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Fastness Improvement of a Crystalline Liquid Thermochromic Print on Cotton Fabric by the Application of Silica Nanoparticles from Rice-Husk

Izboljšanje obstojnosti termokromnega tiska s tekočimi kristali na bombažni tkanini z uporabo nanodelcev silicijevega dioksida iz riževih lupin

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Abstract

Most commercially available thermochromic dyes are not resistant to washing and rubbing when applied to textile materials. This is due to their low affinity for fibre. The addition of silica extracted from rice husk ash using the sol-gel method was performed to improve colour fastness and maintain the stability of thermochromic dyes printed on cotton fabrics. The rice husks used in this study were derived from the *Baroma* rice variety with silica content in ash and silica gel of 97.05% and 99.20%. The morphological structures and particle sizes of the silica obtained were analysed using a scanning electron microscope (SEM) and particle size analyser (PSA). The particle sizes of the silica product, thermochromic dye and silica-dye mixture were 53.64–60.66 nm, 2.603 nm and 5.827 nm, respectively. The printing process of silica: the dye mixture was applied to cotton fabric in a ratio of 1:1. Fluid of silica: the dye showed good stability until the seventh day of observation. Colour fastness to washing assessed using a staining scale was better with the addition of silica than without silica, i.e. 3–4. Similarly, fastness to rubbing was also better with the addition of silica, i.e. 3–4 dry rubbings and 3 wet rubbings. Moreover, the combination of silica, binder, PDMS and dye (in a ratio of 1 : 1 : 1 : 1) gave the best colour fastness to washing and rubbing.

Keywords: rice husk, silica, thermochromic dyes, liquid crystal, printing

Izvleček

Večina komercialno dostopnih termokromnih barvil, nanesenih na tekstilne materiale, ni odporna proti pranju in drgnjenju. To je posledica njihove nizke afinitete do vlaken. Dodatek silicijevega dioksida, ekstrahiranega iz pepela riževih lupin z metodo sol-gel, je bil namenjen izboljšanju barvne obstojnosti in ohranitvi stabilnosti termokromnega barvila, natisnjenega na bombažne tkanine. V tej študiji so bile uporabljene riževe lupine sorte riža Baroma z vsebnostjo silicijevega dioksida v pepelu in silikagelu 97,05 % in 99,20 %. Morfološke strukture in velikost delcev dobljenega silicijevega dioksida so bili analizirani s pomočjo vrstičnega elektronskega mikroskopa (SEM) in analizatorja velikosti delcev

(PSA). Velikosti delcev silicijevega dioksida, termokromnega barvila in mešanice silicijevega dioksida in barvila so bile 53,64–60,66 nm; 2,603 nm oziroma 5,827 nm. Tiskanje na bombažno tkanino je bilo izvedeno z mešanico silicijevega dioksida in barvila v razmerju 1:1. Tekoča mešanica silicijevega dioksida : barvilo je pokazala dobro stabilnost do sedmega dneva opazovanja. Barvna obstojnost pri pranju, ocenjena s prehodom barvila na spremljevalno tkanino, je bila ob dodatku silicijevega dioksida boljša kot brez silicijevega dioksida, tj. ocena 3–4. Podobno je bila tudi obstojnost pri drgnjenju boljša ob dodatku silicijevega dioksida, in sicer ocena 3–4 pri suhem in ocena 3 pri mokrem drgnjenju. Poleg tega je kombinacija silicijevega dioksida : veziva : PDMS (polidimetilsiloksana) : barvila v razmerju 1 : 1 : 1 : 1 dala najboljšo barvno obstojnost pri pranju in drgnjenju.

Ključne besede: riževe luščine, silicijev dioksid, termokromna barvila, tekoči kristal, tisk

1 Introduction

Thermochromic dyes, the most frequently used smart dyes among other developed chromic materials, change colour reversibly or irreversibly when the temperature of the surrounding environment changes [1], even in the context of a minor temperature change [2]. Based on their ability to respond to the stimuli of changing temperature, thermochromic dyes are divided into two types: leuco and crystalline liquid. As seen in Figure 1 [3], the leuco type exhibits a single colour change through a molecular rearrangement, while the crystalline liquid, which is made of a cholesteric liquid crystal, can demonstrate a spectrum of colour change [4]. The colour change shown by thermochromic liquid crystal (TLC) is initially colourless at room temperature, then red when the temperature increases to yellow, green, blue, and purple, and then colourless again, depending on the reflected wavelength at a certain temperature [5]. Both types of thermochromic dyes have been widely used in various smart textile applications, primarily for sensor applications or for aesthetic purposes in fashion products. For these purposes, the smart properties of the thermochromic dyes can be expanded if their technical properties can be improved.

One of the important properties to be improved in terms of thermochromic print on cotton is colour fastness. It is evident from available literature that some thermochromic dyes are susceptible to photochemical reactions, which causes colour fading, which in turn indicates a low affinity to fibres and poor fastness to light [6]. Some commercially available thermochromic dyes were also reported to be unwashable when applied to textiles [7, 8]. Previous studies reported that silica nanoparticles could effectively increase the fastness properties of thermochromic dyes, either by immobilizing the thermochromic dyes in the silica nanoparticles [9] or by coating the silica sol-gel on the surface of the thermochromic dye-printed textile materials [10]. Silica is generally prepared using vapor-phase reaction, sol-gel and thermal decomposition methods. Various techniques have been used to produce pure nano-sized silica with a high surface area using an

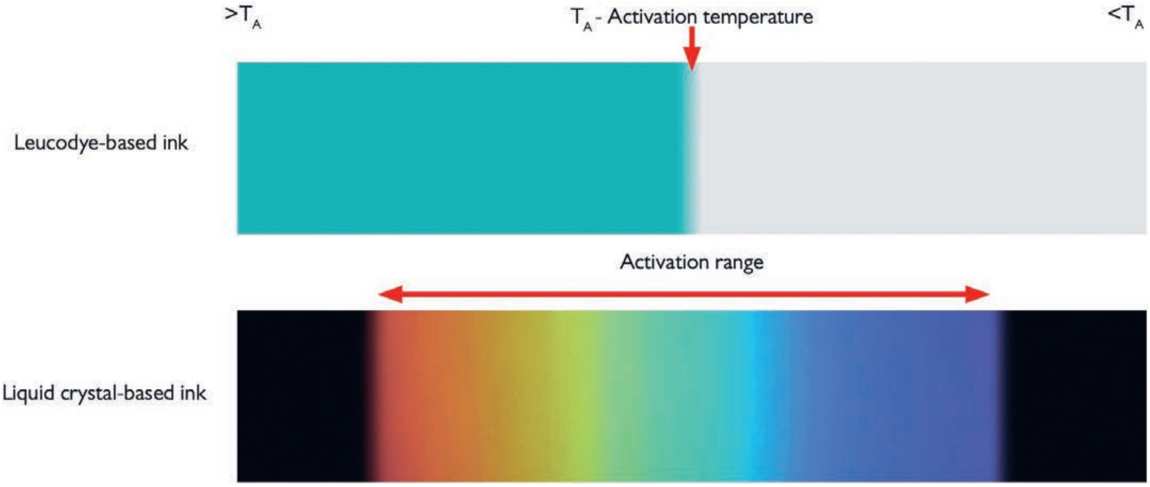


Figure 1: Changes in leuco and liquid crystal types of dyes [3]

easy-to-use alkaline extraction followed by an acid precipitation method. This method can be used conventionally and has the advantages of being simple, cost-effective, and reproducible. The results of previous studies indicate that the use of silica nanoparticles to improve the fastness of thermochromic dyes is still the subject of a great deal of additional study, and is thus the background of this study.

In this study, silica was synthesized from rice husk biomass. Using the proper preparation treatment of silica from rice, husks can be used in the textile sector. The utilization of rice husks is potentially promising, including in Indonesia, which is an agricultural country, with rice as one of its most important commodities. Based on the results of a BPS (Indonesian Central Bureau of Statistics) survey, Indonesia recorded very high grain production in 2021 of about 54.42 million tons of GKG (milled dry grain) [11]. From each rice milling process, rice husks usually account for between 20–30% of the initial weight of the grain. Rice husk waste is widely found in rural areas as a by-product of rice milling, and has great potential. The silica content in rice husk is 15–20% [12]. If the rice husk is converted into ash, the silica content is 99% [13]. The rice sample used in this study was the *Baroma* variety in the form of grain as shown in Figure 2. It was therefore necessary to carry out a milling process to separate the rice and rice husks.

Rice husk has many organic and inorganic compounds that are quite complex. Several steps are thus required to achieve pure silica form. The many methods used to obtain silica nanoparticles include the sol-gel method, reverse micro emulsion, and heat synthesis. The sol-gel method was used to produce pure silica because it can control particle size, size distribution and morphology through reaction parameters [14]. The silica used was the result of synthesis using sol-gel as shown in Figure 3. One of the potential uses of nanometre-sized silica in textile materials is to improve the properties or characteristics of various smart dyes.

Figure 3: Silica gel from a sol-gel synthesis process

The colouring of a textile material can be achieved using a dye that is applied through dyeing or by printing. Printing using a flatscreen is the oldest but easiest method because of its simple application [15]. In this study, a printing process was selected as the method of application of the thermochromic

a) *b)*

Figure 2: Rice grain (a) and rice husk (b) of the Baroma variety

dye. The effect of nano-silica from rice husks and its combination with other additives (binding agent and polydimethylsiloxane) to the fastness of the printing results was studied.

2 Materials and methods

2.1 Materials

Silica nanoparticle gels were synthesized from the rice husk of the Baroma variety obtained from the Indonesian Centre for Rice Research at the Ministry of Agriculture. The detailed process of making silica nanoparticles is not described in this study. However, the production steps referred to in [16, 17] are mentioned here, with some modifications. The resulting silica characterized using particle size analysis (PSA; Zetasizer Nano Range, Malvern Instrument) showed that the mean size of the silica obtained from the rice husk ash and from the sol-gel process were 30.06 nm–46.44 nm and 53.64–60.66 nm, respectively. The surface area, pore radius and silica pore volume analysed using Brunauer–Emmett–Teller analysis (BET Quantachrome QuadraWin ©2000-16, Quantachrome Instruments) gave the results of 224.1660 m^2/g, 4.16759 nm, and 0.4671 cm^3/g, respectively. The amorphous properties of the silica were shown using X-ray diffraction analysis (XRD Shimadzu XRD-7000). The thermochromic liquid crystal used for this study has the commercial name of Temperature Responsive Liquid Crystal Sprayable Ink, with an activation temperature of 24–29 °C. It is manufactured by Good Life Innovations Ltd (Special FX Creative). Stabiprint B–PK 400 binder (acrylic copolymers) was purchased from a local supplier. Polydimethylsiloxane (PDMS) linker was purchased from Wacker. The 100% black cotton fabric was obtained from the stock in our laboratory.

2.2 Methods

2.2.1 Preparation of the thermochromic print on cotton

Before being printed on the prepared cotton fabric, the thermochromic dye and mixtures thereof were stirred at 500 rpm for 60 minutes [18]. Flat screen printing was selected as the best method among others, such as padding or spraying to obtain an even distribution of the TLC ink on the fabric surface. The same method was also reported previously by other researchers [19]. The method was also suitable for the TLC used in this study, as suggested by the supplier, [20] and it demonstrated minimum viscosity for the flat screen-printing process, even without the addition of thickeners or other auxiliaries. The screen used was a monofilament polyester (70–80 threads/cm), as suggested in the product technical data sheet. Furthermore, the addition of binder and silica nanoparticles in the form of sol-gel could also increase the viscosity of the print paste. Four variations of mixture were prepared as follows: (1) V1: TLC (thermochromic liquid crystal) + binder; (2) V2: TLC + silica; (3) V3: TLC + binder + silica; and (4) V4: TLC + binder + silica + PDMS. In addition, printing fabric with only TLC (without binder) was also prepared for comparison purposes, particularly for testing the washing fastness. Printing the TLC with binder (V1) is a commonly applied composition. In V2, binder was not added to compare the effect between silica and binder to the washing fastness of the printed fabric. The mixture effect of binder and silica was represented in V3 and, finally, PDMS was added to the mixture of V3 to study its effect on improving the washing fastness of the printed fabric. All variations were prepared with a composition of each ingredient in a ratio of 1 : 1. The prepared mixtures (Table 1) were then flat screen printed using a T80 screen. Each printed fabric was then dried at a tem-

Table 1: Variations of printing paste mixtures

Printing paste	Concentration (g/100 g)				
	TLC	Binder	Silica	PDMS	Distilled water
Blank	50.0	/	/	/	50.0
V1	33.3	33.3	/	/	33.3
V2	33.3	/	33.3		33.3
V3	25.0	25.0	25.0	/	25.0
V4	20.0	20.0	20.0	20.0	20.0

perature of 60 °C with a drying distance of 30 cm from the fabric for two minutes. Based on product technical information [21] (Good Life Innovations Ltd (Special FX Creative), n.d.), this type of thermochromic dye is not resistant to heat. For this reason, curing at a high temperature was not performed in this experiment.

2.2.2 Fluid stability test

Sedimentation photography is the main method for studying sedimentation in fluids. A decrease in fluid stability can be caused by the distribution of particles that tend to agglomerate when stored for a certain period of time. In this method, a number of synthesized nanofluids containing silica gel were stored in a tube to take photos at regular intervals for seven days. Visual analysis was carried out to determine the stability. The observation was carried out at room temperature for seven days to see if there was any separation and phase change, following the method described in a previous study [22].

2.2.3 Visual colour-change response test

The colour change evaluation of each printed sample was performed 30 times to observe the temperature when changing colour. A Peltier cooler box, equipped with thermo-control as presented in Figure 4, was used as a container to observe changes in the colour response of the fabric that can be adjusted at a certain temperature. The colour changes of the fabric were observed.

2.2.4 Evaluation of colour fastness to rubbing and washing

The colour fastness to rubbing of the thermochromic cotton fabrics was tested according to SNI ISO 105-X12 (E): 2016 (Textiles – Tests for colour fastness – Part X12: Colour fastness to rubbing). Samples were separately rubbed to and from in a straight line at a rate of one cycle per second, 20 times, 10 times to and 10 times from, along a track (104 ± 3) mm, with dry and wet standard crocking clothes under vertical pressure (downward force of (9 ± 0,2) N by a manual crocking fastness tester with a rubbing finger appropriate for solid colour fabrics. Before testing, samples and rubbing clothes were conditioned for at least four hours in the standard atmosphere defined in ISO 139. The evaluation was carried out by assessing the staining of the cotton rubbing cloths with the grey scale for staining under suitable illumination, in accordance with ISO 105-A03. While evaluating, each tested rubbing cloth was backed by three layers of the identical rubbing cloth. The colour fastness to washing was tested according to SNI ISO 105-C06:2010 (Textiles – Tests for colour fastness – Part C06: Colour Fastness to domestic and commercial laundering). Two-single fabrics made of cotton and wool were attached to the different sides of the tested fabric, in accordance with relevant sections F01 to F08 of ISO 105-F:1985. The washing conditions followed the test number A1M in Table 2 in the standard: at 40 °C for 45 minutes in 150 ml washing

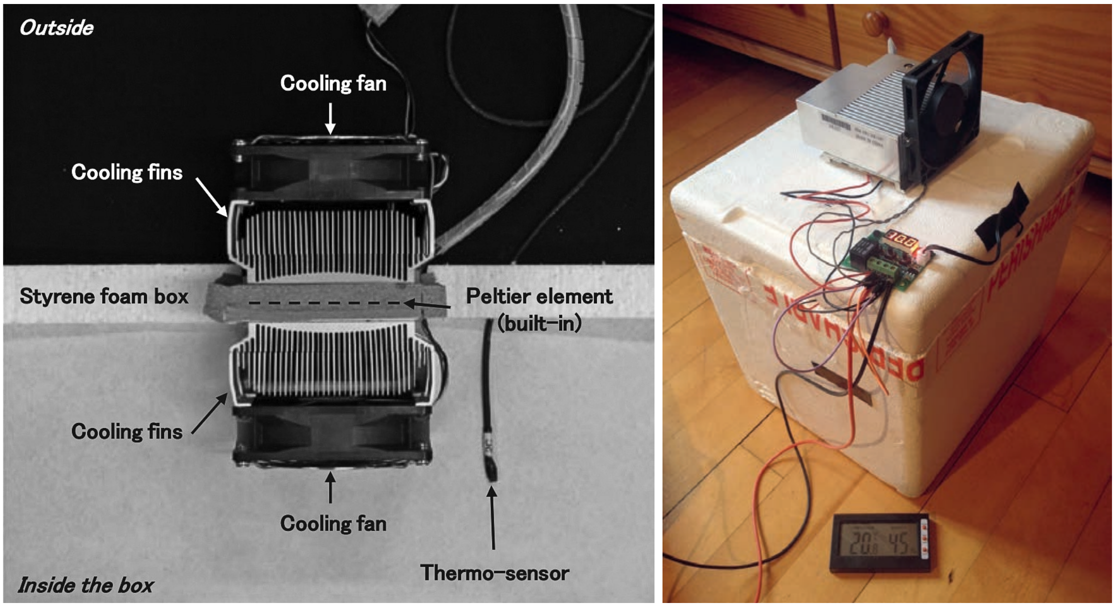


Figure 4: Temperature control design [23]

liquor containing 4 g/l ECE phosphate reference detergent, without an optical brightening agent, and 10 steel balls. The test number A1M is equivalent to five cycles of domestic washing. The evaluation was carried out by assessing the change in colour of the sample and the staining of the adjacent fabrics using the grey scale, according to ISO 105-A03. In order to verify that the thermochromic effect was still active, all the tested samples were re-evaluated in a Peltier cooler box according to the aforementioned procedures (2.2.3).

3 Results and discussion

The silica nanoparticles used in this study were a product of rice husk ash, which was extracted from the Baroma variety of rice using the sol-gel method. The result was in the form of a gel that was used as an additional material in the printing process on fabrics. Silica gel was an inorganic and amorphous polymer formed by the condensation of silicate tetrahedrons using oxygen as a binding site, giving rise to siloxane (Si-O-Si) bonds. The synthesis method of the silica gel will be reported separately, so it is not described in details in this study. The particle size of the silica from the rice husk analysed by PSA was distributed between 53.64–60.66 nm, while the original size of the thermochromic dyes (TLC) used in this study was 2.603 nm. The large size of the dye was caused by aggregation during the analysis process. In the process of mixing silica gel and dye, a stirring process was applied using a magnetic stirrer at a speed of 500 rpm to allow movement for the dye to fill the pores and stick to the silica surface as illustrated in Figure 5. This followed one of mechanisms described by Pilkington et al. [24] about immobilization techniques, which were divided into four major groups, i.e. based on the physical mechanisms of immobilization, adsorption to a pre-formed carrier, physical entrapment within a porous matrix, self-aggregation in floes and the containment of cells behind a barrier. The result of the particle size obtained after this process was 5.827 nm. The distribution of thermochromic dyes filling the pores of the nano silica gel and making a physical bonding with the silica surface could be the reason for an increase in the particle size during analysis.

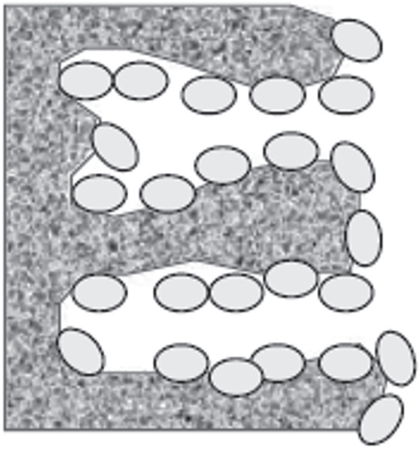


Figure 5: Illustration of immobilization of particles in substance pores [25]

The mixture stability for each variation provided, i.e. thermochromic liquid crystal dye (TLC) + binder, TLC + silica, TLC + binder + silica, and TLC + binder + silica + PDMS was observed as previously explained for seven days. The predetermined time interval was set to observe the stability of the mixtures. Sedimentation was not shown by all mixtures, as can be seen from the image in Figure 6. All mixtures kept showing agglomerations after being stored for seven days, which occurred because of the Van der Waals forces between very reactive nanoparticles. This agglomeration must be maintained until all the particles were dispersed in the entire fluid. Although agglomeration has become one of obstacles in the manufacture of mixed flow, stability was demonstrated in this case.

Five printed fabrics with different composition of chemicals were evaluated, in particular for their thermochromic effects and fastness. As previously mentioned, the five printed fabrics were treated differently, i.e. blank, V1), V2, V3 and V4. A Peltier cooler box, equipped with a thermo-control in a container, was used to observe the activation temperature of each sample. To determine the typical activation temperature (T) of the dye, the test was repeated 30 times. From the test, it was determined that the average temperatures to turn the dye coloured and colourless were 24.13 °C and 29.37 °C, respectively. These two activation temperatures were then used as a standard temperature to verify the thermochromic effect after each treatment. The black fabric used for the application of thermochromic dyes changed from colourless to red, green, and

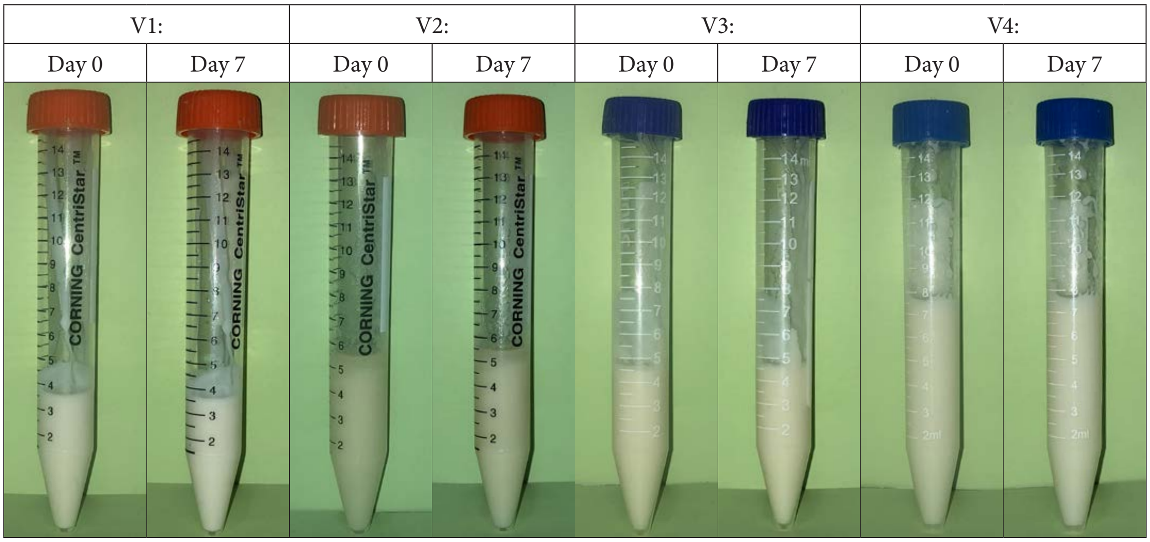
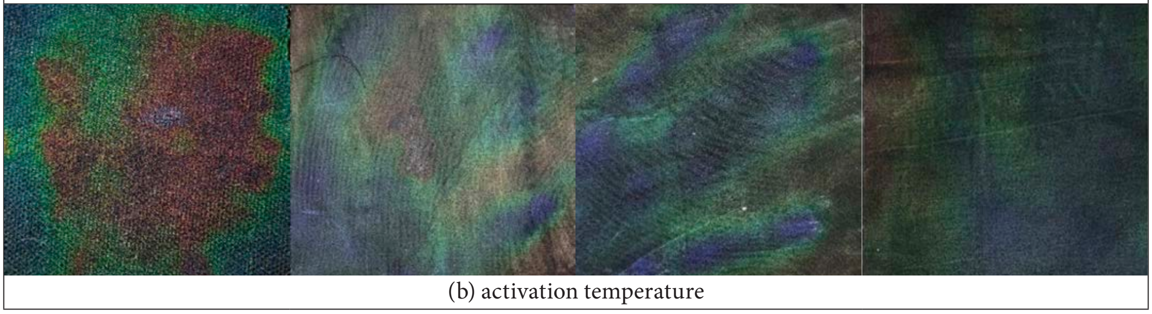


Figure 6: Visual appearances of fluid stability of various printing substance mixtures

blue and then turned colourless again at the optimal temperature (29 °C). Reversibility was demonstrated in this test due to the alternating changes of the dyestuff structure, depending on the ambient temperature. As previously mentioned, based on observations of the printed fabric, the colour change of the TLC started at an average of 24 °C, while the optimum temperature change was at 29 °C. This dye has the special feature of changing the colour spectrum due to temperature. Colour emerged from changes in the liquid crystal orientation structure with regard to temperature and the way light interacts with liquid crystals to produce coloured reflection by interference [26]. TLC is capable of rotating the plane of polarization of linearly polarized light and reflecting colours in the visible light spectrum from the red to the blue spectrum, depending on temperature [5]. This explains why TLC has an activation temperature range of 24–29 °C. Figure 7 shows the visual appearance of each printed fabric with all variations with different composition at ambient temperature (32 °C), as well as the colour changing at their activation temperature (24–29 °C).

(a) ambient temperature



(b) activation temperature

Figure 7: Visual observation of the thermochromic effect of the printed fabrics

The evaluation of fastness to washing and rubbing was carried out for all printed fabrics. The thermochromic effect of each fabric after being washed and rubbed was also observed. The results of the fastness tests are presented in Table 1. It can be seen that the addition of silica to the commonly used composition of the TLC printing process (V3) improved its washing and rubbing fastnesses from 3 or 3–4 to 4. The addition of PDMS resulted in further improved, giving staining scales of 4–5 and 4 for washing and rubbing fastness, respectively. Moreover, the resulting thermochromic cotton fabrics presented good thermochromic performances after washing and rubbing. In other words, the washings did not change the thermochromic capability of the TLC applied to the fabrics. On the contrary, the washing fastness of each fabric printed with TLC + binder and TLC + silica alone (V1 and V2) did not show better results. It appears that the binder and silica resulted in similar effects with regard to the strength of the physical interaction between TLC and the fabric, which in turn affected their fastnesses to washing and rubbing. This is possible because the diffusion of dyes into the pores of silica provided protection to the dyes from direct interaction to washing and rubbing, but could not improve the interaction with the fabric. Likewise, the binding agent helped the dyes interact with the fabric. After washing or rubbing, however, the interactions were weakened, as there was no protection similar to the silica-dye combination. When combined, both effects were obtained.

As observed, the silica had an -OH group that was expected to help improve fastness properties against both washing and rubbing. Silica is a material that contains a large number of small 'nano-sized' pores, making it possible to be used as a matrix material to accommodate a variety of functional materials. A thermochromic dye interacted with the surface of the silica matrix. The tiny pores of silica provided free space for the dye molecules to fill. In the presence of -OH on the silica and -OH on the fabric, hydrogen bonds occurred together with the formation of a physical bond (Van der Waals). These bonds played a role by providing the effect of increasing the fastness of the dye.

The addition of a binder in the printing process can generally increase colour fastness. This is because the binder is a film-forming agent composed of long-chain macromolecules, which when applied to the textile together with the pigment, produce a three-dimensional network. However, this process requires several supportive conditions such as heat and change in pH value [27]. The TLC used in this study was very unstable to an increase in temperature. For this reason, heating to allow complete polymerization and thus the formation of the three-dimensional network was not applied. This explains why the addition of a binder to the mixture did not work optimally as expected. PDMS in this study was added as a long chain alkyl agent and has excellent water-repellent properties [28]. The addition of PDMS also had a good effect on the surface of the printed fabric because it removed the white effect of the added silica (see V4 in Figure 7). The addition of these chemicals also reduced the surface tension properties of the fabric. From the observations, it could be seen that printing only with dyes gave the worst fastness results, in both washing and rubbing, which was expected. The evaluation of the fabric with the addition of binder and silica successively gave better fastness results than before. The addition of PDMS to the mixture then gave the best results in colour resistance to both washing and rubbing. This is due to the long alkyl chain which has a water-repelling effect that reduces the solubility of the dye during washing, as seen in Figure 8.

Table 2: Colour fastnesses of the thermochromic print fabrics

Samples	Colour fastness to washing			Colour fastness to rubbing		Thermochromic effect	
	Grey scale for staining		Grey scale for colour change	Grey scale for staining		After washing	After rubbing
	on cotton	on wool		On dry rubbing cloth	On wet rubbing cloth		
Blank	3	3	3	3	2-3	√	-
V1	3-4	3-4	3	3-4	3	√	√
V2	3-4	3-4	3-4	3-4	3	√	√
V3	4	4	4	4	4	√	√
V4	4-5	4	4-5	4	4	√	√

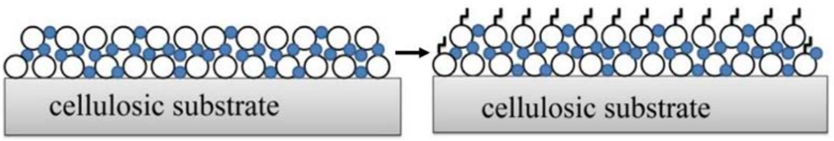


Figure 8: Illustration of fabric surface scheme after the printing process with and without PDMS [29]

4 Conclusion

Durable, reversible colour-changing cotton fabrics were successfully prepared using printing TLC with silica nanoparticles. Moreover, the thermochromic fabrics demonstrated improved colour fastness due to the silica nanoparticle hydrogen and physical bond structures among the fibres. Washing and rubbing fastnesses all exceeded 3–4. The evaluation of colour fastness to washing and rubbing gave better results with the addition of silica than without that addition, but variations of silica, binder, PDMS and dye (in a ratio of 1:1:1:1) gave the best results.

Acknowledgments

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