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*Published in:* Materials and Design

*DOI:* 10.1016/j.matdes.2021.110175

Published: 15/12/2021

*Document Version*
Publisher's PDF, also known as Version of record

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*Please cite the original version:*
Textile integrable mechanochromic strain sensor based on the interplay of supramolecular interactions

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Highlights
- A simple supramolecular polymer/chromophore (polyvinylpyrrolidone/Disperse Red 1) coating on PDMS was demonstrated to show gradual stepless colour changing from orange to red upon elongation.
- Dip-coating was employed to fabricate naked-eye observable mechanochromic strain sensor on commercial polyamide yarns.
- Sensor yarns being able to stretch up to 75% elongation without breaking were fabricated.
- Colour-changing can be quantitatively characterized by both UV–Visible spectroscopy and simple photography through RGB analysis.

Graphical Abstract

Abstract
Mechanochromic materials, when exposed to mechanical deformation, undergo a modification of optical properties. This behaviour can stem from either conformational rearrangements, disruptions of intermolecular interactions, or molecular structure changes affecting absorption, emission, or reflection abilities. Here reversible colour change of Disperse Red 1/polyvinylpyrrolidone films resulting from humidity annealing and subsequent stretching is reported. Due to the humidity-induced blue shift of the absorbance peak related to exciton coupling of the chromophores, the tone of films abruptly changes from red to orange. Upon stretching, the gradual disaggregation of the chromophores takes place and therefore the colour switches back to red in a stepless manner. Using either red–green–blue analysis of time lapse photography or UV–Visible measurements, this transformation, which is also well visible by the naked eye, can be followed with high accuracy. This work offers the opportunity to apply the strain sensor in humid environments to prevent the mechanical failures by showing a colour change in areas subjected to undesired stress. Moreover, dip-coating yarns with mechanochromic coating allows fabrication of functional yarns that change their colour based on their stretching state – thus enabling preparation of colour-changing stretchable textiles was demonstrated.

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1. Introduction

The novel naked-eye readable stretchable strain sensors that do not consume energy for displaying the state of elongation, and
thus, do not need to be plugged in a power source, can assist in warning about mechanical deformations, fractures and failures in bulk materials, being especially useful in prevention of hazardous accidents [1]. Such sensors, fundamentally different on the most commonly studied strain sensors based on coupling of a conducive strain-sensing coating to a stretchable support [2,3], are non-invasive and non-destructive devices that allow real-time strain measurements. They can be applied on various materials surfaces like plastics, coatings, or composites and in different industries, such as architecture, packaging, medicine or even fashion [4,5]. A special interest is to integrate these types of sensorial materials onto textile yarns, which would enable not only textile integration, but would also outperform conventional rigid sensors in detecting human body motions, thanks to yarn-based sensors being lightweight, highly stretchable and accounting for user comfort [6].

Such integrated devices have demonstrated promising potential to be applied in wearable devices [7,8]. Furthermore, mechanochromic molecular systems changing their optical outputs as a result of mechanical deformations are an ideal candidate for the active component of naked-eye readable stretchable strain sensors [4]. Significant efforts have been dedicated to fabrication of fibre-shaped mechanochromic system with the prospect of facile textile integration, however, either the synthesis of the functional materials or the fabrication method of the colour-changing fibres have been highly complex implying significant costs [9–12].

In mechanochromic materials, mechanically-induced molecular structure variations, intermolecular isomerization, and conformational rearrangements lead to optical responses, such as alterations in absorption, reflection, and emission of light. For instance, poly(-diacetylene)s exhibit red-to-blue chromism due to the conformational rearrangements of the polymer back-bone as a response to a mechanical force [13]. Upon mechanical shearing, the maximum of the absorption wavelength shifts from 540 nm to 630 nm, resulting in a change of the fluorescent emission spectra [14]. Another example is the change of molecular packing of chrophophores with conjugated ε-electron systems. This type of aggregation in nonplanar 1-methyl-1,2,3,4,5-pentaphenylsilole leads to intensive fluorescence emission [13]. Moreover, Peterson et al. reported 3D-printable mechanochromic materials based on poly(ε-caprolactone) (PCL) polymers containing spiropyran. Elongation of the fabricated polymer filaments causes stress, accumulation of which activates the mechanochromic ring-opening isomerization reaction and therefore a colour change from brown to purple in the absorption occurs [15]. Even though polymeric materials are natural choice for detecting of mechanical deformations, such as shear and compression, mechanochromism in polymer systems is not often reported [16].

At the same time, the change of displayed colours that takes place in the nature is essential for species that hide from predators, want to seduce their victims, communicate or reproduce [17,18]. Spatial structures, pigments and bioluminescence are the most frequent methods of achieving the desired colour. For example, the tropical fish species Paracheirodon innesi, known also as neon tetra, possesses the extraordinary ability to change the colours displayed on its photonic crystals. The change of the reflected light results from variations in angle or spacing between the reflective platelets located in a soft matrix of their scales or the reflective platelets result from variations in angle or spacing between the reflective platelets located in a soft matrix of their scales or 

Inspired by the abovementioned biological examples, a goal to find a material system was set, in which the interplay between different supramolecular interactions could be easily altered by elongation of the material. As one such system, having the additional advantage of a naked-eye observable shift in the absorption upon aggregation of adjacent chromophores, previously reported supramolecular complexes between Disperse Red 1 (DR1) and polyvinylpyrrolidone (PVP) emerged [19]. In this system, the DR1 molecules bond noncovalently to the polymer backbone, which can accept a hydrogen bond from the hydroxyl group of DR1, as illustrated in Fig. 1. In contrast to covalently bonded systems, in this case, no complicated organic synthesis is required [20]. Also, the dye/polymer ratio can be easily adjusted. Upon exposure to humidity, an intense colour shift from red to orange attributed to the water molecules displacing DR1 hydrogen-bonded to PVP and thus enabling formation of DR1–DR1 aggregates was observed [19]. Since this system consists of multiple competing supramolecular interactions, it is hypothesized that applying a mechanical strain on these films could shift the balance back towards non-aggregated DR1 molecules exhibiting red colour.

In the present article, this hypothesis was tested and a highly stretchable strain sensor fabricated from a DR1/PVP supramolecular complex deposited on a stretchable polydimethylsiloxane (PDMS) substrate was reported. This sensor is based on the antiparallel stacking of molecular dipoles of DR1 molecules (referred to as H-aggregation) in the swollen PVP polymer and delinate mechanical-force induced alterations in the aggregation state of the chromophores. Therefore, a well visible wavelength shift upon mechanical deformation is observed. To observe the expected change in colour from red to orange and back to red, in case of the deposited film, first humidity annealing and then stretching with 5% increment were used. Furthermore, the state of the elongation of the prepared samples by using the red–green–blue (RGB) analysis of their photographs was confirmed. Also, a potential textile integrability of DR1/PVP humidity annealing is demonstrated by functionalizing a commercial polyamide (PA) yarn with abovementioned supramolecular complex. Additionally, the tensile test was conducted on both pure and coated PA yarns to characterize the mechanical properties of the device. The cycle stretch/release experiment was performed on the coated PA samples to indicate the repeatability of the colour changing.

2. Materials and methods

2.1. Materials

Disperse Red 1 (DR1) (Dye content 95%) was purchased from Aldrich. Co. Polyvinylpyrrolidone (PVP) (Average mol wt 360,000) was purchased from Sigma. Chloroform (CHCl3) was purchased from Honeywell. For fabrication of polydimethylsiloxane (PDMS) Silicone Elastomer Curing Agent and Silicone Elastomer Base were purchased from Sylgard®. All the chemicals were used as received, thus without further purification. Glass slides were purchased from VWR. Nine different yarn types were purchased from several manufacturers which was summarized in Table 1.

![Fig. 1. Chemical structures of bonding of the hydrogen group of the dye DR1 and the carbonyl group of the polymer PVP.](image-url)
Table 1
List of the purchased yarns used in the experiments including their types, commercial names, and manufacturers.

<table>
<thead>
<tr>
<th>Yarn type</th>
<th>Commercial name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastan (100%)</td>
<td></td>
<td>Prym</td>
</tr>
<tr>
<td>Elastan (100%)</td>
<td></td>
<td>Asahi Kasei Corporation</td>
</tr>
<tr>
<td>Extrafine merino wool with PBT (95:5%)</td>
<td>Evolution</td>
<td>Tolegno 1900</td>
</tr>
<tr>
<td>Linen/hyaca (90:10%)</td>
<td></td>
<td>Unknown</td>
</tr>
<tr>
<td>Nylon</td>
<td></td>
<td>Kinetic</td>
</tr>
<tr>
<td>Poly(urethane)/nylon (50:50%)</td>
<td></td>
<td>Kinetic</td>
</tr>
<tr>
<td>Polyamide (PA) yarn (Nylon 66)</td>
<td>Bollicine</td>
<td>Alpes Manifaturra Filati</td>
</tr>
<tr>
<td>Polyester (PES)/elastan (90:10%)</td>
<td>Baktron 1300</td>
<td>Elasten</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td></td>
<td>Uppingham Yarns</td>
</tr>
<tr>
<td>Wool</td>
<td>Capri</td>
<td>Sidwolle Group</td>
</tr>
</tbody>
</table>

2.2. Preparation of the solution

2 wt% and 4 wt% of DR1 and PVP were dissolved in CHCl3. DR1 composed of 1 wt%, 5 wt%, 10 wt%, 25 wt%, and 50 wt% of both powders. Next, the prepared solutions were spin-coated on glass slides to determine the most suitable spin coating speed and afterwards, on PDMS.

2.3. Preparation of PDMS

To prepare flexible samples of PDMS, Silicone Elastomer Base and Silicone Elastomer Curing Agent were used in the ratio of 10:1. To prepare the PDMS substrate with uniformed thickness, 8 ml of silicon elastomer base and 0.8 ml of silicon elastomer curing agent were mixed in a petri dish. Then the mixture was put into a vacuum oven to degas 30 min and then for 7 h into an oven at 60°C to harden. Next, specimens with the following dimensions of 2 cm x 1 cm were cut out.

2.4. Spin coating

The solutions containing both DR1 and PVP were spin coated at 1000 rpm, 2000 rpm and 4000 rpm with a WS-650MZ-23NPPM 0 Laurell device. The acceleration time was 5 s, the spin cycle was 30 s, and the slowing down 3 s.

2.5. Humidity annealing

A self-built humidity chamber connected to a nitrogen gas cylinder was used for the research purposes. Samples were placed under the chamber box for the time of 30 s to 5 min. As a rule of thumb, complete colour change from red to orange required less time on thin film samples deposited on PDMS, which changed the colour within 1 min, as compared to polymer complex deposited on the yarns, which required up to 5 min for a complete colour conversion.

2.6. Profilometry

To measure the film thicknesses, a Dektak 6 M Stylus profilometer was used. Uniform scratches were made to films. Next, the thickness was determined as a difference between the film surface and the bottom of the scratch.

2.7. Dip coating

All yarns were dip coated at 10 mm/min in a solution containing 10 wt% of DR1 in 4 wt% of DR1 and PVP in CHCl3 for 30 s and withdrawn at 10 mm/min using a KSV NIMA Dip Coater produced by Biolin Scientific.

2.8. UV–Visible spectra

UV–Visible spectra of fabricated films were recorded using a Shimadzu UV-2600 with ISR-2600 Plus Integrating Sphere Attachment spectrophotometer.

2.9. RGB analysis

Photographs of manufactured and humidity annealed samples were taken using a Raspberry Pi High Quality V1.0 camera and a NOIR V2.1 camera. A close-up lens nr 4 manufactured by Hoya was used to achieve greater zoom in of the HQ camera. The samples were stretched with an increment of 5%. A self-created program was used to obtain the red (R), green (G), blue (B) channel values from a rectangle in the middle of the coloured area of a photograph [21].

All experiments were conducted in room temperature.

2.10. Tensile test

The tensile test was performed by Instron-33R4204 on both substrate PA yarns and coated PA yarns. All the samples were placed under the controlled condition with constant relative humidity at 50% and temperature at 23°C for 48 h before the characterization. The stretching speed was 5 mm/min with the 20 mm length of the samples.

3. Results and discussion

3.1. Fundamental properties of the DR1/PVP system when applied on glass and PDMS substrate

3.1.1. Non-stretched specimens before humidity annealing

To study the effect of the proportional content of DR1 in the material system, the mixture with 1 wt%, 5 wt%, 10 wt%, 25 wt% and 50 wt% DR1 in PVP were prepared. These systems were dissolved as 2 wt% and 4 wt% of dry content in CHCl3. It is assumed that the thickness deposited on the glass slide is approximately equal to the film thicknesses fabricated on PDMS with the same spin-coating parameters. Profilometry results, shown in Table 2, demonstrated that the thickness of a polymer/azobenzene film increases with decreasing spinning speed as well as with increasing solution concentration. As expected, the absorption intensity, confirmed by UV–Vis measurements, increases as a function of increasing film thickness. Thus, for making the material suitable for naked-eye readable sensors, thick films, prepared with 1000 rpm from 4 wt% solution were selected for the further study.

To understand the relevance of the DR1 concentration with respect to the polymer matrix, UV–Vis measurements at fixed spin-coating parameters were conducted, and the results are presented in Fig. 2. The results indicate that the absorption peak for the films of 1–10 wt% DR1 in PVP corresponds to 511 nm. This result can be attributed to the unaggregated DR1 molecules [22,23]. The results of the samples containing 25 wt% and 50 wt% DR1 showed a gradual spectral shift towards shorter wavelength, which is referred to as blue shift, caused by the partial excitonic coupling of adjacent DR1 molecules [24]. Furthermore, excitonic coupling can be also dependent on the pH [25], crystallite size or concentration of the solution [26]. In this case, the DR1 chromophores aggregation is caused by decreased intermolecular distance due to increased chromophores concentration.
To give further support for the hypothesis of the aggregation mechanism, nominal intermolecular distance can be calculated, assuming that the DR1 molecules are equally distributed in the polymer films. The intermolecular distance \( r \) was calculated based on the following equation, adapted from Koskela et al. [27]:

\[
r = \sqrt{\frac{1}{N}} = \sqrt{\frac{M}{w_1 q N_A}}
\]

where \( N \) is the number density of the chromophores, \( M \) is the molar mass of the chromophore, \( w_1 \) is the chromophore weight fraction, \( q \) is the material density, and \( N_A \) is the Avogadro’s number. The DR1 density amounts to 1.1523 g cm\(^{-3}\) [28], whereas the density of PVP equals to 1.2000 g cm\(^{-3}\) [29].

Fig. 3 illustrates that with increasing chromophore concentration, the intermolecular distance decreases. In comparison, Pirrotta et al. showed through simulations that the excitonic coupling can be controlled through manipulation of molecular dimers with single-molecule force spectroscopy. The intermolecular distances of excitonic coupling were computed using the transition atomic charge method and amounted to 0.5–3.4 nm [24]. In this work, the calculated intermolecular distance values amount from 0.96 nm to 3.52 nm. Combining the intermolecular distance results with the UV–Vis results from Fig. 2, the sample containing 10 wt% DR1 in PVP has an intensive absorption peak at 511 nm and an intermolecular distance as 1.94 nm, while excitonic coupling observed in UV–Vis spectroscopy is negligible. On the other hand, for the sample of 25 wt%, the intermolecular distance of 1.21 nm is already reflected as molecular aggregation in the UV–Vis spectra. Consequently, 10 wt% DR1/polymer ratio was chosen for further humidity and stretching test.

3.1.2. Non-stretched specimens after humidity annealing

The sample containing 10 wt% DR1 in PVP was then spin coated on the PDMS substrate and treated by humidity annealing. The UV–Vis measurement was carried out before and after the humidity exposure. As indicated by Fig. 4, the blue shift of the main peak of excitonic coupling were computed using the transition atomic charge method and amounted to 0.5–3.4 nm [24]. In this work, the calculated intermolecular distance values amount from 0.96 nm to 3.52 nm. Combining the intermolecular distance results with the UV–Vis results from Fig. 2, the sample containing 10 wt% DR1 in PVP has an intensive absorption peak at 511 nm and an intermolecular distance as 1.94 nm, while excitonic coupling observed in UV–Vis spectroscopy is negligible. On the other hand, for the sample of 25 wt%, the intermolecular distance of 1.21 nm is already reflected as molecular aggregation in the UV–Vis spectra. Consequently, 10 wt% DR1/polymer ratio was chosen for further humidity and stretching test.

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Fig. 3. Decreasing intermolecular distance as a function of increasing from 0 wt% to 50 wt% DR1 chromophore concentration.

Fig. 4. UV–Vis absorption spectra of DR1/PVP films on PDMS before (red) and after (orange) humidity annealing. The more intensive red peak is located at 511 nm, whereas the less intensive orange peak at 402 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Spinning speed [rpm]</th>
<th>Thickness [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt%</td>
<td>1000</td>
<td>6120.6</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>4241.4</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>3558.4</td>
</tr>
<tr>
<td>5 wt%</td>
<td>1000</td>
<td>6402.8</td>
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<tr>
<td></td>
<td>2000</td>
<td>4328.0</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>3201.5</td>
</tr>
<tr>
<td>10 wt%</td>
<td>1000</td>
<td>6560.7</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>4016.6</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>3554.9</td>
</tr>
<tr>
<td>4 wt%</td>
<td>1000</td>
<td>2422.7</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>16555.8</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>13771.6</td>
</tr>
<tr>
<td>5 wt%</td>
<td>1000</td>
<td>15209.5</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>12760.4</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>11750.2</td>
</tr>
<tr>
<td>10 wt%</td>
<td>1000</td>
<td>16472.6</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>12457.4</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>11171.1</td>
</tr>
</tbody>
</table>

Fig. 2. UV–Vis spectra of the solutions consisting of 1 wt%, 5 wt%, 10 wt%, 25 wt%, and 50 wt% DR1 in 4 wt% of DR1 and PVP in CHCl₃ spin coated at 1000 rpm on glass slides. It should be noted that for the 50 wt% sample the spectrum is saturated due to high number density of chromophores in the film.
occurred from 511 nm to 402 nm upon humidity annealing of the samples. Similar colour change upon humidity annealing was described in the previous research by Schoelch et al. [19] This colour change is visible to naked eye, stable, and it can last for weeks in a low humidity or dry environment.

The humidity-induced colour change can be rationalized by DR1 being hydrophobic compound, while PVP is hydrophilic. When the thin films are exposed to humidity, PVP bounds with water because of water molecules donating stronger hydrogen bonds to PVP, as compared to DR1. At the same time, humidity annealing increases the mobility of DR1 molecules and allows the molecules to come closer to other DR1 molecules than average estimate distance. When the intermolecular distance decreases below the threshold, DR1 favours local phase separation, which means that molecular dipoles stack antiparallel. This state is referred to as H-aggregation [27], which leads to the colour change from red to the orange.

When these films are then exposed to stretching, gradual disaggregation of DR1 aggregates occurs, resulting in the colour change back to red. As is well known, the excitonic coupling is very sensitive towards the intermolecular distance and its variations. Analogously, the computational study of Pirrotta et al. reports tuning the energy of exciton coupling from 0.02 eV at the folded structure to 0.15 eV at the elongated form of the dimer [24]. In the current system, advantage of the interplay of multiple supramolecular interactions in the molecular system was taken allowing creating a system that is very sensitive to mechanical deformation.

3.1.3. Stretched specimens after humidity annealing

For better understanding of the work, a schematic of the stretcher used throughout the experiments is shown in Fig. 5a. By applying a horizontal force and therefore stretching the sample located in the middle of the device, the colour gradually changes from orange to red. Fig. 5b presents photographs of the PDMS samples in the stretcher as a function of elongation. The non-stretched film (0% elongation) has an orange tone. The higher percentage of stretching, the more visible the colour change towards red is. Notably, elongating the double layer of humidity-annealed DR1/PVP complex and PDMS substrate does not give rise to a surface wrinkling, as is typical for analogous non-humidity exposed system [30]. Thus, the molecular mobility in the present humidity-annealed system is enough to prevent buckling as well, as to enable gradual increasing of intermolecular distance and therefore weakening of exciton coupling, upon stretching up to 80%.

A well visible mechanochromic colour change of the film was also confirmed with UV–Vis spectrometry. Fig. 6a shows that the peak at 511 nm becomes more pronounced as compared to the peak of the aggregated DR1 at 402 nm with the increasing percentage of stretching, thus indicating an overall colour change. In Fig. 6, the difference in the red peak amounts to 0.16 as the starting peak is at 0.63 and the final peak at 0.79. The increase equals to 25%. The results were obtained for 3 samples, all elongated to at least 55%, and therefore it can be concluded that such mechanochromic behaviour is repeatable. Analogous results were presented by Rossi et al., who showed mechanochromatic changes in the emission spectra of [3-(pyren-1-ylmethoxy)propyl]triethoxysilane (Py-TEOS) labelled PDMS elastomer upon elongation to 16.7% of strain. Emission values decreased due to relaxation and the effect was reproducible over the surface of the sample [31]. In contrast to the reference article, current material exhibits mechanochromism in directly observable absorption, which enables a less complicated assessment. Moreover, this material enables elongation coupled to stepless colour change to higher strain values. Based on the UV–Vis results, the ratio of absorption intensity at 402 nm and 511 nm can be employed as the key parameter correlating linearly with the strain of the material, as shown in Fig. 6b.

In order to confirm the continuous colour change from orange to red, RGB analysis of the photographs for the humidity annealed samples was performed. RGB analysis can be used to obtain more accurate stretching state as compared to the naked eye. It is a reliable method used for different applications especially popular in indicating freshness of food, such as apples [32], chicken meat [33], fishes [34] and bell pepper fruits [35]. Furthermore, the RGB data could help to build modelling then estimate and predict the quality and status of the agricultures [36–38].

The RGB results, shown in Fig. 7, indicate that the red, green, and blue channel values decrease gradually with the increasing percentage of stretching. Thus, the colour intensity of the sample decreases. As shown in Fig. 7, red values decreased by 2.2%, green by 7.8%, and blue by 4.0% when stretched from 0% up to 85%. Since the red channel decreases the least in comparison to the green and blue channels, and these two channels decrease significantly, the final film appears more red. This demonstrates that the mechanically-induced gradual changes of the intermolecular interactions can be easily observed as a change of the hue of films captured by digital time lapse photography.

3.2. Fundamental properties of the DR1/PVP system when applied on a yarn

The mechanochromic DR1/PVP films described in this article can also be integrated into textiles. To prove the concept, experiments on different yarns were carried out. Such yarns have to fulfill three requirements, namely they have to be elastic enough to stretch to at least 50%, their materials cannot interact destructively with the polymer nor chromophore, and their colour should not influence the output. A summary of tested yarns with observations is presented in Table 3. According to the tests, a nylon yarn was
stretched to maximum 30–35% which is not enough to observe the full spectrum of colour change from orange to red. On the other hand, a white yarn consisting of 50% nylon and 50% poly(urethane) was stretchable, but the desired tone change was not observed. Upon stretching, the red colour became brighter due to the white shade of the yarn and wrinkles appeared.

PA yarn consisting of Nylon 66 met all aforementioned requirements. Thus, it was decided to use it in the further experiments.

The PA yarns were dip-coated at 10 mm/min in the DR1/PVP solution and left to soak for 30 s. Next, the yarns were withdrawn at 10 mm/min. Alike in case of PDMS samples, dip-coated yarns were subjected to humidity annealing for the average time of 1.5 min. After humidity annealing, the yarns were stretched up to 75% elongation, as shown in Fig. 8. The colour changing before and after stretching is visible to the naked eyes. The tone of the non-stretched yarn is clearly dark orange, whereas the yarn becomes dark red when stretched to 75% state. To determine the mechanical properties of the stretchable yarn samples, the tensile test was performed for both the uncoated and coated PA yarns. The results of the strains at the breaking point were 51.6 ± 4.2% for pure PA yarn, whereas the coated PA yarns broke at 51.6 ± 5.2% strain, which indicated that the stretchability is mainly dependent on the mechanical properties of the substrates.

The dip-coated yarns were analysed with the time lapse photography. Fig. 9 presents the RGB analysis of all R, G, and B channels of the yarn samples as a function of stretching. The value of the red channel decreased by 2.3%, the value of the green channel decreased by 31.6%, and the blue channel decreased by 12.2%. The colour of the substrate is an important difference between films deposited on PDMS and these PA yarns, the yarns being white, whereas PDMS being transparent. Thus, due to the difference in the transparency of the substrate – and the directly-related apparent colour, the slope inclination in all channels of the resulting colour change shown in Fig. 9 slightly varies as compared to Fig. 7.

Cyclic stretch/release experiment was conducted to present the repeatability of the textile samples. The cyclic samples were prepared with abovementioned methods. However, considering the mechanical properties of the yarns, after humidity annealing, the samples were stretched with 5% increment to 30% strain and then released and left in ambient condition to recover the colour back to

---

**Table 3**

Summary of all yarn types used in the experiments including the desired stretchability (>50%) and observation of the aimed colour change from red to orange.

<table>
<thead>
<tr>
<th>Yarn type</th>
<th>Desired stretchability</th>
<th>Observed colour change</th>
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</thead>
<tbody>
<tr>
<td>Elastan (100%)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Elastan (100%)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Extrafine merino wool with PBT (95:5%)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Linen/lycra (90:10%)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Nylon</td>
<td>No</td>
<td>–</td>
</tr>
<tr>
<td>Poly(urethane)/nylon (50:50%)</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Polyamide (PA) yarn (Nylon 66)</td>
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<td>Yes</td>
</tr>
<tr>
<td>Polyester (PES):elastan (90:10%)</td>
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<td>No</td>
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<tr>
<td>Polypropylene (PP)</td>
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<td>No</td>
</tr>
<tr>
<td>Wool</td>
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</table>

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Fig. 6. a) Normalized UV–Vis absorption spectra dependent on the percentage of stretching of the samples. The lower stretching values starting from 0% are marked with darker colours. The maximum elongation percentage amounts to 55%. The well-visible increase of the 511 nm peak area proves the increasing red colour tone. b) The ratio of absorption intensity at 402 nm to 511 nm as a function of the materials strain, the dash line is the linear fitting. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Decrease of the red, green, and blue channel values as a function of stretching from 0% to 85% of the DR1/PVP film deposited by spin coating on the flexible substrate PDMS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Additionally, heating by a heating plate can speed up the recovery process. The colour changing was analysed by the RGB of the photography taken at each stretched state. However, due to the mechanical failure of the PA yarns, the samples broke during the 4th cycle. The raw data of R, G and B channels from cyclic experiment of one sample was presented in Fig. 10a, which indicated that upon each cycle, the colour change and recovery occurred upon stretch and removal of the humidity. However, the efficiency of the colour change decreased upon repeating. As shown in Fig. 10b, the ratio of values at each stretching step to the original value from the green channel increased with the cycle number, which indicated the decrease of colour change efficiency.

To contextualize the application potential of these type of textile-integrable sensors, the mechanochromic yarns have shown great potential to be applied in numerous fields from previous reports. Compression therapy, in which controlled pressure gradient is applied to a patient’s body part like limb, is used in treating post-surgical hematoma, lymphedema, chronic venous ulceration, burn-related wounds and other medical conditions. Sandt et al. [39] have demonstrated how slightly more complex PDMS-based yarns can be employed in sensing the bandage pressure. By implementing stretchable PDMS/polystyrene- polyisoprene triblock copolymer (PSPI) fibres in the bandage and stretching the yarns up to 75%, colour change occurs. This colour change informs a patient about a dangerous pressure put on a limb instantaneously and prevents from resulting medical conditions advancing sub-bandage pressure measurements. The phenomenon is visible for the naked eye in form of colour change from red, through orange, yellow, green, and light blue, to dark blue due to variations in location of fibres’ reflection band in the visible light spectrum as the fibre’s diameter and cladding layer period change.

To sum up, the demonstration of a mechanochromic yarn that can be stretched up to 75% is a straightforward step towards integrating the elements constituting the textile and the functional coating into one single entity. This approach can overcome the problems of a conventional textile integration of imprinting or implementing functional elements of the surface of textiles causing many problems due to the mismatch of the mechanical properties [40,41]. Moreover, as compared to typical strain sensors based on elongation-induced resistance changes in conductive materials, this system, which is based on the elongation-induced changes of molecular aggregates in a soft material, is easier to integrate on purely soft materials substrates without the need of complex fabrication processes, such as layering of different nanocomposites [3]. Furthermore, although the DR1/PVP film is sensitive to humidity, according to the previous research [19] and the cyclic experi-
ments, the humidity during the stretching process can be considered relatively constant for the timescale of hours. However, when a humidity annealed DR1/PVP film is exposed to room temperature for a longer time, the colour will change back to red because of the slow evaporation. Therefore, in case longer device lifetime would be required, the device could be encapsulated.

4. Conclusions

The mechanochromic polymer/azobenzene supramolecular complex was optimized both for thickness and for the relative chromophore content to give films of gradual colour changes upon stretching. Unlike conventional strain-sensors based on elongation-induced changes in resistivity, the sensor presented in this article is based on delicate changes in molecular aggregation, directly reflected in the UV–Vis absorption spectra of the samples. This extremely simple, although sensitive system can be easily integrated in many different organic substrates without the need of adding bulky extra components, such as power source or electronic contacts.

The colour changes from red to orange due to the humidity exposure and gradually back to red as a result of stretching were characterized. The physical principle behind this sensor can be assigned to variation in antiparallel stacking of DR1 molecules, which is directly reflected in the UV–Vis absorption. This allows preparing mechanical sensors based on simple time-lapse photography and RGB analysis. The potential integrability with fabrics was demonstrated by depositing the film on yarns and reproducing the experiment. Yarn samples were stretched to 75% and the RGB analysis, which showed a gradual decrease of all three channel values, was performed. Furthermore, the colour change on the yarns is repeatable with a slight decrease in efficiency upon three cycles. All in all, as compared to conventional strain sensors, the fabricated sensor based on elongation-induced changes of molecular aggregates is much easier to integrate on substrates of soft materials due to a simple fabrication process.

Declaration of Competing Interest

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

Acknowledgements

The work was performed in the School of Chemical Engineering at Aalto University. The profilometry measurements were performed in Nanotalo which is a part of the Department of Applied Physics in the School of Science at Aalto University. The work was supported by Academy of Finland SUPER-WEAR project (decision number: 322214).

Data statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

References


