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Colorimetric properties and application of temperature indicator thermochromic pigment for thermal woven textile

Yuanfang Zhao and Li Li*

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong

*Corresponding Author:

Li Li, The Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hunghom, Kowloon, Hong Kong. Email: li.lilly@polyu.edu.hk

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Abstract

Currently, the thermometer, infrared thermal imaging camera and temperature sensor are the main instruments for the temperature measurement of thermal products. However, these instruments are either inconvenient or too expensive to afford. For researchers, these are common to approach, whereas for designers or salespeople who work in the thermal textile field, new tools that are more convenient to access, easily affordable and have design possibilities need to be invented. This study aims to select a temperature indicator thermochromic pigment amount of four pigments (red, yellow, green and blue) for thermal woven textiles by analyzing the colorimetric properties and making a fast indicator demonstration prototype to achieve the concept. The pigment samples are heated respectively and the decolorization color at 40°C, 50°C, 60°C and 70°C under illuminant D65 are real-time measured by a spectroradiometer. The L*, a*, b*, Δ L*, Δ a*, Δ b*, K/S and color difference CMC 2:1 values are calculated and analyzed. In this experiment, blue pigment has the best performance and thus results in the top selection of the indicator pigment, which is used in production for a fast, convenient and visualized temperature indicator for thermal woven textiles.

Keywords

colorimetric properties, temperature indicator, thermochromic pigment, thermal woven textile

Introduction

There are a variety of different classes of color-changing materials. Energy source changes lead to the alteration of their optical properties. Thermochromic materials change color with temperature change. Most of them are reversible, but some are not. Thermochromic pigments are produced and commercialized by many chemical companies in various fields of application. These pigments are used to produce paints and inks for surface treatment or mixed with other materials, such as polymers, for batch coloring. Peversible thermochromic organic materials generally consist of at least three components, a color former, color developer and solvent. Color formers are electron donors, which are colorless dyes. When the pH changes, these compounds are halochromic and thus change color. Their reaction with the electron-accepting developer determines the position of the longest wavelength absorption that results in coloration/decoloration. At lower temperatures where the solvent is solid, it produces a colored dye developer complex; at higher temperatures, the solvent

developer interaction dominates when the solvent melts. As a result, the dye developer complex is destroyed, turning the system into a colorless state.^{8–10} To date, leuco dye-developer–solvent composites are the most important systems for achieving thermochromic properties using organic materials.¹¹

Temperature indicating paint (TIP) is one of the thermochromic pigments that is coated onto the surface of the subject to indicate the temperature change and distribution. When the TIP coating is heated to the trigger temperature, the pigment color changes.¹² A Germany company invented the earliest TIP in 1938. In the 1940s and 1970s, there was a great development in the research and application of TIP. In this period, easy-to-use and sensitive TIP sheets and reversible TIP were produced. After that, the research focus gradually shifted to the area of low trigger temperature and reversible TIP.¹² Currently, researchers have conducted much work and have made encouraging progress.¹³ In general, TIP technology is becoming a mature and widely recognized reliable test technology of temperature measurement.¹⁴ The application areas of TIP are various, including mercury thermometers, millivoltmeters, temperature measurement for which high-radiation meters are not suitable and the temperature distribution measurement of continuous operation components and large-area surfaces. 12-17 For instance, it can be used for the overtemperature alarm of chemical, refining and reactor walls, as well as the temperature measurement and temperature distribution measurement of aircraft engines, internal instruments and skin structures. The advantage of TIP is that it can be adopted on occasions where the traditional temperature measurement instrument cannot reach. It can measure surface temperature distribution, which is convenient and equipment free. The disadvantage is that it is limited by the conditions of use and has poor accuracy.12-17

Thermal products are rapidly increasing in the e-textile industry. Taking thermal pads, for example, there are generally three common ways to measure the heating temperature: thermometer, infrared thermal imaging camera and temperature sensor. When selling the products, it is difficult to measure the thermal pads using the three methods mentioned above due to the accuracy requirement or the price budget. As for designers, these instruments may be difficult to operate and too technical, which may affect their use in design-related products. Therefore, an easier, cheaper, more rapid and convenient method needs to be found. In this case, a thermochromic pigment like TIP can be a very useful method, with the use of which customers can more intuitively feel the temperature change and range. In addition, the colorimetric result of different thermochromic pigments can also help designers to create various pattern

designs, which can be cleverly combined with the thermal products and thus add additional value. This study aims to analyze the colorimetric properties of four thermochromic pigments and determine the best temperature indicator pigment for thermal woven textiles.

Experimental details

Four thermochromic pigments, produced by Zhongshan JIAHUA Printing Material Company, China, in red, yellow, green and blue, were used (Figure 1(a)). According to the manufacturer's specification, the activation temperature is 31°C. Each color was brushed onto a 3 cm \times 5.5 cm thin gray fabric around 2 cm \times 2 cm. The pigment samples were placed in a thermostatic room at 20°C for 3 hours in advance. They were heated respectively by a 5.9 inches × 4.8 inches thermal woven fabric (Figure 1(c)), which was woven by a CCI tech automatic dobby sampling loom with plain structure, weft density of 30 picks/inch and warp density of 40 ends/inch. The conductive path was woven by silver-coated conductive Yarn A (Figure 1(d)), while the heating area was woven by silver-coated conductive Yarn B (Figure 1(e)) and was designed as shown in Figures 1(f) and (g), in which Yarn B was woven every other pick. The samples were measured at 40°C (Figure 1(h)), 50°C (Figure 1(i)), 60°C (Figure 1(i)) and 70°C (Figure 1(k)) under an illuminant D65 light box, as shown in Figure 1(b). The thermal woven fabric was given electricity at 8.5, 11, 13 and 14.8 V by a DaXin digital direct current (DC) power supply DX3005DS (Figure 1(p)) and the temperature was measured by an FLIR Thermal imaging camera E33, as demonstrated in Figure 1(o). A color assessment cabinet, VeriVide CAC 120 (Figure 1(1)), provided the light source. The colors were measured by a Konica Minolta CS-2000 spectroradiometer (Figure 1-m) in real time when the temperature was rising. A GIT20 tripod (Figure 1(n)) held the spectroradiometer to keep the focal distance fixed.

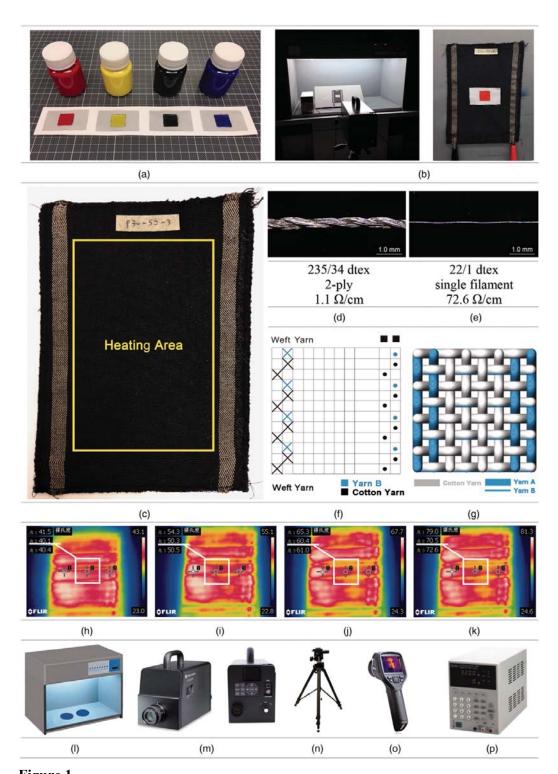


Figure 1.

Experimental images: (a) thermochromic pigment samples; (b) experiment process; (c) thermal woven

fabric; (d) Yarn A; (e) Yarn B; (f) fabrication design; (g) three-dimensional fabric concept design; (h) 40°C; (i) 50°C; (j) 60°C; (k) 70°C; (l) light box; (m) spectroradiometer; (n) tripod; (o) thermal imaging camera; (p) power supply.

Results and discussion

Data processing

The Konica Minolta CS-2000 spectroradiometer is a measuring instrument with high accuracy; thus, the data generated by which are quite precise – an interval of 1 nm, compared to the spectrophotometer Datacolor 650, for which the data interval is 10 nm. For further data analysis, the raw data need to be processed in 10 nm interval (Figure 2(c)). In addition, as displayed in Figure 2(a), the diagram contains several peeks, which means there is a light source in the data. After measuring the white board, the diagram shows the same peek position (Figure 2(b)). Because the XYZ data measured by spectroradiometer are relative values rather than absolute values, the X value, Y value and Z value of four color data must be divided by the white board data, which will eliminate the influence of the light source (Figure 2(c)). There are two ways to correct the raw data: the first is to divide the XYZ values of color data by the Y value of the white board data; the second is to divide the XYZ values of color data by the XYZ value of the white board data. Comparing the two correction results, it is obvious that the $X_w Y_w Z_w$ correction has greater deviation than the Y_w correction. As listed in Figure 2(c), all colors corrected by the $X_wY_wZ_w$ value were a little reddish. Apparently, the deviation of the blue group is the largest, and the blue color even changes to a purple color. Therefore, in this study, all raw data will be processed with the Y_w correction method to maintain the smallest deviation. In this case, the data of L^* , a^* , b^* , ΔL^* , Δa^* , Δb^* , K/S and CMC 2:1 can be correctly calculated.

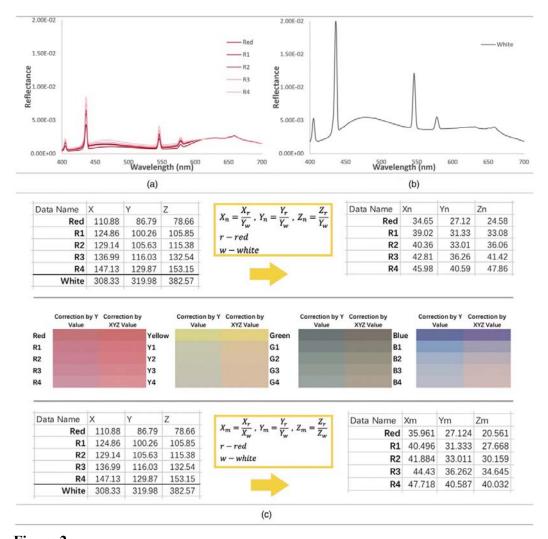


Figure 2.

Raw data process: (a) raw data diagram of the red color; (b) raw data diagram of the white board; (c) raw data processed by the $X_wY_wZ_w$ correction and the Y_w correction and their color differences.

CIELAB allows the specification of color stimuli in terms of a three-dimensional space. The L^* -axis is known as the lightness, and extends from 0 (black) to 100 (white). The other two coordinates, a^* and b^* , represent redness–greenness and yellowness–blueness, respectively. Samples for which $a^* = b^* = 0$ are achromatic and, thus, the L^* -axis represents the achromatic scale of gray from black to white. The quantities L^* , a^* and b^* are obtained from the tristimulus values according to the following transformations, where X_0 , Y_0 and Z_0 are the standard tristimulus values, which are 95.05, 100 and 108.91, respectively, under D65

$$L^* = 116(Y/YY_0Y_0)^{1/3} - 16, Y/YY_0Y_0 > 0.008856$$
 (1)

$$a^* = 500 \left[\left(X/XX_o X_o \right)^{1/123} - \left(Y/YY_o Y_o \right)^{1/123} \right], X/XX_o X_o > 0.008856$$
 (2)

$$b^* = 200[(Y/YY_0Y_0)^{1/123} - (Z/ZZ_0Z_0)^{1/123}], Z/ZZ_0Z_0 > 0.008856$$
 (3)

The CIE 1976 ($L^*a^*b^*$) color space provides a useful three-dimensional representation for the perception of color stimuli. If two points in space, representing two stimuli, are coincident then the color difference between the two stimuli is zero. As the distance in space between two points (L^*1 , a^*1 , b^*1 and L^*2 , a^*2 , b^*2) increases, it is reasonable to assume that the perceived color difference between the stimuli that the two points represent increases accordingly. One measure of the difference in color between two stimuli is therefore the Euclidean distance ΔE^* between the two points in the three-dimensional space. This Euclidean distance can be computed as below, where $\Delta L^* = L_1^* - L_2^*$ and Δa^* and Δb^* are similarly defined

$$\Delta E_{ab}^* = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \tag{4}$$

The CMC color difference formula allows the calculation of tolerance ellipsoids around the target standard, where the dimensions of the ellipsoid are a function of the position in the color space of the target. The design of this formula allows for two user-definable coefficients, l and c, and the formula is thus normally specified as CMC (l:c). The values of l and c modify the relative importance that is given to differences in lightness and chroma, respectively. The equation is listed as follows,

where $L_s^*, C_{ab,s}^*$ and $h_{ab,s}^*$ represent the standard colorimetric parameter

$$\Delta E_{CMC(l:c)}^* = \sqrt{(\Delta L^*/lS_L)^2 + (\Delta C_{ab}^*/cS_C)^2 + (\Delta H_{ab}^*/S_H)^2}$$
 (5)

$$S_L = \begin{cases} 0.040975L_S^*/0.040975L_S^*(1+0.01765L_S^*), & (1+0.01765L_S^*), & L_S^* \ge 16\\ 0.511, & L_S^* \le 16 \end{cases}$$
(6)

$$S_C = 0.0638C_{ab,s}^*/0.0638C_{ab,s}^* \left(1 + 0.0131C_{ab,s}^*\right) + 0.638\left(1 + 0.0131C_{ab,s}^*\right) + 0.638 \tag{7}$$

$$S_H = S_C (F^*T + 1 - F)$$
 (8)

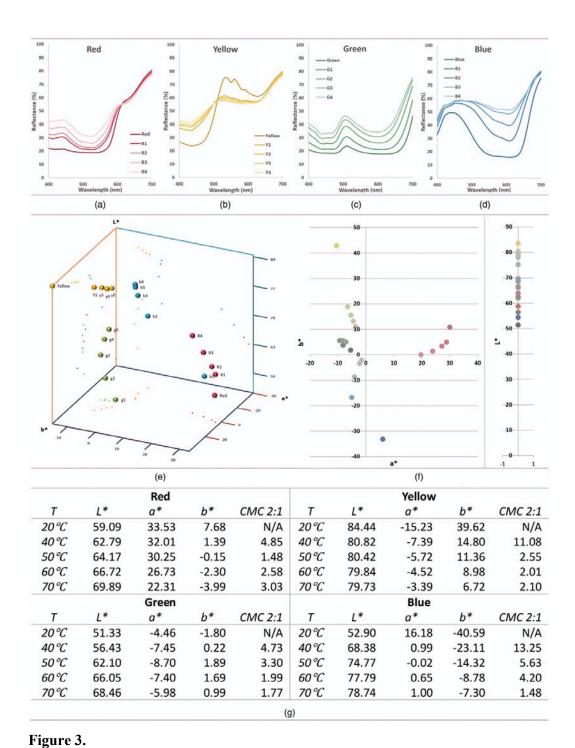
$$F = \sqrt{(C_{ab,s}^*)^4/[(C_{ab,s}^*)^4 + 1900]}$$
(9)

$$T = \begin{cases} 0.36 + |0.4\cos(h_{ab,s}^* + 35)|, \\ h_{ab,s}^* > 345^* \text{ or } h_{ab,s}^* < 164^* \\ 0.56 + |0.2\cos(h_{ab,s}^* + 168)|, \\ 164^* \le h_{ab,s}^* \le 345^* \end{cases}$$
(10)

In the textile industry, the coefficient l is normally set as 2, which allows ΔL^* to have greater tolerance. The coefficient c is the chroma weighting, which is always equal to 1.0. The CMC (2:1) version of the formula has been shown to be useful for the estimation of the acceptability of color difference evaluations. The CMC (2:1) equation is a British Standard (BS: 6923) for the assessment of small color differences and is currently being considered as an International Organization for Standardization (ISO) standard.

Colorimetric properties

All pigment samples were heated up from 20°C to 70°C. They were measured at 40°C, 50°C, 60°C and 70°C during the decolorization progress by a spectroradiometer. After processing the raw data, the correct data were generated. The reflectance spectra of the four color groups are shown in Figures 3(a)–(d). The decolorization colors at certain temperatures are displayed in Figure 3(e) and the *L*a*b** distribution is displayed in Figure 3(f). All *L**, *a**, *b** values and CMC 2:1 values during the color change are listed in Figure 3(g). *T* represents the heating temperature. CMC 2:1 represents the color difference when the temperature changed from 20°C to 40°C, 40°C to 50°C, etc. As illustrated in Figure 3, it is obvious that the decolorization processes of red, green and blue colors are continuous without abrupt changes. However, the color yellow is to some extent different. The color yellow has an obvious change compared to color Y1, while colors Y1, Y2, Y3 and Y4 change slightly, which makes yellow pigment an unsuitable indicator thermochromic pigment for thermal woven textiles. The red and green groups change evenly but with little difference, which will lead to difficulty in being distinguished by eye.



Decolorization color images: (a) reflectance of the red color group; (b) reflectance of the yellow color group; (c) reflectance of the green color group; (d) reflectance of the blue color group; (e)

decolorization colors in CIELAB space; (f) $L^*a^*b^*$ distribution of decolorization colors; (g) L^* , a^* , b^* values and CMC 2:1 color difference values during color change.

The a^* , b^* value and L^* values describe the color path of changing at heating. In Figure 4(a), almost all a^* and b^* values, except values of the green color group, are decreased when the temperature increased, which means that when the temperature is increased, the color components reduce. Particularly in the range between 20°C to 40°C, the color components diminished rapidly. The a^* and b^* values of the green group are first increased and then decrease from 50°C. Figure 4(b) illustrates the lightness changing during temperature increasing. The red, green and blue color groups become lighter when heating up, while the yellow color group is the opposite. The yellow pigment became lighter quickly and was nearly invisible, so that the background gray color of the sample appeared. The measured color to a large extent had been influenced by the gray color, which leads to the lightness decreasing of the yellow color group. Among all four pigments, the blue pigment has the largest slope, which means this color has a more obvious change in lightness during temperature alteration.

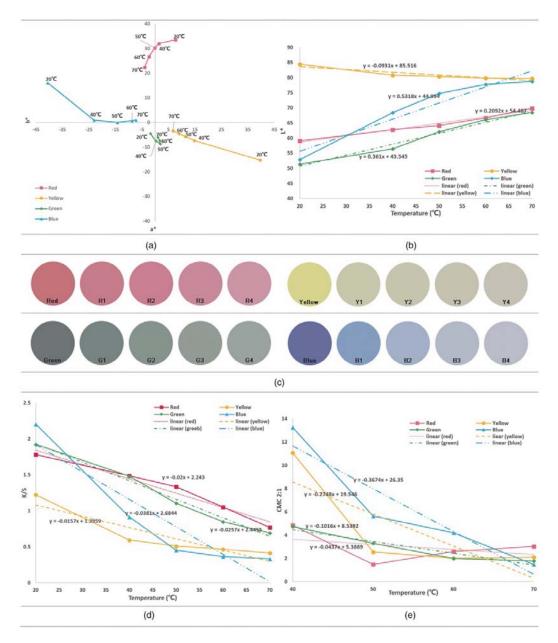


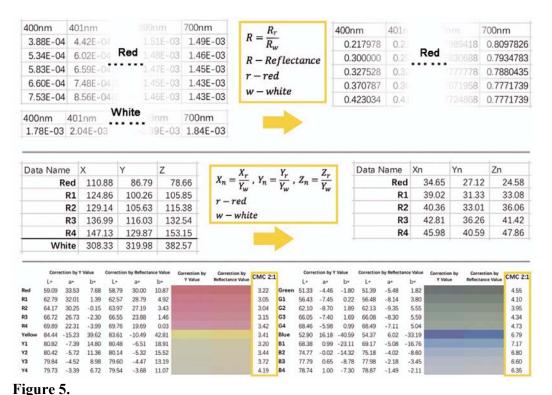
Figure 4. Comparison diagrams of four color groups: (a) CIELAB values in the a^* and b^* planes at heating; (b) CIELAB lightness L^* in dependence on temperature at heating; (c) measured color by the spectroradiometer; (d) K/S in dependence on temperature at heating; (e) CMC 2:1 color difference in dependence on temperature at heating.

The measured colors are listed in Figure 4(c). Apparently, red, green and blue colors change constantly, while the yellow color has a sudden change between yellow and Y1. As concluded previously, the map demonstrates a similar result in that the red and green colors are slightly different from one another. As demonstrated in Figure 4(d),

the K/S rate describes the color depth of all pigments during changing. They all rapidly lose their color depth between 20°C and 40°C. The red and green colors constantly and evenly reduce color depth up to 70°C. The yellow color diminished in color depth in the first change and almost no change occurred at the other positions. Combining the former figures, the change of the yellow color becomes difficult to distinguish when the temperature increased. In contrast, the blue color has the largest slope, which means that the color depth decreased. Compared with CMC 2:1 values, Figure 4(e) shows the result that the color difference of the red color is not stable, which decreased first and then increased. The color difference of the green color is rather small, which makes it difficult to distinguish. The yellow color has the largest color difference between yellow and Y1 and the lowest color difference amount from Y1 to Y4, so definitely cannot be used as an indicator pigment. On the contrary, the blue color has nearly the largest color difference between each temperature position and the largest slope among all colors, which means that the blue color has obvious color changing during the decolorization process. Combining the previous results, the blue pigment is the best thermochromic indicator pigment for thermal woven textiles.

Error analysis

There is another way to process the raw data measured by spectroradiometer – the reflectance data of colors divided by the reflectance data of the white board. The concept is similar to that of the Y_w correction, as they both aim to remove the light source influence. However, the results show some differences between these two methods. As listed in Figure 5, the CMC 2:1 color difference of both methods cannot be ignored. Some of them even reach 7.17. The red group is around 3, the yellow group is around 3.6 and the green group is around 4.5. The blue group shows the largest color difference, which is approximately 6.8. The reason why there are such notable color differences may be the different methods of the integral during calculation of the $L^*a^*b^*$ value. To guarantee the accuracy of all colors, this study adopted the Y_w correction because the XYZ data were calculated by the spectroradiometer after measuring, which is the smallest deviation before data processing.



Color difference between the R_w correction and the Y_w correction.

Because of the limitation of instruments, different light sources and imperfect calibration, the measurement results between the Konica Minolta CS-2000 spectroradiometer and the spectrophotometer Datacolor 650 have significant color deviation. Figures 6–9 display the measured color of pigment samples under 20°C using different instrument. The red, yellow, green and blue represent the color of the pigment samples measured by the spectroradiometer and dRed, dYellow, dGreen and dBlue represent the color of the pigment samples measured by the spectrophotometer. The CMC 2:1 values are 12.15, 13.47, 15.03 and 8.02, respectively. Apparently, these four pairs of colors have significant color deviation. The red, yellow and green colors are quite different between the two instruments, while the blue color has the smallest color deviation but still reached 8. Almost every color in Figures 69 shows that there are large differences in the blue color reflectance area and gradually diminish until the red color reflectance area. In the red color reflectance area, the graphs are almost overlapping. All four colors have over 10 value biases in lightness, which explains why the color measured by the spectroradiometer appears dark and grayish.

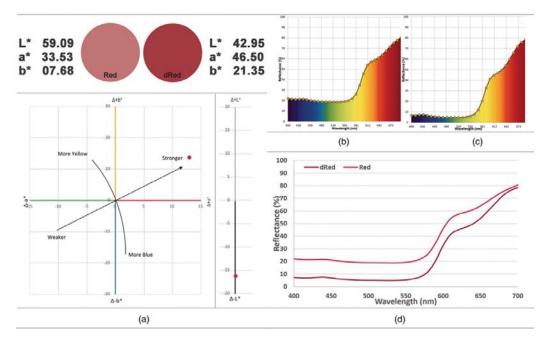


Figure 6.

Color difference between the red pigment sample measured by the spectroradiometer (red) and the spectrophotometer (dRed): (a) - diagram of ΔL^* , Δa^* , Δb^* ; (b) spectrogram of red color; (c) spectrogram of dRed color; (d) diagram of measured wavelength comparison.

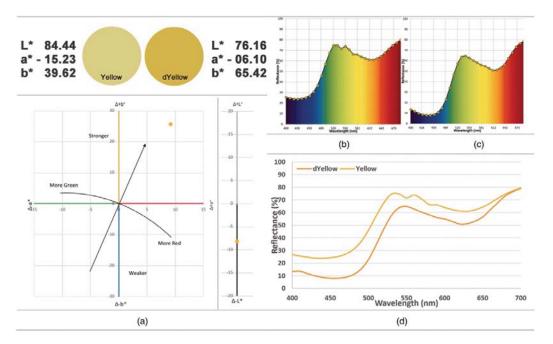


Figure 7.

Color difference between the yellow pigment sample measured by the spectroradiometer (yellow) and the spectrophotometer (dYellow): (a) diagram of ΔL^* , Δa^* , Δb^* ; (b) spectrogram of yellow color; (c) spectrogram of dYellow color; (d) diagram of measured wavelength comparison.

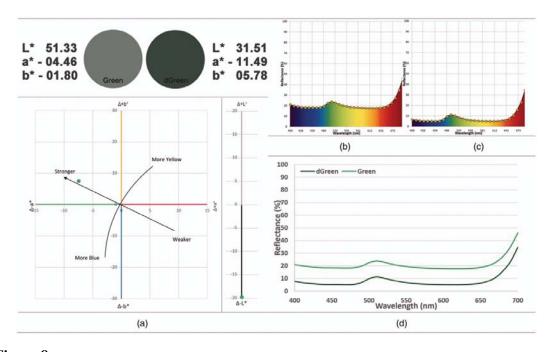


Figure 8. Color difference between the green pigment sample measured by the spectroradiometer (green) and the spectrophotometer (dGreen): (a) diagram of ΔL^* , Δa^* , Δb^* ; (b) spectrogram of green color; (c) spectrogram of dGreen color; (d) diagram of measured wavelength comparison.

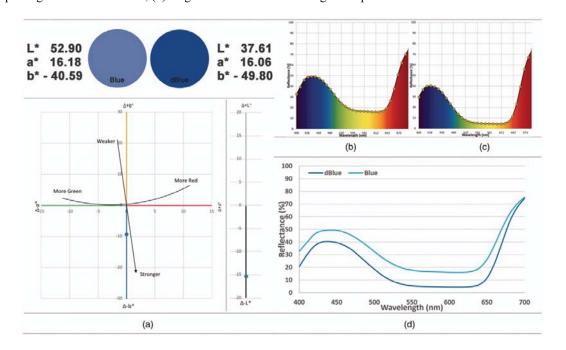


Figure 9. Color difference between the blue pigment sample measured by the spectroradiometer (blue) and the spectrophotometer (dBlue): (a) diagram of ΔL^* , Δa^* , Δb^* ; (b) spectrogram of blue color; (c) spectrogram of dBlue color; (d) diagram of measured wavelength comparison.

The most probable reason for this may be the different light source influence. The spectroradiometer measured samples under a real light source – illuminant D65 from the light box – while the spectrophotometer used theoretical illuminant D65 as the light source. These two light sources are supposed to be the same; however, they result in different measurements. Moreover, these two instruments have different measuring methods. The spectroradiometer measures the relative value, which needs to be divided by the white board value. During the calculation process, deviation may be introduced. In contrast, the spectrophotometer provides an absolute value, which does not need further processing. Lastly, the calibration of the spectroradiometer is much more difficult than that of the spectrophotometer, which may cause the deviation in the calibration phase.

Application design

In this application design, the conceptional design flow and prototype demonstration will be introduced. The first step is "Color Matching." In this phase, a Nikon D90 SLR camera (Figure 10(a)), GIT20 tripod (Figure 10(b)), DaXin digital DC power supply DX3005DS (Figure 10(c)), FLIR thermal imaging camera E33 (Figure 10(d)), spectrophotometer Datacolor 650 (Figure 10(e)) and Fuji Xerox DoCuColor 1450 GA printing machine (Figure 10(f)) were used. Due to the color matching necessary for professional instruments and software to achieve, this part of the study only provides a conceptional prototype, for which deviations are allowed to exist. Due to the blue color having the best performance among the four colors, the temperature indicator prototype will select the blue pigment to produce. Since the colors measured by the spectroradiometer are rather different from the colors as we see them, it will combine the two methods to match a similar indicating color. First, as shown in Figure 10(1), the SLR camera was used to take color photos in the decoloration process with fixed exposure while the spectroradiometer was measuring them at the same time. All the colors were read by MATLAB 2016 software and the average color was calculated. The color image is read by the software and pixel information is provided. Two coordinates, $A(x_1, y_1)$ and $B(x_2, y_2)$, are selected to fix the fetch area. After calculation, the $L^*a^*b^*$ values of the average color are generated. The codes are presented as follows

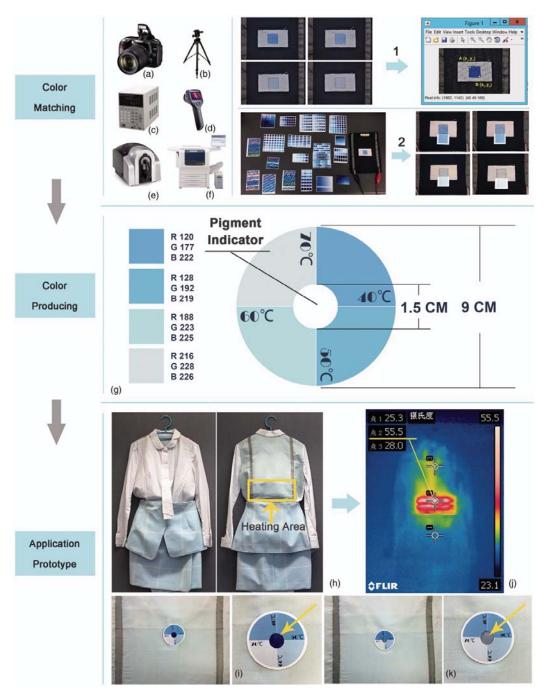


Figure 10.

Application design flow and prototype demonstration: (a) SLR camera; (b) tripod; (c) power supply; (d) thermal imaging camera; (e) spectrophotometer; (f) color printing machine; (1) color matching by SLR camera photos and MATLAB calculation; (2) color matching by color database; (g) indicator prototype design; (h) thermal woven garment; (i) indicator prototype before heating up the garment; (j) thermal image of the thermal woven garment under heating up; (k) indicator prototype after heating up the garment.

```
im=imread ('picture name.jpg');
imshow
impixelinfo
tmp=im (y1: y2, x1:x2, :);
tmp=reshape (tmp, [],3);
tmp=mean(tmp);
tmp=tmp/255;
lab=rgb21ab(tmp,'WhitePoint','d65');
```

Second, as shown in Figure 10(2), the blue color database is used to match the experimental blue color to select the best match. The combination of the results of the two methods is used to print the best match and to compare again until the differences cannot be distinguished by human eye. This method is just a substitute method for this prototype making. For real product making, the professional instrument and software will be adopted.

The second phase is "Color Producing." All best match colors for each temperature position are measured by the spectrophotometer (Figure 10(e)). The red, green, blue (RGB) values will be generated and are used to color design the temperature indicator prototype, as shown in Figure 10(g). The pie shape is divided into four even sections, each of which represents a temperature color, such as 40°C, 50°C, 60°C or 70°C. In the center, there is a hollow circle in which to place the blue thermochromic pigment, which will change color during heating up.

The last phase is "Application Prototype." In Figures 10(h)–(k), when heating up the thermal woven garment to 55°C, the indicator prototype successfully changes the blue color to the indicating color between 50°C to 60°C, which means that the user will know the thermal fabric is now heating up to around 50–60°C. After modifying the instruments and producing the indicator under industrial assistance, a more accurate product can be produced and thus it will indicate the temperature within a small range.

Conclusion

This paper aims to propose a possible method to select a thermochromic pigment indicator for thermal textiles to show the temperature in a fast and convenient way for potential customers. Four thermochromic pigment samples were heated respectively and the decolorization color was measured by spectroradiometer at 40°C, 50°C, 60°C and 70°C under an illuminant D65 light source. When the temperature increased, the

color component decreased while lightness increased. The color depth reduced when heated up, especially between 20°C and 40°C. The color difference of yellow, red and green colors are unstable. Combining all of the analysis results, in this experiment, the blue color is the ideal indicator for thermal woven textiles, which can provide the temperature range in a rapid and convenient way. Color deviation was analyzed, and the major causes may be instrument limitation, light source difference and calibration variation. A successful temperature indicator prototype using a thermochromic pigment was produced and the working effect was demonstrated. In future work, the modification can be adopted to accurately indicate the temperature range with industrial assistance when producing a professional product. In addition, pigments from different companies will be used to conduct contrast tests to verify if the method can be used in any scenario.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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