic dyes is well-explored and established using conventional textile production techniques such as screen-printing, dyeing, padding or mass dyeing. However, in comparison to the large amount of research activities in the domain, photochromic textiles do not meet the expected success in terms of market presence. Market success of photochromic textiles may among other, be restricted due to the high material cost of specialty dyes and the inflexibility of conventional textile processes, which is not in favor of the production of small batches. Therefore, we choose a technology-driven approach using a resource-efficient production to eventually facilitate the success of photochromic textiles in sensor applications. The aim of the thesis is to investigate the necessary steps and factors of influence towards the design of smart textile UV sensors based on photochromic dyes primarily using inkjet printing and UV curing. This includes the research steps of the formulation and development of functional photochromic inks and their characterization according to the printing process, the effect of printing and curing parameters on the color performance of the photochromic prints and the effect of fastness tests on the durability and handle of the prints. In all studies one type of fabric, a plain-woven polyester fabric was used to limit the research to the just named effects.

5.1 Ink Development

The photochromic UV-curable inkjet inks are formulated as free radical system using four main components:

- Photochromic dye
- Monomer
- Oligomer
- Photo-initiator

The ink varnish is made of monomers, oligomers and a photo-initiator and is then combined with the photochromic dye in solution. A fifth component, a solvent is used to dissolve the photochromic dyes, which is removed from the ink after stirring by vacuum pumping.

5.1.1 Choice of Photochromic Dyes

The photochromic dyes, which are used in the ink formulation and production of the UV-responsive textiles are chosen with the requirements of i) high absorbance, which results in strong color yield, ii) least solvent toxicity possible and iii) stability towards temperature for application in wearables. The photochromic textiles should show stable coloration in a practical range of temperature and especially around 20 °C to be suitable in wearable applications, if desired. Figure 12 shows the absorbance of five commercial photochromic dyes from Vivimed Labs and two pure photochromic dyes purchased from Sigma Aldrich as function of temperature with a concentration of 0.05 mg/ml in three different solvents. Hexane and toluene are representatives of non-polar solvents (dipole moments of 0.00 and 0.36 respectively) and acetonitrile as polar solvent (dipole moment of 3.92). Sea green, Oxford blue, Palatinate purple and spirooxazine are dyes of the spirooxazine class, Ruby red and Corn yellow belong to the naphthopyran class and spiropyran is a spiropyran dye. As can be seen in Figure 12, the different dyes, even of the same class behave distinctly in regards to solvent effects and as function of temperature. The absorbance maximum (given as wavelength) shifts in different solvents, which can be a bathochromic, i.e. red, shift towards longer wavelengths or a hypsochromic, i.e. blue, shift towards shorter wavelengths.
5.1.2 Design of the UV-Curable Varnish

The combination of components in the UV-curable varnish was selected based on their physical properties to ensure ink jettability, sufficient reactivity for curing of the ink, flexibility/elasticity in regards to the printable textile substrate and relative resin hardness for a durable end product. In UV-curable inkjet printing the main challenge is to balance the oligomer-monomer-ratio to achieve low enough ink viscosity but necessary curing efficiency. Whereas the type of oligomer is generally decisive for the mechanical properties of the cured resin, the type of monomer has largest impact on the cure reactivity of the resin and its amount can dilute the ink to achieve a lower viscosity. As for the photo-initiator, UV-LED photo-initiators are used for energy-saving and efficient curing of the resin.

The main properties of inkjet inks, which need to be met according to specifications of the chosen print head, are the viscosity, surface tension, particle size (if applicable) and stability of the ink. Ink formulations using the material listed in Table 3 have been adjusted to meet these requirements.

Table 3: List of materials used to formulate UV-curable varnish.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Supplier</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPGDA</td>
<td>Allnex</td>
<td>&gt; 99 %, 11.2 mPas</td>
</tr>
<tr>
<td>DDDA (1,10-decanediol diacrylate)</td>
<td>Sartomer</td>
<td>SR 595, 100 %, 10 mPas</td>
</tr>
<tr>
<td>Alkyl acrylate/ lauryl acrylate</td>
<td>Sartomer</td>
<td>SR 335, 100 %, 5 mPas</td>
</tr>
<tr>
<td>1,10-decamethylene glycol dimethacrylate</td>
<td>Sartomer</td>
<td>SR 261, &gt; 97 %, 9.1 mPas</td>
</tr>
<tr>
<td>IDMA (isodecyl methacrylate)</td>
<td>Sartomer</td>
<td>SR 242, 5 mPas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Supplier</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Genomer 3497</td>
<td>RAHN AG</td>
<td>Modified polyetherpolyl acrylate, 600 mPas (25 °C)</td>
</tr>
<tr>
<td>Genomer 5275</td>
<td>RAHN AG</td>
<td>Acrylated oligoamine resin, 4000 mPas (25 °C)</td>
</tr>
<tr>
<td>Ebecryl 81</td>
<td>Allnex</td>
<td>Amine modified polyetheracrylate</td>
</tr>
<tr>
<td>Ebecryl 853</td>
<td>Allnex</td>
<td>Acrylated resin</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photo-initiator</th>
<th>Supplier</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Hydroxy-2-methylpropiophenone</td>
<td>Sigma</td>
<td>Absorbance max. 245 nm</td>
</tr>
<tr>
<td>4,4’-Bis(diethy lamino)benzophenone</td>
<td>Sigma</td>
<td>Absorbance max. 380 (245) nm</td>
</tr>
<tr>
<td>Genocure TPO-L (Ethyl(2,4,6-trimethylbenzoylelphosphinate)</td>
<td>RAHN AG</td>
<td>UV LED range 370 (275) nm</td>
</tr>
</tbody>
</table>

Figure 12: Absorbance at maximum wavelength of commercial and pure photochromic dyes in hexane, toluene and acetonitrile as function of temperature.
5.1.3 Stabilization Mechanisms

A side project in this thesis resulted in a preliminary study on stabilization mechanisms of photochromic UV-curable inkjet prints. The effect of physical barriers on the color yield of photochromic prints was compared to the effect of a chemical approach by the addition of hindered amine light stabilizer (HALS) in the UV-curable photochromic ink formulation. Polyurethane coatings and non-toxic, edible substances as waxes, protein and starch have been used to explore their potential in physically shielding and therewith stabilizing the photochromic dyes in UV-cured prints as listed in Table 4. Wax coating has shown to be a useful oxygen barrier given that the temperature during curing does not melt the coating. Recent studies focus on the oxygen and water barrier properties, strength of whey protein films and their antioxidant behavior for the use in food packaging.

Table 4: List of materials used for chemical and physical stabilization of photochromic prints.

<table>
<thead>
<tr>
<th>Product name</th>
<th>Supplier</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tinuvin 292</td>
<td>BASF</td>
<td>Hindered amine light stabilizer (HALS)</td>
</tr>
<tr>
<td>Physical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whey powder</td>
<td>Star Nutriton</td>
<td>Whey protein isolate</td>
</tr>
<tr>
<td>β-lactoglobulin</td>
<td>Sigma Aldrich</td>
<td>Protein concentrate from bovine milk</td>
</tr>
<tr>
<td>Greenland wax</td>
<td>Fjällriven Sigma Aldrich</td>
<td>65% paraffin wax, 35% bee wax</td>
</tr>
<tr>
<td>Amylose</td>
<td>Sigma Aldrich</td>
<td>Starch from potato</td>
</tr>
</tbody>
</table>

5.2 Production Process Parameters

Two different types of inkjet printing systems have been used in this research. The printing systems are differentiated in the type of print head used and the printing mode, i.e. multi-pass (Xennia ink fluid development system) with a Sapphire QS 10 print head from Fujifilm Dimatix (native resolution of 100 dpi, 256 nozzles), or single-pass mode (modular inkjet printing system) with a Starfire SA print head from Fujifilm Dimatix (native resolution of 400 dpi, 1024 nozzles). Whereas the Xennia ink fluid development system was used in the studies of papers II, IV and V, the modular inkjet printing system was used in paper III. In paper I, the same print head as in the modular printing system was used. In paper VI, the fabric was dyed using a lab-scale beam type scCO\textsubscript{2} device.

The Xennia ink fluid development system is fitted with one print head that is mounted on a rotating plate. It is movable in x-, y- and z-direction whilst the printing substrate is static (Figure 13a and Figure 14a). The printable substrate is placed on a porous board, which is connected to a vacuum system to prohibit a shift of the substrate while printing. Compliant with the printable image data, the head moves along the substrate in x- and y-direction to print the imagery in multi-pass mode. The resolution of the printed image is adjustable up to 300 dpi.

Figure 13: (a) Xennia ink fluid development system with UV protection box and (b) modular inkjet printing system with UV curing bridge.

The modular inkjet printing system is a continuous inkjet printer with two bridges for printing of aqueous, solvent or UV-curable inks and one bridge for curing with a UV-LED lamp (Figure 13b and Figure 14b). The printable substrate is transported with a conveyor belt, which is adjustable in z-direction to change the distance between print head and substrate.

Figure 14: (a) Multi-pass printing and curing process using the Xennia ink fluid system and modular printer and (b) continuous printing and curing process using the modular printer only.
5.2.1 Printing Parameters

Parameters in the printing process are i) the amount of applied ink on the PET fabric and ii) the speed of the conveyor belt speed, which transports the printable PET toward the print head. The Xennia ink fluid development system with a Sapphire QS 10 print head prints in multi-pass mode, which allows the application of several printing passes, i.e. layers. In paper II, one, three, five, seven and ten printing passes have been applied on PET fabric. The printing speed is constant (60 mm s⁻¹) in this discontinuous process. The modular inkjet printing system with a Starfire SA print head prints in single-pass mode, which allows printing of four different shades in one printing pass. In paper III, the darkest shade, i.e. grey-scale was used.

5.2.2 UV Curing Parameters

Parameters in the curing process are i) the speed of the conveyor belt and ii) the lamp intensity of the UV-LED lamp using the modular inkjet printer as seen in Figure 14b. Irrespective of the printing process, curing of the photochromic prints exclusively results in the continuous process. In paper II and IV, six combinations of the belt speed of 50 mm s⁻¹ or 300 mm s⁻¹ with 1, 25 or 80% of the maximum lamp intensity of 6 W cm² were used. In paper III, four combinations of the belt speed of 50 mm s⁻¹ or 300 mm s⁻¹ with 1 or 80% of the maximum lamp intensity were used.

5.2.3 scCO₂ Dyeing Parameters

In paper VI, dyeing was performed using a batch type scCO₂ 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 a cooling element. The textile is wrapped around a small beam during dyeing. Dye amount of 0.027% of Reversacol Ruby red and Sea green relative to the weight of the PET fabric were added to the dyeing vessels. The chosen dye amount conforms to the amount of dye applied on PET by inkjet printing of the UV-curable photochromic ink in the darkest shade using the modular printing system. Dyeing of the PET fabric was carried out at a temperature of 120 °C and a pressure of 25 MPa for one hour.

![Figure 15: Scheme of scCO₂ lab dyeing procedure with (1) CO₂ tank, (2) freezer, (3) dyeing vessel and (4) high-temperature oil bath.](image)

5.2.4 Stabilization Parameters

Photochromic prints with 4 g L⁻¹ of Ruby red dye were stabilized before and after UV curing with impregnation of protein and starch emulsions and wax coating. Emulsions of whey powder, β-lactoglobulin and amyllose in distilled water were prepared for impregnation. For amyllose emulsion the distilled water was preheated to 50 °C. For impregnation with whey powder six different concentrations (1, 3, 5, 10, 15 and 20 wt%) were used, whereas 10 wt% showed best results. β-lactoglobulin and amyllose were applied with 10 wt% only. The printed fabrics were soaked in the emulsions for 2 min and then dried in an oven at 70 °C for 20 min. Wax coating was made by smearing 10 layers of wax on top of the photochromic prints using a wax block and afterwards heating it for 20 s in a heat transfer press at 100 °C. To compare the performance of physical stabilization layers using impregnation and coating to a standard chemical stabilization, photochromic ink containing 2 wt% Tinuvin 292 (HALS) was prepared. UV curing was made at a belt speed of 50 mm s⁻¹ and a lamp intensity of 25 %.
6. Experimental Methods

In the following chapter, the used methods to evaluate the stages of ink development, curing efficiency of the printed ink, color assessment of the sensor material and the resulting fastness properties, which are important for textile products in use, are described.

6.1 Ink Development and Characterization

Developed inkjet ink formulations are characterized according to their physical-chemical properties such as surface tension, viscosity and visualization of the jettability.

6.1.1 Surface Tension

For ink development in papers I, II, III, IV and V the pendant drop method using an optical tensiometer Attension Theta from Biolin Scientific. Three individual measurements with a drop size of 6 µl at 22 °C were made to measure the surface tension of inks, which is based on the Young-Laplace equation (Equation 10).

6.1.2 Viscosity

For ink development in papers I, II, III, IV and V, the viscosity of the ink was measured in a double gap cylindrical cell with Poiseuille flow using a rheometer Physica MCR500 from Paar Physica. The viscosity was measured at the maximum shear rate of the rheometer of 10000 s⁻¹ in a temperature sweep from 20 – 40 °C and 40 – 20 °C, which was repeated twice. The viscosity is an important measure of the jettability of a fluid in a specific print head. In inkjet printing specifically, a shear thinning viscosity is desired when the ink is jetted through the print head compared to when stored ⁴².

6.1.3 Drop Formation

In paper I, jettability of photochromic inks was assessed visually with a high-speed camera, Uridium drop watch, which records the formation of ink drops ejected from a print head as function of a chosen parameter, i.e. temperature, voltage etc. In paper I, visual drop formation, drop volume and velocity were recorded as function of temperature.

6.1.4 Particle Size

Next to the surface tension and the viscosity of the fluid, particle size is another important requirement for inkjet inks. The maximum size of particles according to the nozzle dimensions of the specific print head and the colloidal stability of the particles is to be measured prior to ink jetting in order to avoid clogging of the nozzles. For the Fujifilm Dimatix print heads Sapphire QS 10 and Starfire SA a maximum particle size of < 0.1 µm is required. In the case of jetting of photochromic dyes in a mixture of photo-polymers, particles as such are not apparent in the ink formulation. Photochromic dyes dissolve on molecular level and no sedimentation was observed for the concentrations of dyes used in the ink formulations. However, for precaution photochromic ink was filtrated initially through nylon syringe filters with pore size of 0.45 and 0.2 µm for qualitative analysis.

6.2 Degree of Cure of the Ink

6.2.1 Fourier-Transform Infra-Red Spectroscopy (FTIR)

Using FTIR spectroscopy it is possible to determine the infrared spectrum by excitation of molecules into a vibrational state, which gives, among other, information on specific bonds in the material. To determine the degree of cure in acrylated UV-curable material, the conversion of the C=C double bond at a wavenumber around 1650 cm⁻¹ is looked into. FTIR spectra were measured using a Nicolet iS10 from Thermo Fisher Scientific.

6.2.2 Differential Scanning Calorimetry (DSC)

In paper II, DSC was used for indirect analysis of the degree of cure of the UV-curable photochromic ink on PET fabric. By measuring the shift of the melting peak Tₘ of pure PET compared to printed PET samples using a Q1000 DSC from TA Instruments, USA, the influence of deposited ink amount and curing conditions on the curing efficiency can indirectly be determined. During a heating and cooling cycle from 25 °C to 290 °C and back to 25 °C with a rate of 10 °C min⁻¹ the heat flow of samples of about 5.0 mg was measured. The released energy ΔH of the endothermic reaction during melting of the material gives indirect information on the degree of polymer crosslinking at the interface between the PET fabric and the photochromic UV-cured ink.

6.2.3 Dynamic Mechanical Analysis (DMA)

DMA evaluates a samples response to mechanical deformation. In the analysis of photochromic prints on the PET fabric a Q800 DMA (TA Instruments, USA) is used to measure the influence of the different curing settings on the prints’ mechanical properties. Via measurement of the storage modulus as a function of frequency the stiffness of the UV-sensing textile is determined. In paper IV, the storage modulus was measured at a frequency sweep between 1 and 12 Hz with a preload force of 0.01 N.

6.2.4 Spectroscopy

Dyes in solution have been analyzed with UV/Vis spectroscopy, whereas color intensity of the photochromic textiles was measured with conventional visible reflectance spectroscopy or dynamic spectrophotometry.
6.2.4.1 UV/Visible Spectroscopy

UV/Visible spectroscopy, also electronic spectroscopy, is a useful technique to characterize colors of dyes or pigments. For analysis of the effect of temperature and solvent polarity of the commercial photochromic dyes in solution a temperature-controlled UV/Vis spectrophotometer Agilent 8453 from Hewlett Packard has been used. To affirm fit of the photo-initiator for the UV-LED lamp of the pilot-scale inkjet printer and to determine the influence of UV-varnish on the absorption spectra of the RR dye a Libra S60 double beam spectrophotometer from Biochrom and a UV-3101PC double beam spectrophotometer with integrated sphere accessory from Shimadzu have been used.

6.2.4.2 Visible Reflectance Spectroscopy

Color measurement based on visible reflectance spectroscopy is made in the CIE L*a*b* color space with standardized set of factors of light source/ object/ human observer. L* defines the lightness coordinate (black = 0 and white = 100), a* the green-red coordinate (greenness = - a* and redness = + a*) and b* the blue-yellow coordinate (blueness = - b* and yellowness = + b*) 13,14. Hue is the color appearance and chroma the saturation of a color. A color is defined as a point in the CIE L* a* b* color space and the distance between two points is the color difference ΔE. ΔE is a common measure of color intensity of photochromic materials using traditional spectrophotometers with separate UV exposure 7, 10, 22, 23, 27. The flaw of traditional spectrophotometry for photochromic materials is that a delay after UV activation is caused before color measurement because activation and measurement are performed separately. Neither does such a setup allow calculations of dye kinetics. The method was used in the analysis of stabilization layers (chapter 7 - Ways to Extend the Life Time of a Printed Textile UV-Sensor) and to analyze background colors in paper VI.

6.2.4.3 Dynamic Spectrophotometry

Dynamic or also referred to as online color measurement of photochromic materials upon excitation and relaxation of the material with UV light requires a special measurement setup. A specifically designed spectrophotometer LCAM Photochrom 3 was used to analyze the photochromic inkjet prints on fabric. The device enables simultaneous UV excitation and color measurement of the photochromic material, which gives precise results about the reaction kinetics as depicted in Figure 8. The method was used for analysis of the color performance based on K/S values in papers II, III, IV and VI.

6.3 Textile Properties

In the development of functional and smart textiles for wearable applications product reliability in terms of durability of the functionality and wearing comfort in terms of flexibility and breathability of the functionalized fabric are important. Therefore, the photochromic textiles are characterized according to fastness tests, i.e. washing and abrasion and objective evaluation of the textile handle using a Kawabata evaluation system and scanning electron microscopy.

6.3.1 Fastness Properties

As the various photochromic dyes have inherently different kinetic switching and fatigue properties, fastness properties to determine the durability and adhesion of the UV-cured photochromic prints as in washing and abrasion is an important measure of the novel material. Fastness tests have been used to determine the impact on the color yield and kinetic rate constants of a spirolloxazine and a naphthopyran dye.

6.3.1.1 Abrasion Resistance

In paper III, 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 evaluate the influence of mechanical action on the print durability and adhesion.

6.3.1.2 Wash Fastness

The print durability of photochromic prints was determined after single and ten washing cycles in papers II and III. In paper VI, the effect of a single wash was investigated on the color performance of scCO2-dyed photochromic textiles. Washing was conducted according to ISO 6330:2012 using procedure 4N and reference detergent 3. The samples were dried using drip flat drying. In paper II, washing tests also gave information on the physical durability, i.e. the adhesion of the ink on the PET surface, which is indicated by the difference in melting peak temperature ΔTm,ashed of the photochromic prints before and after washing.

6.3.2 Kawabata Evaluation System (KES)

KES is designed to objectively measure properties of textile fabrics and predict the aesthetic quantities perceived by human touch based on primary hand values (HV). From the primary hand values, which include the stiffness (koshii), smoothness (numeri), fullness and softness (fukurami), crispness (shari) and anti-drape stiffness (hari), the total hand value (THV) is calculated. Calculations are based on tensile, shear, bending, compression, and surface properties of the fabrics. HVs are evaluated 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 chosen application. In the evaluation of inkjet-printed photochromic fabrics in paper III, the change in handle of the plain-woven PET compared to after printing with Ruby red ink and after washing for 10
cycles a KES instrument at the Technical University of Liberec, Czech Republic was used.

6.3.3 Scanning Electron Microscopy (SEM)
SEM is commonly used to analyze the morphology and surface properties of textile structures. In the characterization of photochromic prints in paper III, the impact of the inkjet functionalization on the inter-yarn pores in the textile is evaluated using a JEOL JSM-6301F. Images were taken at an acceleration voltage of 6 kV and a working distance of 39 mm.

6.4 Statistical Analysis
Scientific results in this work are statistically underpinned using ANOVA analyses at a confidence interval of 95%.

7. Summary of Results

7.1 Design of UV-Curable Photochromic Inkjet Inks
Naphthopyran dye Ruby red (RR) and spirozaxine dye Sea green (SG) were chosen as dyes for the design of UV-curable photochromic inks. Both RR and SG were relatively stable over the practical range of temperatures between 0 and 30 °C (as seen in Figure 12). RR shows stronger absorbance in polar and SG in non-polar solvents. Color analyses of the photochromic dyes as prints on textile are made at wavelengths, which correspond to the dyes’ absorbance maxima in solvents: 500 nm for RR in ethyl acetate and 620 nm for SG in hexane as shown in Figure 16.
Prerequisite for fully functional UV-curable photochromic ink is that the photo-initiator used in the ink formulation conforms to the UV light source, which is used to initiate photo-polymerization. In Figure 16, it can be seen that the photo-initiator TPO-L has an absorption peak between 340 and 410 nm, which conforms to the LED-UV lamp used for curing with emission wavelengths between 380 and 420 nm.

![Figure 16: Absorbance spectra of photo-initiator TPO-L, Ruby red in ethyl acetate and Sea green in hexane.](image-url)
For ink formulation, the physical properties of the ink have to follow the print head requirements. This means that the following has to be met for Fujifilm Dimatix print heads Sapphire QS 10 and Starfire SA:

- Surface tension: 30 – 35 mN m⁻¹
- Viscosity: 0.008 – 0.020 Pa s (ideally 0.010 – 0.014 Pa s)
- Particle size: < 0.1 μm

As mentioned earlier, no particles are used in the formulation, but filtration using syringe filters has been initially made without an affecting the ink.

The viscosity had been identified as the most crucial physical property, which is decisive for the jettability of the formulated ink. Combinations of different monomers and oligomers (as listed in Table 3) have been tested initially to evaluate, which combination is suitable for the development of photochromic ink. According to Figure 17, mixtures with oligomers Genomer 3497 and Genomer 5275 resulted in too high viscosity (> 15 mPa s) and mixtures with monomer ACLA in too low viscosity (< 10 mPa s). It was also observed that the polymer mixtures with ACLA were turbid and could not be homogenized sufficiently.

As can be seen in Figure 18 and Figure 19, different combinations of monomers and oligomers and different ratios of ink components do not largely affect the surface tension of the ink. With the exception of the combinations of Genomer 3497/ DPGDA and Genomer 3497/ DDDA, all other combinations were within the jettable range according to print head requirements. Eventually, the mixture of monomer DPGDA and oligomer Ebecryl 81 was chosen as basis for the varnish for further development of photochromic ink. This combination fulfilled requirements in regards to the surface tension, viscosity and showed best preliminary curing efficiency when combining with the photo-initiator TPO-L.
Figure 19: Influence of different ratios of ink components on the surface tension (●) and the viscosity (■) of the ink formulations at 20 °C.

Eventually, the formulation of monomer DPGDA, oligomer Ebecryl 81 and photoinitiator TPO-L was finalized for printing and curing studies (paper II, III and IV) with the ratio of 21:1:1 and RR/SG photochromic dyes with concentrations of 2.5 and 4 g L⁻¹ in ethyl acetate and hexane, respectively.

As can be seen in Figure 20a, the viscosity of the varnish and RR and SG inks decreases as function of increasing shear rate from 1 to 10000 s⁻¹. The UV-curable varnish as mixture of polymers with different chain length may be responsible for the shear-thinning behavior of the ink. Thus, UV-curable photochromic inks behave as non-Newtonian fluids. In comparison, functional waterborne ink containing polysiloxane shows Newtonian behavior and weak temperature-dependence, which is discussed in paper V. An increase of 20 °C affects the functional waterborne ink with a viscosity decrease of ca. 15% (from ca. 0.012 Pa·s to 0.010 Pa·s). Photochromic UV inks are more affected by temperature with a 30% decrease in viscosity from 20 °C to 40 °C as seen in Figure 20b (from ca. 0.015 Pa·s to 0.0105 Pa·s).

Figure 20: Viscosity of RR ink, SG ink and ink varnish as function of (a) shear rate from 1 to 10000 s⁻¹ at 20 °C and of (b) temperature from 20 to 40 °C at 10000 s⁻¹.

Despite similar viscosity and surface tension of RR and SG inks, differences were observed in relation to the velocity of the droplets upon jetting and the drop volume. SG ink drops exhibit remarkably lower velocity at room temperature and generally lower drop volume than RR ink. Such difference can be explained by the distinct molecular structures of the dyes. With SG being non-planar in the ring-closed state, jetting of the ink can be similarly affected as the dye kinetics in a UV resin with different crosslinking densities as discussed in papers II and III. During jetting, higher temperatures enable more flexibility in the ink and smoother ink flow. The bulky structure of spirooxazines could cause a bottleneck at the orifice and result in smaller drop volumes.
As described in *Ink Jettability* in chapter 4, jettability of ink can be evaluated by calculations of dimensionless numbers *We*, *Re* and *Z*, which are based on the jettable fluids’ physical properties. In paper I, the aim was to determine the jettability of the formulated photochromic UV inks based on RR and SG dyes theoretically using calculations and visually using a high-speed camera Uridium drop watcher. According to Derby, a fluid is classified as jettable with stable drop formation (see Figure 10) in the range of 1 < *Z* < 10. According to calculations of the dimensionless numbers based on the density, viscosity, surface tension and velocity of the inks and the dimension of the jetting orifice, RR ink and SG ink show *Z* values of 1.28 and 1.24, respectively, at room temperature (22 °C). This suggests stable drop formation of the photochromic inks. With increasing temperature *Z* increases and hence the jettability improves. For RR ink an optimal *Z* of 1.99 is achieved at 35 °C and for SG ink *Z* was highest at 40 °C with 1.7. As a conclusion, temperature has an important role in influencing the jetting behavior of UV-curable photochromic inks. Therefore, inks were jetted at 35 °C for the production of samples used in paper II, II and IV.

However, visual analysis disclosed that satellite droplets, as categorized in Figure 10, are formed for both RR and SG ink. Despite calculated and perceived improvement of ink jettability in print tests, the result seen in Figure 21 points out a discrepancy between theory and visual analysis. The formation of satellite drops for the photochromic UV inks might result from the more complex rheological behavior of non-Newtonian fluids compared to Newtonian fluids. Theory and computational models are principally based on Newtonian fluids. Until today, a limited number of computational models for ink jetting has been introduced, which takes both temperature and strain dependence of non-Newtonian fluids into account. Apart from adjustments of the viscosity and the workflow, which have proven to improve drop formation, better understanding and optimization of the UV-curable photochromic inks can be made by investigation on defined models for non-Newtonian fluids.

### 7.2 Degree of Cure of the Inkjet-Printed and UV-Cured Ink on Textile

After printing of the ink, curing via a UV light source results, which necessitates the analysis and specific quantification of the degree of cure of the ink in order to optimize the system. The settings in the technical process of UV curing affect the chemical process of polymer crosslinking. There both the degree of polymer crosslinking and the crosslinking density of the resin are influenced. However, within this thesis no differentiation between the degree and density of crosslinking is aimed at. The degree of cure is relevant in three respects – i) impact of the resin rigidity on the dye kinetics, ii) influence of the degree of cure on the durability of a photochromic print on textile and iii) health concern of the UV resin in liquid form.

Usually, FTIR is a common method to determine the degree of cure as cleavage of the C=C in UV-curable material. However, in the case of our material FTIR was not suitable to determine the degree of cure of the ink-jetted photochromic ink on the plain-woven PET fabric. As seen in Figure 22, the PET reference and printed PET show equal FTIR-spectra, which shows that the thin layer of photochromic ink cannot be detected by FTIR on the porous textile structure. As seen in Figure 23, monomer cleavage of the C=C double bond at 1636 and 1619 cm<sup>-1</sup> is observed for a drop of ink with a volume of 1 μl on a glass plate. Here, it can be seen that the amount of broken C=C increases with increasing curing intensity as compared to the liquid photochromic ink drop, which allows qualitative analysis. However, the amount of a 1-μl ink drop on glass and the ink-jetted material on plain-woven PET fabric are quantitatively incomparable.
Therefore, DSC measurements in the first place, but also DMA measurements were made in order to be able to analyze the ink-jetted UV-cured photochromic ink on textile. As discussed in papers II and IV, the curing intensity and hence the crosslinking density of the UV-curable polymer resin affect the color intensity and kinetic switching speeds of the coloration and decoloration reaction. Stronger curing increases the rigidity of the polymer resin and reduces the free volume for the photochromic dye molecule to move within. The impact of the degree of cure on the color performance and kinetics of the photochromic prints will be discussed in detail later in this chapter in Color Performance of the Textile UV Sensors. DSC results in Figure 24 show that the melting peak temperature increases with increasing curing intensity. Data acquired by DSC can possibly be interpreted as stated in paper II; the shift of the melting peak \( T_m \) towards higher temperatures compared to the \( T_m \) of unprinted, pure PET fabric indicates that an insulating layer is built around the textile yarn/fibre, which affects the heat flow into PET. As a result of more intense curing (lower belt speed and higher lamp intensity) a thicker heat insulation layer of the ink resin may be formed.

Further measurements, exceeding the outcome of paper II show that UV curing of the unprinted PET with different curing intensities, i.e. 300 mm s\(^{-1}\) + 1%, 50 mm s\(^{-1}\) + 1% and 50 mm s\(^{-1}\) + 80%, and at different distances of the conveyor belt to the UV-LED lamp, i.e. 10 mm, 20 mm and 28 mm, increases the \( T_m \) of PET as such (see Figure 25). The observed increase of \( T_m \) of PET accounts for approx. 1 °C and therewith indicates...
that UV radiation influences the textile material by itself. However, the increase of $T_m$ of UV cured ink on PET accounts for a successive increase of 1 °C of the melting peak, with an observed systematic increase with increasing curing intensity. Because the extended measurements of UV-treated unprinted PET are not statistically representable, but indicate a factor, which was not regarded in paper II, other methods for quantitative analysis might be necessary to clarify the degree of cure of the photochromic ink on a textile as a result of curing intensity.

Figure 25: Melting temperature $T_m$ of unprinted PET treated with different intensities ($\tilde{\text{}}$) of UV-LED light and at different distances between the conveyor belt and the UV lamp ($\text{\textbullet}$) compared to untreated PET ($\text{\textbullet}$).

DMA measurements confirm the trend of increasing degree of cure with increasing curing intensity in relation to stiffness of the printed and cured photochromic material on PET fabric. The storage modulus as function of frequency between 1 and 12 Hz increases with increasing curing intensity as can be seen in Figure 26. Whereas the PET reference has a storage modulus around 300 MPa, PET printed with RR ink increases the storage modulus to ca. 1000 MPa for an ink with low crosslinking density and to 1400 MPa with an ink with high crosslinking density.

Figure 26: Storage modulus as function of frequency of PET reference fabric and prints cured with different intensities on PET

7.3 Development of an Extended Kinetic Model

Color measurements with the LCAM Photochrom 3 spectrophotometer have shown that the first-order kinetic model for the coloration reaction (Equation 8) is only valid for photochromic prints with a high polymer crosslinking density, i.e. printed and cured at a belt speed of 50 mm s$^{-1}$ and lamp intensity of 80%. For all other printing and curing parameters, the application of Equation 8 resulted in a poor and unacceptable fit ($R^2 < 0.45$) of the coloration data, as seen in Figure 27. The deviation of the coloration data from the first-order kinetic model was found to be in line with the degree of polymer crosslinking in the following order, starting from the curing settings with the highest deviation:

$300 \text{ mm s}^{-1}/1\% > 300 \text{ mm s}^{-1}/25\% > 50 \text{ mm s}^{-1}/1\% > 50 \text{ mm s}^{-1}/25\% > 300 \text{ mm s}^{-1}/80\% > 50 \text{ mm s}^{-1}/80\%$

Therefore, the development of an extended kinetic model for photochromic UV-curable prints with a low degree of polymer crosslinking was required in order to be able to characterize the material. The difference between the first-order kinetic model and the extended kinetic model is that the extended model also takes into account and corrects for a decay mechanism upon coloration of the photochromic prints.
Figure 27: Coloration data (•) and first-order curve fitting (—) according to Equation 8 of a photochromic print with 19 g m⁻² deposited ink, cured at belt speed of 50 mm s⁻¹ and 1% lamp intensity in cycle 1 with a fitting value $R^2 < 0.45$.

7.3.1 Challenging Role of UV Light for Curing and Activation

By combining photochromic and UV-curable material a challenging relationship exists between the mechanisms of color activation and polymerization, both initiated by molecular excitation via UV light. Upon UV excitation during color measurement of the photochromic prints, photochromic dyes are activated, as well as free radical polymerization of the UV-curable material can be initiated.

As mentioned earlier, photochromic materials show fatigue, which degrades the photochromic color switching effect over time. Also, curing of a UV-curable resin requires sufficient light intensity and time in order for the free radical polymerization reaction to be terminated. While high UV radiation improves the cure speed of the resin¹²⁹,¹³⁰ and longer irradiance increases the degree of polymer crosslinking¹³¹, photo-degradation of photochromic dyes is commonly observed under prolonged UV irradiance¹²,⁶⁹,¹³².

This means that if the polymer crosslinking density of photochromic prints is high, no further curing takes place while color measurement, which is the case for prints produced at 50 mm s⁻¹ and 80%. Photochromic dyes are also better protected against fatigue when fixed in a fully cured matrix. However, a partially liquid resin has a lower viscosity, which facilitates oxygen diffusion¹³⁰. Hence dye degradation as a result of photo-oxidation is more likely to occur in a softer resin compared to when the dye is fixed in a solid matrix. Therefore, for prints with a low degree of polymer crosslinking, polymer crosslinking continues during color measurements and a simultaneous secondary decay mechanism is observed, which affects the color behavior of photochromic dyes.

7.3.2 Model Development and Application

For photochromic prints with a low polymer crosslinking density an extended kinetic model is introduced, which defines the kinetics of a decay mechanism owing to continuous curing while color measurement and which reconstructs the actual coloration curve (see Figure 28). For UV-curable photochromic ink systems with the aim to characterize photochromic material and to optimize its curing conditions, the following extended kinetic model is proposed.

\[
\Delta \frac{K}{S_{\text{col}}} = \left( \frac{K}{S_{\text{col}}^\circ} - \frac{K}{S_{\text{col}}^\text{dec}} \right) \cdot e^{-\left( k_{\text{col}}^\circ + k_{\text{col}}^\text{dec} \right) t} + \frac{K}{S_{\text{col}}^\text{dec}} \cdot e^{\left( -k_{\text{dec}}^\text{dec} \right) t} \]

where $K/S_{\text{col}}^\circ$ is the initial color value for the coloration reaction, $K/S_{\text{col}}^\text{dec}$ is the maximum coloration value, $K/S_{\text{dec}}$ is the initial value of the decay and $K/S_{\text{dec}}$ is the final value of the secondary decay for each activation cycle. Kinetic rate constants for the coloration reaction and decay are defined as $k_{\text{col}}^\circ$ and $k_{\text{dec}}$, respectively.

Under the boundary condition that the processes of coloration and decay start simultaneously upon UV excitation and at $\Delta K/S = 0$, which means that $K/S_{\text{col}}^\circ = 0$ and $K/S_{\text{dec}} = 0$, Equation 17 reduces to

\[
\Delta \frac{K}{S_{\text{col}}} = \frac{K}{S_{\text{col}}^\text{dec}} \cdot \left( 1 - e^{-\left( k_{\text{col}}^\circ \right) t} \right) - \frac{K}{S_{\text{dec}}} \cdot \left( 1 - e^{-\left( k_{\text{dec}}^\text{dec} \right) t} \right) \]

As seen in Figure 28, the color intensity $K/S$ of photochromic prints produced and cured at a belt speed of 300 mm s⁻¹ and a lamp intensity of 1% is decreased throughout the activation cycles 1 to 5 (i.e.) during color measurement. Furthermore, the secondary decay is most pronounced during the first activation cycle and decreases gradually during continuing cycles. For the print in Figure 28 degradation becomes statistically ineffective in activation cycle 5 (v). Eventually, the application of Equation 18 allows the distinction of a decay mechanism and the reconstruction of the achievable coloration curve for given curing settings. Vice versa, via the extended kinetic model respective curing parameters can be chosen for a desired photochromic performance of the material.
Figure 28: Activation cycles 1-5 (i-v) of a print with 19 g m\(^{-2}\) deposited ink cured at 300 mm s\(^{-1}\) and 1%. Measured K/S (■) includes decay (—·) and coloration (–). Calculated sum of decay and coloration (—–) validates the model.

7.4 Color Performance of the Textile UV Sensors

In this section, the color performance of inkjet-printed photochromic textiles as a result of different production process parameters and fastness tests is described, as well as the implications of these factors on the durability and textile handle of the photochromic prints are summarized. Furthermore, the color performance of scCO\(_2\)-dyed photochromic textiles and the effect of washing on the uniformly dyed fabrics is described.

7.4.1 Inkjet-Printed Photochromic Textiles

The performance of inkjet-printed photochromic textiles was studied extensively in regards to several factors; the amount of deposited ink on the textile, production process parameters, durability and textile properties.

7.4.1.1 Deposited Ink Amount

In paper II, single-pass printing of photochromic ink with RR dye was used to study the effect of printing passes between 1 and 10, i.e. the amount of deposited ink on the textile, and the effect of printing and curing parameters on the print’s color performance. Color performance implies the color intensity \(\Delta K/S\) of the photochromic prints and the kinetic rate constants of the coloration and decoloration reaction \(k_{col}\) and \(k_{dcol}\) as seen in Figure 29. It was found that the color intensity \(\Delta K/S\) is linear towards the deposited amount of ink irrespective of the curing intensity of the prints. Aldib \(^27\) also observed linear increase of \(\Delta K/S\) of photochromic prints in an earlier study applying solvent-based photochromic inkjet ink. Deeper shades of a color are expected with increasing layer thickness, i.e. lower surface-bulk ratio and reduced colorless reflection \(^26, 40\). It is noted that all measured color intensities \(\Delta K/S\) are visible by the naked eye, with the lowest printable amount, i.e. one printing pass, corresponding to ca. 2 wt% of ink deposited on PET. The kinetic rate constants \(k_{col}\) and \(k_{dcol}\) are influenced by the amount of deposited ink, where more material causes weakened and hence slower activation of the dyes with increasing layer thickness.\(^33\)
Figure 29: (a) Color yield $\Delta K/S$, (b) coloration rate constant $k_{col}$, (c) decoloration rate constant $k_{decol}$ of printed (■) and washed (£) RR prints as function of printing passes and (d) inactive (l), printed (P) and washed (W) RR prints with 1, 5 and 10 printing passes cured at 50 mm s$^{-1}$ and 80%.

### 7.4.1.2 Production Process Parameters

Tuning of dye kinetics as means of controlling the properties of the dye-carrying media is a topic of interest in many studies. The viscosity of the media, the chain length of polymers or the specific placement of the dye molecule in the polymer matrix can influence dye kinetics \(134-141\). In this thesis, control of dye kinetics as means of using production process parameters, i.e., conveyor belt speed and lamp intensity was investigated. The principle is based on enabling enough space for the photochromic dyes to undergo quick isomerization from the orthogonal ring-closed to the co-planar ring-opened form as visualized in Figure 30.

The lower the crosslinking density of the UV-ink, the least rigid becomes the dye-carrying varnish. Less rigidity implies a higher degree of freedom for isomerization of the dye, which enables faster kinetic switching and higher color yields as can be seen in color performance values in Table 5. Eventually, prints produced with the highest belt speed of 300 mm s$^{-1}$ combined with the lowest lamp intensity 1% achieve high color yields $\Delta K/S$ with 0.47 after printing and 0.25 after washing, fastest isomerization with $k_{col}$ of 0.16 s$^{-1}$ after printing and 0.11 s$^{-1}$ after washing and good durability after washing with 54.1% of the initial $\Delta K/S$, despite lowest polymer crosslinking density.

Figure 31: Change in $k_{col}$ before and after washing of RR prints as function of curing intensity with low (●), intermediate (▲) and strong (■) curing.
Summarizing, the effect achieved by production process parameters on dye kinetics is less as other means of polymer architecture. For example via polymer conjugation an effective change of \( k_{col} \) of up to a 5-fold was achieved compared to an increase of \( k_{decol} \) of 1.4 using belt speed and lamp intensity.

One advantage of inkjet printing is the ability of fast, flexible and precise pattern printing and hence makes it an ideal technology for multi-colored photochromic applications. The use of several colors, i.e. dye types, also brings along differences in dye-specific color performance, which can either be beneficial or challenging. This depends on the application of the photochromic textile sensor, which may either require different activation and deactivation speeds or the need for synchronization of the dyes. In paper III, where two types of photochromic dyes were used, molecular differences between the spiropyrane dye and the naphthopyran dye caused distinct kinetic effects. For spirooxazine-based prints (SG) color yield \( \Delta K/S \) is lower and color build-up and reversion will be slower than for naphthopyran-based prints (RR). However, SG prints were more influenced by changes in the crosslinking density owing to their inherently faster dye kinetics and more bulky structure. Spirooxazines, which are more non-planar and have higher molecular weight, are influenced stronger if the dye-carrying resin loosens. Therefore, \( k_{col} \) of SG prints increased a 5-fold with approx. 0.071 \( s^{-1} \) when produced at a belt speed of 300 mm s\(^{-1}\) and a lamp intensity of 1% compared to 50 mm s\(^{-1}\) and 80% with approx. 0.015 s\(^{-1}\). For RR prints an increase of a 2-fold from \( k_{col} \) of ca. 0.056 s\(^{-1}\) to ca. 0.116 s\(^{-1}\) can be achieved with the same change of production process parameters and resulting crosslinking density. In order to achieve synchronized dye kinetics of combined RR and SG prints with similar \( k_{col} \) of 0.05 – 0.08 s\(^{-1}\), RR should be preferably cured with a strong intensity (50 mm s\(^{-1}\) + 80%) and SG with a low intensity (300 mm s\(^{-1}\) and 1%). Eventually, production process parameters can be used to intensify or balance out differences in dye kinetics of multi-colored textiles, which may depend on the requirements of the desired application.

### 7.4.1.3 Durability

Durability of photochromic prints for UV sensor applications is a measure of two factors – i) adhesion of the photochromic ink on PET and ii) performance of the photochromic effect over time. Whereas adhesion is influenced and determined by fastness tests as washing and abrasion and indirectly via melting peak temperatures, the performance over time is influenced by the materials’ fatigue properties.

In paper III, exceeding the findings to controlling dye kinetics via production process parameters, we could also confirm that curing intensity influences the durability of photochromic prints. In general, it was observed that a reduced rigidity of the host matrix improves print durability. Wearing of textiles typically is caused mechanically as in abrasion or chemical-mechanically as in washing. As seen in the factor analysis (Figure 32), color performance as in \( \Delta K/S \), \( k_{col} \) and \( k_{decol} \) is less affected by treatments with mechanical action via abrasion with 20000 rubbing cycles than by chemical-mechanical action via one or 10 washing cycles. Washing has a harsher effect than abrasion.

<table>
<thead>
<tr>
<th>Belt speed (mm s(^{-1}))</th>
<th>Lamp intensity (%)</th>
<th>( \Delta K/S )</th>
<th>( k_{col} ) (s(^{-1}))</th>
<th>( k_{decol} ) (s(^{-1}))</th>
<th>( k_{decol} ) (%)</th>
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<tbody>
<tr>
<td>300</td>
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<td>0.467 ±0.038</td>
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<td>0.070 ±0.008</td>
<td>0.008 ±0.001</td>
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</table>

<table>
<thead>
<tr>
<th>Belt speed (mm s(^{-1}))</th>
<th>Lamp intensity (%)</th>
<th>( \Delta K/S )</th>
<th>( k_{col} ) (s(^{-1}))</th>
<th>( k_{decol} ) (s(^{-1}))</th>
<th>( k_{decol} ) (%)</th>
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</tr>
</tbody>
</table>

Figure 32: Effects of the factors curing intensity ( ), dye type ( ) and treatment ( ) on (a) \( \Delta K/S \), (b) \( k_{col} \) and (c) \( k_{decol} \).
The abrasion resistance of UV-curable inks is in general very good. Comparing the color performance of SG and RR prints, SG prints are more durable as a result of abrasion cycles. Whereas, RR prints show a steady decrease of $\Delta K/S$ and $k_{col}$ as function of abrasion cycles, SG prints are not as systematically affected (see Figure 33).

Figure 33: 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$^{-1}$ and 80% (50_80) and 300 mm s$^{-1}$ and 1% (300_1) on and on $k_{col}$ of RR (c) and SG (d) prints cured at 50 mm s$^{-1}$ and 80% (50_80) and 300 mm s$^{-1}$ and 1% (300_1).

After a first washing cycle, photochromic prints are influenced noticeably. Prints with lower crosslinking density, however, are less affected both for RR and SG dyes. When washing the prints more extensively, prints with high crosslinking density show a steady decrease in $\Delta K/S$, $k_{col}$ and $k_{decol}$ but prints with low crosslinking density dispose of stable values between 1 and 10 washes, which is also seen for multiple activations. It is important to know how the inkjet-printed material behaves after extensive washing and multiple activations in regard to maintenance and repeatability of potential textile UV sensors. Additionally, extensive washing is suggested as reduction process with respect to health concerns of uncured monomer, not just to remove potentially uncured ink of prints with low crosslinking density but also to achieve durable and reliable prints for long-term use.

A remarkable difference between RR and SG prints is the initial increase of $\Delta K/S$ of SG prints after initial washing or abrasion (as seen in Figure 33b and Figure 34b). This phenomenon has been observed in other prior studies, where the loosening effect of a washing procedure on the matrix believes to facilitate isomerization. Eventually, when multi-colored and synchronized prints are desired for a specific application, the durability of RR and SG prints will be uneven. As stronger curing of RR prints is needed for synchronized rate constants with SG, which was mentioned earlier, the durability against abrasion and washing of RR dyes will be weakened.

Figure 34: 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$^{-1}$ and 80% (■, ▲, △) and 300 mm s$^{-1}$ and 1% (█, □, ▼) and of (b) SG prints cured at 50 mm s$^{-1}$ and 80% (■, ▼, ▼) and 300 mm s$^{-1}$ and 1% (█, □, ▼).
In paper II, adhesion of the UV-curable ink as such on PET was investigated indirectly as in the difference of melting peak temperature after printing and after washing \(AT_{washed}\). The smaller \(AT_{washed}\), the more UV-cured ink is left on PET after a washing procedure and the more durable the prints are. We could observe a difference between the strongly cross-linked prints produced with 50 mm s\(^{-1}\) and 80% with a melting temperature after washing of \(T_{washed} = 255.2^\circ\text{C}\) and a \(AT_{washed}\) of 0.2 \(^\circ\text{C}\) and the less cross-linked prints produced with 300 mm s\(^{-1}\) and 1% with \(T_{washed} = 254.3^\circ\text{C}\) and a \(AT_{washed}\) of 0.1 \(^\circ\text{C}\). Although the differences in adhesion are minor, knowing that the color performance is superior for photochromic prints with reduced matrix rigidity, it can be concluded that stronger curing than with a belt speed of 300 mm s\(^{-1}\) and 1% lamp intensity is not more beneficial for the durability of the print. Furthermore, a lower curing intensity is most energy and cost effective.

### 7.4.1.4 Textile Properties

In paper III, the effect of a photochromic, inkjet-printed surface layer on the textile properties is evaluated and discussed. KES measurements confirm a stiffening effect of the PET fabric after inkjet printing with the photochromic ink, which is expressed in several values. The values of stiffness (koshi) and anti-drape stiffness (hari) increase after printing, but decrease again after washing. The fabric’s fullness and softness (fukurami) in return, decreases after printing, but is revoked again after washing. Another property, which confirms stiffening after inkjet printing of PET, is the bending moment of the fabric. The bending moment of printed PET decreases after washing from \(B = 0.249\) g·cm\(^{-2}\)·cm\(^{-1}\) to 0.221 g·cm\(^{-2}\)·cm\(^{-1}\). As a result, KES measurements support the hand feel that when bending the fabric, which is mentioned in paper IV, functionalization with UV-curable photochromic ink obviously stiffens the fabric. After extensive washing, the stiffening however is revoked. Through from color measurements it is proven that the inkjet-printed photochromic layer is effective both before and after washing. SEM pictures (see Figure 35) also show that the photochromic ink barely influences the textile, as the ink layer does not affect the fabric structure, i.e. space between the yarns and fibers. Hence, it can be expected that the fabrics’ porosity and breathability are not influenced.

![Figure 35: PET fabric printed with 19 g m\(^{-2}\) of RR ink cured at 100 mm s\(^{-1}\) belt speed and 25% lamp intensity (a, c) compared to PET reference (b, d).](image_url)

### 7.4.2 ScCO\(_2\)-Dyed Photochromic Textiles

The representative dyes RR and SG of the naphthopyran (NP) and spirooxazine (SO) class respectively, were applied by scCO\(_2\) dyeing onto PET. The uniformly colored fabrics exhibit reversible color-changing properties when exposed to UV light. The two photochromic dyes on PET performed differently in terms of the rate of photochromic coloration \(k_{col}\) and decoloration \(k_{decol}\) color yield \(\Delta K/S\) and in terms of wash fastness. Before washing, PET dyed with spirooxazine dye SG and naphthopyran dye RR exhibit similar \(\Delta K/S\) with 0.096 and 0.088, respectively. However, after one washing cycle SG-dyed PET exhibits a lower color yield with \(\Delta K/S = 0.026\) than RR-dyed samples with \(\Delta K/S = 0.068\). The spiromaxazine-dyed fabric shows faster coloration and decoloration speeds with \(k_{col} = 0.141\) s\(^{-1}\) and \(k_{decol} = 0.072\) s\(^{-1}\) in comparison with naphthopyran-dyed fabrics. RR fabrics have a \(k_{col} = 0.020\) s\(^{-1}\) and \(k_{decol} = 0.007\) s\(^{-1}\). The wash fastness of SG fabrics is poor compared with when dyed with RR dye as can be seen in the reduced K/S values in Figure 36.
Results obtained by scCO₂ dyeing of PET with RR and SG dyes can be compared to UV-curable inkjet printing in terms of a bulk versus a surface treatment of the dyes on textile, but also in terms of how a polymer matrix influences isomerization and hence kinetics of the dyes. A general observation is that the color performance of RR and SG dyes, respectively, is opposite when applied by inkjet printing compared to scCO₂ dyeing. Whereas RR prints show higher color yields, faster kinetics, but worse durability after abrasion and a first washing cycle, SG prints show lower color yields, slower rate constants but better fastness properties. ScCO₂-dyed samples show opposing behavior. The common reason for both the poor fastness properties of the SG-dyed samples and the slow kinetics of SG prints is presumed to be due to the non-planar ring-closed form and more bulky molecular structure of spirooxazine dyes. Molecular non-planarity impedes the penetration of the dye into a polymer matrix and thus prevents SG dyes from penetrating into the bulk of the polymer matrix. Instead the dyes are believed to be more concentrated on the fiber surface, which results in poor wash fastness. For SG inkjet prints, the bulky structure of the dyes influences a larger relative increase of kinetics with a decreasing polymer crosslinking density of the ink. Explanation for why RR dyes are stronger colored and faster switching in UV ink than in scCO₂-dyed PET has not been possible to account for yet. It might be influenced by the polarity of the surrounding media.

The fact that photochromic dyes can successfully be applied on PET fabric by scCO₂ dyeing widens the scope of application of the technology. This shows the potential and may be a contributing factor for the yet uncommon technology to reach a breakthrough.

7.5 Ways to Extend the Lifetime of an Inkjet-Printed Textile UV Sensor

UV-curable photochromic prints suffer from oxygen inhibition during curing of the ink resin and from photo-oxidation when exposed to UV radiation, which will reduce their color switching effect over time. Firstly, during the curing process oxygen reacts with the produced free radicals, which limits the initiation and reduces the rate of polymerization. Secondly, the fatigue behavior of photochromic dyes is influenced by photo-oxidation and leads to a lower color effect of the print. Hence, means of light stabilization have been explored to protect the photochromic dyes in a UV resin from oxygen inhibition and photo-oxidation in these two stages, producing a print with extended lifetime. It has been studied how different treatments applied before and after the curing process affect the color performance of the photochromic prints both directly and over time. The aim is to reduce photo-oxidation in the prints by a physical shield layer, which improves both the curing efficiency and color yields during activations, compared to means of chemical stabilization using hindered amine light stabilizers.

It has been shown that it is possible to enhance the color yield of photochromic prints cured with UV-LED radiation by impregnating photochromic ink on PET fabric with whey powder or coating it with wax (Figure 37). Starch based impregnation using amylase did not improve the coloration performance of photochromic prints, but rather had a reducing effect as can be seen in Figure 38, which could also be concluded statistically. The poor protective properties against photo-oxidation of amylase are assumed to result from poor adhesion of amylase to the fabric.
As seen in Figure 39 and Figure 40, where trend lines are used to guide the eye, both before and after washing photochromic prints treated with protein or wax exhibit higher color difference $\Delta E$ than prints containing HALS. However, over the course of 10 activation days washed prints containing HALS show an increasing trend of coloration as compared to protein and wax treatments, which decrease in coloration.

The residual color difference, as ratio of the color difference $\Delta E$ before washing and the color difference $\Delta E_{washed}$ after washing, determines the fatigue of the photochromic prints and the durability of the physical stabilization layers after a washing procedure. As seen in Table 6, impregnation of RR prints with whey powder before curing achieved highest residual color difference with 64.5% for single activation. Upon multiple activations, i.e. after 10 days, wax coating applied after curing could protect
the photochromic prints best with 83.1% residual color difference. Also, whey powder impregnations before and after curing show high remaining color with 82.6% and 81.6%, respectively. Wax coating applied before curing exhibits a remarkably lower value of 58.1% similar to the non-stabilized RR print with 60%.

The trend is seen that higher color difference is achieved if samples are coated or impregnated before the curing process. This is valid for both unwashed and washed prints, but with generally higher coloration values for unwashed prints. This suggests that wax and protein treatments work well in protecting the print from oxygen inhibition during curing. After washing the fatigue behavior as in relative loss of color difference from day 1 to 10 of photochromic prints improved, but with a lower initial $\Delta E$ as presented in Table 6.

Table 6: Color difference $\Delta E$ and residual color difference $\Delta E/\Delta E_{\text{washed}}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color difference $\Delta E$</th>
<th>Residual color difference $\Delta E/\Delta E_{\text{washed}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single activation</td>
<td>Multiple activations</td>
</tr>
<tr>
<td></td>
<td>Unwashed</td>
<td>Washed</td>
</tr>
<tr>
<td>RR print cured</td>
<td>8.8</td>
<td>4.2</td>
</tr>
<tr>
<td>RR print + HALS</td>
<td>9.3</td>
<td>4.1</td>
</tr>
<tr>
<td>RR print + wax before curing</td>
<td>12.8</td>
<td>5.9</td>
</tr>
<tr>
<td>RR print + wax after curing</td>
<td>10.6</td>
<td>4.8</td>
</tr>
<tr>
<td>RR print + whey before curing</td>
<td>12.5</td>
<td>7.6</td>
</tr>
<tr>
<td>RR print + whey after curing</td>
<td>9.2</td>
<td>5.2</td>
</tr>
</tbody>
</table>

To investigate if the amount of protein is decisive, impregnations have been made with $\beta$-lactoglobulin (pure protein) and whey powder (87 wt% protein). $\beta$-lactoglobulin applied before curing showed lower $\Delta E$ than whey powder for unwashed prints and higher $\Delta E$ for washed prints. However, statistically no significance can be stated. FTIR analysis clarifies that whey powder and $\beta$-lactoglobulin have the same chemical structure. Therefore, whey powder and $\beta$-lactoglobulin can be seen to have the same color enhancing effect, but from an economic perspective whey powder is the more attractive substance.

As a conclusion, physical shield layers using wax and protein can be used to improve the fatigue behavior of photochromic prints. However, the initial studies conducted in this thesis cannot discard the findings from earlier studies that chemical stabilization with hydrogen donors, such as amine substances as HALS is well suited for increasing the lifetime of the coloration effect of photochromic textiles. Also, further investigations have to be made to understand the mechanisms behind the effectiveness of wax and protein, as well as the adhesion of the stabilizing layers and their impact on the degree of cure on the photochromic prints.

8. Conclusions

This thesis presents a technology-driven approach to explore the application and performance characteristics of photochromic dyes primarily using inkjet printing and UV curing but including scCO$_2$ dyeing on textiles. The general aim in this thesis is to facilitate a flexible and economic production of functional and smart textiles towards the intended use in sensor applications. Hereof, the following knowledge was gained in the resource-efficient production of novel photochromic textiles:

- UV-curable photochromic inkjet inks exhibit complex rheological behavior, which limits the evaluation of their jetting behavior with established theory. Temperature was identified as an important factor to influence the jettability of photochromic inks.
- Production process parameters, i.e. conveyor belt speed and lamp intensity, can be used to modify the crosslinking density of the UV-curable ink, which alters the rigidity of the dye-carrying matrix and hence can be used to tune dye kinetics. Low crosslinking density facilitates isomerization and provides faster kinetic switching between colorless and colored states.
  - The use of UV light for both curing and activation of the photochromic material necessitated the introduction of an extended kinetic model to describe the reaction of UV-cured photochromic prints with low crosslinking density.
- Production process parameters also influence the durability of photochromic prints towards washing and abrasion. More durable photochromic prints are achieved for prints with low crosslinking density, which are produced using least intense curing conditions. The textile properties are not influenced negatively as a result of inkjet printing with photochromic ink.
- Impregnation with whey protein and coating with wax as physical layers deliver promising results after single and multiple activations in protecting the photochromic prints against photo-oxidation and therewith can extend the lifetime of the prints.
- Dyeing with scCO$_2$ is a promising technique for uniform coloration of photochromic textiles. In contrast to inkjet printing of photochromic ink, spiroxazine dye Sea green is faster switching than naphthopyran dye Ruby red.
- Differences in behavior between the two commercial dyes used in this thesis are inherent to their molecular structure and isomers and were observed in i) distinct jetting behavior of the inks, ii) different kinetic behavior after UV curing of the photochromic dyes and iii) varying penetration of the dyes into the fiber matrix after scCO$_2$ dyeing.

With these results important challenges towards the resource-efficient production and design of a smart textile UV sensor have been met. Contrary to logic expectations, we could prove that photochromic materials can be cured with UV light and that this
combination gives extended information on the photochromic properties manifested in an extended model. We could also highlight a discrepancy of theory and visual assessment in regards to the jetting of photochromic UV ink, which creates new research prospects in the domain of ink development. Overall findings in this thesis present a substantial step towards a resource-efficient production of photochromic textiles for surface and pattern applications using ink jetting and UV curing and for uniform through-coloration using scCO₂ dyeing. This may open new opportunities for the market of functional and smart textiles with biggest potential of inkjet printing for a flexible and small-batch production. The successful application of photochromic dyes by scCO₂ dyeing may be a contributing factor for the breakthrough of the technology.

9. Future Work

Despite our comprehensive study in developing inkjet-printed photochromic textiles for potential use as smart textile sensor, several aspects need to be investigated further before a resource-efficient smart textile UV sensor is ready for commercialization on the market. Specific challenges and aspects of interest, which can be studied in the future are elaborated below.

Regarding the jetting behavior of the UV-curable photochromic inks, further optimization of the ink formulation can avoid the formation of satellite drops and hence improve the printability, which is important also once patterning and resolution is studied in detail. Furthermore, by including the moment of splashing when the ink drop hits the fabric surface analysis can be deepened and theoretical calculations of the printability of ink can be expanded. The wetting and spreading of the photochromic ink can be investigated further also in relation to resource-efficient pretreatments using plasma or spray coating, which may affect both the resolution and durability of the photochromic prints. Moreover, the establishment of new models and calculations of ink jetting due to the discrepancy between current theory for Newtonian fluids and the rheological behavior of non-Newtonian may open up new research prospects.

In regards to the effect of process parameters, as the obtained results from DSC analysis observed in a change in melting temperature leave room for interpretation, complementing methods may be necessary to clarify the influence of process parameters on the degree of cure of the photochromic ink on PET.

Additionally, looking into other aspects during the production of the photochromic prints, a correlation between the amount of applied ink and sharpness of printed patterns, as well as resulting stiffness of the material will be interesting.

So far, we have classed the degrading mechanism of the color yield of photochromic ink upon simultaneous curing and color measurement as decay. However, it would be a breakthrough to distinguish between the effect of degradation and curing. If degradation and curing mechanisms can be separated, the extended mathematical model could be specified further with individual rate constants.

Another interesting property to study is the porosity of printed fabric as function of deposited ink amount and curing intensity. Although SEM pictures showed that the photochromic ink did not alter the morphology of the textile strongly visually, small changes might be detected with porosity measurements.

Furthermore, the use of different monomer and oligomer types in the UV resin can be explored, which allow a more porous structure of the matrix and thus more space for the photochromic dyes to undergo isomerization without having to compromise on curing efficiency.

Physical stabilization using protein and wax has shown potential in extending the lifetime of photochromic inkjet prints. However, comprehensive analysis in regards to polymerization density of the physically stabilized photochromic prints and online
color measurements to determine K/S values and kinetic rate constants during coloration and decoloration is necessary to be able to draw more precise conclusions. Exceeding the current scope of this thesis, other forms of curing using near infra-red (NIR) rays as light curing method would be interesting to study. Here, an advantage could be that photochromic dyes and the curing light source would not be in direct competition.

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Influence of physical parameters and temperature on ink jetting of UV-curable photochromic inks for smart textile applications
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Manuscript submitted
Effect of physical parameters and temperature on the piezo-electric jetting behaviour of UV-curable photochromic inks

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Abstract

Although resource-efficient processes like inkjet printing have a large potential to foster the development of smart and functional textiles, one bottleneck still is the development of functional inks. To make inkjet printing and UV curing given production techniques for smart and functional specialty products, e.g. photochromic textiles, development and jet ability of functional ink is needed. This paper focuses on the formulation and performance of UV-responsive and UV-curable inkjet inks, which are based on photochromic dyes and their application to produce UV-responsive textiles. Two commercial photochromic dyes – Reversacol® Ruby red and Sea green, which are especially feasible for textile applications in regards to their temperature-stability, have been used to develop the inks. Ruby red (RR) and Sea green (SG) represent dyes of the naphthopyran and spirooxazine class, respectively. The specially designed photochromic inks are characterized according to their physical-chemical and rheological properties in respect to temperature. The influence of temperature on the jetting performance and drop formation of the inks is analyzed using a high-speed camera and gives important information on the jettability of the ink. The printability of the RR and SG inks is framed and underpinned by theoretical calculations of the Z number. Discrepancies are observed and discussed between existing theory of ink jettability and visual evaluation of the photochromic ink.

Keywords: Inkjet printing, UV curing, photochromic ink, jettability, drop formation

1. Introduction

Digital inkjet technology offers a great opportunity for the textile industry not only through the conservation of resources, but also through its high potential to cultivate innovation. Through inkjet printing a flexible textile functionalization process for small batches with a reduced ecological footprint can be realized. Next to the minimized consumption of energy, water and chemicals, the functional chemistry can be applied locally and with complex designs while retaining the textile properties. Functional finishes on textiles offer an enriching possibility to create smart textile materials and find new fields of application. Until now, a major challenge having to be faced in fostering the technology is to formulate inks beyond the established colorants and instead with advanced and smart functions to cater to future trends and industrial development. According to Mendes-Felipe et al.¹ the symbiosis of ink jetting technology and UV-curable materials has large potential as resource-efficient, sustainable and versatile production method for next generation devices and smart solutions.

Drop-on-demand (DOD) inkjet printing is the most common type of inkjet printing, where tiny droplets with a volume of approx. 10 picolitres are precisely deposited on the surface of the printable substrate. As the name implies, in DOD printing a drop is formed when there is a demand for it according to the print pattern. The ink is fired upon an electric signal and a droplet with characteristic tail formation is ejected from the nozzle. Through polarization of the lead zirconium titanate the crystal undergoes distortion creating a pressure pulse in the ink chamber ². The Starfire SA Dimatix print head used in this study is a typical industrial print head for textile printing, which features a total number of 1024 nozzles.

Drop formation of an ink is influenced by the properties of the mixture of fluids – viscosity, surface tension, density – and by the velocity and size of the droplet ³. Electric voltage and pulse shape influence the drop formation related to the nozzle geometrics as well ²,¹. As the ink reservoir is not pressurized, the surface tension in the printer prevents unwanted ink flow from the nozzles when in standby mode. Therefore, pressure initiated by the piezoelectric signal helps to overcome a certain surface tension in order for a drop to be formed at the orifice. The pressure difference, which has to be exceeded, is ⁴,

\[ \Delta P = \frac{2\gamma}{r} \]  

(Equation 1)

where \( \gamma \) is the surface tension and \( r \) the radius of the nozzle.

The theoretical printability of ink, which has been widely discussed in literature ⁵-⁹ can be calculated by a combination of dimensionless numbers, which depend on various physical-chemical properties of the printable fluid and dimensions of the printing orifice. The Reynolds number \( Re \) and the Weber number \( We \) specify the relative magnitude of the fluid’s interfacial, viscous and inertial forces ³,⁶,⁷.
\[ Re = \frac{u \rho}{\eta} \]  
(Equation 2)

\[ We = \frac{u^2 \rho r}{\gamma} \]  
(Equation 3)

where \( u \) is the velocity, \( \rho \) the density and \( \eta \) the viscosity. The Reynolds number defines the fluid’s inertia to its viscosity, whereas the Weber number specifies the ratio of inertia to its surface tension.

Fromm\(^7\) has developed a solution based on the Navier-Stokes equations\(^10\) to express the limitations of drop ejection in regards to interfacial, viscous and inertial properties of the fluid\(^3\).

\[ Z = \frac{(\gamma \rho r)^{1/2}}{\eta} = \frac{1}{Oh} = \frac{Re}{We^{1/2}} \]  
(Equation 4)

\( Z \) is the inverse of the Ohnesorge number \( Oh \) and is defined as the ratio of the Reynolds number and the square root of the Weber number; also known as Laplace number \( La \).

The initial specification from Fromm\(^7\) that \( Z > 2 \) is required for the ejection of stable droplets was revised and updated by Derby\(^11\) to an acceptable range of \( 1 < Z < 10 \).

The formation of stable droplets implies single droplets with tail formation (c) as seen in Figure 1. If these conditions cannot be met, so-called satellite droplets (b) will be formed, which impede print quality.

Figure 1: Scheme of (a) continuous fluid flow, (b) satellite drops and (c) stable drop with tail.

Looking closer into the effects on how a droplet with tail is formed, a cylindrical fluid shape flowing out of the nozzle is assumed in the beginning of the process. During the process a droplet develops from the cylindrically shaped fluid flow and forms a filament combining fluid cylinder and droplet. With continuous approach of the droplet towards the solid surface the filament eventually breaks and a flying droplet is formed\(^12\). At flight a spherical droplet with a specific and constant volume will form before landing on the printable substrate.

This paper focuses on the exploration of the jettability of UV-curable photochromic inks and their drop formation as function of temperature and its effect of changed physical fluid properties on the drop formulation. The results entail empirical data, which is embedded in and confirmed using theoretical calculations based on the dimensionless numbers \( We, Re \) and \( Z \).

2. Materials and Methods

2.1 Ink formulation

In the formulation of photochromic UV-curable inkjet inks two commercial heterocyclic spiro-compounds are used. Reversacol\(^8\) Ruby Red (RR), a naphthopyran-type and Reversacol\(^8\) Sea Green (SG), a spirooxazine-type dye from Vivimed Labs, UK are combined with a UV-curable varnish to fit print head specifications. The dye concentration in the designed inkjet inks is 4 g/l. The UV-curable varnish consists of dipropylene glycole diacrylate monomers (DPGDA), amine modified polyetheracrylate oligomers (Ebecryl\(^8\) 81) supplied by Allnex SA/NV, Belgium and a UV-LED photo-initiator (Genocure\(^8\) TPO-L) supplied by Rahn AG, Switzerland. The ratio of component parts for monomer/oligomer/photo-initiator is 21/1/1. For dissolution and homogeneous dye dispersion solvents are used in the ink formulation, which are removed after stirring by vacuum pumping. Ethyl acetate, 99.9\% (Chromasolv\(^8\) Plus) is used for RR and hexane, ≥ 97\% (Chromasolv\(^8\) HPLC) for SG, both purchased from Sigma-Aldrich. A mixture of isomers, dipropylene glycol methyl ether acetate (DPGMEA) purchased from Sigma-Aldrich, is used as standard cleaning fluid for the Starfire SA print head and serves as a reference fluid for the evaluation of the ink jettability of the photochromic inks. DPGMEA has a surface tension of 31.1 mN/m and a viscosity of 4.8 mPas at 20 °C.

2.2 Rheological and physical properties

The viscosity was measured using a rheometer Physica MCR500 from Paar Physica with a double gap cylindrical cell. The viscosity was acquired at the maximum shear rate of the rheometer of 10000 1/s at a temperature sweep from 20 – 40 °C and 40 – 20 °C, which was repeated twice. A shear rate of 10000 1/s simulates the conditions upon jetting as the estimated shear rate at the nozzle tip of a Dimatix print head could reach 40000 1/s. The surface tension of the ink fluids was measured using an optical tensiometer Attension Theta from Biolin Scientific. Three individual measurements were made with the pendant drop method and drop size of 6 μl at 22 °C.

2.3 Visual evaluation of ink jettability

The two photochromic inks and DPGMEA are jetted with a Starfire SA print head from Fujifilm Dimatix, which prints with a resolution of 400 dpi and in three different grey scales. The radius of the orifices featured in the print head is estimated to 10 μm and the printable range is specified with \( \eta = 8 – 20 \) mPas (recommended 10 – 14
mPas) and γ = 20 – 35 mN/m. Visual analysis of the drop formation is made with a Uridium drop watcher high-speed camera. Jetting results at a head voltage of 110 V, max. frequency of 14 kHz and with a waveform of three pulses with increasing amplitudes of 50/70/90 V resulting in three dots per drop (DPD). The photochromic inks’ behaviour as function of temperature was analysed in detail in regards to drop volume and drop velocity at a delay of 200 μs, which is optimal for picture processing. The temperature was increased in steps of 5 °C between 25 °C and 40 °C with a waiting time of 30 min for conditioning.

For comparison of the visual analysis with the fluids’ theoretical jetting behavior, the printability of the fluids RR ink, SG ink and DPGMEA are calculated based on their physical properties using Equations 2 – 4.

3. Results and Discussion

3.1 Ink characterization

UV-curable photochromic inks are specialty inks, which are designed for photochromic sensory applications on textile surfaces. The UV-curable photochromic inks RR and SG ink are characterized according to their absorbance for the expected photochromic color effects and to their physical properties in order to match print head requirements. Color effects of photochromic dyes are inherent to the respective dye class, influenced by solvent polarity and temperature with generally higher thermal conversion at higher temperatures\textsuperscript{13,14}. Naphthopyran dyes are inherently more stable and less temperature-sensitive than spirooxazine dyes\textsuperscript{15-17}. As can be seen in Figure 2, RR has stronger absorbance in polar solvents as acetonitrile, whereas SG has stronger absorbance in non-polar as hexane. Both these specific commercial photochromic dyes exhibit rather low temperature-dependence, which is desirable for the application at varying temperatures for wearable or other non-wearable smart applications.

In Figure 3, the typical behavior of the inversely proportional relation between temperature and a substance’s viscosity is seen. The increase in temperature has a thinning effect on the different ink formulations. The viscosity of both the varnish (Figure 3a) and the photochromic inks (Figure 3b-d), irrespective of dye concentration and dye type, decreases with increasing temperature. The viscosity has been measured twice at a temperature sweep from 20 °C to 40 °C for the formulations after a cooling phase. It can be seen that for the second set of measurements the viscosity is lower at the starting temperature for all ink formulations, which is a characteristic of the inks’ inertia. On average a 20 °C increase in temperature lowers the viscosity from 0.014 Pas to 0.010 Pas, which approximates a decrease of 0.001 Pas per 5 °C. The change in viscosity as function of temperature seems to be characteristic for the UV-curable varnish, which is neither influenced by the type or concentration of photochromic dye.

[Figure 2: Temperature and solvent dependency of absorbance of (a) Ruby Red (RR) and (b) Sea Green (SG) photochromic dyes]

[Figure 3: Influence of temperature on the viscosity of UV-curable varnish (a) and photochromic inks with 2.5 g/l of RR (b), 4 g/l of RR (c) and 4 g/l SG (d) measured in two sweeps each (.1/.2)]

In terms of physical properties as viscosity and surface tension, RR and SG ink are similar with a viscosity of ca. 14.5 mPas and a surface tension of 31 mN/m as listed in table 1. SG ink has a lower density with 1024 kg/m\(^3\) compared to RR ink with 1077 kg/m\(^3\). Despite differences in density, the resulting \(Z\), which determines the ink printability, reaches similar values with 1.28 for RR ink and 1.24 for SG ink. In respect to drop velocity and calculated dimensionless numbers \(Re\) and \(We\), RR and SG inks distinguish themselves more from one another. Whereas RR ink drops reach a velocity of 4.35 m/s at a delay of 200 μs, SG ink drops are slower with a velocity of...
2.39 m/s. This also has an impact on the Reynolds and Weber number, which both are higher for RR ink than SG ink.

To compare the jetting behavior of the ink formulations with a standard fluid, DPGMEA is used. Compared with the photochromic inks, DPGMEA has a similar density of 980 kg/m³, a similar surface tension of 31.1 mN/m, but a three-fold lower viscosity with 4.8 mPas. The lower viscosity affects the dimensionless numbers Re, We and Z with increased values. Z of DPGMEA reaches a nearly three-fold higher value with 3.64 compared to the photochromic ink formulations. According to the original specification of ink jettability of Fromm⁷ that $Z > 2$, this would mean that DPGMEA is printable, but RR and SG inks are not. According to Reis and Derby’s¹⁸ further refinement, however, both photochromic inks and DPGMEA are classed as printable with stable drop formation.

Table 1: Physical properties and dimensionless numbers of ink fluids at 22 °C.

<table>
<thead>
<tr>
<th>Ink fluid</th>
<th>Density (kg/m³)</th>
<th>Viscosity (Pas)</th>
<th>Surface tension (N/m)</th>
<th>Velocity at delay of 200μs (m/s)</th>
<th>Reynolds number (Re)</th>
<th>Weber number (We)</th>
<th>Inverse (Z) of Ohnesorge number (Oh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR</td>
<td>1077 ±31.8</td>
<td>0.0143 ±0.001</td>
<td>0.031 ±0.0002</td>
<td>4.35 ±0.14</td>
<td>3.28 ±0.11</td>
<td>6.58 ±0.44</td>
<td>1.28 ±0.44</td>
</tr>
<tr>
<td>SG</td>
<td>1024 ±20.2</td>
<td>0.0144 ±0.0004</td>
<td>0.0309 ±0.0002</td>
<td>2.39 ±0.4</td>
<td>1.71 ±0.28</td>
<td>1.92 ±0.63</td>
<td>1.24 ±0.63</td>
</tr>
<tr>
<td>DPGMEA</td>
<td>980 ±0.0001</td>
<td>0.0048 ±0.0004</td>
<td>0.0311 ±0.0002</td>
<td>6.73 ±0.1</td>
<td>13.74 ±0.27</td>
<td>14.27 ±0.42</td>
<td>3.64 ±0.42</td>
</tr>
</tbody>
</table>

3.2 Visual jetting performance

The jetting behavior as function of temperature of the photochromic inks in relation to DPGMEA as a standard fluid is visually analyzed at a delay sweep between 50 and 200 μs. When ink is printed on a substrate, the substrate will be positioned at a distance of 2-3 mm from the nozzle plate, which means that according to the jetting sequences (Figure 4 – 6), UV-curable ink drops have travelled half way towards the substrate at a delay of 200 μs at 35 – 40 °C. Visual analysis is complemented by calculations using the dimensionless numbers Re, We and Z, which determine the printability of ink based on the physical properties of the fluid viscosity $\eta$, surface tension $\gamma$ and drop velocity $v$.

As seen in the representative photo sequences, after firing of two ink drops of RR ink and SG ink (Figure 4 and 5, respectively), they initially are attached to the ligament, i.e. tail, until the tail dissipates in many small drops, i.e. satellite drops. For DPGMEA, unstable drop formation without definition of ligament and drop occurs from the start (Figure 6).

Figure 4: Representative photo sequence of drop formation of RR ink at a delay between 50 and 200 μs at varying temperatures of (a) 25 °C, (b) 30 °C, (c) 35 °C and (d) 40 °C.
Figure 5: Representative photo sequence of drop formation of SG ink at a delay between 50 and 200 μs at varying temperatures of (a) 25 °C, (b) 30 °C, (c) 35 °C and (d) 40 °C.

Figure 6: Representative photo sequence of drop formation of DPGMEA fluid at a delay between 50 and 200 μs at varying temperatures of (a) 25 °C, (b) 30 °C, (c) 35 °C and (d) 40 °C.
3.3 Effect of temperature

Changes in velocity as a result of change in temperature have an impact on the drop formation, which is seen in Figures 4 – 6, but also in calculated \( Z \) numbers (Table 2). Changes in \( Z \), eventually mean that also the expected print quality is affected, which however is not experimentally evaluated in this study. The impact of temperature on the surface tension of the fluids is neglected as of very small changes in the range of room temperature to 40 °C. Hence, \( \gamma \) is constant in the calculations of the Weber number \( We \).

When applying Equations 2 – 4 with available experimental data, i.e. temperature-dependent viscosity and velocity values, it can be understood that the jettability improves based on increasing \( Z \) values. For RR ink \( Z \) increases from 1.27 at room temperature to 4.5 at 35 °C. An explanation for the difference in jettability at lower temperatures can be due to the more bulky and rigid structure and higher molecular weight of spirooxazines \(^{19,20}\), which impedes jetting of the ink from the orifice. At temperatures from 35 °C the lower viscosity of the varnish enables more flexibility for the dye to move and hence smoother jetting flow.

Another critical difference between the ink formulations RR and SG is the drop volume. Whereas, temperature does not have a significant and coherent effect on the drop volume, the type of dye has. SG ink exhibits generally smaller drops with 27 – 32 pL compared with RR ink, which jets larger drops of 32 – 37 pL. The reason for a smaller drop volume could also be owing to the difference in molecular structure of the dyes. As mentioned earlier, spirooxazines are more rigid than naphthopyrans and non-planar in their inactivated state, which is the case upon jetting. Spirooxazines also have a higher molecular weight than naphthopyrans, which however is not specified for the commercial dyes RR and SG. As the difference in molecular structure between the two dyes has shown to have a distinct effect on the color kinetics of photochromic prints using RR and SG \(^{21}\), it is likely to affect drop formation and can cause a bottleneck at the orifice resulting in smaller drop volumes.

Table 2: Temperature dependence of physical properties and dimensionless numbers of photochromic inks.

<table>
<thead>
<tr>
<th>Ink fluid</th>
<th>Temperature (°C)</th>
<th>Viscosity (Pas)</th>
<th>Volume (pL)</th>
<th>Velocity at delay of 200μs (m/s)</th>
<th>Reynolds number (Re)</th>
<th>Weber number (We)</th>
<th>Inverse (Z) of Ohnesorge number (Oh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR ink</td>
<td>25</td>
<td>0.0121 ± 0.0014</td>
<td>35.3 ± 7</td>
<td>4.54 ± 0.02</td>
<td>4.04 ± 0.01</td>
<td>7.17 ± 0.05</td>
<td>1.51 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.0114 ± 0.0009</td>
<td>32.3 ± 1.2</td>
<td>5.27 ± 0.12</td>
<td>5.12 ± 0.11</td>
<td>9.66 ± 0.11</td>
<td>1.61 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.0092 ± 0.0040</td>
<td>32.0 ± 1.4</td>
<td>6.04 ± 0.06</td>
<td>6.09 ± 0.07</td>
<td>12.63 ± 0.42</td>
<td>1.99 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.0100 ± 0.0006</td>
<td>37.0 ± 1.7</td>
<td>6.60 ± 0.06</td>
<td>7.09 ± 0.06</td>
<td>15.12 ± 0.27</td>
<td>1.82 ± 0.27</td>
</tr>
<tr>
<td>SG ink</td>
<td>25</td>
<td>0.0133 ± 0.0006</td>
<td>31 ± 5</td>
<td>2.43 ± 0.13</td>
<td>1.87 ± 0.1</td>
<td>1.96 ± 0.02</td>
<td>1.34 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.0123 ± 0.0010</td>
<td>29.7 ± 2.9</td>
<td>4.17 ± 0.12</td>
<td>3.48 ± 0.1</td>
<td>5.76 ± 0.12</td>
<td>1.45 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.0111 ± 0.0003</td>
<td>31.7 ± 1.2</td>
<td>4.95 ± 0.1</td>
<td>4.58 ± 0.09</td>
<td>8.11 ± 0.32</td>
<td>1.61 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.0105 ± 0.0002</td>
<td>27.3 ± 1.2</td>
<td>5.54 ± 0.13</td>
<td>5.42 ± 0.07</td>
<td>10.19 ± 0.47</td>
<td>1.7 ± 0.07</td>
</tr>
</tbody>
</table>

Despite similar physical properties, i.e. surface tension and viscosity as presented in Table 1, of RR and SG inks, visual analysis reveals distinct jetting behavior of the photochromic inks. At room temperature (22 – 23 °C) and 25 °C droplets of SG ink have a remarkably lower velocity (ca. 2 m/s) with 2.4 m/s than RR ink droplets with 4.5 m/s. At higher temperatures the difference is smaller (ca. 1 m/s) with \( v_{SG} = 5 – 5.5 \) m/s and \( v_{RR} = 6 – 6.6 \) m/s. An explanation for the difference in jettability at lower temperatures can be due to the more bulky and rigid structure and higher molecular density of 1080 kg/m³ results in a \( Z = 0.8 \), which predicts that the fluid is not printable. A \( Z < 1 \) would prevent drop ejection due to viscous dissipation \(^{28}\). Despite the fact that this formulation is non-jettable, it shows that an increase in viscosity can decrease the \( Z \) value.

According to print head specifications of the Starfire SA, the physical properties of DPGMEA are partially challenging. Whereas a surface tension of 31.1 mN/m is in the
jetting range, the three-fold lower viscosity than the photochromic inkjet inks of 4 – 5 mPas is below the recommended range for the Starfire SA print head. This would make DPGMEA not an ideal fluid for good print quality. However, according to calculations based on the physical properties of DPGMEA with \( Re = 13.74, We = 14.27 \) and a resulting \( Z = 3.64 \), the fluid is within the printable region of \( 1 < Z < 10 \). It is though obvious from the photo sequence (Figure 6) that due to the low viscosity of the fluid uncontrolled dripping results and satellite drops dominate. It can also be seen that temperature does not have a decisive effect in changing the jetting behavior as compared to photochromic inks, where it is obvious that with increasing temperature the tail becomes longer, a distinct drop forms earlier and the velocity increases (Figures 4 and 5).

3.5 Tail formation
The length of the formed tail upon jetting as mentioned above varies as effect of temperature, but also between RR and SG inks as seen in Figure 4 and 5. SG ink tends to exhibit shorter tails than RR ink, with generally increasing length with higher temperature. This visual observation is contradictory to the improved calculated \( Z \) value as a result of temperature, as a longer tail is supportive of the formation of satellite drops. Vice versa, a short tail and an optimum viscoelastic behavior of the fluid will lead to that the tail is instantly pulled into the drop after ejection and jet breakup at the nozzle 29. If the formed tail separates from the drop head this is either caused by Rayleigh-Plateau instability or end pinching 30. The tail length is predominantly influenced by the printable fluid’s density, where a small increase in density may reduce the tail length significantly 31. But also, a decrease in viscosity can reduce the tail length non-linearly of polymer-loaded ink solutions. The decrease in viscosity of polymer-containing inks in the production of scaffolds to stabilize tail formation 31 suggests the opposite trend compared to an increase in viscosity of Newtonian fluids proposed by Jo et al. 27. As an increase in viscosity of the photochromic ink negatively influenced the calculated \( Z \) value, change in density in the ink formulation may be help to stabilize drop formation by achieving shorter tail length. However, although SG ink has most stable drop formation with shortest tail at 25 °C, drop velocity at this temperature with 2.4 m/s is very low, which impeded printing on a textile substrate. Therefore, not just in theoretical calculations but also in practice, it could be shown that temperature is an important means of improving ink jettability and resulting print quality. For inkjet printing of photochromic inks on polyester fabric the print head temperature was set to 35 °C 21,32. However, these studied did not include the analysis of resolution and sharpness of the printed patterns, which possibly improves with more stable drop formation.

3.6 Jet breakup
The formation of satellite drops, despite measured and calculated values for stable drop formation, necessitates the discussion in relation to breakup of liquid jets. Several factors influence the behavior of fluids upon breakup of liquid jets, which is decisive for how a drop is formed and the resulting print quality. Although the print quality is not subject to this study, it is known that the instability and breakup of a liquid jet into fine secondary drops while travelling to the printable substrate, results in loss of print quality 33,34. Vastly studied phenomena in primary and secondary breakup of jets are distinguished with four modes of primary breakup, initially observed by Ohnesorge 25 and Reitz 36. Primary breakup occurs closer to the nozzle plate, where larger ligaments and drops detach from a liquid jet. With increasing perturbation effects in primary breakup, the Rayleigh, first and second wind induced and atomization mode are distinguished 37,38. According to the definitions, RR and SG inks mainly exhibit Rayleigh behavior, where a liquid jet is disrupted by capillary instability caused by axisymmetric perturbations. Drops, which are formed have similar or larger diameter as the jet itself. DPGMEA shows larger instability with agreement of what is defined as first wind induced breakup, where perturbations on the jet surface are present, formed drops are smaller, vary more in size distribution and satellite drops can occur in between main drops.

In secondary breakup further deformation and breakup of the larger ligaments and drops into smaller ones continues until a stable drop is formed 37. Here, for fluids with a Weber number below the critical value of \( We = 12 \), drops are impacted by oscillation, which cause deformation and eventually vibrational breakup 39,40. This is the case for SG and RR ink, although drops of SG ink are more stable with a lower \( We \) of 1.9 than for RR ink with \( We = 6.6 \). DPGMEA has a \( We \) of 14.3, which is classified as bag breakup \( (We > 12) \), where drops initially deform into a spherical cap and then to a flat disk 39,42.

4. Conclusion
This paper points out the discrepancy between theory of jetting of ink, which is based on Newtonian fluids and its application for functional inkjet inks with non-Newtonian behavior. Although calculation of the dimensionless numbers \( We, Re \) and \( Z \) categorizes ink printability with stable drop formation of RR and SG inks, visual analysis displays flaws and the formation of satellite drops. Phenomena affecting the jettability of UV-curable photochromic ink as non-Newtonian fluid behavior, tail formation and jet breakup to explain the formation of satellite drops of different ink formulations are discussed. Temperature is a main factor in changing the jettability of UV-curable photochromic and spirooxazine-based UV-curable photochromic inks.

Higher temperature increases drop velocity and improves the theoretical printability of the ink expressed in the \( Z \) number. Eventually, a temperature of 35 °C is preferable for ink jetting of both RR and SG ink on a substrate. The combination of visual and theoretical analysis enables investigation of the special jetting behavior of functional inks. Thereewith, the design of functional inks, exceeding photochromic inks, can be optimized and eventually facilitate the production of smart and functional textiles with inkjet printing and UV curing as given production techniques.

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Author contributions
S.S., J.Y. and V.A.N. established the conception, research questions and experimental design in this study. S.S. conducted all experiments, data acquisition, initial analysis and interpretation. Further analysis of the results, evaluation and discussion were equally done by all authors. S.S. prepared the manuscript draft and graphics, whereas improved versions were equally contributed to by all authors.

Competing interests
The authors declare no competing interests.

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Inkjet printing and UV-LED curing of photochromic dyes for functional and smart textile applications

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Inkjet printing and UV-LED curing of photochromic dyes for functional and smart textile applications†

Sina Seipel,*a Junchun Yu,a Aravin P. Periyasamy,a,b Martina Viková,b Michael Vir,b and Vincent A. Nierstraszb

Health concerns as a result of harmful UV-rays drive the development of UV-sensors of different kinds. In this research, a UV-responsive, smart textile is produced by ink jet printing and UV-LED curing of a specifically designed photochromic ink on PET fabric. This paper focuses on tuning and characterizing the colour performance of a photochromic dye embedded in a UV-curable ink resin. The influence of the industrial fabrication parameters on the crosslinking density of the UV-resin and hence on the colour kinetics is investigated. A lower crosslinking density of the UV-resin increases the kinetic switching speed of the photochromic dye molecules upon isomerization. By introducing an extended kinetic model, which defines rate constants $k_{\text{isocyanation}}, k_{\text{ring}}$ and $k_{\text{crosslinkation}}$, the colour performance of photochromatic textiles can be predicted. Fabrication parameters present a flexible and fast alternative to polymer conjugation to control kinetics of photochromic dyes in a resin. In particular, industrial fabrication parameters during printing and curing of the photochromic ink are used to set the colour yield, colouration/decolourisation rates and the durability, which are important characteristics towards the development of a UV-sensor for smart textile applications.

Introduction

The main drivers and motivation behind the sensor technology of smart textiles are the changing environment, an increasing need for protection mechanisms and a demand for lightweight products with highly integrated functions. Smart textiles help the user to sense and respond to external stimuli, and ideally adapt therewith warn the user of the presence of harmful UV-radiation, i.e., to protect and control skin from the long-term effects of solar UV-radiation and sunburn.

In the recent literature, the development of UV-sensing textiles using photochromic dyes has been paid much attention. The integration of photochromatic dyes into textile structures has been proven successful with traditional textile production techniques such as screen-printing, Additionally, UV-curable coatings distinguish themselves from thermally curing mechanisms by the benefits of controllable and industrially applicable process. Altering the curing intensity of the photochromic ink on the textile during fabrication, influences the rigidity of the UV-resin, the dye-polymer matrix interaction and hence the degree of freedom of the dye to switch between isomers in the matrix. In particular, the photo-switching of the molecular structure of the dye, which is reversible either through visible light or heat. The isomers A and B of the dye have different absorption spectra. In recent literature, the development of UV-sensing textiles using photochromic dyes has been paid much attention. The integration of photochromatic dyes into textile structures has been proven successful with traditional textile production techniques such as screen-printing, (...)

Moreover, the application of photochromic dyes using novel production techniques has emerged. Whereas, Alldíñ† investigated the potential of digital inkjet printing of solvent-based ink to produce photochromic textiles, Fu et al. studied photochromic curing to produce a photochromic cross-linked polymer. In other areas of textile colouration such as pigment printing, the advantages of inkjet printing in combination with photo-curing of an aqueous polyeurethane acrylate system or by mini-emulsion encapsulation were explored. To the best of our knowledge, the combination of digital inkjet printing and UV-LED curing has not yet been studied in the industrially applicable fabrication of a UV-sensing smart textile using photochromic dye.

UV-curable coatings distinguish themselves from thermally dried coating or binder systems, such as water-based acrylic binders typically used in screen-printing, by their high rigidity and three-dimensional cross-linked structure. According to Schwan et al. and Agarwal, depending on the chemistry, i.e., the choice of oligomers and monomers in the formulation, the coating’s flexibility, adhesion and hardness can be controlled.

Substrate-ink adhesion and flexibility are particularly important when printing on flexible substrates like textiles. In general, UV-curable inkjet inks exhibit good adhesion to porous substrates as compared to solvent-based alternatives. Inkjet printing and UV-curing also allow a wider design and control of colour via colourants or photochromic dyes for functional and smart textile applications. The sublimation of the printed ink and the cross-linked network can be controlled. Eventually, a high degree of crosslinking is desired to achieve good adhesion of dyes in a solid ink matrix onto the textile surface and to ensure a durable functional surface treatment. The degree of polymer crosslinking of the carrying ink also affects the rate of the switching reaction of photochromic dyes such as spirooxazines or naphthopyrans between their ring-closed colourless and ring-opened coloured state. (Fig. 1(a)). A 90° rotation in the molecular structure between non-planar and planar isomers requires space.

In this paper, we explore and tune the colour performance of a novel UV-responsive textile using fabrication parameters of an industrially applicable process. Altering the curing intensity of the photochromic ink on the textile during fabrication, influences the rigidity of the UV-resin, the dye-polymer matrix interaction and hence the degree of freedom of the dye to switch between isomers in the matrix. In particular, the photo-switching of the photochromic textiles is influenced by the combination of two challenging functions of electromagnetic radiation during production and characterization. The photochromic textile, which is fabricated by inkjet printing and UV-LED curing is activated by UV-light once in use. The impact of UV-rays during curing and activation requires the introduction of an extended kinetic model to describe the kinetics of UV-curable photochromic materials. The lowest curing intensity achieves highest colour yields and fastest switching behaviour between the coloured and colourless state of the photochromic dye Ruby Red in a UV-curable resin. The proposed kinetic model is an important step towards the development of a smart textile UV-sensor and allows the prediction of the colour performance based on fabrication parameters.
UV-Vis spectroscopy

UV-Vis spectra were collected using a Libra 960 double beam spectrophotometer from Biochrom, UK and a UV-1010FC from Shimadzu, Japan double beam spectrophotometer with integrated sphere accessory to affirm fit of the photo-initiator for the UV-LED lamp of the pilot-scale inkjet printing system and to determine the influence of UV-variability on the absorbance spectra of the dye.

Colour analysis

The colour behaviour of the photochromic prints was measured using an LCAM Photochrom 3 spectrophotometer, which allows continuous colour measurement upon cycles of UV-exposure and relaxation\(^*\) (Fig. 2). The activation light source was an Edison UV-LED lamp (ED8UV-31A1) with a radiometric power \(P_t\) of 150 mW and an emission peak with wavelengths between 395 nm and 410 nm. The measuring light source was a dual light source system of combined high power white LEDs with CCTs of 4000, 5000 and 7000 K. The measuring light source system illuminates samples with an illuminance of 60 klx. This illuminate is a compromise between brightest sunlight intensity (120 klx) and daylight intensity without direct sunlight at noon (20 klx). In addition, the measuring light source is equipped with a set of high-pass filters preserving light transmission below 420 nm, which decrease possible activation of photochromic composition. Colour values \(K_S\) were measured from reflectance values \(R_m\) using the Kubelka-Munk function:

\[
\frac{K}{S} = \left( \frac{1 - R_m^2}{2R_m} \right) e^{-\alpha R_m} \tag{1}
\]

The kinetic model shown in eqn (2) follows first-order kinetics and is generally used to describe photochromic colour behaviour for both the colouration and decolouration reaction as seen in Fig. 2.\(^*\)

\[
A \left( \frac{K}{S} \right) = \left[ \left( \frac{K}{S} \right) - \left( \frac{K}{S} \right)_0 \right] e^{-\alpha T} + \left( \frac{K}{S} \right)_0 \tag{2}
\]

Based on the kinetic model, the sensor functionality was specified by its achieved colour intensity \(K/\)upon activation with UV-light, its rate constant of colour increase \(K_\text{rate}\), to achieve maximum colouration \(K_\text{max}\), and its rate constant of colour decrease to revert to the initial colourless state \(K_\text{col}\).

**DSC analysis**

The influence of deposited ink amount and curing conditions on the curing efficiency was determined indirectly by analysing the shift of the melting peak \(T_m\) of PET using a Q1000 DSC from TA Instruments, USA. The DSC samples sealed in aluminum pans were weighted. The balance (Kern) has 99.96% accuracy when calibrated against a standard weight of 100 mg. The heat flow of samples of about 5.0 mg was measured during a heating and cooling cycle from 25 °C to 290 °C and back to 25 °C with a rate of 10 °C min\(^{-1}\). The released energy \(\Delta H\) of the endothermic reaction during melting of the material gives indirect information on the degree of polymer crosslinking at the interface between the PET fabric and the photochromic UV-cured ink. The shift of the melting peak \(T_m\) towards higher temperatures compared to the \(T_m\) of pure PET fabricated indicates that an insulating layer is built surrounding the textile yarn/ fiber. Depending on the curing intensity, the insulation effect of the print varies. The adhesion of the ink on the PET surface is indicated by the difference in melting peak temperature \(\Delta T_m\) of the photochromic prints before and after washing. Washing hence gives information about the durability of the photochromic, UV-cured surface treatment on PET.

**Statistical analysis**

Statistical analysis of colour measurement and DSC data was conducted in Origin 2017 from OriginLab Corporation, USA at a confidence interval of 95%. One-way ANOVAs were used to determine the effect of washing on the crosslinking density of the ink, colour yields and rate constants of the dye. Two-way ANOVAs were used to determine the effect of the production parameters belt speed and lamp intensity, as well as the significance of their interaction.

**Results and discussion**

**Design of the UV-curable ink**

UV-Vis spectra confirm the fit of photo-initiator (absorption peak between 340 and 410 nm) used in the ink formulation with the UV-LED light source (emission band of 380 to 420 nm) to initiate polymer crosslinking. First-order kinetics was used to determine the absorption peaks of the photochromic dye in solvent and UV-resin conform to each other. Ruby Red has an absorption peak of 500 nm in ethyl acetate and 490 nm in the UV-curable resin (Fig. S1 in ESI†). Analysis of the measured colour values, rate constants for colour development and reversion are hence made at a wave-length of 500 nm.

**DSC analysis of crosslinks in the UV-curable ink**

Effect of deposited ink amount and curing settings on the crosslinking density. Thermal analysis of the interface between the printed photochromic ink and the PET fibre was measured by DSC. The cross-linked UV-ink gives no endothermic behaviour, however, it behaves as heat insulation layer, which affects the heat flow into PET during DSC measurement. The DSC measurement therefore gives indirect information on the polymer crosslinking density of the photochromic ink by measuring the melting temperature \(T_m\) of the PET fabric with UV-cured photochromic prints. For cured ink with increased ink deposition, or cured with higher intensity, i.e. higher lamp intensity and/or lower belt speed, the ink has a higher crosslinking density. Hence, it forms a thicker or more distinct insulation layer on the PET fabric surface. This in return increases the \(T_m\) and differences in the melting peak temperature, i.e. \(\Delta T_m\) of the PET fabric with photochromic prints on its surface compared to the untreated PET fabric. Inkjet-printed samples with different printing passes cured at a belt speed of 50 mm s\(^{-1}\) and 80% of the maximum lamp power (Fig. 3), showed a linear increase of \(T_m\) from 252.8 °C for 1 pass to 253.4 °C for ten passes. Prints with more amount of cross-linked polymer deviate more from the \(T_m\) of 252.9 °C of untreated PET fabric as they provide progressively more insulation. Furthermore, the prints showed a more significant shift of \(T_m\) with higher curing intensity (in combination with lamp intensity and belt speed). As shown in Fig. 4, an increase of lamp intensity, 1% to 25%, promotes the \(T_m\) of the photochromic prints on PET. The prints produced at 300 mm s\(^{-1}\) showed a progressive increase of \(T_m\) from 254.4 °C, 255.0 °C and 255.4 °C, i.e. \(\Delta T_m\) of 1.5 °C, 2.1 °C and 2.5 °C. A similarly increasing trend of \(T_m\) was detected for prints produced at 50 mm s\(^{-1}\) with various curing intensities but with less significant variation in \(\Delta T_m\) i.e. 2.3 °C, 2.4 °C and 2.5 °C respectively. The saturation of \(T_m\) in prints produced at 50 mm s\(^{-1}\) indicates that the increase of curing power cannot further increase the crosslinking density in the UV-curable ink. The inkjet-printed photochromic material accounts for about 10% of the measured DSC sample. To ensure representative measurements, the \(T_m\) and the standard deviation were taken from three independently measured samples. The largest standard deviation in DSC measurements is ±0.5 °C, which is in general smaller than presented in Table 1. Furthermore, an indium sample was measured three times with a \(T_m\) of 156.9 ± 0.05 °C, which is comparable with literature, where indium is reported with a \(T_m\) of 156.6 °C. Moreover, in order to exclude the effect of UV-radiation on the \(T_m\) of the PET fabric, the \(T_m\) of UV-cured PET fabric only, i.e. non-printed, was measured by DSC with 254.0 ± 0.1 °C. In this case, the detected variation of \(\Delta T_m\) (measured samples subtracted by 254.0 °C, Fig. 6) which is reduced to 0 to 1.5 °C, however, is still more significant than the measurement error. It can be concluded that the detected variation of \(\Delta T_m\) is small in DSC in general, but as it shows systematic variation and higher significance than the measurement error, it supports the validity of the experimental setup.

Moreover, fitting and extrapolation of the data (Fig. S2 in ESI†) suggested that the \(T_m\) increased exponentially as a function of printing passes, which saturates at around 50 printed passes and a \(T_m\) of 357.1 °C. This indicates that measuring \(T_m\) with DSC can approximate the amount of cross-linked UV-ink at a certain curing condition on the PET fabric.

**Colour performance of the photochromic textile**

**Extended kinetic model for the colouration reaction.**

Colour measurements with the LCAM Photochrom 3 spectrophotometer have shown that the first-order kinetic model for the colouration reaction (eqn (2)) is only valid for photochromic prints with a high polymer crosslinking density, i.e. a belt speed of 50 mm s\(^{-1}\) and 80% lamp dosage (Fig. S3 in ESI†). For cured prints with a low polymer crosslinking density, hence lower \(T_m\), polymer crosslinking continues during colour measurements and a simultaneous secondary decay mechanism occurs. The trend of deviation from normal photochromic colouration behaviour is supported by DSC measurements. The lower the speed of the transportation belt and the higher the lamp intensity for curing, the higher is the \(T_m\) and hence the insulation effect of the cured ink on PET (Fig. 4). When using
a conveyor belt speed of 50 mm s$^{-1}$, the differences in polymer crosslinking density through curing at different radiation intensities, 1, 25 or 80%, become less crucial. At high belt speed, i.e. 300 mm s$^{-1}$, increasing lamp power plays a decisive role in the crosslinking density that is achieved. Deviation from eqn (2) for the colouration reaction is in line with the degree of polymer crosslinking in the following order, starting from the curing settings with the highest deviation:

300 mm s$^{-1}$ > 150 mm s$^{-1}$ > 50 mm s$^{-1}$, with the highest deviation from the kinetic model in the first colouration cycle as a result of lower polymer crosslinking density. This conforms to the colour data, which shows that UV-light exposure during colouration of samples with low crosslinking density decreases $\Delta K_{\text{colouration}}$ in the subsequent colouration cycles 2, 3, and 4 (Fig. 5). This can be a result of continuous curing and simultaneous dye degradation. High UV-irradiation improves the cure speed of the resin$^{[15]}$ and longer irradiance increases the degree of polymer crosslinking.$^{[16]}$ Meanwhile, photo-degradation of photochromic dyes is commonly observed under prolonged UV-irradiation.$^{[29]}$

Therefore, for prints with lower polymer crosslinking density, we introduce a model that defines the kinetics of a decay mechanism as a result of continuous curing while colour measurement and reconstructs the actual colouration curve (Fig. 5). For ink systems, where UV-light is used to cure the photochromic prints with the aim to optimize curing conditions, the following extended kinetic model is proposed.

$$\Delta K_{\text{colouration}} = \Delta K_{\text{residual}} \left(1 - e^{-\left(\Delta K_{\text{residual}} / \Delta K_{\text{decolouration}}\right)}\right)$$

where $K_{\text{residual}}$ is the initial colour value for the colouration reaction, $K_{\text{residual}}$ the maximum colouration value, $K_{\text{decolouration}}$ the initial value of the decay and $K_{\text{decolouration}}$ the final value of the degrading reaction for each activation cycle. Kinetic rate constants for the colouration reaction and decay are defined as $k_{\text{colouration}}$ and $k_{\text{decolouration}}$, respectively.

$$\Delta K_{\text{decolouration}} = \Delta K_{\text{residual}} \left(1 - e^{-\left(\Delta K_{\text{residual}} / \Delta K_{\text{decolouration}}\right)}\right)$$

$$\Delta K_{\text{residual}} = \Delta K_{\text{decolouration}} / \left[\ln\left(1 + \frac{1}{\Delta K_{\text{residual}} / \Delta K_{\text{decolouration}}}\right)\right]$$

where $K_{\text{residual}}$ is the initial colour value for the colouration reaction, $K_{\text{decolouration}}$ the maximum colouration value, $K_{\text{residual}}$ the initial value of the decay and $K_{\text{decolouration}}$ the final value of the degrading reaction for each activation cycle. Kinetic rate constants for the colouration reaction and decay are defined as $k_{\text{colouration}}$ and $k_{\text{decolouration}}$, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Lamp intensity (%)</th>
<th>$T_{\text{residual}}$ (°C)</th>
<th>$T_{\text{residual}}$ (°C) washed</th>
<th>$\Delta K_{\text{residual}}$ (°C) washed</th>
<th>$\Delta K_{\text{residual}}$ (°C) untreated PET</th>
<th>$\Delta K_{\text{decolouration}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>252.6 ± 0.6</td>
<td>254.3 ± 0.3</td>
<td>0.4</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>25</td>
<td>255.6 ± 0.0</td>
<td>254.6 ± 0.3</td>
<td>1.0</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>50</td>
<td>254.6 ± 0.2</td>
<td>258.4 ± 0.2</td>
<td>1.4</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>1</td>
<td>255.6 ± 0.0</td>
<td>257.4 ± 0.0</td>
<td>1.2</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>25</td>
<td>255.6 ± 0.0</td>
<td>257.4 ± 0.0</td>
<td>1.2</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>255.6 ± 0.0</td>
<td>257.4 ± 0.0</td>
<td>1.2</td>
<td>0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Lamp intensity (%)</th>
<th>$K_{\text{dec}}$ (°C)</th>
<th>$K_{\text{res}}$ (°C)</th>
<th>$K_{\text{coloration}}$ (°C)</th>
<th>$K_{\text{decolouration}}$ (°C)</th>
<th>$K_{\text{residual}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.467 ± 0.038</td>
<td>0.375 ± 0.018</td>
<td>0.011 ± 0.001</td>
<td>0.003 ± 0.003</td>
<td>0.006 ± 0.003</td>
</tr>
<tr>
<td>25</td>
<td>0.505 ± 0.049</td>
<td>0.328 ± 0.019</td>
<td>0.011 ± 0.001</td>
<td>0.004 ± 0.002</td>
<td>0.008 ± 0.002</td>
</tr>
<tr>
<td>80</td>
<td>0.434 ± 0.006</td>
<td>0.114 ± 0.018</td>
<td>0.010 ± 0.003</td>
<td>0.004 ± 0.002</td>
<td>0.005 ± 0.004</td>
</tr>
<tr>
<td>1</td>
<td>0.376 ± 0.012</td>
<td>0.372 ± 0.012</td>
<td>0.010 ± 0.003</td>
<td>0.002 ± 0.001</td>
<td>0.001 ± 0.001</td>
</tr>
<tr>
<td>25</td>
<td>0.278 ± 0.025</td>
<td>0.070 ± 0.008</td>
<td>0.000 ± 0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 5

Extended model for reconstruction of photochromic colouration throughout colouration cycles 1–5 ($\Delta K_{\text{decolouration}}$) of a print with 19 g 100% deposited ink cured at belt speed of 300 mm s$^{-1}$ and 1% lamp intensity. Measured K/S data ($K_{\text{decolouration}}$) consists of reaction processes of decay ($K_{\text{decolouration}}$) and colouration ($K_{\text{decolouration}}$) during colour measurement. The model for the decay term ($K_{\text{decolouration}}$) successfully validates the model. For this print degradation becomes statistically ineffective in activate cycle 5 ($\Delta K_{\text{decolouration}}$).

### RSC Advances

$\Delta K_{\text{colouration}}$, throughout the five UV-exposure cycles during the colouration reaction, which add up to 1500 s.

The extended kinetic model, eqn (4), has been applied to the colour data of inkjet-printed samples with a deviation from eqn (2), i.e. $W^2 < 0.95$, to reconstruct the $\Delta K_{\text{decolouration}}$ and a secondary decay, which obviously reduces $\Delta K_{\text{decolouration}}$ and colour reaction kinetics.

**Effect of amount of ink deposition on the colouration reaction.** It was found that the achieved colour intensity $\Delta K_{\text{decolouration}}$ of printed and washed samples was linear towards the deposited amount of photochromic ink irrespective of curing conditions (Fig. 7), which agrees with the linearly increasing $T_{\text{residual}}$ as function of ink amount. Stronger colour yields with increasing ink amount are visible by eye for both printed and washed samples as can be seen in Fig. 1(c). According to Vikovska et al.$^{[19]}$ and Periyasamy et al.$^{[29]}$ deeper shades are expected with increased layer thickness as a result of lower surface-bulk ratio and hence, less colourless reflection. Additionally, also observed the trend of a continuous increase in colour yield from 1 to 10 inkjet printing passes of the same dye type but for solvent-based ink. This indicates that the crosslinking density and the adhesion of the UV-resin to the textile surface are not affected by the amount of ink deposition.

The amount of printed photochromic ink on PET influences the kinetics of the colouration reaction. Similar to the trend in decrease in $K_{\text{decolouration}}$, an increasing amount of applied material lowers $K_{\text{decolouration}}$ as seen in Fig. 6(b) for prints cured at a belt speed of 50 mm s$^{-1}$ and 80% of lamp intensity. A decrease in $K_{\text{decolouration}}$ as function of printing passes can be explained by weakened activation of the photochromic dye with increased layer thickness.$^{[29]}$ Washing has a significant effect on the colouration behaviour of the photochromic prints. Both $\Delta K_{\text{decolouration}}$ and $K_{\text{decolouration}}$ significantly decrease as a result of oxygen diffusion.$^{[29]}$ It can be assumed that during the washing cycle, a result of photo-oxidation occurs in the soft component of the resin, which is more prominent compared to when the dye is fixed in a solid matrix. However, cut-off effects of the dye carrying medium, i.e. shift in reflectance properties as a result of changed degree of cure and media thickness have also been investigated.$^{[29]}$ We therefore consider the observed decrease a secondary decay, which obviously reduces $\Delta K_{\text{decolouration}}$ and colour reaction kinetics.
compared to 40% at 1 pass, \( \Delta K_{\text{decolouration}} \) is less affected with increasing layer thickness.

**Effect of crosslinking density on the colouration reaction.** The production parameters belt speed and lamp intensity have a significant effect on \( \Delta K_{\text{decolouration}} \) and rate constants \( \Delta K_{\text{decolouration}} \) and \( \Delta K_{\text{decolouration}} \). In Fig. 7, curing parameters belt speed and lamp intensity, 300 mm s\(^{-1}\) by 1%, 50 mm s\(^{-1}\) by 1% and 50 mm s\(^{-1}\) by 80% represent settings, which result in low, intermediate, and high crosslinking density, respectively. It is with high crosslinking density have experienced strongest curing, which increases the rigidity of the UV-resin but may also cause dye degradation. As a result, \( \Delta K_{\text{decolouration}} \) is lowered. As seen in Table 2, highest \( \Delta K_{\text{decolouration}} \) in all curing conditions, with maximum remaining 55.5% to minimum 48.3% for 10-pass prints. It can be concluded that stronger curing conditions result in low absolute \( \Delta K_{\text{decolouration}} \) and low \( \Delta K_{\text{decolouration}} \) and \( \Delta K_{\text{decolouration}} \). A low polymer crosslinking density of the carrier matrix exhibits a higher amount of soft component in the photochromator, which enables more flexibility and free volume for faster switching of the photochromic dye molecule.\(^{28,39}\) A comparison of colour intensities and colouration values for all curing combinations of curing settings reveals that the setting with the lowest curing intensity, i.e. belt speed of 300 mm s\(^{-1}\) and lamp intensity of 1%, is the most favourable. High \( \Delta K_{\text{decolouration}} \) and fast kinetic switching with \( \Delta K_{\text{decolouration}} \) of 0.157 s\(^{-1}\) after printing and 0.199 s\(^{-1}\) after washing between the uncoulored and coloured state of the textile UV-sensor is achieved. A higher cross-linked resin results in lower rates of colouration with \( \Delta K_{\text{decolouration}} \) of 0.079 s\(^{-1}\) before and 0.047 s\(^{-1}\) after washing for 10-pass prints cured at 30 mm s\(^{-1}\) and 80%. Vlkova\(^{40}\) applied naphthopyran dyes on textiles in a screen-printing paste and achieved colouration rates of 0.09 s\(^{-1}\) and 0.25 s\(^{-1}\) with a concentration of 0.25 wt% at lamp intensity of 100 mW cm\(^{-2}\). The same dye applied with a concentration of 1 wt% in a spin dope, which was melt-blown to a non-woven achieved colouration rates between 0.01 s\(^{-1}\) and 0.03 s\(^{-1}\). With respect to different concentrations and activation powers it can be assumed that similar dye types to reversescal Ruby Red applied via a UV-cured matrix obtain \( \Delta K_{\text{decolouration}} \) which are higher than in a fibre structure but lower than in a water-based and thermally cured acrylic paste.

**Effect of amount of ink deposition on the decolouration reaction.** The decolouration reaction as shown in Fig. 2 of naphthopyran dye Ruby Red is a thermal reaction, which takes place in the dark and therewith is independent from the colouration reaction.\(^{28,39}\) Decolouration yields \( \Delta K_{\text{decolouration}} \) which correspond to \( \Delta K_{\text{decolouration}} \) and independent decolouration rates \( \Delta K_{\text{decolouration}} \) are calculated using eqn (2). A significant difference is seen for \( \Delta K_{\text{decolouration}} \) after printing and after a washing cycle. The same behaviour as for \( \Delta K_{\text{decolouration}} \) is seen for decolouration intensities. As seen in Fig. 6(c), \( \Delta K_{\text{decolouration}} \) increase linearly as function of printing passes and exhibit approx. 60% of the initial yields after washing. It is not affected by the printed ink and temperature after washing (T\(_{\text{wash}}\)). The effect of washing (T\(_{\text{wash}}\)) gives indirect information on the durability of the cross-linked photochromic ink and its adhesion to the surface of PET.

Washed samples exhibit a statistically significantly lowered melting temperature (T\(_m\)) regardless of the curing condition, as shown in Fig. 4. The decreased T\(_{\text{wash}}\) is ascribed in Table 1, is a measure for durability in terms of adhesion of the cured photochromic photo print to the PET fabric surface. While the T\(_{\text{wash}}\) for prints cured at 100 mm s\(^{-1}\) with 1% lamp power remains nearly unchanged with a decrease of 0.1°C, for prints transported at a belt speed of 50 mm s\(^{-1}\), the trend of the T\(_{\text{wash}}\) as a function of lamp intensity changes after washing. Photochromic prints that underwent strongest curing at 80% of the maximum lamp power had almost no change in T\(_{\text{wash}}\) (0.2°C within the measurement error). Prints that have been cured at both 25% and 1% lamp intensity have a T\(_{\text{wash}}\) of 254.7°C. This gives the curing intensity, 0.4°C and 0.5°C for lamp powers 25% and 1%, respectively. The result for the samples processed with 50 mm s\(^{-1}\) suggested that higher lamp power could increase the crosslinking density in the printed UV-ink.

Fig. 7 Linear increase of \( K_{\text{decolouration}} \) a function in a printing passes for low, intermediate and strong curing conditions, i.e 300 mm s\(^{-1}\) by 1%, 50 mm s\(^{-1}\) by 1% and 50 mm s\(^{-1}\) by 80% respectively after printing (a) and washing (b) and (washed).
Furthermore, the weight of printed and washed functional layers is complimentary to DSC and colour measurements. Additionally, photochromic inkjet printing has large potential to trigger innovative products and to promote the small-batch production of functional high-end and smart textiles.

Conflicts of interest
There are no conflicts to declare.

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

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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

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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. Alidh [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 present 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) represent dyes of two different dye classes, naphthopyran and spirooxazine, respectively. The dye concentration in the host matrix can be influenced through different ways of polymer architecture by varying the type, dye placement, or surface functionalization is effective without influencing the textile character. 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.

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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.
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/m² 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/cm² 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 times after printing and curing. Washing was conducted on the print durability, samples were washed once and ten times after printing and curing. Washing was conducted on the print durability, samples were washed once and ten times after printing and curing.

Color Analysis

To evaluate the color behavior upon excitation (coloration) and relaxation (decoloration) of the photochromic prints an LCAM Photocrom 3 spectrophotometer was used. The specially designed device allows continuous color measurement 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 Edxion UV-LED lamp (EDEV-3LA1) with a radiometric power ≥300 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 kIx was used. Measured reflectance values are calculated to color values K/S using the Kubelka-Munk equation.

\[ \frac{K}{S} = \frac{(1-R)R}{2R} \]

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].

\[ \frac{S}{S_\infty} = 1 - e^{-kt} \]

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 reconstruction of actual color density is [8].

\[ \frac{S}{S_\infty} = 1 - e^{-kt} - \frac{(1-e^{-kt})}{k_c} (-\frac{1-e^{-kt}}{k_c}) \]

where, under the boundary condition that the processes of coloration and decay start simultaneously and at ΔK/S=0, K/S_∞ is the maximum coloration value and K/S_0 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_c and k_d, respectively.

Based on the kinetic models, the performance of the textile UV-sensors was specified by its achieved color intensity ΔK/S upon activation with UV-light, its rate constant of color increase k_c to achieve maximum coloration K/S_∞ and its rate constant of color decrease k_d 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 spiropyrane dye Sea green analysis was made at 620 nm.

Kawahata 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 sum 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 ΔK/S of 0.27, whereas after abrasion with 20000 rubs (Figure 3(b)), ΔK/S is lowered to 0.2. However, when fitting the color data of SG prints, ΔK/S of the printed sample (Figure 3(c)) with a value of 0.06 is lower than after abrasion with ΔK/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 spiropyrans 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 spiropyrane 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
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 \( k_{\text{col}} \) and \( k_{\text{decol}} \). 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 naphtopyran dye Ruby red (RR) and spiroxazine 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 \( k_{\text{col}} \) (Figure 4b) 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 \( k_{\text{col}} \) as compared to printed samples. The same trend in regards to the effect of curing intensity, dye, and treatment is seen for \( k_{\text{decol}} \) (Figure 4c). Higher \( k_{\text{decol}} \) 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 naphtopyrans [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 displays stronger \( k_{\text{col}} \) and higher switching rates \( k_{\text{col}} \) and \( k_{\text{decol}} \). 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, 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 \( \Delta E \) 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 spiroxazine dye than for naphtopyran 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 \( k_{\text{decol}} \) 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, spiroxazines are generically faster switching dyes than naphtopyrans, but they also are more rigid in structure with a higher molecular weight and non-planarity in the colorless state than naphtopyrans [4,22,29]. If a dye that is generally fast-switching, but rigid

\[ \Delta K(S)/S \]

\[ k_{\text{col}} \]

\[ k_{\text{decol}} \]

\[ \Delta E \]

\[ \Delta K/S \]

\[ k_{\text{col}} \]

\[ k_{\text{decol}} \]
Table 1. Color yields ΔK/S and rate constants $k_{\text{col}}$ and $k_{\text{dec}}$ of RR prints printed, 1+ and 10× washed and hydrolyzed with 5000, 10000, 15000, and 20000 cycles

<table>
<thead>
<tr>
<th></th>
<th>50 mm/s×80 %</th>
<th>300 mm/s×1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔK/S</td>
<td>$k_{\text{col}}$</td>
<td>$k_{\text{dec}}$</td>
</tr>
<tr>
<td>Printed</td>
<td>0.103±0.009</td>
<td>0.089±0.007</td>
</tr>
<tr>
<td>1+ washed</td>
<td>0.062±0.002</td>
<td>0.059±0.008</td>
</tr>
<tr>
<td>10× washed</td>
<td>0.039±0.003</td>
<td>0.048±0.009</td>
</tr>
<tr>
<td>5000 rubs</td>
<td>0.086±0.008</td>
<td>0.066±0.000</td>
</tr>
<tr>
<td>10000 rubs</td>
<td>0.077±0.013</td>
<td>0.056±0.002</td>
</tr>
<tr>
<td>15000 rubs</td>
<td>0.079±0.002</td>
<td>0.056±0.002</td>
</tr>
<tr>
<td>20000 rubs</td>
<td>0.075±0.004</td>
<td>0.053±0.001</td>
</tr>
</tbody>
</table>

Table 2. Color yields ΔK/S and rate constants $k_{\text{col}}$ and $k_{\text{dec}}$ of SG prints printed, 1+ and 10× washed and hydrolyzed with 5000, 10000, 15000, and 20000 cycles

<table>
<thead>
<tr>
<th></th>
<th>50 mm/s×80 %</th>
<th>300 mm/s×1 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔK/S</td>
<td>$k_{\text{col}}$</td>
<td>$k_{\text{dec}}$</td>
</tr>
<tr>
<td>Printed</td>
<td>0.107±0.002</td>
<td>0.020±0.002</td>
</tr>
<tr>
<td>1+ washed</td>
<td>0.086±0.025</td>
<td>0.017±0.004</td>
</tr>
<tr>
<td>10× washed</td>
<td>0.050±0.006</td>
<td>0.012±0.001</td>
</tr>
<tr>
<td>5000 rubs</td>
<td>0.085±0.006</td>
<td>0.016±0.000</td>
</tr>
<tr>
<td>10000 rubs</td>
<td>0.085±0.003</td>
<td>0.016±0.000</td>
</tr>
<tr>
<td>15000 rubs</td>
<td>0.073±0.003</td>
<td>0.014±0.000</td>
</tr>
<tr>
<td>20000 rubs</td>
<td>0.063±0.000</td>
<td>0.013±0.000</td>
</tr>
</tbody>
</table>

Inkjet-Printed and UV-Cured Photochromic Textiles

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 ΔK/S width of 103 (50_80) is lower for prints with high polymer crosslinking density compared to prints with low crosslinking density with ΔK/S=0.235 (300_1) as seen in Table 1. Lower ΔK/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 ΔK/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 ΔK/S=0.225 compared to initial 0.235. Washing after 10 cycles, however, results in a significantly lower ΔK/S=0.136. Rate constants of the coloration reaction $k_{\text{col}}$ differ between 300_1 and 50_80 RR prints. Prints with a low degree of polymer crosslinking (300_1) show higher switching speeds with $k_{\text{col}}=0.114 1/\text{s}$ compared to prints with high matrix rigidity (50_80) with $k_{\text{col}}=0.089 1/\text{s}$ of printed samples. After washing, rate constants are lowered for all RR prints. Whereas washing with different densities gradually reduces the rate of photoswitching 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 $k_{\text{col}}=0.102$ 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 $k_{\text{col}}$. 50_80 RR prints dispose of 54 % the initial $k_{\text{col}}$. The speed of the decoloration reaction is approximately one order of magnitude slower than $k_{\text{col}}=0.011 1/\text{s}$ 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 $k_{\text{col}}$ can be seen for rate constants under color reversion. Whereas $k_{\text{dec}}$ of 50_80 RR prints decreases continuously after 1 to 10 washing cycles from 0.011 to 0.009 to 0.008 1/s, $k_{\text{dec}}$ of 300_1 prints is stable after a single washing (Figure 6(a)). With $k_{\text{dec}}=0.013 1/\text{s}$ after 10 washing cycles compared to the initial $k_{\text{dec}}=0.014 1/\text{s}$ 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 faster 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), ΔK/S of 300_1 printed, i.e. 0 washing cycles, with 0.079 is lower than after 1 washing cycle with 0.153 and after 10 washing cycles with 0.202. Washing with 0.079 is lower than after 1 washing cycle with 0.153 and after 10 washing cycles with 0.202. Washing gradually decreases color yields of SG prints with a high degree of polymer crosslinking from ΔK/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 ΔK/S.

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Figure 6. Effect of 0, 1, and 10 washing cycles on ΔK/S, $k_{\text{col}}$, and $k_{\text{dec}}$ 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 \( k_{\text{col}} = 0.080 \text{ } \text{1/s} \) than 50_80 prints with \( k_{\text{col}} = 0.020 \text{ } \text{1/s} \). 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 decoloration rate of 62 % after 10 washing cycles. Prints with high crosslinking density affect \( k_{\text{decol}} \) of SG with a 40 % decrease. The decoloration reaction, which has approx. 3 times slower \( k_{\text{decol}} \) compared to \( k_{\text{col}} \), is also significantly affected by washing. A continuous decrease in \( k_{\text{decol}} \) 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 \( k_{\text{decol}} \) 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, the coloration rate \( k_{\text{col}} \) decreases over five cycles of coloration and 4 cycles of decoloration. 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 drop after washing. The fabric's 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 also slightly decreases 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 \( B = 0.249 \text{ } \text{g/cm} \text{cm}^2 \text{ cm} \). After 10 washing cycles \( B \) is reduced to 0.221 g/cm cm². The larger the value of \( B \) is, the harder is the object. Therefore according to the definition the printed fabric's comfort is lower than the reference PET and the 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 slightly increases, which 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 7.93 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.

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.

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.
photochromic textile is less comfortable and the washed photochromic textile is more comfortable than the non-
printed reference PET. 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 of 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 the inkjetting 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.

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References

Resource-efficient production of a smart textile UV sensor using photochromic dyes: Characterization and optimization

S. Seipel, J. Yu, A. Periyasamy, M. Viková, M. Vik and V. A. Nierstrasz

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Resource-Efficient Production of a Smart Textile UV Sensor Using Photochromic Dyes: Characterization and Optimization

Sina Seipel, Junchun Yu, Aravin P. Periyasamy, Martina Viková, Michal Vik and Vincent A. Nierstrasz

Abstract Niche products like smart textiles and other technical high-end products require resource-efficient processes and small batches contrary to conventional textile processes that require larger batches and are water-, chemical- and energy-intensive. This study focuses on digital inkjet printing and UV light curing as a flexible and resource-efficient and therewith economic production process of a smart textile UV sensor. The UV sensor is based on a UV-curable inkjet ink and a commercial photochromic dye. The inkjet ink is cured via free radical polymerization initiated by a UV–LED lamp. This system contains two photoactive compounds for which UV light both cures and activates the prints. An important challenge is therefore polymer crosslinking of the resin and UV-sensing performance of the photochromic dye. In this paper, we present performance as a function of belt speed and lamp intensity during curing. Via wash tests, we investigate the durability of the photochromic prints. The UV-sensing textile is characterized by color measurements, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

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1 Introduction

Today, smart textile UV sensors can typically be produced using screen printing [1–3], conventional dyeing [4, 5] and compounding and melt spinning [3, 6]. Successful UV-sensing textiles have been produced using these conventional technologies. However, due to the large production scale of these conventional processes and the fact that photochromic dyes are costly chemicals, this did not lead to an economically industrial-viable process. This paper therefore focuses on the potential of both digital inkjet printing and UV light curing in the production of a smart textile UV sensor using photochromic dyes. UV radiation triggers a reversible colour change in photochromic dyes as a result of a change in absorption spectra as shown in Fig. 1. The colour change is caused by ring-opening isomerization initiated by high photoelectric energy. Depending on the type of photochromic dye, the reverse reaction to the dye’s uncoloured state is triggered by visible light (P-type) or by temperature (T-type) [7, 8].

Both digital inkjet printing and UV-curing are resource-efficient technologies, which conserve unnecessary amounts of chemicals and energy, as well as waste that is produced. Furthermore, the combination of these technologies introduces process flexibility in regards to produced run lengths, change in pattern and ink [9–11].

Digital inkjet printing puts high physical requirements on the development of the printing ink to guarantee ink jet ability and storage. Properties like the ink’s stability, particle size, surface tension and viscosity have to be compatible with the chosen print head.

In this paper, ink has been developed containing a commercial photochromic dye, mixture of acrylate monomer and oligomer and a UV–LED photo-initiator. The role of UV light as curing initiator and activator of the photochromic colour change and its influence on the performance of the UV-sensing prints is explored. The production of the textile UV sensor using digital inkjet printing and UV-curing
is optimized using different UV light intensities; 1, 25 and 80% of the maximum dosage, and two different conveyor belt speeds; 50 and 300 mm/s, during curing. The smart textile UV sensor is characterized and evaluated in terms of colour yield, colouration and decolouration rates and degree of polymer crosslinking of the ink on the textile surface. The mechanical properties of the UV-sensing textile are influenced by the different curing intensities. The change in stiffness of the photochromic prints is determined via DMA measurements.

2 Experimental Part

As described previously [12], a photochromic inkjet ink, which consists of a UV-curable carrier and a commercial photochromic dye Reversacol Ruby Red (Vivimed Labs, UK), was used to produce photochromic prints on plain-woven polyester fabric of 147 g/m² (FOV Fabrics, Sweden). The UV-curable carrier consists of dipropylene glycole diacrylate monomers (DPGDA), amine modified polyetheracrylate oligomers Ebecryl 81 (Allnex, Belgium) and a UV–LED photo-initiator Genocure TPO-L (Rahn AG, Switzerland). A digital inkjet printing system featuring a piezoelectric drop-on-demand print head Sapphire QS-256/10 AAA (Fujifilm Dimatix, USA) was used to produce prints in multi-pass mode with 3, 5 and 10 layers of photochromic ink (Fig. 2a). To cure the prints, a FireJet UV–LED lamp (Phoseon Technology, USA) with emission wavelengths of 380 to 420 nm was used (Fig. 2b).

Ink characterization is done to ensure jetting of the ink formulation and desired drop placement on the textile. Essential ink properties and specifications according to the print head requirements are the fluid’s surface tension, viscosity, overall stability of the ink and the particle size. The surface tension of the ink is measured using a tensiometer One Attension (Biolin Scientific, Sweden) as pendant drop. The ink viscosity is measured at a shear rate of 10,000 s⁻¹ at 20 °C using a rheometer.

![Fig. 2](image1.png) **Fig. 2** a Digital inkjet printing system featuring a piezoelectric print head for UV-curable ink and b curing of photochromic ink using a UV–LED lamp with emission wavelengths of 380–420 nm on plain-woven polyester fabric

Physica MCR 500 (Anton Paar, Austria). Particle size assessment is done via filtration and ink stability is tested via storage tests.

For process and sensor optimization, curing parameters were varied by (i) change in transportation speed of the print passing the UV source, i.e. conveyor belt speed, and (ii) intensity of the maximum UV–LED lamp power, i.e. lamp intensity. Conveyor belt speeds varied among 50 or 300 mm/s and were combined with 1, 25 or 80% of the maximum lamp intensity as the production process scheme shows in Fig. 3.

The inkjet-printed and UV-cured photochromic ink on polyester fabric is heated from 25 to 290 °C at a scanning rate of 10 °C per min using a Q1000 DSC (TA Instruments, USA). The shift of the melting peak of polyester is used to analyse the degree of crosslinking of the ink for each curing setting; respective belt speed and lamp intensity. The photochromic print’s colour properties were measured using a custom-made LCAM Photochrome spectrophotometer (Technical University of Liberec, Czech Republic), which enables continuous colour measurements upon various cycles of UV activation and reversion [13]. The textile UV sensor’s performance is characterized by the achieved colour yield ΔK/Δ, colouration rate \( k_{\text{colouration}} \) and decolouration rate \( k_{\text{decolouration}} \) upon isomerization between the uncoloured and coloured state of the photochromic dye. The influence of the different curing settings on the mechanical properties of the photochromic prints on the polyester fabric is measured using a Q800 DMA (TA Instruments, USA). The stiffness of the textile UV sensors is determined via the storage modulus as a function of frequency. The storage modulus was measured at a frequency sweep between 1 and 12 Hz with a preload force of 0.01 N.

![Fig. 3](image2.png) **Fig. 3** Production process scheme of a printing and b curing of photochromic prints on polyester fabric
3 Results and Discussion

The developed UV-curable photochromic ink fulfills the requirements of the Sapphire QS-256/10 AAA print head with the following specifications:

- Surface tension: ca. 35 mN/m
- Viscosity: 10–14 mPa s
- Particle size: <0.1 μm
- Ink stability.

The different curing settings; combinations of 50 mm/s and 300 mm/s belt speeds and 1, 25 and 80% of maximum lamp intensity influence the crosslinking densities of the printed polyester fabrics and alter achievable colouration yields, as well as colouration and decolouration rates. High colour yields $K/S$ and fast reaction rates $k_{\text{colouration}}$ and $k_{\text{decolouration}}$ of the photochromic dye in the UV-curable matrix between the uncoloured and coloured states are favoured by high belt speed and low lamp intensity.

As shown in Fig. 4a, the storage modulus of the inkjet-printed and UV-cured polyester fabric obtained a higher storage modulus than the nonprinted polyester sample. The crosslinking of the UV-curable ink increased the hardness of the overall textile sensor. Furthermore, the sample cured at higher UV dosage, i.e. at 50 mm/s belt speed with 80% lamp intensity, had a higher storage modulus. At a frequency of 12 Hz, the polyester fabric without print has a storage modulus of 300 MPa. A photochromic print cured at low intensity, i.e. conveyor belt speed of 300 mm/s and lamp power of 1%, increases the storage modulus to ca. 1000 MPa. For prints, which undergo strong curing, i.e. 50 mm/s belt speed and 80% lamp intensity, the storage modulus reaches 1400 MPa. This suggests that there are more crosslinks of the sample cured under higher dosage of UV exposure. The same trend is confirmed by DSC measurements, which present an increase in melting peak as a function of curing intensity. However, the textile sensor is still bendable and rather flexible for the sample cured at 50 mm/s belt speed with 80% lamp intensity (Fig. 4b).

4 Challenges and Conclusion

This paper demonstrates the potential of combined digital inkjet printing and UV–LED curing in a resource- and cost-efficient textile production process. We conclude that changes in UV light intensity and belt speed during the curing process achieve distinct results in terms of colouration yields and kinetics of the colouration and decolouration reaction of the photochromic dye. These changes also affect the degree of polymer crosslinking, which influences the durability of the smart textile UV sensor in use. The degree of polymer crosslinking also influences the stiffness of the UV-sensing textiles. The stronger the curing intensity, the higher is the storage modulus of the printed fabrics as a result of higher degree of polymer crosslinking. However, in use, the flexibility of the photochromic prints, irrespective of curing intensity, is suitable for wearable applications, such as smart textile sensors.

In addition, we explore the effect of washing on the colour performance and switching reactions of the textile UV sensor. High belt speed and lower UV–LED light intensity enables faster colour changing and higher colour yield. The same effect is seen after washing despite a lower degree of polymer crosslinking.

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References


**Paper V**

Digital inkjet functionalization of water-repellent textile for smart textile application

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Digital inkjet functionalization of water-repellent textile for smart textile application

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ABSTRACT

Digital inkjet printing is a production technology with high potential in resource efficient processes, which features both flexibility and productivity. In this research, waterborne, fluorocarbon-free ink containing polysiloxane in the form of micro-emulsion is formulated for the application of water-repellent sports- and work wear. The physicochemical properties of the ink such as surface tension, rheological properties and particle size are characterized, and thereafter inkjet printed as solid square pattern (10 × 10 cm) on polyester and polyamide 66 fabrics. The water contact angle (WCA) of the functional surfaces is increased from <90° to ca. 140° after 10 inkjet printing passes. Moreover, the functional surface shows resistance to wash and abrasion. The WCA of functional surfaces of micro-emulsion is formulated for the application of water-repellent sports- and work wear. The physicochemical properties of the ink such as surface tension, rheological properties and particle size are characterized, and thereafter inkjet printed as solid square pattern (10 × 10 cm) on polyester and polyamide 66 fabrics. The water contact angle (WCA) of the functional surfaces is increased from <90° to ca. 140° after 10 inkjet printing passes. Moreover, the functional surface shows resistance to wash and abrasion. The WCA of functional surfaces of micro-emulsion is formulated for the application of water-repellent sports- and work wear. The physicochemical properties of the ink such as surface tension, rheological properties and particle size are characterized, and thereafter inkjet printed as solid square pattern (10 × 10 cm) on polyester and polyamide 66 fabrics. The water contact angle (WCA) of the functional surfaces is increased from <90° to ca. 140° after 10 inkjet printing passes. Moreover, the functional surface shows resistance to wash and abrasion. The WCA of functional surfaces of micro-emulsion is formulated for the application of water-repellent sports- and work wear.

In this study, we investigated an alternative solution that stresses a resource efficient process, inkjet printing and environmental-friendly polysiloxane ink, to replace conventional large run machineries with fluorocarbon chemistry. Polysiloxane used in this work is a linear-type polysiloxane (estimated as Mw ≈ 70000 and n ≈ 900, defined as middle-high molecular weight polysiloxane by Mojeskiewicz-Piotrowska et al. [26]) which does not pose threat to organisms via the respiratory system (when n ≥ 4) and therefore is favorable for textile application. Furthermore, middle-high molecular weight polysiloxane features low toxicity and does not bio-accumulate once it enters the environment according to existing studies [26].

Despite desired functionalities, the fastness properties of functionalized textile toward wash and abrasion are a fundamental challenge [27]. Zhou et al. [28] demonstrated a durable super-hydrophobic SiO2/PDMS nanocomposite coating on polyester fabrics by dip-coating. The WCA of the functional layer maintained almost the same (~170°) after 500 wash cycles or after abrasion testing (Martindale method) of 28000 cycles under 12-kPa load. Liu et al. [1] introduced a cross-linking agent, and therefore, the covalently bonded functional layer is capable to stand 20 wash cycles without significant changes in WCA (decreases from 153° to 148°).

In this research, we used inkjet printing to deposit water-repellent ink on polyester and polyamide 66, which is commonly used in the application of functional (technical) textile. There is a lack of publication concerning hydrophobic functionalization by inkjet printing.
printing on a porous and absorbent (textile) substrate. We focus on the inkjet formulation, the inkjet printing process and ink-substrate interaction for the application of functional textiles in sports- and work wear.

Materials and methods

Raw polysiloxane micro-emulsion dispersion in water (Dow Corning Corporation) was kindly supplied by Univar Inc. The substrates used for inkjet printing were 100% plain woven polyester fabric (PET, FOV Fabrics AB, Sweden) and 100% plain woven polyamide 66 fabric (PA, FOV Fabrics AB, Sweden). The PET fabric has a zero twist two ply yarn warp (336 dtx) and weft of 306 dtx and a weight of 145 g m⁻². The weft/warp count is 22/20 cm⁻¹ for PET. The PA fabric has a warp and weft of 188 dtex and a weight of 118 g m⁻². The weft/warp count is 27/39 cm⁻¹ for PA. The fabrics were received as washed and preset from the production line and thereafter soaked and rinsed by deionized water and iron dried before inkjet printing. Reference PET and PA samples with the same construction but without polysiloxane dispersion were received as washed and preset from the production line.

The polysiloxane dispersion used in the inkjet printing process contains amino functional dimethyl polysiloxane dispersion (so-called the functional ink). The amino functional dimethyl polysiloxane dispersion was used as it is after inkjet printing. Reference PET and PA were inkjet printed with the optical tensiometer (Attension Theta). Three to five random spots on a textile substrate were selected and thereafter soaked and rinsed by deionized water and iron dried before inkjet printing. Reference PET and PA samples with the same construction but without polysiloxane dispersion were received as washed and preset from the production line. The functional ink contains amino functional dimethyl polysiloxane (MareCarnelian 100 inkjet development and analysis system equipped with a piezoelectric type, Dimatix Sapphire Q2-256/10 AAA print head. The print head features a fundamental printable drop size of 10 pl. Solid square pattern (10 × 10 cm) and custom-designed patterns were inkjet printed at a resolution of 300 dpi on PET and PA substrates by multi-pass. Thereafter, the inkjet-printed samples were heated in an oven at 150 °C for 5 min to dry the functional ink. The dried samples that could still be hydrophilic at the functional surface were immersed in excessive amount of water to remove the water-soluble component in the ink. Eventually the samples were air-dried, and the functional surface became hydrophobic.

Results and discussion

Polysiloxane was chosen as fluorocarbon-free and water-repellent compound in the functional ink. As shown in Fig. 1a, the viscosity of the functional ink was compared with one type of Dimatix test ink. The viscosity of the functional ink shows a rather flat trend with increased amount of functional ink in the ink. Eventually the viscosity of 9.9 mPa s at 100 s⁻¹ (14.8 mPa s for Dimatix test ink) and 10.1 mPa s at 1000 s⁻¹ (14.6 mPa s for Dimatix test ink) at 25 °C. The Newtonian behavior of the fluid and weak temperature-dependent viscosity of the ink suggested that it is reasonable to present the viscosity of 9.9 mPa s of functional ink at 1000 s⁻¹ (high shear rate) and 35 °C (inkjet printing temperature) for ink characterization at inkjet printing conditions. The presented viscosity of 9.9 mPa s of functional ink fits the inkjet printable range, i.e., from 8 to 14 mPa s.

The surface tension and particle size were analyzed by pendant drop method and filtration test, respectively. The functional ink has a surface tension of 23.9 mN m⁻¹, which is slightly below but still around the typically acceptable surface tension for inkjet printing between 25 and 35 mN m⁻¹ [3]. The transparent functional ink containing polysiloxane in the form of a micro-emulsion should have a particle size distribution between 50 and 100 nm. The particle size (15 nm) is considerably below 200 nm, which is an experienced particle size limitation to avoid agglomeration of particles in the printing nozzle (31). The functional ink was able to filter through nylon syringe filters with pore sizes of 0.45 and 0.2 μm, respectively, which confirms that the functional particles are compatible with the inkjet printing process. The results obtained from measurements of surface tension, surface tension and particle size suggested that the functional ink fulfilled the print head specifications.

The functional ink was inkjet printed as solid square (10 × 10 cm) or as other customized pattern at a resolution of 300 dpi by printing of 1, 3, 5 and 10 passes. The hydrophobicity of inkjet-printed samples was characterized by WCA measurements. As shown in Fig. 2a, untreated PET and PA woven fabrics showed overall hydrophilic surfaces with WCA < 90°, even though PET fiber is inherently hydrophobic but PA fiber is inherently hydrophilic. The inkjet functionalized surfaces showed significantly increased WCA. The one-pass printed PET (PET × 1) and PA (PA × 1) already show that WCA increased from < 90° to more than 130°. With increased amount of functional inks, the 10-pass printed PET (PET × 1)
Jin et al. Moreover, the inkjet-printed samples polysiloxane with periodic pitch pattern reported by 40 and 50 tiles could be equivalent to a periodic pitch between 110 and 130, respectively. This indicates that the surface roughness of the textile for more than 10 min without visually wetting the surface (Fig. 2d). A drop testing kit with the surface of PET. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on PA, which, however, is less obvious on PET and shows higher WCA than literature reported on smooth, solid form polysiloxane film (~ 110°) [32]. This indicates that the surface roughness of the textiles could be equivalent to a periodic pitch between 40 and 50 μm, in comparison with laser etched polysiloxane with periodic pitch pattern reported by Jin et al. [32]. Moreover, the inkjet-printed samples are all able to hold the water and other water-based droplets such as milk, coffee and blue-colored ink on the surface for more than 10 min without visually wetting the surface (Fig. 3d). A drop testing kit with various mixtures of isopropanol and water (0, 2, 5, 10, 20, 30 and 40 vol% of isopropanol/water mixture) supports the WCA result (SI, Table S2).

SEM was applied to study the morphology of the functional layer. As shown in Fig. 5a, d the functional ink formed a thin layer wrapped around the textile filament. Besides, the functional ink formed uneven circular layers on the surface of PA filament (Fig. 5d), so-called coffee-stain effect after drying of the functional ink [3]. The formation of coffee-stain effect on the PA, which, however, is less obvious on PET and indicates that the inkjet-printed ink was spread more evenly on PET. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed on PA × 10 sample.

As shown in EDX spectrum in Fig. 5b, O and Si were the main element detected which are the components of the functional ink (O could contribute from PA substrate as well but less likely due to detectable depth of EDX). Element mapping of Si by EDX was also performed locally on one filament of the PA × 10 (SI, Fig. S5a). Accumulation of Si was detected as layer wrapped around the filament. The above results support that the hydrophobicity of the PET and PA surface is introduced by covering the surface with a thin layer of polysiloxane that is the active compound in the ink formulation.

Inkjet printing can deposit functional fluid on demand. The SEM images in Fig. 3a characterized the inkjet printing boundary of the solid square of PET × 10 sample. The side with smooth and dark appearance is the side with deposited functional ink which is clearly separated from the untreated PET side with rougher and brighter appearance. Moreover, logos of University of Borås and FOV fabrics are inkjet printed (with original pattern in SI, Fig. S4a, b). Demonstration of water repellency of the functional surface to water, milk, coffee and blue-colored droplets. The weight of the deposited functional material as function of printing passes on PA (red color) and PA (open red triangles), reference PET (open squares) and PA (open red triangles) with fluorocarbon finishing were presented. The error bar is the standard deviation from three to five independent measurements. The weight of the deposited functional material on PA × 10 sample to blue-colored ink. The logos of University of Borås and FOV fabrics are inkjet printed (with original pattern in SI, Fig. S4a, b). Demonstration of water repellency of the functional surface to water, milk, coffee and blue-colored droplets. PET × 10 sample, and PET × 10. Wash × 10 sample. The blue pen marked area is functionalized with water repellency. The scale bar in the figure is 1 cm.

Of the fabric and did not penetrate through the fabric (SEM in SI, Fig. S5a, b). The observation in microstructure was supported by WCA measurement that the printed front side of PET × 1 after 10 washes showed WCA of ~ 11° higher than printed backside surfaces. It is good to note that the PET and PA used in this work are not pre-treated to promote surface absorption. Necyhoruch et al. [13] found that the strike through of inkjet-printed pigment colorants on cotton was ca. 50% of the thickness of fabric and can be further constrained to the surface.
with a porous top coating. Inkjet printing has the advantage of efficient materials usage in comparison with other coating technologies. It is only possible to deposit the same amount of materials homogeneously all over the bulk textile by dip-coating, or other dipping methods. For single-side deposition technology such as knife coating, Liu et al. [1] demonstrated a fluorocarbon foam, which can typically apply 1.8 g m\(^{-2}\) on textile. This amount of material is slightly higher than the case for 10 passes of inkjet printing. However, other components such as rheology modifiers needed to be added in the formulation but was removed after deposition. For formulation with high solid content (> ca. 50 wt.%), high viscosity (a few tens of Pa s) and low shear rate (~ 2000 s\(^{-1}\)) in knife coating, the materials applied (processing speed dependent) are often higher than a few tens of grams per square meter [53, 54]. Although dip-coating and knife coating hypothetically are flexible in production length, inkjet printing still has the advantage to efficiently deposit costly functional materials. Thanks to the precisely controllable deposition of ink volume in pl. range, the key textile features such as textile feeling and breathability are not affected after functionalization. As shown in the SEM pictures (Fig. 5), the inkjet-printed functional ink formed a thin layer that does not block the inter-yarn pores of the woven textiles, therefore maintaining the tactile feeling and breathability of the textile after inkjet functionalization.

The durability of the functional layer toward wash and abrasion is assessed to simulate the usage of functional textiles in a daily environment. The functionalized textiles were washed at 40 °C according to ISO 6330 standard. During washing, the functional surface is exposed thoroughly to agitation by detergent, mechanical vibration and elevated temperature. As plotted in Fig. 4a, the PET × 10 and PA × 10 samples preserved similar level of WCA after 10 wash cycles. The WCA of PET × 10 was 136° and became 133°; the WCA of PA × 10 was 137° and became 131° after 10 wash cycles. In comparison, the reference PET with fluorocarbon finishing has a decreased WCA from 143° to 126° whereas the reference PA with fluorocarbon finishing has a decreased WCA from 140° to 128° after 10 wash cycles. The results showed the functional layer demonstrated resistance to wash. The WCA almost stayed the same after 10 wash cycles. SEM analysis was performed on PET × 10 and PA × 10 samples after 1 and 10 wash cycles. After one wash, there are spherical-shaped particles and agglomerated clusters of such particles formed at the functional surface for both PET × 10 and PA × 10 samples (Fig. 5b, e). The formed particle has a diameter smaller than 5 μm after one wash but became progressively denser and tended to form clusters larger than 10 μm with various shapes and dimensions after 10 wash cycles (Fig. 5c, B). A tenable assumption is that the washing process abraded the functional surface and partially rubbed off some functional material to form the spherical particles. As shown in Fig. 5i, O, Si, Na and Ca were the main elements detected on PET × 10 Wash × 10 sample. The detection of O and Si elements suggested that the functional ink remains at the textile surface. The Na and Ca could be residuals from detergents added during wash tests (referring to surfactant, zeolites, etc., as component in the washing detergent). The proportion of elements is not shown since EDX is a qualitative method. Furthermore, element mapping of Si confirmed that Si accumulated locally on a few aggregated spherical particles on one filament of PET × 10 Wash samples (SI, Fig. S5b). This suggested that the functional ink was mechanically abraded, chemically agitated and thereafter formed spherical particles, which stick to the textile substrate by physical interaction, or are partially removed (damaged) from the filament. As shown in Fig. 5g (see arrow), the washing process might attack the functional layer in a similar way like peeling an onion, i.e., layer by layer. The textile could preserve the hydrophobicity as long as there is some functional material wrapped around/sticking to the filament, regardless if it is a form of flat layer or in other spherical-like shapes. However, the change in microstructure indicated damage or disturbance of the inkjet-printed functional layer. Various liquids were placed on a PET × 10 Wash × 10 samples to verify the water repellency after washing. As shown in Fig. 2e, the inkjet-printed area of PET × 10 Wash × 10 sample showed repellency to water, coffee and blue-colored ink. However, we noticed that the time for the textile to hold the water droplet after 10 washes is reduced. The WCA started to decrease after drop placement within 3–5 min. The deterioration of water repellency of the functional layer agreed with the damage of the functional layer in microstructure. The durability of the functional layers on textile is challenging and demanding. Similar comparison can be made with functional layers produced with other methods, and Vasiljevic et al. [35] produced a hierarchically roughened surface with SiO\(_2\) nanoparticles covered by fluorooalkyl functional oligosiloxane by pad-dry-cure method. During wash fastness testing, the functional layer starts to change after 10 domestic washes. Schwarz et al. [36] produced thin copper films on para-aramid yarns via
Furthermore, transportation of the functional ink is assessed theoretically and experimentally. The Washburn–Lucas equation \( \text{(1)} \) describes the transportation of liquid within a two-end open pore with external pressure opposing capillary flow. By assuming the opposition pressure is negligible, the equation became:

\[
I = \frac{\gamma \cdot \cos \theta}{4 \cdot \eta} \cdot t
\]

where \( I \) is the distance penetrated by a liquid, \( \gamma \) is the effective capillary radius of the pores, \( \theta \) is the surface tension of the applied liquid, \( \eta \) is the liquid/pore contact angle, \( \gamma \) is the viscosity of the liquid and \( I \) is the time. The wicking property of the fabric was assessed by the absorption rate of the ink on the substrate (5). As shown in Fig. 5, the absorption of the functional ink on PET is more or less linear in speed as in Eq. (1), and faster than the absorption on PA. Furthermore, the absorption of the functional ink on PA is a two-stage or exponential decay process. The ink was absorbed faster at the beginning but got slower with time. Moreover, in capillary height measurement in warp and weft direction of untreated PA and PET, the absorption rate of water in untreated PET is higher than PA (SI, Fig. S1). The results suggested that untreated PET could have larger pores, i.e., inter- and intra-yarn spaces, than PA in Eq. (1); therefore, larger PET was observed experimentally (assumed \( \cos \theta_{\text{PET}} \approx \cos \theta_{\text{PA}} \)). As a result, the ink spread more on the surface of PA rather than transporting it deeper. This could be deduced by experimentally measured smaller \( r_{\text{PA}} \) (average pore size of PA of 11.2 \( \mu \text{m} \) by BET, Fig. 6) suggested that the functional layer was not affected very much in both PET \( \times 10 \) and PA \( \times 10 \) samples after 20000 rubs. In comparison, the untreated PET and PA samples showed no improved WCA after abrasion tests. The SEM images (Fig. 6) suggested that the functional layer was not affected very much in both PET \( \times 10 \) and PA \( \times 10 \) samples after 20000 rubs. The microstructure is significantly different compared with inkjet functionalized textiles after wash fastness tests. Furthermore, the reference PET had a slightly decreased WCA from 143° to 127°, whereas the reference PA remained the hydrophobicity from 140° to 133° after 20000 rubs. We noticed that the abrasion tests could produce a fluffy surface due to abrasion of textile substrate against the abrasing material. At microscopic level, the inkjet functionalized textile became planar functionalized woven yarns with protruding filaments with functional wrapping. According to Cassie–Baxter equation \( \text{(43, 44)} \),

\[
\cos \theta_{\text{PA}} = f_s \cdot (\cos \theta_1 + 1) - 1
\]

where \( \theta_1 \) is the Cassie–Baxter contact angle on the rough surface, \( f_s \) is the fractions of the solid area divided by the projected surface area on the surface, and \( \theta_1 \) is the contact angle on smooth surface. Therefore, WCA of a surface is affected by the surface roughness. These small protruding filaments with hydrophobic functionalization on the top surface may boost the hydrophobicity by reducing \( f_s \) (higher WCA \( \theta_{\text{PA}} \) in Eq. 2). The resistance to abrasion of inkjet functionalized samples is comparable or slightly better than fluorocarbon–finished reference PET and PA. Abrasion tests were performed on PET \( \times 1 \), PET \( \times 3 \), PA \( \times 1 \) and PA \( \times 3 \) samples. As plotted in Fig. 4d, PET \( \times 1 \) and PET \( \times 3 \) samples have WCA of 130° and 121° after 20000 rubs. But
PA × 1 and PA × 3 samples became hydrophilic after 10000 and 20000 rubs. The PET × 1 and PET × 3 samples showed better abrasion resistance compared to PA × 1 and PA × 3 samples. The results suggested that the functional ink adhered better/interacted stronger with PET. However, the capability of samples to hold water droplets decreased significantly, suggesting damage of the functional layer. After 3000 rubs, the droplets can wet PET × 1, PET × 3, PA × 1, and PA × 3 samples within 5 min, despite a high initial WCA.

The ink transportation and ink-filament interaction are crucial to understand the durability of the functional layer in abrasion. Two factors, porosity/effective pore size of the textile substrate and ink-filament interaction played a key role. As shown experimentally in capillary height and functional ink absorption measures in Fig. S1 and S2, as well as theoretical deduction in Eq. (1), the functional ink penetrates deeper in PET fabrics. This can be the reason to obtain better abrasion resistance with PET. The inkjet-printed ink first covered the top layer of the textile surface and thereafter transported deeper through inter- and intra-yarn spaces into the bulky textiles. The ink transported deeper into the textile could offer better resistance, whereas functional ink accumulated on the top of the surface is more vulnerable to abrasion. Furthermore, PET indicates stronger ink-filament interaction with the functional ink. The functional ink adhered better on PET × 1 and × 3 samples than PA × 1 and × 3 samples, which agreed with previous wash fastness results. Moreover, the filaments wrapped around with a thicker layer of functional material are more resistant to abrasion. As shown in Fig. S4d, the sample with less functional material (PET × 1, ×3 and PA × 1, ×3, <1 g m⁻²) is more vulnerable to abrasion tests than PET × 10 and PA × 10 samples (1.6 g m⁻²). Overall, the inkjet-printed PET and PA surface with polysiloxane showed moderately high WCA, wash fastness and abrasive property. However, due to the nature of non-covalent interaction between the functional layer and textile substrate, the fastness properties are constrained. To improve water repellency, as well as fastness properties, it could be interesting to introduce covalent bonding between the functional layer and textile substrates in combination with nanoscale surface roughening.

Conclusion

Waterborne, fluorocarbon-free and water-repellent ink with polysiloxane micro-emulsion was formulated and inkjet printed on plain woven PET and PA textile substrates, in order to functionalize the textile with water repellency. The PET and PA have a WCA from <90° to 140° after inkjet functionalization. The functional textile has a microstructure with polysiloxane wrapped around the filament which modified the surface property of the textiles. Furthermore, the functional surfaces show resistance to wash and abrasion. The 10-pass printed PET (PET × 10) preserved a WCA of 133° after 20000 rubs and a WCA of 140° after 20000 rubs. We found that the ink transportation in the textile structure as well as the ink-filament interaction plays a key role in the durability of the functional layer. The functional ink was transported faster and deeper in PET, and with stronger non-covalent ink-filament interaction with PET than with PA. Therefore, PET showed better wash fastness and abrasion resistance. The microscopic images showed that inkjet printing did not or had little impact on the tactile feeling of the textile, i.e., the hand feeling and softness of textile is well preserved. Inkjet printing demonstrated selective and efficient deposition of functional material on textiles, as a promising resource-efficient process in the applications of functional and smart textiles.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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Paper VI

Supercritical CO2 dyeing of polyester fabric with photochromic dyes to fabricate UV sensing smart textiles
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Manuscript submitted
Supercritical CO₂ dyeing of polyester fabric with photochromic dyes to fabricate UV sensing smart textiles

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Abstract

Photochromic molecules are well-established colourants in the manufacturing of niche products, providing reversible colour change effects when irradiated with ultraviolet (UV) light. The high material cost of such speciality dyes along with the general high carbon footprint and extensive water consumption of textile products necessitates resource-efficient production processes. The use of supercritical CO₂ (scCO₂) dyeing technique enables the economic production of textile high-end products, where a uniform through colouration is desired. This study investigates the potential application of two commercial photochromic dyes based on spirooxazine (Sea Green – SO-SG) and naphthopyran (Ruby Red – NP-RR) to polyester fabric using scCO₂ dyeing technique and examines their photochromic behaviour. The dyeing was carried out at 120 °C and 25 MPa for one hour. The photochromic performance was evaluated using a specially designed online colour measurement system capable of simultaneous UV irradiation and continuous measurement of photochromic colour change even after the shutdown of the UV source. The colour yields (K/S values), photoswitching rates and durability against washing were the main parameters examined. The results showed that scCO₂ dyed polyester fabrics exhibited reversible colour changing properties upon UV exposure and removal. The samples dyed with SO-SG demonstrated a comparable degree of photo-colouration, lower background colour, faster colouration and decolouration speeds, but inferior wash fastness compared with NP-RR dyed samples. Particularly, the same class of dyes applied by scCO₂ dyeing showed faster fading rates compared with conventionally dyed samples. This study shows that scCO₂ dyeing method is a potential alternative to develop uniformly coloured photochromic textiles providing excellent photochromic performance with additional economic and environmental benefits.

Keywords: Supercritical carbon dioxide (scCO₂) dyeing, polyester, textile, photochromic dye, spirooxazine, naphthopyran

1. Introduction

Photochromic colourants change their colour from colourless to a coloured state when irradiated by UV light and revert to their original colourless state when exposed to visible light or increased temperature. Photochromic materials have been used in different application areas including ophthalmic lenses, optical data recording and storage, memories, light control filters, security printing, sensors and displays [1, 2], but their use in textiles has been limited. Nowadays, however, the interest in using photochromic textiles has risen especially due to their important and potentially fun applications in smart and functional textiles [3]. Applications in textiles range from everyday clothing to high-tech smart and functional textiles such as in fashion and intelligent design, security and brand protection, anti-counterfeit, camouflage, textile UV sensors, and active protective clothes [4]. Photochromic textiles have the advantage of quickly changing colour in response to light while maintaining general textile properties. For example, UV sensing textiles show higher flexibility, are easily customizable and require low maintenance compared to conventional sensor systems [5]. Despite the availability of significant interest, commercial development of photochromic textiles is limited mainly due to technical issues associated with application methods and performance [1]. Several techniques have been reported for the preparation of photochromic textiles, including screen-printing [6-11], digital inkjet printing [12-
exhaust dyeing [15, 17-20], sol-gel coating [21, 22], pad-dry method [23, 24], electrospinning [25, 26], and mass colouration [27, 28]. Details about the different methods of production of photochromic textiles, their properties, and applications in the textile field were reviewed by Periyasami et al. [29]. Among the methods, screen-printing and conventional exhaust dyeing are the most widely used methods. Screen-printing has been successfully used to apply photochromic dyes to textiles. While good photochromic effects have been obtained, the binder used usually imparts a relatively harsh handle to the fabrics, which affects their comfort characteristics. It also has relatively poor fastness and photostability properties compared with the exhaust dyeing method [3]. Exhaust dyeing of photochromic dyes as disperse dyes to various textile substrates has also been widely investigated [15, 18, 19]. It is commonly considered as the most convenient and easy technique compared with mass colouration and printing methods. However, exhaust dyeing has many inevitable problems such as the requirement of long dyeing time at high temperature, a large amount of water and auxiliary chemicals, incomplete exhaustion and fixation even with salts and alkalis, and the discharge of the contaminated wastewater, which makes it ecologically and environmentally less safe. During exhaust dyeing, approximately 5-10% of the dyes are not used and ends up in wastewater [30]. In addition, the exhaustion and colour build-up properties of photochromic dyes were reported rather low [18, 19], which makes the process even more costly given the high cost of photochromic colourants. Attempts to replace water with organic solvents was also challenged by issues such as toxicity, recoverability, and cost [24]. Recently, application of photochromic colourants using digital inkjet printing has presented promising results for one-sided patterned applications [12, 16, 21]. Despite its advantages over conventional screen-printing in regards to resource efficiency and process flexibility, the requirement of inks, which meet the stringent physical, chemical, and environmental criteria along with the associated print qualities remain a challenge. Overall, most of the conventional techniques currently used to produce photochromic textiles have common issues such as higher cost of production, lower level of colour development, and insufficient durability, that need to be addressed for successful commercial application [4]. Therefore, appropriate production techniques, which meet the necessary commercial requirements, are still needed.

For uniformly through-coloured applications, the dying process in scCO2 is an attractive alternative to aqueous and solvent-based processes offering significant environmental and economic benefits [32]. The primary advantage is that it avoids the use of freshwater and auxiliaries and the associated hazardous effluent. It has simpler dye formulation with a small amount of dyestuff particularly advantageous in the case of expensive materials such as photochromic dyes. The dying process in scCO2 is generally faster due to its low viscosity and high diffusivity properties. Briefly, the dye is dissolved in supercritical medium, transported to the fibre, and penetrates into the fibre relatively fast achieving uniform dyeing in a short time. In addition, CO2 can swell and plasticize the polymer which also facilitates the diffusion of dye molecules. At the end of the process, CO2 and excess dye can be recycled and no drying is required. Thus, it is a resource-efficient and economical production process offering an overall 50% lower operating cost [33-35]. Furthermore, the use of scCO2 as a solvent avoids any undesirable solvent effect on the photochromic properties as the CO2 can be easily removed from the polymer during pressure release after completion of the dying procedure.

Photochromic dyes are suitable colourants to be applied in scCO2 medium owing to similar molecular structure as the conventional disperse dyes in that they are small to medium-sized neutral molecules with a balance of hydrophilic and hydrophobic character [36]. They displayed the same dyeing behaviour as disperse dyes when applied to polyester fabric using exhaust dyeing method [19]. Application of some photochromic dyes in polymeric matrixes using scCO2 has been proven to be feasible. Glagolev and his research group [37-40] investigated the potential of scCO2 impregnation to produce different photochromic polymeric materials using various photoactive compounds. Lima et al. [41] also studied the impregnation of polycarbonate and silica gel composite film into a photochromic dye Reversacol Graphite in scCO2 medium to fabricate photochromic lenses. To the best of our knowledge, however, the application of photochromic dyes to polyester fabrics using scCO2 dyeing method has not yet been investigated.

This study investigates the potential application of selected commercial photochromic dyes, i.e. spirooxazine and naphthopyran based dyes, to polyester fabric using the scCO2 dyeing technique to produce UV sensing smart textiles. The photo-colouration and fading properties of the photochromic dyed samples were performed using an online colour measurement system. The
colour yield and switching rates and their durability against washing were examined. Results showed that both photochromic dyes were successfully incorporated into the polyester fabric using scCO₂ technique displaying comparable performance in terms of colour yield but a distinct rate of colour build-up and wash fastness properties. This study provides an insight into the behaviour of photochromic dyes applied directly as disperse dyes to the polyester fabric from scCO₂ media with a large potential to facilitate the development of uniformly coloured photochromic textiles in an eco-friendly and resource-efficient way.

2. Experimental

2.1 Materials

The substrate used in this study was a heat-set plain-woven polyester fabric (147 g/m²) supplied by FOV Fabrics (Sweden). Two commercial photochromic dyes; Reversacol Ruby Red and Sea Green (Vivimed Labs, UK) were selected (Table 1) and their generalized structures are illustrated in Scheme 1. The CO₂ used in all experiments was supplied by AGA industrial gases (Sweden) and has 99.5 % purity.

Table 1. Commercial photochromic dyes used and their notations

<table>
<thead>
<tr>
<th>Notation</th>
<th>Colour</th>
<th>Chemical class</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO-SG</td>
<td>Sea Green</td>
<td>Spirooxazine</td>
</tr>
<tr>
<td>NP-RR</td>
<td>Ruby Red</td>
<td>Naphthopyran</td>
</tr>
</tbody>
</table>

2.2 Dyeing procedure

Dyeing was performed using a batch type scCO₂ dyeing apparatus (Figure 1) 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 apparatus is a beam type dyeing machine, where the polyester fabric (21×30 cm, ca. 10 g) was
wrapped around a Teflon mesh, suspended inside the dyeing vessel (with internal volume = 290 mL, \( P_{\text{max}} = 30 \) MPa, and \( T_{\text{max}} = 130 \) °C) and the photochromic dye (0.027% owf ~ 2.56 mg) was placed below the fabric at the bottom of the vessel. The amount of colourant was selected on the basis to compare results of photochromic textiles produced with digital inkjet printing [16].

As illustrated in Figure 1, the dyeing vessel (3) was pre-cooled in a separate freezer (2) and afterwards filled with the required amount of CO\(_2\). Then, the vessels were mounted on the shaft rotating inside the pre-heated oil bath (4) and the temperature rose at a rate of 3 °C per minute to the working temperature. For all samples, dyeing was carried out using the same dyeing condition of 120 °C and 25 MPa for one hour. After dyeing, the vessels were removed from the oil bath and the CO\(_2\) was vented slowly and the samples were taken out for further analysis without reduction cleaning procedure.

**2.3 Dynamic colour measurement**

The colouration and decolouration properties of the photochromic textiles were measured using an LCAM Photochrom 3 spectrophotometer (Technical University of Liberec, Czech Republic), which can measure the colour development and fading performance continuously over various cycles of UV- exposure and relaxation. The LCAM Photochrom 3 is equipped with LED Engine LZ1-00UV00 LED as an activation light source with a radiometric power 1680 mW and an emission peak with a wavelength of 365 nm. The measuring light source is a dual system of combined high-power white LEDs with CCTs of 4000, 5000 and 7000 K. Upon measurement, samples are illuminated with 60 klx, which constitutes an illuminance between brightest sunlight intensity (120 klx) and daylight intensity without direct sunlight at noon (20 klx). The temperature of the samples was controlled to around 21 °C and reflectance values were recorded in intervals of 2 s during continuous UV irradiation and shutdown. Colour analysis of each dye is made at their dominant wavelength, which is 500 nm for NP-RR and 620 nm for SO-SG. The colour values (K/S) were calculated from the reflectance spectra using the Kubelka-Munk function, Equation (1).

\[
\frac{K}{S} = \frac{(1 - R)^2}{2R} \tag{1}
\]

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

The colouration and fading kinetics, determined from the K/S-time datasets, were fitted to an extension of the first-order kinetic model, Equation (2). This model is generally used to describe the behaviour of photochromic dyes incorporated into the textile matrix during colouration and decolouration [42].

\[
\Delta \frac{K}{S} = \left( \frac{K}{S_0} - \frac{K}{S_{\infty}} \right) \cdot e^{(-kt)} + \frac{K}{S_{\infty}} \tag{2}
\]
where: \( K/S_0 \) and \( K/S_\infty \) are the initial and final (saturated) 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 subscripts define the time relationships: \((0)\) = time in the beginning and \((\infty)\) = time at infinity. From this equation, the halftime of colour change \( (t_{1/2}) \) was calculated using Equation (3) \([43]\).

\[
t_{1/2} = \frac{\ln 2}{k} \quad [8]
\]

Thus, the photochromic performance of scCO\(_2\) dyed photochromic polyester fabrics were evaluated in terms of the colour yield \( \Delta K/S \) upon activation with UV-light, rate constants of colour increase \( (k_{\text{col}}) \) to achieve maximum colouration \( (K/S_\infty) \), and rate constant of colour decrease \( (k_{\text{decol}}) \) to revert to the ring-closed colourless state \( (K/S_0) \), and half-lives \( (t_{1/2}) \) of colouration and decolouration.

### 2.4 Background colour measurement

The conventional colour measurement system was conducted to evaluate the background colour of photochromic fabric samples in order to estimate the permanent shade developed in their inactive state due to the high-temperature dyeing process. The background colour is expressed as the colour difference \( \Delta E \) (CMC) between the non-dyed polyester fabric and the photochromic dyed samples without UV irradiation. Datacolor Check Pro spectrophotometer (USA) was used under the condition of D65 illuminant and 10\(^\circ\) standard observer. Three measurements were read at different sites of the same sample and average values are reported. All measurements were performed at room temperature (approx. 22 °C) without UV irradiation.

### 2.5 Durability towards washing

To evaluate the durability property, samples were washed once according to ISO 6330:2012, domestic washing and drying procedure (at 40 ±3 °C, using 20 ±1 g reference detergent for 30 min) using a domestic laundry machine. Sufficient ballasts of 100 % polyester fabric were added in order to achieve the specified weight in the reference washing machine. A comparative study on the photochromic properties of samples before and after washing was performed to evaluate their performance against washing. The decrease in colour yield \( (K/S) \) after washing can be used to express the washing fastness of the photochromic effect. The fastness is evaluated according to a relative loss in percentage using Equation (4), which measures the magnitude of the residual photochromic performance after washing.

\[
\text{Fastness (\%)} = \frac{K/S(2)}{K/S(1)} \times 100
\]

where: \( K/S(1) \) and \( K/S(2) \) are the colour yield of the photochromic fabric before and after the standard washing respectively, upon UV exposure.

### 2.6 Statistical analysis

Two replicate samples were produced, and three measurements were taken for each sample where each measurement contains three cycles of continuous colouration and two cycles of decolouration. The obtained data were fitted to the first-order kinetic model, Equation (2) using Origin Lab software. The factor effects such as the type of the photochromic dye, washing condition, and the number of UV exposure and fading cycles on the colour yield and rate of colouration and decolouration were analysed using Minitab 17 software according to the criteria \( p \leq 0.05 \).

### 3. Results and discussion

The photochromic behaviour of the scCO\(_2\) dyed polyester samples was evaluated by continuous measurement of the photo-colouration during UV irradiation and the decolouration after UV light is removed. For each sample, three cycles of colouration and two cycles of decolouration were measured continuously and the experimental data were fitted using the first-order kinetic model, Equation (2). All photochromic samples developed in scCO\(_2\) changed their colour when exposed to UV light and reverted to their original colour when UV light was removed. The samples produced using the two dye types generally showed comparable performance in terms of colour
yield but distinct kinetics and durability towards washing were obtained. The repeated UV exposure and fading cycles had no significant effect on the colour yield and kinetics of both dyes. This indicates good fatigue resistance although more cycles are required for a better understanding of the fatigue behaviour.

3.1 Data fitting

The experimental data fitting procedure is presented here to show how the data was analysed. The experimental data sets contain reflectance values (converted into K/S values) collected at intervals of 2 s. For SO-SG dyed samples, the photochromic textile is activated upon 300 s (150 data points) and deactivated upon 400 s (200 data points). For NP-RR dyed samples 500 s activation and 1000 s deactivation intervals were used, which account for 250 and 500 data points, respectively. The experimental data sets contain three replicates for each sample type and three cycles of colouration and two cycles of decolouration were collected for each replicate. Therefore, each sample has nine colouration and six decolouration data sets and these data sets were fitted to the first-order kinetic model (Equation (3)) for comprehensive analysis. The experimental data of the colouration and fading of the second cycle measurement of the second replicate samples are shown as a representative sample as seen in Figure 2.

The obtained R² values suggest that the fit was satisfactory for analysis of the kinetics of the photochromic dyes applied to polyester fabric. The model fits well for all samples and conditions except for NP-RR samples (unwashed samples only) seemingly underestimates the level of the photo colouration compared with the average values of the fitted data (Figure 2) based on qualitative observation of the graphs. However, the differences between the colour strength values of both dyes were insignificant suggesting similar colourability properties.

3.2 Colour yield (ΔK/S)

The collected reflectance values during continuous UV exposure and relaxation were converted into K/S values using the Kubelka-Munk function. Generally, the K/S value corresponds to the intensity of the developed colour; the higher the value the deeper the developed colour. From the results, samples dyed with NP-RR exhibited a slightly lower colour yield with ΔK/S of 0.088 compared with SO-SG dyed samples with ΔK/S of 0.096, which is displayed in the fitted experimental data of the average colour yield of photochromic dyed samples (see Table 2). Thus, the obtained intensities of the developed colour by both dyes were similar. According to previous research, differences in the degree of colouration between dye classes were observed. However, there was no obvious correlation between the degree of photo colouration and the chemical class.
of the dyes. The difference is mostly related to the particular chemical nature of individual dye structures [19]. Accordingly, it can be concluded that these specific dye structures used in this study have a similar degree of colouration when applied from the scCO₂ solvent. In comparison to results of inkjet printing with UV-curable photochromic inks with the same types and amounts of dye deposited on polyester, colour yields of NP-RR dyes are similar both before and after washing incorporated in an ink resin with high crosslinking density. Ink-jetted and UV-cured prints showed an initial ΔK/S of 0.103, which is reduced to ΔK/S of 0.062 after one wash. SO-SG prints with the same crosslinking density, display similar initial colour strength after printing with ΔK/S of 0.107. However, after one wash (ΔK/S = 0.086), not as much colour is lost during washing compared with scCO₂-dyed samples [16]. Thus, the results of the colour yields in both methods showed that the dyes have similar colourability property but different washing performances.

Table 2. Average colour yield (K/S) of photochromic dyed polyester samples upon UV exposure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unwashed</th>
<th>Washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO-SG</td>
<td>0.096±0.016</td>
<td>0.026±0.013</td>
</tr>
<tr>
<td>NP-RR</td>
<td>0.088±0.004</td>
<td>0.068±0.007</td>
</tr>
</tbody>
</table>

3.3 The rates of colouration and decolouration

Before the actual measurement, representative samples were exposed to UV light to estimate the time required to reach their saturation colouration and fading back to their uncoloured states. From the results, samples dyed with NP-RR took a relatively long time to reach their maximum colouration (500 s) and to revert to their uncoloured state (1000 s) while samples dyed with SO-SG needed only 300 s and 400 s for complete colouration and decolouration, respectively. Thus, all further investigations and measurements were carried out based on these time intervals.

3.3.1 Kinetic rate constants

Figure 3 shows the fitted average experimental data of photochromic dyed samples measured upon UV exposure and relaxation. As seen in the fitted curves, samples dyed with SO-SG showed a significantly higher rate of colour development and faded more rapidly than NP-RR dyed samples.

Figure 3. Average fitted plots for colouration (I) and decolouration (II) curves of photochromic dyed samples (a) SO-SG unwashed (b) SO-SG washed, (c) NP-RR unwashed, (d) NP-RR washed. The values are normalized to have the same initial and final values for the colouration and decolouration curves, respectively.
According to the rate constant values in Table 3, SO-SG samples have a $k_{col}$ of 0.141 s$^{-1}$ and NP-RR samples have a $k_{col}$ of 0.020 s$^{-1}$, in which SO-SG had more than seven-fold faster colour development compared with NP-RR. This difference in rate kinetics between the two dyes could arise from the intrinsic difference between the two dye classes. Spirooxazines are inherently faster-switching dyes and more temperature-dependent dyes, whereas naphthopyrans are more durable, but slow-switching [8, 44]. A faster colour development by spiroxazine dyes printed on the polyester fabric was also reported compared with naphthopyrans [6]. Naphthopyran based dyes applied to polyester using the inkjet printing method also showed lower fading rates compared with spiroxazine based dyes [12]. Thus, the results obtained in the current study are consistent with previously reported ones. In addition to the inherent characteristics of the dyes, the polymer matrix and the relative position of the dye molecules in the polymer matrix could affect the reaction kinetics. This observation was made, when inkjet printing SO-SG and NP-RR dyes in UV-curable ink onto polyester fabric [16]. Here, the inherently faster switching SO-SG dye showed a slower rate constant than NP-RR dyes. However, SO-SG was more affected by changes in the matrix rigidity of the dye-carrying ink, with a higher relative increase of reaction kinetics compared with NP-RR dyes. A less rigid matrix resulted in a five-fold increase of $k_{col}$ of SO-SG prints compared to a two-fold increase of NP-RR prints. Furthermore, the weak fastness properties displayed by SO-SG dyed samples (Section 3.5) suggests limited dye penetration. This promotes fast response upon isomerization, as the dye concentration used was small and the dye molecules located near the surface provide free space, which facilitates faster ring opening and closing. In contrast, samples dyed with NP-RR displayed better wash fastness property, indicative of deeper dye penetration or the presence of more number of dye molecules locked within the polymer matrix. Owing to the semi-crystalline and hydrophobic nature of polyester, these deeply penetrated NP-RR dye molecules are more constrained with limited space requiring a relatively long time for the photo transformation to occur. Matrix rigidity influences the behaviour of photochromic dyes significantly, which has been discussed in prior studies [16, 31, 45-48]. Thus, the assumed location of the dye in the fibre structure has an effect on dye kinetics and does not interfere with the inherent properties of the different photochromic dyes. As mentioned earlier, spirooxazines are generally faster-switching dyes, but naphthopyrans are more durable.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{col}$ Before wash</th>
<th>$k_{col}$ After wash</th>
<th>$k_{decol}$ Before wash</th>
<th>$k_{decol}$ After wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO-SG</td>
<td>0.141 ±0.038</td>
<td>0.022 ±0.003</td>
<td>0.072 ±0.004</td>
<td>0.016 ±0.001</td>
</tr>
<tr>
<td>NP-RR</td>
<td>0.020 ±0.003</td>
<td>0.011 ±0.001</td>
<td>0.007 ±0.001</td>
<td>0.005 ±0.000</td>
</tr>
</tbody>
</table>

For both dyes and for all washing conditions, the fading rate is slower than the rate of colour build-up, which is a common behaviour of photochromic dyes. Unwashed samples of SO-SG have a two-fold slower and NP-RR an approx. three-fold slower decolouration reaction than colouration reaction. The fading curves of samples dyed with SO-SG and NP-RR are shown in Figure 3. As can be seen from the curves, SO-SG dyed samples demonstrated fast fading rate compared with NP-RR dyed samples. SO-SG and NP-RR samples have an average $k_{decol}$ of 0.072 s$^{-1}$ and 0.007 s$^{-1}$, respectively (see Table 3). In both cases, the dyes start fading immediately upon the removal of the UV-light source. After washing, SO-SG dyed samples showed a dramatic decrease in fading rate while the washing effect was less significant for NP-RR dyed samples.

### 3.3.2 Half-lives

The half-life ($t_{1/2}$) of colouration/fading is a common measure to express the colour switching speeds of photochromic materials. Unlike the overall rate behaviour described above, the half-life values give information about the kinetic behaviour of dyes during their initial colouration and decolouration phases. Generally, the initial colouration and decolouration rates are faster compared with the rates near to saturation and towards the end of decolouration. This phenomenon is related to the half-life of the photochromic reaction which has important practical implications. The half-life of colouration ($t_{1/2col}$) is the time required to reach half of the total photochromic response upon exposure to UV irradiation and similarly, the half-life of fading ($t_{1/2decol}$) is the time taken to revert half of the developed colour (K/S$\infty$) [22]. This means that smaller numerical values of $t_{1/2}$ indicate faster colouration and decolouration speeds and vice
versa. As can be seen from the results in Table 4, SO-SG dyed samples showed relatively higher colouration and fading rates, expressed by lower half-lives of colouration and fading, compared with NP-RR dyed samples regardless of the washing condition. For both dyes, the half-lives of colouration and decolouration increased after washing, which means slower colouration and fading. These results are expected and consistent with the kinetic results obtained in the previous section. The same trend has also been observed in previous studies of the same classes of photochromic dyes applied to polyester fabric using exhaust dyeing and screen printing method [6, 19]. In fact, a higher rate of colouration and fading by spirooxazine-based dyes compared with naphthopyrans was consistently reported in agreement with this study.

Table 4. Half-lives (t$_{1/2}$) of colouration and decolouration of dyes applied to the polyester fabric using scCO$_2$ dyeing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t$_{1/2}$ (s)</th>
<th>Colouration</th>
<th>Fading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unwashed</td>
<td>Washed</td>
<td>Unwashed</td>
</tr>
<tr>
<td>SO-SG</td>
<td>5.2 ±1.3</td>
<td>31.5 ±4.3</td>
<td>9.6 ±0.5</td>
</tr>
<tr>
<td>NP-RR</td>
<td>35.6 ±4.9</td>
<td>65.3 ±4.2</td>
<td>100.2 ±6.2</td>
</tr>
</tbody>
</table>

One notable observation was that the half-live of fading of the same class of dyes applied by scCO$_2$ dyeing are significantly lower than those obtained when applied by aqueous or solvent-based dyeing methods [19, 24] and comparable with digital inkjet printing as presented in Table 5 [12, 16, 31]. The shortest time (t$_{1/2}$decol = 0.15 min) was achieved for scCO$_2$ dyed samples with spirooxazine (SO-SG) followed by inkjet printing of spirooxazine in a UV-curable ink and solvent-based ink. This is an additional advantage by scCO$_2$ dyeing since a minimum half-life of fading is commercially useful. Faster reaction rates upon activation and deactivation can be preferable for improved product reliability depending on the application. The advantage of scCO$_2$ dyeing towards conventional dyeing techniques includes the simplicity of the process and the absence of auxiliary chemicals. As only CO$_2$ is used as dyeing medium and photochromic dyes are involved in the process, kinetic switching is not disturbed by the solvent or other material and hence is faster than with exhaust and solvent dyeing.

Table 5. Half-lives of fading of photochromic dyes applied to the polyester fabric by using different application methods

<table>
<thead>
<tr>
<th>Application method</th>
<th>Dye class</th>
<th>t$_{1/2}$decol (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exhaust dyeing</td>
<td>Spirooxazine</td>
<td>3.1*</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>Naphthopyran</td>
<td>18.1*</td>
<td></td>
</tr>
<tr>
<td>Solvent dyeing</td>
<td>Spirooxazine</td>
<td>3.1*</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>Naphthopyran</td>
<td>11.5*</td>
<td></td>
</tr>
<tr>
<td>Digital inkjet printing</td>
<td>Spirooxazine</td>
<td>1.0, 0.9*</td>
<td>[12], [16]</td>
</tr>
<tr>
<td></td>
<td>Naphthopyran</td>
<td>5.1, 0.8*</td>
<td></td>
</tr>
<tr>
<td>scCO$_2$ dyeing</td>
<td>Spirooxazine</td>
<td>0.15</td>
<td>Current work</td>
</tr>
<tr>
<td></td>
<td>Naphthopyran</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

*Minimum half-life values were taken to show the fastest achievable fading kinetics.

### 3.4 Background colour

Background colour measurement was performed to evaluate the permanent shade of the photochromic textiles in their inactive state influenced by the dyeing process. During the dyeing process, high temperatures may thermally influence isomerization of photochromic dyes and hence the background colour. The background colour has shown to affect the degree of photocoloration [12]. The colour strength expressed by K/S (Figure 4) and ΔE (CMC) values (Table 6) were used to evaluate the background colour of dyed samples. The ΔE refers to the colour difference values between the dyed and non-dyed polyester fabrics without UV irradiation. From the background K/S values, it was evident that samples dyed with NP-RR have relatively higher K/S value (deeper colour) compared with samples dyed with SO-SG. A similar trend was also observed from the AE values as presented in Table 6. Higher ΔE values displayed by NP-RR dyed samples with a ΔE value of 2.81 imply higher background colour compared with those dyed with SO-SG with ΔE = 1.47 before washing.
Generally, the ring-closed form of photochromic dyes is usually uncoloured. However, because of the textile application process, a characteristic background colour is often observed. The presence of thermochromism and thermal instability of the dyes under application conditions were mentioned as the two main factors for the development of background colour. Among these factors, the degree of thermochromism is believed to be the dominant one \[19, 24\]. At a higher treatment temperature, the ring-closed form of some photochromic dye molecules is converted thermally to their coloured open (merocyanine) form and subsequently locked in this form within the structure of the textile fibre, resulting in a permanent colour \[6\]. Thus, the difference in the level of background colour between the two dyes could be due to a difference in their thermal sensitivity as well as the penetration level of the dyes in their ring-opened form. Generally, spirooxazines are more sensitive to temperature than naphthopyrans \[1\]. On the other hand, NP-RR dye molecules seem to be deeper penetrated into the fibre bulk compared to SO-SG dyes as established from the wash fastness result. Deeper penetration into the bulk compared to if the dyes are predominantly situated on the fibre surface, results in more restricted space for the dyes to move and thus locks them in their coloured form.

Table 6. Average CMC ΔE values of the background colour of photochromic dyed polyester fabrics and their washed counterparts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Unwashed</th>
<th>Washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO-SG</td>
<td>1.47 ±0.12</td>
<td>1.35 ±0.13</td>
</tr>
<tr>
<td>NP-RR</td>
<td>2.81 ±0.15</td>
<td>2.69 ±0.08</td>
</tr>
</tbody>
</table>

3.5 Durability towards washing

Washing was used as a measure of the durability of the photochromic behaviour and to gain knowledge about the dye penetration level and the affinity of the dye towards the polyester fabric. To assess the durability of photochromic dyed samples, a comparative study on the photochromic colour build-up and fading properties of the samples before and after a standard washing cycle was used. According to the results discussed above, all samples generally displayed inferior photochromic performance after washing irrespective of the type of photochromic dye used. The mean ΔK/S of the two dyes before and after washing, expressed as fastness percentage, was significantly different. Compared with each other, samples dyed with NP-RR exhibited better fastness percentage (77 %) compared with SO-SG dyed samples with a significantly lower fastness percentage of 27 %. This result is in line with the general behaviour of the two dye classes applied on textiles. The relatively better wash fastness behaviour by NP-
RR dyed samples suggests enhanced penetration or better affinity towards polyester compared to SO-SG.

The wash fastness properties of the background colours of both dyed samples were also evaluated. Background colours of the photochromic samples with a generally deeper shade of NP-RR samples (see Figure 5b) decrease slightly after washing. According to ΔE values, the background colour of SO-SG samples reduces to 92% from 1.47 to 1.35 compared to 96% from 2.81 to 2.69 for NP-RR samples (see Table 6). The higher decrease in the background colour of spirooxazine dyed polyester is likely to result from the removal of more dyestuff due to that SO-SG dyes are located more on the fibre surface.

![Figure 5. (a) Activation of the photochromic textiles using a UVA light torch and (b) Locally activated SO-SG (left) and NP-RR (right) samples after washing.](image)

Furthermore, the washing has also a significant effect on the rate of colouration and decolouration of samples developed with both dye types. As presented in Table 3, for SO-SG dyed samples, the washing lowers the colouration rate by 84% and decolouration rate by 77%. Similarly, for NP-RR dyed samples, \( k_{\text{col}} \) decreased by 46%, and \( k_{\text{decol}} \) by 35%. Nevertheless, samples dyed with SO-SG still displayed a significantly higher rate of colouration (\( k_{\text{col}} = 0.022 \, \text{s}^{-1} \)) and fading (\( k_{\text{decol}} = 0.016 \, \text{s}^{-1} \)) after washing compared with NP-RR dyed samples, which has a two-fold lower rate of colouration and three times lower decolouration speed. This result correlates with the inherent property of the specific dye classes with a more durable character of naphthopyrans and faster kinetics of spirooxazines. According to previous reports and which is in line with the current results, spirooxazines showed higher thermal sensitivity, which causes faster thermally driven decolouration than naphthopyrans [6, 49].

4. Conclusions

This paper presents a novelty of water-free dyeing of UV sensing smart textiles using photochromic dyes with superior colour performance compared to conventional dyeing techniques. Two photochromic dyes belonging to the spirooxazine and naphthopyran dye classes were successfully applied to the polyester fabric using scCO₂ dyeing. The uniformly coloured photochromic polyester fabrics prepared using scCO₂ dyeing technique exhibit significant reversible colour changing properties when exposed to UV light. The two photochromic dyes on polyester fabrics showed comparable performance in terms of colour yield and distinct characteristics in terms of reaction kinetics, background colour, and wash fastness properties. Sea green from the spirooxazine family had faster reaction kinetics, lower background colour, and reduced wash fastness properties compared with the ruby red from the naphthopyran dye class. Notably, the photochromic fabric produced by scCO₂ dyeing exhibited faster dye kinetics compared to photochromic textiles produced with conventional exhaust and solvent dyeing techniques. Improving the durability properties could be of interest in future research for effective utilization of this technique. Overall, the experimental findings suggest that scCO₂ dyeing technique is a promising alternative to conventional processes for uniform colouration, not only because of its economic importance but also due to its environmental advantages such as avoiding the use of water, organic solvents, auxiliary chemicals, and requiring small amounts of dye and short dyeing time. The obtained photochromic textiles can be used for applications such as UV sensing smart textile.

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