



## Utilizing Smart Chromic Dyes in the Textile Sector

Amina L. Mohamed<sup>1</sup>, Hager M. Y. Okda<sup>1</sup>, and Mohamed Salama<sup>2</sup>

<sup>1</sup> National Research Centre (NRC), Textile Research and Technology Institute (TRTI), Pre-treatment and Finishing of Cellulose based Textiles Department (PFCTD), El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt

<sup>2</sup> College of Food Science and Technology, Huazhong Agricultural University, Wuhan, Hubei 430070, China

### Abstract

When woven into fabric, color-changing fibers have the potential to extend the capabilities of intelligent wearable devices to a broad variety of configurations. The incorporation of features into conventional fabrics is one of the reasons why chromatic textiles are being considered. The goal of this study is to present and discuss the overall usability of chromic textiles by evaluating recent breakthroughs in order to pave the way for future research in this field. This will be accomplished by describing the overall usability of chromic fabrics. A comprehensive review of the recent advancements in smart chromic textiles is offered here, with the current state of the art serving as the basis for the presentation. All aspects of chromic textiles, including their applications, experimental verification, performance characterization, main barriers, and future research targets, are investigated. Keyword: Smart dyes, color change, chromic dyes, thermchromic, photochromic

### Introduction

Dyes have traditionally been used in textiles for colouring purposes. Previously, consumers purchased textiles for their aesthetic value. Consumers now have several options as they can get a colored textile, not only normal textile dyed with traditional dyes, but also fabrics dyed with a smart dyes that has a chromic effect. [1] Chromic concepts are given names with the suffix chromism followed by a prefix that refers to the stimulus that caused the colour change. [2] Through induced stimuli (temperature, humidity, brittleness, pH, ionic characteristics, chemicals, etc.) as shown in Figure 1, several natural or manmade materials display optical changes (colour, transparency, reflectance). [3] These substances are referred to as "chameleon" or "chromogenic materials" because they are described as color-changing substances even if their optical characteristics do not change. [4]

### Electrochromic dyes

Electrochromic dyes are based on electrochromism, which involves reversible colour changes caused by electricity (electronic gain and loss). This mechanism is common in transition metal oxides, which conduct both electricity and ions. A strong electric field has been found to change the colour of

certain dyes. A good example of electrochromism is phthalocyanine dye. Polyaniline is a common electrochromic substance. Electrochromic dyes can also be used to create smart window curtains that filter sunlight correctly and also camouflage is one of the application of Electrochromic dyes. [1, 5]

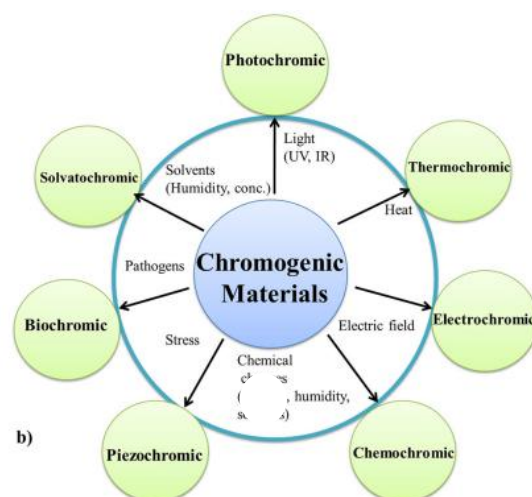


Figure 1: Examples of Color change of chromogenic materials on the basis of the stimuli involved [6]

\*Corresponding author: Mohamed Salama, E-mail: 2506902492@qq.com

Receive Date: 15 July 2024, Accept Date: 01 September 2024

DOI: 10.21608/jtcsps.2024.304625.1384

©2024 National Information and Documentation Center (NIDOC)

### Chemo chromic dyes

Chemo chromic dyes shift colour due to pH variations. pH sensitive dyes include phthalides, fluoranes, triarymethines, and simple azo dyes. As methods of application for chemo chromic dyes, conventional exhaust dyeing, solgel technique, and before addition to electrospinning solution have been reported. Chemo chromic dyes can be used to detect proteins (of particular bacteria) based on colour change. This color-changing identification reveals the presence of bacteria in textiles. As a result, the application field of chemochromic dyes can be expanded to include medical textile bandages. [7, 8]

### Solvatochromic dyes

Solvatochromic dyes operate on the Solvatochromism principle, which corresponds to reversible colour shifts caused by solvent polarity. The colour change is caused by a shift in the maximum absorption of various solvents. [9] Positive solvatochromism and negative solvatochromism are the two forms of solvato chromism. Positive solvatochromism corresponds to a hypsochromic shift caused by a decrease in solvent polarity, while negative solvatochromism is caused by an increase in solvent polarity. [10] Solvatochromic dyes such as pyridinium, merocyanine, and stilbazolium are common examples. Solvatochromic dyes can be used in textiles through the microencapsulation process. The formation of microspheres on fabric produces colour changes while drying and wetting. The use of Solvatochromic dyes in textiles is extremely limited. Because of the colour shift of packaging, these dyes can be used to identify stale or dangerous food. [11]

### Mechanochromic dyes

Mechanochromism is the phenomenon in which the colour of a polymer changes owing to deformation such as elongation and compression. Changes in pH and temperature cause elongation and compression. Mechanochromic dyes are organic dyes that are applied to polymers and create colour variations in response to mechanical pressure. Mechano-chromic dye cannot function alone; it requires a polymer (material) to deform (elongate or compress). Mechano-chromic colourants can be physically distributed in a polymer matrix as supramolecular aggregates. Covalent insertion of chromophoric units into the backbone or side chains of macromolecules has also been employed to apply mechanochromic colourants. Mechanochromic dyes can be used in the footwear and shaped garment industries, where the product's colour can change owing to deformation. [12-14]

### Thermochromic materials

When you hear the suffix thermo, the first thing comes to your mind is heat. Thermochromic materials that used in manufacture aesthetically textiles can

reversibly (or permanently) modify their hue, colour intensity, or transparency, if the temperature changes. [15] When activated by a change in temperature, thermochromic textiles can change their colour reversibly from a colourless to a coloured state. [16, 17]

### Classifications of Thermochromic materials

Depending on the type of thermochromic material, four materials has been discovered: [18]

- 1- Organic substances.
- 2- Inorganic substances.
- 3- Polymers.
- 4- Hydrogels.

### Organic Thermochromic Systems

Organic thermochromic technologies are employed in a variety of applications, including fibers, optics, photo-storage devices, and optical sensors. Depending on the chemical structure, different thermochromic processes may be applied. It can happen as a result of molecular species like acid-base, keto-enol, lactim-lactam, stereoisomers, or different crystal structures interacting. The mechanism is classified into three major groups:

1. Crystal structure modification
2. Stereoisomerism
3. Molecular reorganization

#### Crystal structure modification

Many organic compounds can produce stable transitional phases as they transition from crystalline solid to isotropic liquid. Transitions between phases can be caused by the effect of either temperature (thermotropic mesomorphism) or solvent (lyotropic mesomorphism). [19] The cholesteric (chiral nematic) liquid crystals as shown in Figure 2 are the most essential types of liquid crystals for thermochromic systems, where neighboring molecules are organized in helices.

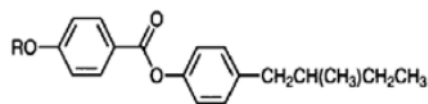


Figure 2: Cholesteric mesophases from chiral molecules [18]

Temperature can affect liquid crystal light reflection by reflecting the structure of helices. The wavelength of reflected light is determined by the liquid crystal's refractive index and the pitch of the molecules' helical configuration as illustrated in Figure 3, when the temperature changes, so does the pitch length. As a result, the wavelength of the reflected light changes, generating a progressive shift in the color spectrum. [20] To generate thermochromic effects in a fabric, the liquid crystal material must be

microencapsulated, and these microcapsules, like pigments, are applied to the fabric using an appropriate resin binder.

### **Stereoisomerism**

Stereoisomerism, which is usually related with ethylenes, is thermochromism caused by changes in stereoisomers. The molecules of these compounds 'switch' between different stereoisomers when the temperature rises. The color of the compounds changes as a result of this transition. The majority of compounds that exhibit stereoisomerism develop color above their melting point, which is typically greater than 150°C. As a result, they are inappropriate for use as thermochromic colorants in textiles. [18]

### **Molecular Rearrangement**

An organic compound's molecular rearrangement can result in increased molecule conjugation and the development of a new chromophore. Temperature changes, changes in the polarity of the solvent, and/or changes in the pH of the solution can all influence this sort of chemical rearrangement. Because the acid-base balance is temperature dependent, pH sensitivity can result in thermochromic behavior. Using crystal violet lactone as an example, the molecular rearrangement of spirolactone dyes can be demonstrated. [18]

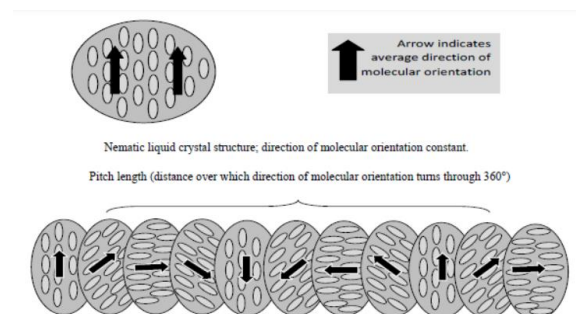


Figure 3: Structure of cholesteric liquid crystal structure, The direction of molecular orientation shifts gradually between layers. [18]

The two types of thermochromic systems that have been effectively implemented on textiles are crystal structure modification and molecular rearrangement.

### **Inorganic Thermochromic Systems**

Many metals and inorganic substances display thermochromic activity in solids or solutions [37-40]. It has been proposed that such thermochromic behavior results from one of the following mechanisms: [41]

- Phase transitions
- Changes in ligand geometry;

- Equilibrium between distinct molecular structures;

- Changes in the quantity of solvent molecules in the co-ordination sphere (e.g. dehydration)

Inorganic thermochromic methods have not been widely used in textiles since the color change happens at high temperatures or in solution. The color change is also irrevocable. These should be reversible, solid (or encapsulated) systems that are suited for dyeing and printing applications if they are to be used on textiles. In addition, it should change color across a narrow temperature range, typically from low ambient temperatures to body temperature for garments. In organic systems, they can be found in crayons that warn of the development of heat spots, heat-indicating paints, and/or a permanent record of an object's thermal history.

### **Polymers used in Thermichromism**

#### **Polymers in inert thermochromism**

This category includes liquid crystalline and conjugated polymers. [21] When exposed to visible light, liquid crystal polymers with chiral molecular structures develop helical superstructures and exhibit a Bragg's reflection kind of thermoresponsive phenomenon. [22] Cholesteric liquid crystalline polymers are the most frequent liquid crystalline phase. The pitch length of this form of liquid crystalline polymer changes with temperature, resulting in thermochromism colour variations. Cholesteric liquid crystalline polymers, polymer gels and thermochromic pigments, which are microencapsulated cholesteric liquid crystals with a low molecular weight, are examples of liquid crystalline polymers. [23] Among these, cholesteric liquid crystalline polymers are the most studied and commercially available. The conjugated polymers are also thermochromic by nature. [21] They have a conjugated p-electron system, which means they have a backbone chain made up of alternate double and single bonds. These polymers are coloured because they absorb visible light, and their colour changes when their conjugation state changes with temperature, resulting in thermochromism. Even minor changes in their structure, such as changes in stereoisomeric form, result in considerable colour shift during a phase transition. [24] Conjugated polymers, in general, have reversible thermochromic effects. However, irreversible thermochromism will be found if the thermal treatment is kinetically controlled. Polyacetylenes, [25] polydiacetylenes (PDA), [26] polysilanes, polythiophenes, [27] and poly-diacetylenes (PDA) are examples of conjugated polymers (phenylenevinylene). [28] Polymers with overcrowded partial stems of polycyclic aromatic groups exhibit another form of inherent thermochromic effect. The thermochromism is noticed for the higher thermal atomic oscillations of the deformed molecules found in the polymer's congested partial stems.

### ***The thermochromic pigments are embedded in polymers.***

Polymer microencapsulated leuco dye-developer-solvent systems are the most often utilised thermochromic pigments. A polymer shell often isolates the thermochromic core, which is essentially a mixture of leuco dye, a developer, and a solvent. They are often pigmented in the solid state but convert to a colourless liquid when heated. There are a few examples of colour changes that occur during the phase shift from liquid to solid. [29] Crystal violet lactone (CVL)-lauryl gallate (LG)-long-chain alcohol (LCA) system is an example of a leuco dye-developer-solvent system. The system is made up of three components mixed in the molar ratio 1:6:40. LG and LCA react violently to generate the colourless chemical (LG)<sub>2</sub>-LCA. LG interacts poorly with LCA and strongly with CVL in the molten state, leading in the production of colourful complexes of the formula (LG)<sub>x</sub>-CVL, where x can vary from 3 to 9. Slow cooling causes the evacuation of CVL from the (LG)<sub>x</sub>-CVL, resulting in the creation of the colourless (LG)<sub>2</sub>-LCA molecule. LCA also functions as a decolorizer in this case by complexing with the CVL and deactivating it. [30, 31] Cholesteric liquid crystals with low molecular weight can also be employed as a component of thermochromic pigment composites. In the case of thermochromic pigments, the typical art for technical progress is microencapsulation of the pigments by a suitable polymer. [32]

### **Hydrogels**

Because of the existence of hydrophilic molecules within their chemical structure, hydrogels are crosslinked or hydrogen-bonded polymeric networks that are swelled with significant amounts of water. Hydrogels can display both thermochromic and thermotropic characteristics and have been successfully produced for a wide range of applications including camouflage fabrics, drug release textiles, drug delivery textiles, temperature sensors, smart windows, and many others. [33-35]

Poly(N-isopropyl acrylamide) (PNIPAM), [36-38] hydroxypropyl cellulose (HPC), [33] poly(acrylic acid), [39] and poly(vinyl alcohol) are examples of thermochromic hydrogels. [40] Phase transformations between isotropic and anisotropic phases via changes in the lyotropic liquid crystalline structure and the generation of temperature-responsive micelles are a common process for thermotropic hydrogels. [32]

### **Mechanism of Thermochromism**

Thermochromic devices change colour in response to temperature changes, which are usually reversible, and can be induced directly or indirectly. [31] The term "**direct thermochromism**" refers to the effect of temperature on a chemical without the use of any other agent. Color changes can occur in

this circumstance due to reversible bond breakage, chemical rearrangements, and stereoisomerism. Color change in **indirect thermochromism** is caused by reversible chemical reactions between a chromophore (a molecular region of a compound where the energy difference between two atomic orbitals falls within the visible spectrum range) and the other components in the system. In this situation, the heating of the system causes these reactions, and the chromophore molecule is not thermochromic in and of itself, but exhibits this behaviour due to interactions with other components of the mixture when the system temperature is raised or decreased. [41]

The **liquid crystalline type** and **leuco dyes** are two thermochromic system kinds that have been used successfully in textiles. [42] The liquid crystals, although this method can produce subtle and very sensitive color effects, they have limited textile applications due to their high cost and low color density. Chiral nematic liquid crystalline homologues of esters as shown in Figure 4 have been applied in commercial thermochromic products. [43]

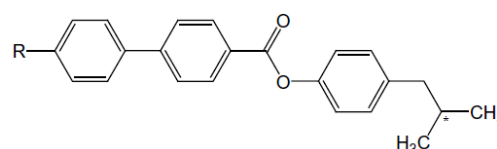


Figure 4: Chiral nematic liquid crystal molecular structure (asymmetric centre)

The most common type of thermochromic dye is leuco dye, which is made up of three components: **dye, solvent (in solid form), and color developer**. [39, 44] The developer's role is to act as a proton donor to the thermochromic compound. [45] The temperature at which the transformation between the colorless and colorful states occurs is controlled by both crystallization and the melting point of the solvent. [29] In this mechanism, two competing reactions occur: between the solvent and the developer and between the developer and the dye, and the facilitation of thermochromism is dependent on the strength of solvation and intermolecular contacts. [46, 47]

Alcohols, hydrocarbons, ester, ketones, thiols, and alcohol-acrylonitrile mixtures are the organic solvents employed in microencapsulation. N-acyl leuco-methylene blue derivatives, fluoran dyes, and diphenylmethane compounds are useful thermochromic colourants. There are numerous chemicals that act as colour developers, including phenol derivatives, notably bisphenol A and bisphenol B. Recently, 1,2,3 triazoles such as 1,2,3 benzotriazole, dibenzotriazole, thioureas, and 4 hydroxy coumarin derivatives have been used in research. [48]

A colorless dye precursor and a color developer are both dissolved in a hydrophobic, non-volatile organic solvent in reversible thermochromic systems, and the solution is then encapsulated so that all three components are retained within a single closed system. The microencapsulation of the leuco dyes ensures the duration of their use, as they are prone to fading without such a barrier. [49, 50] When heated, the organic solvent melts, resulting in either color development or color loss. When the solvent cools, it hardens and the system returns to its original color. [51] Although reversible thermochromic colorants are commercially available with activation temperatures ranging from 15 to 65 °C, most applications are limited to three conventional temperature ranges: cold (about 10 °C), body-heat activated (around 31 °C), and warm (around 43 °C). [52]

At lower temperatures, the dye-developer interactions take precedence while the solvent is solid. The solvent dissolves at high temperatures, increasing its reactivity with the developer and allowing a color change to a colorless state. However, the most typical mechanism of thermochromism in leuco dyes is a change in molecular structure, specifically the lactone ring-opening as shown in . Ring opening, is one of the various mechanisms of thermochromism is illustrated in Figure 5

This ring-opening, aided by a developer in the form of a weak acid, is followed by the development of covalent bonds between an electron donor (chromogenic molecule) and an electron acceptor, allowing for the elongation of conjugation and the formation of its characteristic visible hue. [43, 53]

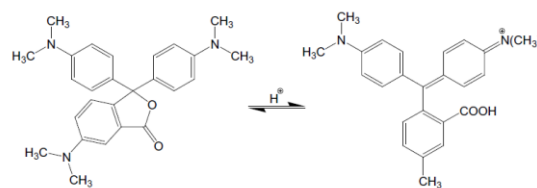


Figure 5: Protonation of crystal violet lactone (thermochromic mechanism) [2]

**Application of Thermochromic dyes in Textiles**

There are many applications of thermochromic dyes in textile industry. It can be applied in spinning of the fibers, dyeing and textile printing.

Li et al. in their work (2022) developed a low-cost, practical, and scalable method for wet spinning thermochromic fibres. It is possible to create flexible fibres with numerous and reversible colour changes by combining various thermochromic microcapsules. The naked eye can easily see these colour changes. Additionally, even after 8000 heat cycles, the fibres still show exceptional color-changing stability. The thermochromic fibres may also be easily woven or implanted into a variety of fabrics with good mechanical performance and can be produced on a big scale. Thermoplastic polyurethane particles ( 1 mm) were cleaned in pure ethanol before being vacuum-dried at 70 °C for about 4 hours. The particles (40 g) were then combined with 180 mL of dimethylacetamide (DMAC, 95%) to create a solution.

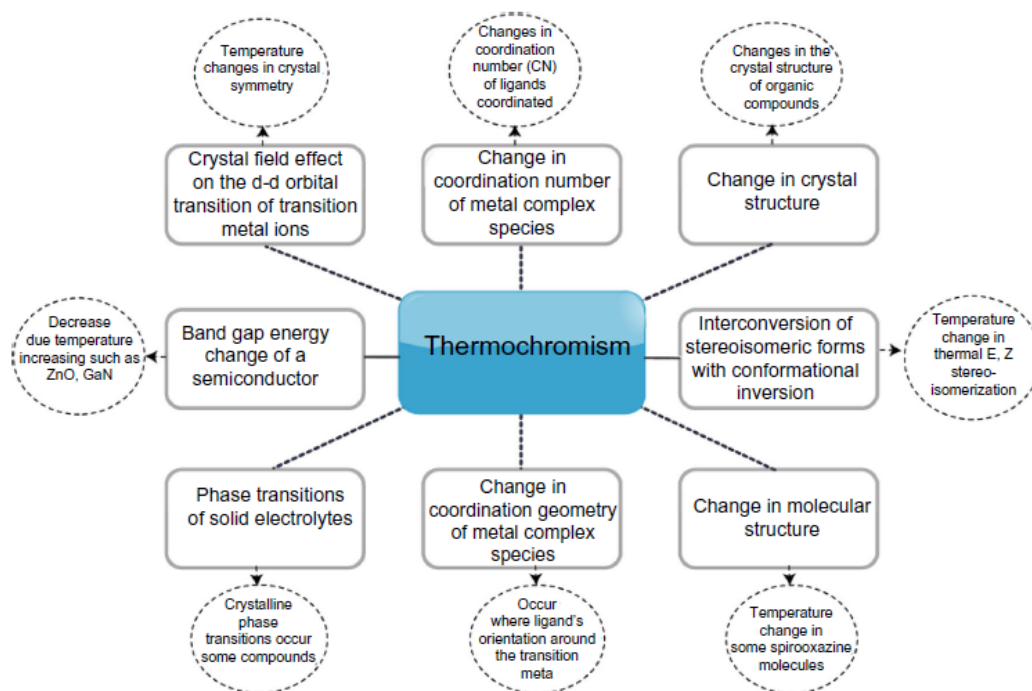


Figure 6: Various mechanisms of thermochromism. [32]

A thermochromic spinning stock solution was created by combining the polymer solution with a thermochromic microcapsule (TCM, 10 g, 9 m). Wet spinning machines made to order were used to create thermochromic fibres. At room temperature, 0.35 mL/min of the thermochromic spinning stock solution was introduced into the coagulation bath (deionized water). The traction motor was used to maintain a constant speed as the thermochromic fibres moved through the coagulation bath. [54]



Figure 7: A continuous spinning mechanism used to create thermochromic fibres [54]

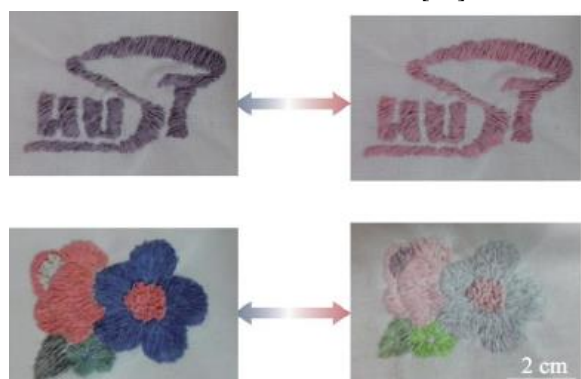


Figure 8: Thermochromic yarns and their color change between 31°C and 55°C [54]

It is proved using temperature control that the patterns on the thermochromic cloth may be modified dynamically. As an example, they created a fabric that displays numbers ranging from 0 to 9. To accomplish this objective, thermochromic fibres and commercial wool were woven into fabric in the shape of a "8," which comprised of seven independent pieces, each of which could be individually changed to 55 °C as illustrated in Figure 9.

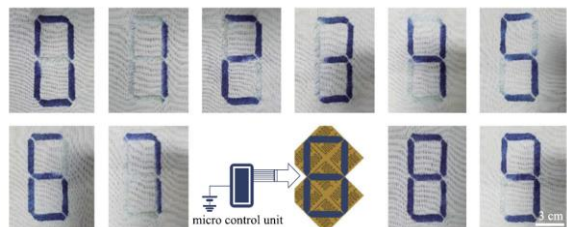


Figure 9: Thermochromic fabric numbers from 0 to 9 with the color change at Temp. 55°C [54]

Zhang *et al.* (2022)[12] used melt spinning to create a series of reversible thermochromic produced fibres incorporating thermochromic pigment microcapsules. There is also advancement in the field of smart textiles with various organic polymers, such as

poly (alkoxythiophenes). When underheated, this polymer's reversible intrinsic thermochromism changes from red-violet to yellow. The process in this situation is based on changes in the crystallinity and molecular conformation of the polymer. [55, 56]

Tozum *et al.* (2022) developed cotton and wool fabrics that have both thermoregulation and thermochromic characteristics. Three-component thermochromic systems (TCTS) were microencapsulated and applied to pure cotton and wool textile fabrics to achieve this goal. The researchers used an emulsion polymerization approach to microencapsulate TCTSs made of crystal violet lactone (CVL), bisphenol A (BPA), and myristyl alcohol in a shell of poly(methyl methacrylate-co-methacrylic acid) (P(MMA-co-MAA)). Under appropriate reaction circumstances, microcapsule wall architectures were engineered to have affinity for cotton and wool fibres. Microcapsules with a spherical form, compact morphology, and an average size of 23.24 nm were successfully manufactured. These microparticles have a latent heat energy storage capacity of 197.7 J/g as well as the necessary thermal stability for textile application process conditions. The exhaustion method was used to apply P(MMA-co-MAA)/TCTS microcapsules to cotton and wool textiles. A substrate absorbs the chemicals in the bath in the procedure, and the affinity between the chemicals and substrate molecules determines the exhaustion process. The structural, colorimetric, and thermal properties of microcapsule-applied fabrics were investigated. The fabrics' colours changed reversibly as a function of temperature. Their colours were blue at room temperature and the original colour of the fabric at temperatures over the thermochromic system's activation point as illustrated in Figure 10. Furthermore, the cotton fabric stored 23.4 J/g of latent heat, but the wool fabric stored 62.1 J/g. They had thermoregulation properties due to the absorbed latent heat. [16]

Karpagam *et al.* (2016) designed printings on cotton fabrics that can change colour (chameleon-like) using thermochromic colourants for military applications. Blue and orange thermochromic colourants combined with turmeric (a natural dye) and graphite have been used to create a variety of coloured coatings, including bright green, dark green, black, brown, and sandal. In order to improve the thermal conductivity of the fabric and make the heat distribution and colour change faster and better than with conventional thermochromic coatings, graphite is added to the thermochromic coatings of the fabric. The printed colour pattern imitates a jungle motif (traditional green and brown camouflage), which when heated by outside sources changes to a desert colour motif (using hot air oven or electrical power). According to the test results, the brown colour was the most sensitive of all the colours tested. Dark green fabrics took a very long time to change colour at 40 °C compared to fabrics dyed brown. Dark-green shade restored its original hue in 63

seconds but brown shade required a very long period or extremely low temperature to do so. For the light-green colour, the colour shift became apparent in 72 seconds, whereas it took 198 seconds for the colour to return to its original state. All colours took less time to change from their original colours as the temperature goes up. But as compared to sandal and brown colours, light green and dark green exhibit better response when considering the ability of their native colours to restore. [57]

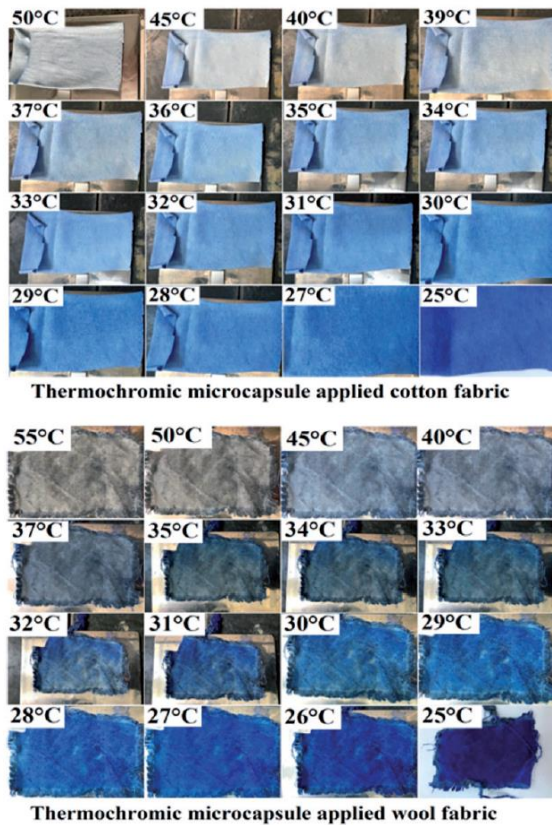


Figure 10: Thermochromic microcapsules applied on cotton&wool fabrics [16]

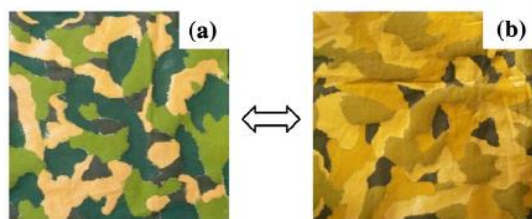


Figure 11: Printed camouflage fabric and its reversible color change  
a)without heating, b)after heating at 60C for 2 min [17]

According to Garcia-Souto (2018), thermochromic pigment applied to a specific region of cloth could be used as a non-invasive and wearable early fever detection device for young babies. As a result, the authors looked into appropriate skin sites and skin temperature threshold values that corresponded

to the development of fever. However, there was no direct application of the thermochromic cloth. Bio-sensing also made use of thermochromic cloth as shown in Figure 12. [58]

**Photochromic dyes**

Photochromism is described as a reversible colour shift caused by light or a reversible transformation between two different chemical structures with different absorption spectra caused by electromagnetic radiations. [11, 12] In photochromism, a colourless molecule becomes coloured in the presence of UV light [4].

Photochromic dyes are classified as either inorganic or organic compounds. Metal oxide, alkaline earth metals, sulphides, copper compounds, and mercury compounds are the most important inorganic kinds. Organic types are effective and environmentally friendly, and they are members of the spiropyrans, spirooxazines, chromomenes, fulgides, fulgimides, and diarylethenes families. Spiropyrans, spirooxazines, and chromomenes are thermally sensitive and revert to a colourless state when exposed to heat or visible light, but fulgides, fulgimides, and diarylethenes are thermally stable. Spiropyrans are of more scientific interest than any other class. [59]

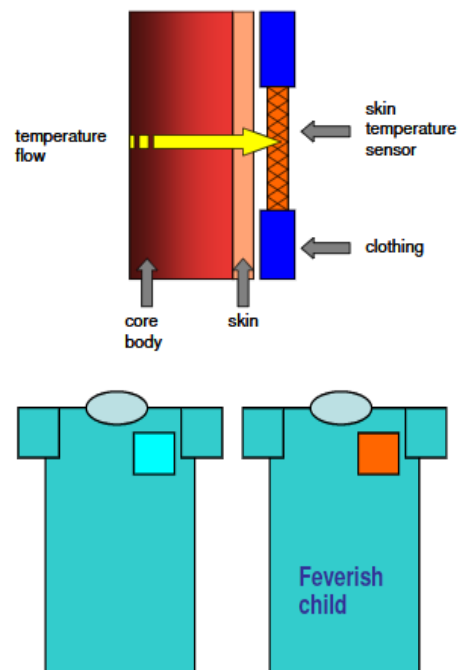


Figure 12: a) Thermochromic applied over the skin, b)possible location of the thermothromic dyes on the garment [58]

**Types of photochromic dyes**

**Spiropyrans**

Spiro compounds have a pyran ring that is bonded to another heterocyclic ring via the spiro group. Because of their ease of production and

ability to create reversible deep hues, spiropyrans have been widely employed in commercial applications. [60, 61] The photochromic effect in spiropyran is caused by a reversible light-stimulated molecular rearrangement of the colourless spiropyran form through ring opening, which results in the formation of the colourful photomerocyanine as shown in Figure 13. Photomerocyanine is usually violet or blue in hue. [43, 62]

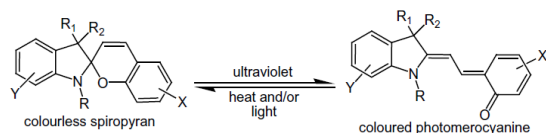
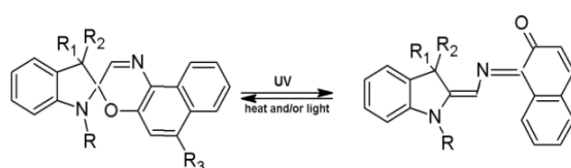


Figure 13: Photochromic performance of spiropyran; R=alkyl; R<sub>1</sub>,R<sub>2</sub>=alkyl; X,Y=H,halogen,nitro [43]

### Spirooxazines

Spirooxazines have a nitrogen atom in place of a carbon atom in the spiro group. These colourless molecules feature a nonplanar structure, which prevents electron delocalization in the molecules. In the presence of UV light, molecules absorb photon energy, causing the -C-O- link in the pyran ring to break and the production of a colourful planar structure molecule. The planarity of the molecule allows electron delocalization, and the molecule becomes coloured. This is a short-term phenomena in which molecules return to their original structure after being exposed to heat or visible light (colorless) as shown in Figure 14. [48, 63]

Spirooxazines, like Spironaphthopyrans, change colour when exposed to UV radiation, from colourless to pale yellow to red, purple, or blue. All compounds are photocolourable due to their huge molar absorption coefficients, high reaction yields, and comparatively delayed bleaching kinetics. Spirooxazines have been studied as nylon, polyester, and acrylic dispersion dyes. They observed that by gently washing the dyes, the strength of the photochromic effect induced may be increased. This could be because aqueous alkaline surfactant treatment enhances dye transport, colourant fibre interactions, and colourant disaggregation inside the fabric, creating more favourable conditions for merocyanine conversion. They discovered that spirooxazines developed colour faster and faded faster than naphthopyrans, and that the latter exhibited a residual colour after fading. [64-66]



(R: alkyl; R<sub>1</sub>, R<sub>2</sub>:alkyl (usually both methyl); R<sub>3</sub>: H, halogen, etc.)

Figure 14: Reversible color change of spiroxazine (photochromic dye) [43]

### Naphthopyrans

The most prevalent type of photochromic chemical used in industry is naphthopyrans. Their photochromism, like that of the spiropyrans and spirooxazines families, is based on light-induced ringopening as illustrated in Figure 15. Because of its changeable colourant chemistry, many other types of functional groups may be added cost-effectively, allowing for a wider colour gamut that spans the visible spectrum from yellows to oranges, reds, purples, and blues. Commercial naphthopyrans, like other known families of photochromic colourants, exhibit high stability and are less temperature sensitive than spirooxazines. [59, 64]

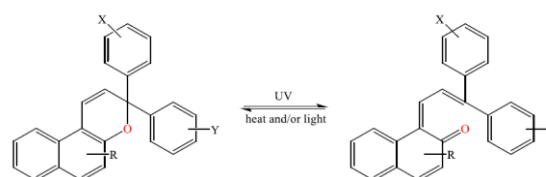


Figure 15: Photochromism of naphthopyrans through ring opening [64]

### Mechanism of photochromism

The photochromic process changes the electronic absorption spectra of molecules. The formation of a new absorption band as a result of electron transitions from various vibrational levels during the excitation of colourless molecules from the S<sub>1</sub>A level to the excited state S<sub>1</sub>B after absorption of an energy photon in the UV region, and then deactivation of the coloured molecules to the ground state S<sub>0</sub>B. Following that, there occurs a spontaneous energy release mechanism, and the molecules return to their original S<sub>0</sub>A ground state. The molecules in the B state are less stable thermodynamically because they have more energy, but after releasing energy, they become colourless and more stable. The transition from state B to A occurs via transition state X, which has a higher energy than the triplet state of coloured form S<sub>0</sub>B and is thermally activated. [48]

The photochromic effect is caused by six mechanisms, which are as follows:

- Triplet triplet photochromism.
- Hetrolytic cleavage
- Hemolytic cleavage
- Trans-cis isomerisation
- Tautomerism
- Photodimerisation

Figure 16 illustrates the transition of molecules at different energy levels following light absorption

### Application of photochromic dyes on textiles

There are many applications of photochromic dyes in textile industry. It can be applied in spinning of the fibers, dyeing and textile printing.



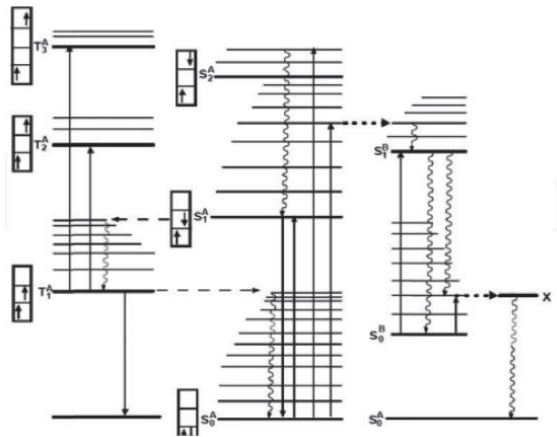


Figure 16: Movement of electronics, radiative and non radiative transitions in photochromic materials [48]

Suju et al. (2022) worked on the as-synthesized AB polymer exceeded the azobenzene (AB) monomolecule in terms of photochromic ability and chemical resistance. Through a simple wet spinning technique as illustrated in Figure 17 an intelligent fibre with photochromic properties may be successfully generated using as-synthesized AB polymer and polyvinylidene fluoride (PVDF). Doping AB polymer in intelligent fibre had little effect on the intrinsic properties of PVDF fibre but drastically changed surface performances such as aesthetics, UV sensing, and shielding. Under UV irradiation, the intelligent fibre may reversibly change colour from pale yellow to orange red, indicating that it could be employed as a flexible UV indicator. The photochromic PVDF fibre demonstrated consistent photochromic responses, reversible optical contrast, and good photo-coloration kinetics as a functional embroidery thread on fabric, considerably increasing the aesthetic and usefulness of the substrate fabric. Furthermore, the fabric knitted with this photochromic fibre may provide UV shielding, as evidenced by the excellent ultraviolet protection factor. Furthermore, the functional fibre was resistant to several solvents, indicating that it might be employed in harsher settings. In comparison to the considerable research on spiropyrans (SPs) and spirooxazines (SOs) in color-changing textiles, this study would be a complimentary study for the use of azobenzenes (ABs) in intelligent textiles as illustrated in Figure 18 and Figure 19. [67] Z

hang et al. (2022) used the interfacial polymerization process to create dyes, multi-color spiropyran and spiroxazine microcapsules with consistent particle sizes by employing compounds of different colours as the core material and polyurethane as the shell material. The hard and soft chemicals are toluene diisocyanate and polyethylene glycol. Polyurethane soft portions, respectively as shown in Figure 20

The colour of spiropyran and spiroxazine microcapsules can transition between colour and colourless with high photo fatigue resistance. The particle

size of microcapsules is 2.951 mm on average, and the particle distribution index is 0.314, indicating that the particle size is small and uniform.

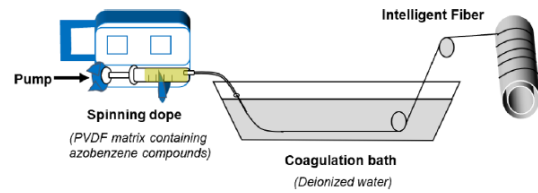


Figure 17: Wet spinning process to develop intelligent PVDF fiber [67]

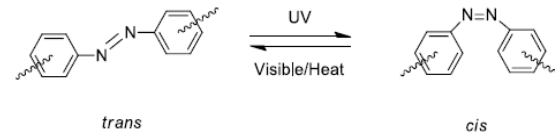


Figure 18: Isomerization of azobenzene derivatives (reversible reaction) [67]

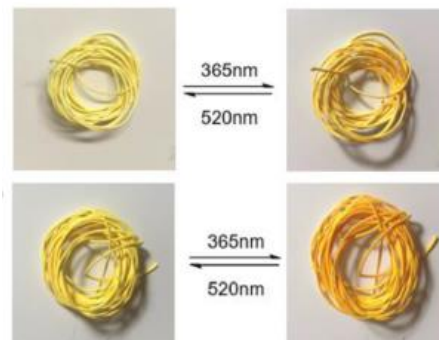


Figure 19: PVDF fiber under various wavelength irradiation [67]

The maximal thermal breakdown temperature is 426 degrees Celsius, indicating excellent thermal stability. The hydrophobic photochromic fabric was created by covering cotton knitted fabric with multi-color spiropyran and spiroxazine microcapsules and applying a hydrophobic treatment. The hydrophobic photochromic fabric is stain resistant and hydrophobic, with multicolor dynamic switching and long-lasting use. Furthermore, spiropyran and spiroxazine microcapsules are used in template and screen printing to give fabrics rich and dynamic color-changing effects, resulting in photochromic fabrics. Photochromic fabrics may have usage in both civilian and military applications as shown in Figure 21. [68, 69]

Khattab et al. (2020) recently reported on immobilising the inorganic Strontium aluminate phosphor at low total content value in an aqueous binder onto cotton fabric via screen printing to produce light-responsive apparel with superior color-exchange performance and colourant stability. To create a dark red backdrop, the photochromic knitted cotton was first dyed conventionally using Reactive Red AEF, followed by screen printing with an aqueous paste including strontium aluminate pigment, binder, diammonium phosphate, synthetic thickener, and ammonium hydroxide.

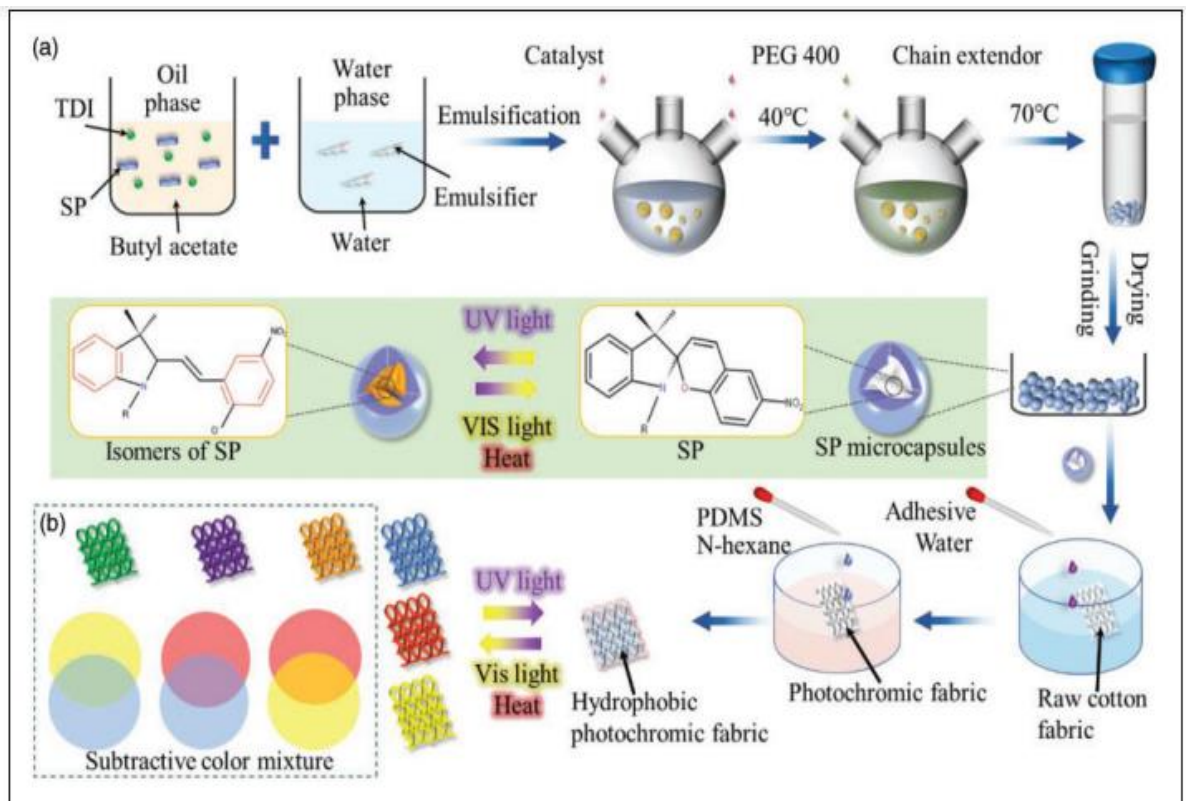


Figure 20: a) Schematic diagram of preparation process of the spiropyran and spiroxazine photochromic microcapsules, b) subtractive color mixture principle. PDMS: polydimethylsiloxane; PEG400: polyethylene glycol400; TDI: toluene diisocyanate; UV: ultraviolet; Vis: visible [68]

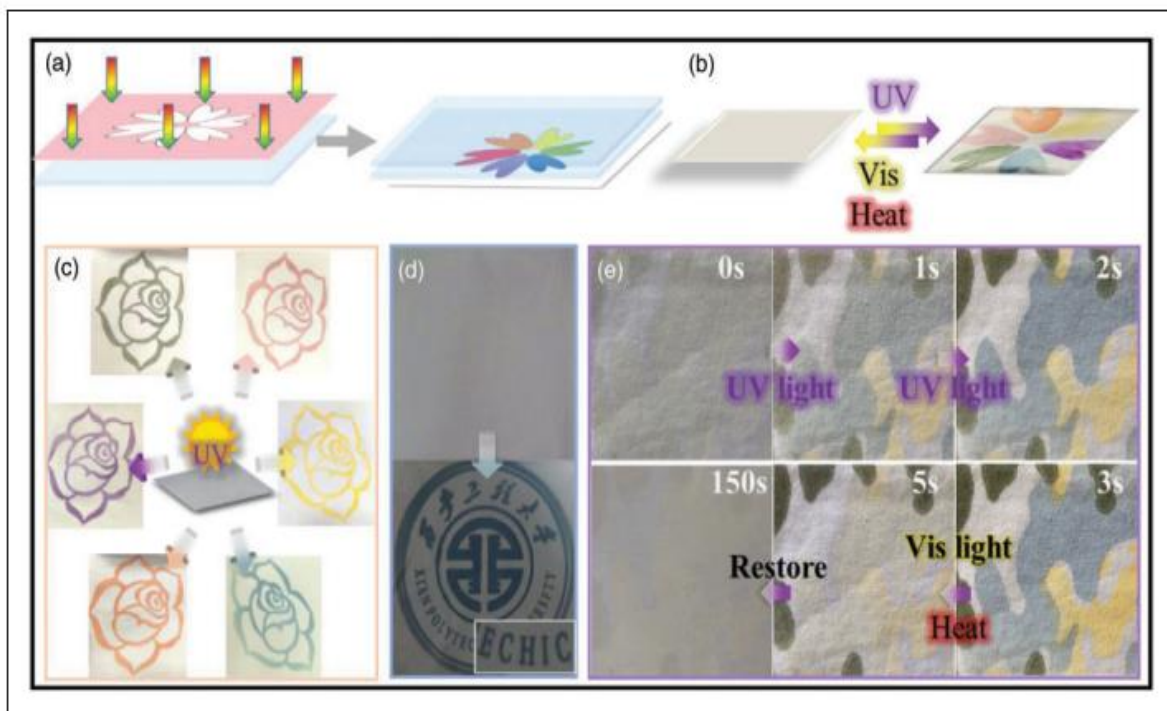


Figure 21: a) Scheme illustrates the fabrication of template print; b) template print fabrics; rewritable fabrics of c) flowers, d) phases of before and after ultraviolet; e) color change of camouflage fabric [68]

The printed cotton was dried at room temperature before being thermofixed at 160 °C. This method was distinguished by its quick and simple application, ease of handling, and low cost, allowing photochromic cotton fabric of great durability without compromising its aesthetic features, such as comfort and handling. Cotton cloth changed colour from red to greenish yellow as shown in Figure 22. It had good fatigue resistance, good colorfastness, great reversibility, and photo- and thermal stability. [43, 70]

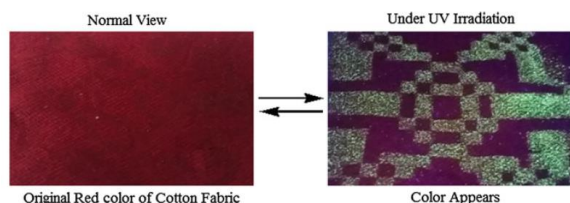


Figure 22: Screen-printed photochromic cotton fabric before and after ultraviolet irradiation [43]

### Summary

The current work provides an overview of the current state of the art in smart chromic fabrics. The applications, experimental verification, performance characterization of chromic textiles have all been covered. Chromic textiles are still a new field with chances to create unique items that can change the way people interact with their clothes. In recent years, there has been an increase in research and development of chromic fabrics and fibres, with an emphasis on improving and expanding textile functionality. Chromic textiles are a type of high-tech textile with enormous promise in a variety of fields. Because of their potential applications in sectors such as wearable displays, sensors, camouflage, and even the military industry, smart colour change fabrics have become an important topic. The research effort in the smart textile sector has steadily increased, and the multidisciplinary approach has been a fundamental reason in this extraordinary expansion. Circuit design, smart materials, microelectronics, and chemical knowledge are fundamentally combined with a thorough understanding of textile fabrication.

### Funds

No fund

### Conflict of Interest

The authors declared no competing interests in the publication of this article

### Acknowledgment

The authors are gratefully grateful to acknowledge the National research Centre.

### References

- Pargai, D. Application of smart and functional dyes in textiles, IntechOpen, (2021).
- CHRISTIE, R.M. Chromic materials for technical textile applications, Advances in the dyeing and finishing of technical textiles, Woodhead Publishing Limitedpp. 3-36, (2013).
- Ferrara, M. and Bengisu, M. Intelligent design with chromogenic materials, *The Journal of the International Colour Association*, **13** 54-66 (2014).
- Li, Q. Intelligent stimuli-responsive materials: From well-defined nanostructures to applications, JohnWiley & Sons, Hoboken, NJ, USA, (2013).
- A., M., H., B., D., H., S., K., R., N. and R., S. Electrochromic dye system for smart window applications, *Advanced material*, **13**(23) 1825-1828 (2001).
- Sadeghi, K., Yoon, J.-Y. and Seo, J. Chromogenic polymers and their packaging applications: A review, *Polymer Reviews*, **60** 1-51 (2019).
- V., S. and ., K.M. Design of ph responsive textile as a sensor material for acid rain, *Polymers*, **12**(10) (2020).
- M., C.R. Chromic materials for technical textile applications, Advances in the dyeing and finishing of technical textiles, Woodhead Publishing, UK; Cambridge, pp. 3-36, (2013).
- S., N. and S., R. Principles and applications of solvatochromism, *Appl Spectrosc*, **55**(11) (2001).
- Papadakis, R. and Tsolomitis, A. Synthesis, substituent and solvent effects on the uv-vis spectra of 4-pentacyanoferrate-4'-aryl substituted bipyridinium complex salts, (2008).
- X., G., C., H., Zhang Q, L.Y. and H., W. Solvatochromic structural color fabrics with favorable wearability properties, *Journal of Material chemistry*.
- F., C., R., G. and A., P. Dye-containing polymers: Methods for preparation of mechanochromic materials, *Chem Soc Rev*, **42**(3) (2012).
- C., C., Li., H.E., F., M.L., S., S. and C., W. Mechanochromic polymers based on microencapsulated solvatochromic dyes. , *Macromol. Rapid Commun.*, **41**(7) (2020).
- R., C.B., M., B., D., K., A., H., T., M.P., R., S. and C., W. Deformation- induced color changes in mechanochromic polyethylene blends, *Macromolecules*, **40**(7) (2007).
- Kreyenschmidt, J., Christiansen, H., Hübner, A., Raab, V. and Petersen, B. A novel photochromic time-temperature indicator to support cold chain management, *Int J Food Sci Technol*, **45** 208-215 (2010).
- Tozum, M.S., Alkan, C. and Aksoy, S.A. Developing of thermal energy storing visual textile temperature

- indicators based on reversible color change, *Journal of Industrial Textiles*, **51**(2S) 1964S–1988S (2022).
17. Karpagam, K.R., Saranya, K.S., Gopinathan, J. and Bhattacharyya, A. Development of smart clothing for military applications using thermochromic colorants, *The Journal of The Textile Institute*, **108** 1122-1127 (2016).
  18. Chowdhury, M.A., Joshi, M. and Butola, B.S. Photochromic and thermochromic colorants in textile applications, *Journal of Engineered Fibers and Fabrics*, **9**(1) 107-123 (2014).
  19. A. Seeboth, A. Klukowska, Ruhmann, R. and Lotzsch, D. Thermochromic polymer materials, *Chin. J. Polym. Sci.*, **25**(2) 123-135 (2007).
  20. Mather, R.R. Intelligent textiles, *Review of Progress in Coloration and Related Topics*, **31**(1) 36-41 (2001).
  21. Seeboth, A., Löttsch, D., Ruhmann, R. and Muehling, O. Thermochromic polymers—function by design, *Chem. Rev.*, **114**(5) 3037-3068 (2014).
  22. Maćzka, M., Ptak, M., Gaćgor, A., Stefan' ska, D. and Sieradzki, A. Layered lead iodide of [methylhydrazinium]2pb<sub>4</sub> with a reduced band gap: Thermochromic luminescence and switchable dielectric properties triggered by structural phase transitions, *Chemical Materials*, **31**(20) 8563-8575 (2019).
  23. Sage, I. Thermochromic liquid crystals, *Liq. Cryst.*, **38**(11-12) 1551-1561 (2011).
  24. Park, H., Lee, J.S., Choi, H., Ahn, D.J. and Kim, J.M. Rational design of supramolecular conjugated polymers displaying unusual colorimetric stability upon thermal stress, *Adv. Funct. Mater.*, **17**(17) 3447-3455 (2007).
  25. Lam, J.W.Y., Luo, J., Dong, Y., Cheuk, K.K.L. and Tang, B.Z. Functional polyacetylenes: synthesis, thermal stability, liquid crystallinity, and light emission of polypropiolates, *Macromolecules*, **35**(22) 8288-8299 (2002).
  26. Chen, X. and Yoon, J. A thermally reversible temperature sensor based on polydiacetylene: Synthesis and thermochromic properties, *Dyes and Pigments*, **89**(3) 194-198 (2011).
  27. Zhao, X. Synthesis, characterization and structure dependence of thermochromism of polythiophene derivatives, *Journal of Materials Science*, **40**(13) 3423-3428 (2005).
  28. Wang, C.-C., Gao, Y., Shreve, A.P., Zhong, C., Wang, L., Mudalige, K., Wang, H.-L. and Cotlet, M. Thermochromism of a poly(phenylene vinylene): Untangling the roles of polymer aggregate and chain conformation, *The Journal of Physical Chemistry B*, **113**(50) 16110-16117 (2009).
  29. MacLaren, D.C. and White, M.A. Design rules for reversible thermochromic mixtures, *Journal of Materials Science*, **40**(3) 669-676 (2005).
  30. Raditoiu, A., Raditoiu, V., Nicolae, C.A., Raduly, M.F., Amariutei, V. and Wagner, L.E. Optical and structural dynamical behavior of crystal violet lactone – phenolphthalein binary thermochromic systems, *Dyes and Pigments*, **134** 69-76 (2016).
  31. Seeboth, A., Ruhmann, R. and Muehling, O. Thermotropic and thermochromic polymer based materials for adaptive solar control, *Materials*, **3**(12) 5143-5168 (2010).
  32. Hakami, A., Srinivasan, S.S., Biswas, P.K., Krishnegowda, A., Wallen, S.L. and Stefanakos, E.K. Review on thermochromic materials: Development, characterization, and applications, *J. Coat. Technol. Res.*, **19**(2) 377–402 (2022).
  33. Zhang, L., Xia, H., Xia, F., Du, Y., Wu, Y. and Gao, Y. Energy-saving smart windows with hpc/paa hybrid hydrogels as thermochromic materials, *ACS Applied Energy Materials*, **4**(9) 9783-9791 (2021).
  34. Zhou, Y., Dong, X., Mi, Y., Fan, F., Xu, Q., Zhao, H., Wang, S. and Long, Y. Hydrogel smart windows, *Journal of Materials Chemistry A*, **8**(20) 10007-10025 (2020).
  35. Wu, T., Yin, T., Hu, X., Nian, G., Qu, S. and Yang, W. A thermochromic hydrogel for camouflage and soft display, *Advanced Optical Materials*, **8**(9) 2000031 (2020).
  36. Owusu-Nkwantabisah, S., Gillmor, J., Switalski, S., Mis, M.R., Bennett, G., Moody, R., Antalek, B., Gutierrez, R. and Slater, G. Synergistic thermoresponsive optical properties of a composite self-healing hydrogel, *Macromolecules*, **50**(9) 3671-3679 (2017).
  37. Kim, H. and Chang, J.Y. Reversible thermochromic polymer film embedded with fluorescent organogel nanofibers, *Langmuir*, **30**(45) 13673-13679 (2014).
  38. Carlotti, M., Gullo, G., Battisti, A., Martini, F., Borsacchi, S., Geppi, M., Ruggeri, G. and Pucci, A. Thermochromic polyethylene films doped with perylene chromophores: Experimental evidence and methods for characterization of their phase behaviour, *Polymer Chemistry*, **6**(21) 4003-4012 (2015).
  39. Crosby, P. Fully green starch-based thermochromic composites, (2022).
  40. Ambrogio, S., de Melo Baêsson, R., Gomis, A., Rivens, I., Ter Haar, G., Zeqiri, B., Ramnarine, K.V., Fedele, F. and Miloro, P. A polyvinyl alcohol-based thermochromic material for ultrasound therapy phantoms, *Ultrasound in Medicine & Biology*, **46**(11) 3135-3144 (2020).

41. Khattab, T.A., El-Naggar, M.E., Abdelrahman, M.S., Aldalbahi, A. and Hatshan, M.R. Simple development of novel reversible colorimetric thermometer using urea organogel embedded with thermochromic hydrazone chromophore, *Chemosensors*, **8**(4) 132 (2020).
42. Chowdhury, M.A., Butola, B.S. and Joshi, M. Application of thermochromic colorants on textiles: Temperature dependence of colorimetric properties, *Coloration Technology*, **129** 232–237 (2013).
43. Khattab, T.A. and Abdelrahman, M.S. From smart materials to chromic textiles, Springer Singaporepp. 257-274, (2020).
44. Aklujkar, P.S. and Kandasubramanian, B. A review of microencapsulated thermochromic coatings for sustainable building applications, *J. Coat. Technol. Res.*, **18**(1) 19-37 (2021).
45. Tözüm, M.S., Aksoy, S.A. and Alkan, C. Microencapsulation of three-component thermochromic system for reversible color change and thermal energy storage, *Fibers and Polymers*, **19**(3) 660-669 (2018).
46. Liu, B., Rasines Mazo, A., Gurr, P.A. and Qiao, G.G. Reversible nontoxic thermochromic microcapsules, *ACS applied materials & interfaces*, **12**(8) 9782-9789 (2020).
47. Zhu, X., Liu, Y., Li, Z. and Wang, W. Thermochromic microcapsules with highly transparent shells obtained through in-situ polymerization of urea formaldehyde around thermochromic cores for smart wood coatings, *Scientific reports*, **8**(1) 1-10 (2018).
48. Kumar Gupta, V. Photochromic dyes for smart textiles, IntechOpen, (2021).
49. Ramlow, H., Andrade, K.L. and Immich, A.P.S. Smart textiles: An overview of recent progress on chromic textiles, *The Journal of The Textile Institute*, 1-20 (2020).
50. Crosby, P.H.N. and Netravali, A.N. Green thermochromic materials: A brief review, *Advanced Sustainable Systems*, **6**(9) 2200208 (2022).
51. Crosby, P.H.N. and Netravali, A.N. Green thermochromic materials: A brief review, *Advanced Sustainable Systems*, **6**(2200208) 1-12 (2022).
52. Chowdhury, M.A., Butola, B.S. and Joshi, M. Application of thermochromic colorants on textiles: Temperature dependence of colorimetric properties, *Coloration Technology*, **129**(3) 232-237 (2013).
53. Traiphol, N., Rungruangviriyaya, N., Potai, R. and Traiphol, R. Stable polydiacetylene/zno nanocomposites with two-steps reversible and irreversible thermochromism: The influence of strong surface anchoring, *Journal of Colloid and Interface Science*, **356**(2) 481-489 (2011).
54. Li, P., Sun, Z., Wang, R., Gong, Y., Zhou, Y., Wang, Y., Liu, X., Zhou, X., Ouyang, J., Chen, M., Hou, C., Chen, M. and Tao, G. Flexible thermochromic fabrics enabling dynamic colored display, *Frontiers of Optoelectronics*, **15**(40) 1-7 (2022).
55. Oliveira, C.R.S.d., Júnior, A.H.d.S., Immich, A.P.S. and Fiates, J. Use of advanced materials in smart textile manufacturing, *Mater. Lett.*, **316** (2022).
56. Bishnoi, A., Rajaraman, T.S., Dube, C.L. and Ambegaonkar, N.J. Smart nanosensors for textiles: An introduction, *Nanosensors nanodevices smart multifunctional textiles*, Elsevierpp. 7-25, (2021).
57. Karpagam, K.R., Saranya, K.S., Gopinathan, J. and Bhattacharyya, A. Development of smart clothing for military applications using thermochromic colorants, *THE JOURNAL OF THE TEXTILE INSTITUTE*, **108**(7) 1122-1127 (2017).
58. Garcia-Souto, M.D.P. and Dabnichki, P. Non-invasive and wearable early fever detection system for young children, *Measurement*, **116** 216-229 (2018).
59. Morsümbül, S., Kumbasar, E.P.A. and Çay, A. Photochromic microcapsules for textile materials by spray drying—part 3- application of photochromic microcapsules on cotton fabrics, *AATCC Journal of Research*, **9**(2) 63 -73 (2022).
60. AR, T., RB, S., AA, K., IN, S., IN, M., OV, V., TM, V., VA, B. and UM, D. Optically controlled field effect transistors based on photochromic spiropyran and fullerene c60 films, *Mendelev Comm.*, **29**(2) 160-162 (2019).
61. M., G., T., X., Z., L. and Y., W. Layered photochromic films stacked from spiropyranmodified montmorillonite nanosheets, *RSC Advances*, **9**(22) 12325-12330 (2019).
62. AV, C., NA, V., EV, S.e., EB, G., YV, Z., VA, L., VG, V., VN, K. and AV, M. Ion-depended photochromism of oxadiazole containing spiropyran, *Journal of Photochemistry and Photobiology A: Chemistry*, **378** 201-210 (2019).
63. Kortekaas, L. and Browne, W.R. The evolution of spiropyran: Fundamentals and progress of an extraordinarily versatile photochrome, *Chem Soc Rev*, **48**(12) 3406-3424 (2019).
64. Mohamed, M., El-Aty, M.A., Moawaed, S.S., Hashad, A.M.E., Abd-Elaziz, E., Othman, H.A. and Hassabo, A.G. Smart textiles via photochromic and thermochromic colorant, *Journal of Textiles, Coloration and Polymer Science*, **19**(2) 235-243 (2022).
65. MorsÜMbÜL, S. and Kumbasar, E.P.A. Performance characteristics in textile application of photochromic dye capsules, *Textile and Apparel*, **32**(2) 155-161 (2022).

66. Morsümbül, S., Emriye Perrin, A.K. and Çay, A. Photochromic microcapsules for textile materials by spray drying—part 1: Production and characterization of photochromic microcapsules, *AATCC Journal of Research*, **8** 31 - 40 (2021).
67. Fan, S., Lam, Y., Yang, J., Bian, X. and Xin, J.H. Development of photochromic poly(azobenzene)/pvdf fibers by wet spinning for intelligent textile engineering, *Surfaces and Interfaces*, **34** 102383 (2022).
68. Zhang, L., Meng, J.-g., Liu, Y.-m., Wang, Y.-z., Sun, Z.-l., Yu, L.-j., Gao, X.-y. and Zhi, C. Preparation of multicolor microcapsules and their application in smart color-switching textiles, *Textile Research Journal*, 00405175221132013 (2022).
69. A., A., H., R.-M. and al., R.B.e. Photoluminescent and chromic nanomaterials for anticounterfeiting technologies: Recent advances and future challenges, *ACS Nano*, **14** 14417-14492 (2020).
70. TA., K., M., R. and T., H. Smart textile framework: Photochromic and fluorescent cellulosic fabric printed by strontium aluminate pigment, *Carbohydr. Polym.*, **195** 143-152 (2018).

### استخدام الأصباغ الكرومية الذكية في قطاع النسيج

أمينة لطفي محمد<sup>١</sup>، هاجر محمد يوسف عقدة<sup>١</sup>، ومحمد سلامة<sup>٢</sup>

<sup>١</sup> المركز القومي للبحوث، معهد بحوث وتكنولوجيا النسيج، قسم التحضرات والتجهيزات للألياف السليلوزية، شارع البحوث (شارع التحرير سابقاً)، الدقي، ص.ب. ١٢٦٢٢، الجيزة، مصر

<sup>٢</sup> كلية علوم وتكنولوجيا الأغذية، جامعة هواتشونغ الزراعية، ووهان، هوبي ٤٣٠٠٧٠، الصين

### المستخلص

عند نسجها في القماش، تتمتع الألياف المتغيرة اللون بإمكانية توسيع قدرات الأجهزة الذكية القابلة للارتداء إلى مجموعة واسعة من التكوينات. يعد دمج الميزات في الأقمشة التقليدية أحد الأسباب التي تجعل المنسوجات الكروماتيكية قيد النظر. الهدف من هذه الدراسة هو تقديم ومناقشة قابلية الاستخدام الشاملة للمنسوجات الكرومية من خلال تقييم الاختراقات الأخيرة من أجل تمهيد الطريق لبحوث مستقبلية في هذا المجال. سيتم تحقيق ذلك من خلال وصف قابلية الاستخدام الشاملة للأقمشة الكرومية. يتم تقديم مراجعة شاملة للتطورات الأخيرة في المنسوجات الكرومية الذكية هنا، مع وضع الحالة الحالية للفن كأساس للعرض. يتم التحقيق في جميع جوانب المنسوجات الكرومية، بما في ذلك تطبيقاتها، والتحقق التجريبي، وتوصيف الأداء، والحوازج الرئيسية، وأهداف البحث المستقبلية.

الكلمات المفتاحية: الأصباغ الذكية، تغيير اللون، الأصباغ الكرومية، الكروم الحراري، الكروم الضوئي