Thermochromic Dyes: Temperature Dependent Spectral Properties of Solids and Solutions

Introduction

Thermochromic materials are substances which reversibly change color with temperature and are commonly used in a variety of products like textiles and smart windows, among other materials.[1-4] These substances can include liquid crystals as well as organic dyes.[1,5] Leuco dye-based thermochromic substances, like those involving crystal violet lactone (CVL), are a well-studied subcategory of thermochromic materials.[1,5-8] These systems include three main components: the dye, a "developer," and a solvent.[1,5,6] For example, when using CVL as a dye, the developer—an electron acceptor for this system—initiates a change to the aromatic structure of the dye by opening a ring.[8] Changes to the dye's aromaticity leads to a change in the perceived color of the dye. This change in color is initiated by a change in phase of the solvent used.[8] As such, the melting temperature of the solvent is important.

Due to the nature of thermochromic systems, it is important to assess the temperature range at which the thermochromic system changes color as well as how effective the system is at changing the overall color of the system. The use of thermochromic materials in the textile industry also involves specific challenges related to how well a dye is able to adhere to different types of fabrics, and how stabile the dye itself is.[4,9] Consequently, it is often important to assess color fastness, or how susceptible a dye is to fading over time when developing commercially available thermochromic materials. When assessing the usable temperature range and the resistance to this change, a method for assessing the change in color is needed. Because the color changes are observable by human eyes for many of these thermochromic systems, UV-Visible spectroscopic methods can be used.

These spectroscopic techniques involve observing the change in UV-Visible light intensity either transmitted through or reflected off a material as a function of wavelength. Any photons which are not transmitted, reflected, or scattered are absorbed by the material, leading to an electronic transition between ground and excited states of the absorber. As these transitions require specific energy, only photons which are able to meet or surpass this energy level can be absorbed, leading to a wavelength-dependent response. Consequently, a UV-Visible spectrum can be observed which reports the absorbance as a function of wavelength. As this spectral range includes light which is visible to the human eye, it can also be an excellent instrument for assessing the color of an object or solution.

While absorbance measurements are the most common form of reporting UV-Visible spectra for non-scattering liquid solutions, opaque solid materials are more complicated to measure using strictly absorbance measurements. However, similar spectral information can be obtained from the reflectance of light off a material's surface, therefore diffuse reflectance measurements are often employed for these types of materials. Using the Kubelka-Munk formalism $(F(R))$,[10] the reflectance data can be converted to a spectrum proportional to absorbance and can therefore be used for similar analyses as are used for solution-phase samples. Consequently, the UV-Visible reflectance spectra of thermochromic systems can be an invaluable measurement when assessing how effectively the substance can change color as a function of temperature.

Through experiments described herein, the use of UV-Visible spectroscopic techniques to measure the response of a thermochromic system to temperature are demonstrated. Using the Thermo Scientific™ Evolution™ Pro UV-Visible Spectrophotometer, UV-Visible reflectance spectra were collected at room temperature and 65 ˚C mixture of CVL, tannic acid (TA), and 1-octadecanol. Additionally, temperature-dependent measurements of a mixture of CVL and TA without 1-octadeconal were performed. For these experiments, the instrument was equipped with a temperature-controlled Thermo Scientific™ Praying Mantis Diffuse Reflectance Accessory. Using the color calculations built into the Thermo Scientific™ Insight™ Pro Software, a color difference analysis was carried out to determine if the samples measured at two different temperatures were discernable by eye.

Experimental
Sample Preparation
Based on the procedures outlined by Zhu et al.,[6] the thermochromic system was set up using a mass ratio of 1:20:40 CVL:developer:solvent. Briefly, 30.1 mg CVL and 1.2015 g 1-octadecanol, the solvent, were mixed together and allowed to heat to ~ 70 ˚C. This allowed for the melting of 1-octadecanol, to allow for better mixing of the materials. Once the solvent was melted, 606.9 mg of TA, the developer, was added to the CVL/1-octadecanol mixture. With heating the sample was mixed to allow for a homogenous distribution of all components. The color of the final product appeared light blue.

A sampling of the CVL/TA/1-octadecanol mixture was added to ~ 1 mL of water. The mixture was then heated to ~65 ˚C and further mixed. The water layer changed from colorless to deep blue and the 1-octadecanol layer appeared clear and colorless when heated. When cool, the color of the water layer did not change, however the top layer, containing 1-octadecanol and CVL, appeared light blue once solidified.

To prepare the samples for analysis, part of the solid blue layer was spread onto a clean room lab wipe. This wipe was used to mimic fabric. The sample was further heated and cooled using a hot plate held at ~65 ˚C to ensure the sample was able to melt and stick to the fabric. As a control sample, a solid mixture of CVL and TA was made by adding 12.8 mg CVL to 256.0 mg TA. This mixture was not deposited on a fabric but instead analyzed in powder form.

Instrumentation
UV-Visible measurements were collected using a Evolution Pro UV-Visible spectrophotometer equipped with a Praying Mantis (Specac) diffuse reflectance accessory. All reflectance spectra were collected between 400 nm and 800 nm using a 1.0 nm step size, 2.0 nm spectral bandwidth, and 0.5 s integration time. Spectra were converted to Kubelka-Munk units using the Insight Pro software.

For temperature-controlled experiments, a reaction chamber was used as the sample holder for the Praying Mantis equipped with a temperature controller. Measurements were collected at room temperature and at 65 ˚C. A recirculating pump was used to cool the heating element of the reaction chamber with water as needed.

Results/Discussion
Figure 1a includes Kubelka-Munk spectra for the CVL/TA/1-octadecanol system spread on fabric and measured at room temperature and at 65 ˚C. Both spectra include maxima at ~615 nm and ~570 nm. As 65 ˚C is above the melting temperature for 1-octadecanol (~59 ˚C),[11] it is expected that a color change should be observed. As is shown, the overall Kubelka-Munk spectrum decreases as the temperature passes the solvent melting point. As the Kubelka-Munk spectrum is proportional to absorbance,[10] this behavior is consistent with a loss of color in the material, depicted in Figure 1b, matching the results observed by eye. While the observed color change can be seen when comparing these images, it does not appear to be a complete loss of color. In the measured spectrum (Figure 1a), features related to the dye can still be observed however it is significantly lower.
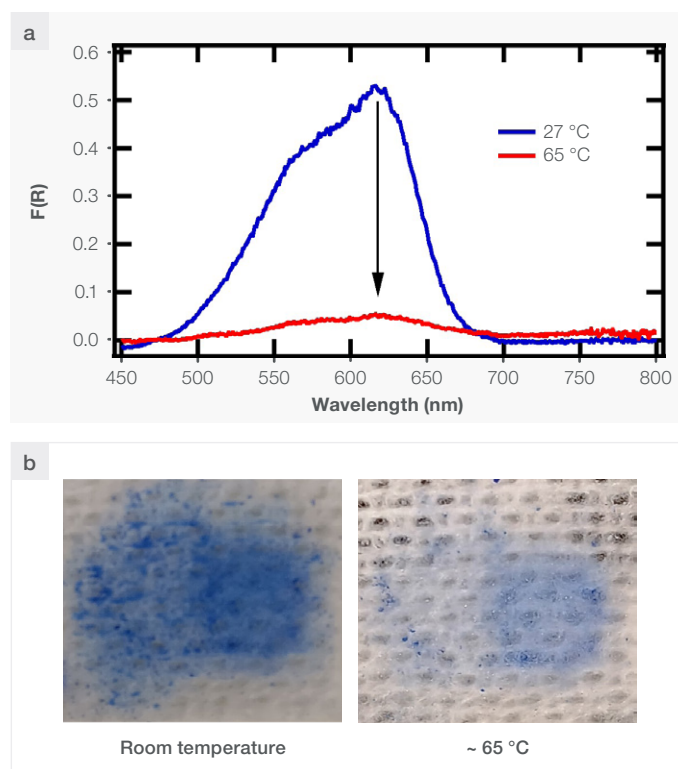
Room temperature   ~ 65 ˚C

Figure 1. (a) UV-Visible Kubelka-Munk spectra of fabric samples with CVL, TA and 1-octadecanol at 27 ˚C (blue) and 65 ˚C (red). Spectra were baseline corrected. (b) Images of fabric with CVL, TA and 1-octadecanol at room temperature and heated to ~ 65 ˚C.

Sample Temperature (˚C)	L*	a*	b*	ΔE* (vs room temperature)
Room	71.99	1.59	-21.88	0.00
65	82.57	-0.80	-4.31	20.65

Table 1. CIE L*a*b* (Illuminant C, 2˚ observer angle) and color difference values for CVL/TA/1-octadecanol at different temperatures. Color difference values were determined against the room temperature CIE L*a*b* color values.

Using the collected spectrum, CIE L*a*b* color values for the room temperature and heated samples were calculated and are included in Table 1. These color coordinates are well characterized and commonly used to convert UV-Visible spectra to a uniform color coordinate, for better sample-to-sample comparison.[12] The color difference ($ΔE$*), determined using the L*a*b* color values, between the measurements at room temperature and at 65 ˚C was found to be 20.65. According to the United States Pharmacopeia (USP), a color difference of greater than 3 suggests the color of two substances appear different by eye.[13] If this value is used as a guideline, then the sample is considered to have a different color when measured at room temperature and 65 ˚C, as expected.

As described previously, the color change is initiated by the melting of the solvent, leading to the tautomerization of the CVL.[6] Without the solvent, there should not be an observable change in color with temperature. To serve as a control experiment, reflectance spectra were collected of a mixture of CVL and TA without 1-octadecanol at 22 ˚C and 65 ˚C. Figure 2 includes the Kubelka-Munk spectra of these samples. As is shown, both spectra include a maximum at ~620 nm. With an increase in temperature, a small increase in the magnitude of the spectra was observed with changes in temperature. However, this change is minimal compared to the change demonstrated in Figure 1a.

The calculated color difference (Table 2) for the sample, calculated using the data collected at room temperature and 65 ˚C was found to be 2.20. This result is significantly lower than the color difference calculated for samples including 1-octadecanol. Considering how close this value is to a color difference of 0, it is likely the color difference at room temperature and 65 ˚C cannot be readily differentiated. While a small change in the spectrum is observed, this color difference further supports the need for a solvent to be present in this thermochromic system.
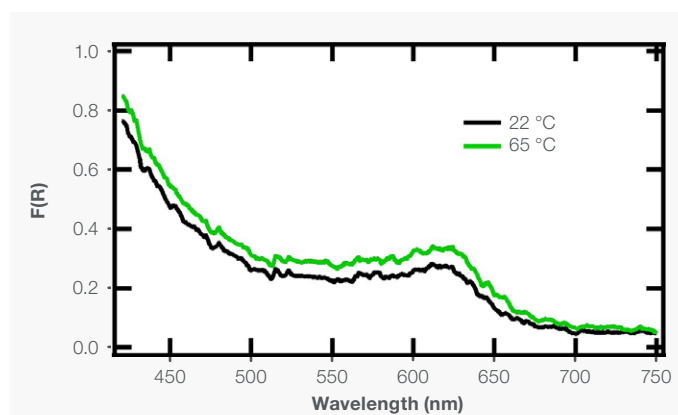

Figure 2. UV-Visible Kubelka - Munk spectra of CVL + TA without solvent.

Sample Temperature (˚C)	L*	a*	b*	ΔE* (vs room temperature)
Room	76.23	-4.59	12.44	0.00
65	74.21	-4.79	11.60	2.20

Table 2. CIE L*a*b* (Illuminant C, 2˚ observer angle) and color difference values for CVL/TA at different temperatures. Color difference values were determined against the room temperature CIE L*a*b* color values.

Conclusions

As demonstrated herein, UV-Visible reflectance techniques can be used to assess the temperature-dependent color change of thermochromic systems. These measurements further outline the ability to monitor this change for both fabric samples as well as powders, using the Evolution Pro UV-Visible spectrophotometer equipped with the temperature-controlled Praying Mantis diffuse reflectance accessory. Additionally, through color calculations carried out using the Insight Pro software, a more uniform method of comparing the color of a substance in different temperature regimes can be utilized. In the development of commercial products which are sensitive to temperature, these attributes of UV-Visible instruments can be highly useful in the development process. This is especially useful for the analysis of solid materials like textiles.

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