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Insight into the evaluation of colour changes of leuco dye based thermochromic systems as a function of temperature

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ABSTRACT

Evaluation of colour change as a function of temperature was studied on twenty eight samples of bulk ternary thermochromic composites using varying concentrations of crystal violet lactone as a colour former, bisphenol A as a developer and tetradecanol as a co-solvent. A number of parameters describing the colour change – reflectance, trichromatic values *X* and *Y*, visual colour densities *DX* and *DY*, and several parameters in CIELAB space, were obtained as a function of temperature. From these functions, the colour contrast, temperature sensitive interval, rate of colour change and width of hysteresis loop as the characteristics of thermochromic composites were evaluated and compared. The results show that cumulative colour difference ΔE_C, representing the length of the path of colour change in CIELAB space, might be the best parameter in such an evaluation. Taking into account both the rate of colour change and the width of hysteresis loop the best performing thermochromic system could be selected.

1. Introduction

Leuco dye based thermochromic (TC) systems are widely used as a carrier of thermally induced colour changes in various applications in smart packaging, security printing, textile colouring, toys and marketing [1–6]. Such TC system can be encapsulated in a polymer envelope and in the form of a pigment deposited in other polymer materials [1,4,7–9] or it can be directly enclosed in polymer fibres or polymer foils [10–12].

Usually three components, a colour former, a developer, and a co-solvent, are needed to produce a system with reversible colour change, and it is driven by their interactions. With the exception of the systems described in Ref. [13], the coloured complex of a colour former and a developer prevails below the melting point of the co-solvent. When the co-solvent melts, the dye–developer complex is destroyed and the TC system becomes colourless [4,14]. Typically, the melting point of the applied co-solvent determines the temperature at which the colour change occurs. However, in some complexes the temperature at which the decolouration appears can be lower than the melting point of the co-solvent [15]. The temperature of colour change is referred to as the switching temperature [4,16], discolouration temperature [17–19], thermochromic temperature [20], clearing temperature [15], and activation temperature [21–26]. The colour change is reversible and exhibits sigmoidal temperature dependence of the parameters describing the colour and colour hysteresis. These effects were observed in commercial TC inks as well as in bulk TC systems [9,15,21–25].

The colour former is an electron donating compound, e.g., spirolactone, fluorane or spiropyran [4,9,27,28]. In most research works on leuco dye based TC composites published so far the crystal violet lactone was applied. The developer is an electron acceptor (proton donor) compound such as Bisphenol A, alkyl gallates, phenols, hydroxybenzoates, and hydroxycoumarin. The co-solvents could be long-chain alkyl alcohols, esters, or acids [4,10–20,27–30]. When the lactone ring of the colour former is closed, then the dye is in its colourless state. The ring opening may be induced by the addition of a proton or through an increase in the polarity of the host environment [20,31–33].

For quantitative colour analyses of TC composites, reflectance at characteristic wavelength R_λ is often used. Mostly it is measured on bulk TC system in its solid form [19,27,29,30]. Colour density as a function of temperature is another widely used parameter in

Abbreviations: TC, thermochromic; CVL, crystal violet lactone; BPA, bisphenol A; TD, tetradecanol; CMF, colour matching functions.

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Table 1
Molar ratios x_{TD}/x_{BPA} in TC composites with constant $x_{CVL} = 1$.

60/1	80/1	100/1	120/1
60/2	80/2	100/2	120/2
60/3	80/3	100/3	120/3
60/4	80/4	100/4	120/4
60/5	80/5	100/5	120/5
60/6	80/6	100/6	120/6
60/7	80/7	100/7	120/7

TC system evaluation. To obtain temperature dependent characteristics, TC system was incorporated in some carrying matter. Coated polyester films [28], impregnated filter paper [9], and ordinary printer paper [14] were used for such measurements. Colour density measurements are also reported in Ref. [20], however, without closer description how the samples were prepared.

Digital photography was used in evaluation of colour changes upon temperature change when the composite was enclosed in polymer fibre [11]. Capturing digital image and its transformation into trichromatic values *XYZ*, with consequent visual colour density calculation from trichromatic *Y* value is also reported [34]. The methodology uses bulk TC composites in vials, tempered in a water bath. After reaching desired temperature, a set of samples was removed from the water bath and an image was acquired by a digital camera with white reference material present in captured area. It is worth of mention that the methodology of digital image acquisition requires uniform stable illumination and camera characterization for any quantitative analyses and therefore the results obtained by this method might not be ideally suited for accurate colour analysis.

Extensive colorimetric studies were performed by Kulčar et al. [22–24], where reflectance spectra of commercial printing inks were obtained, and then used in calculation of colorimetric parameters in CIELAB space. Temperature dependences of lightness L^* and a^* and b^* coordinates as well as colour difference of heated and cooled sample are presented. From the two-dimensional dependences, four temperatures were characterized. The temperature at which the decolouration starts and temperature at which the decolouration stops are characteristic for heated sample and temperatures at which the colouration starts and colouration finishes are characteristic for sample cooling, similarly as in experiments using colour density evaluation of bulk systems [9,28]. Colorimetric parameters can be used in evaluation of total colour contrast and width of hysteresis loop. This technique was also adopted and extended by calculations of size of hysteresis loop's area in CIELAB space and highest decolouration rates [25].

In our previous paper [21] we have presented temperature dependent colour changes of bulk TC composites using 1-octadecanol as a co-solvent with different concentrations of a developer. Temperature sensitive interval, colour and lightness contrast and width of hysteresis loop were computed using regression of $L^*(T)$ dependence by five-parameter sigmoidal function. The sample was measured in a special sample holder, which allowed measuring the sample with constant thickness regardless the temperature, which was properly controlled by tempered water block. This methodology was adopted and further adjusted by

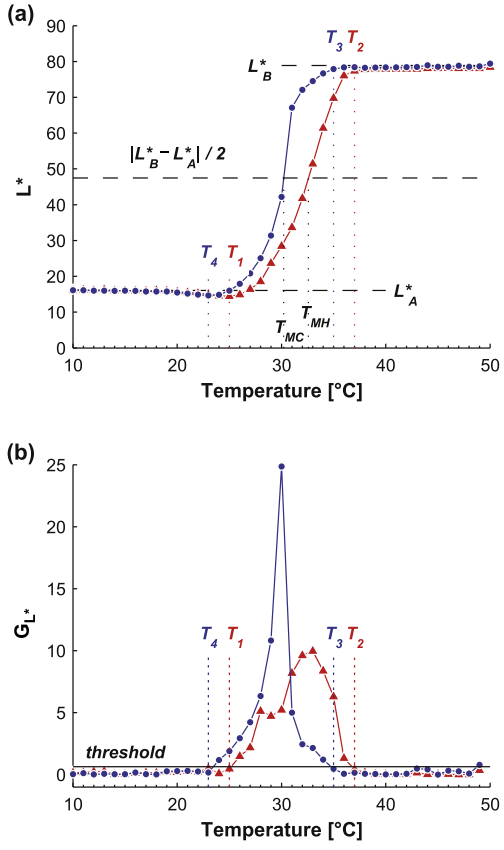

Fig. 1. Illustration of finding temperatures T_{MC} and T_{MH} corresponding to the middle value of colouration (L_A^*) and decolouration (L_B^*) interval (a) and finding T_1, T_2, T_3, T_4 temperatures from gradient G_{L^*} (b), where triangles represent heating and circles cooling of the sample.

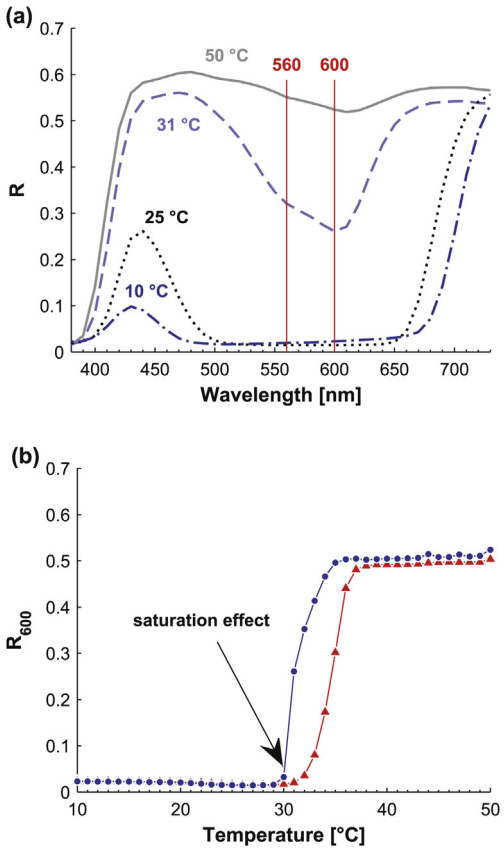

Fig. 2. Reflectance spectra of TC composite with molar ratio x_{TD}/x_{BPA} = 100/6 measured at different temperatures while cooling (a) and reflectance at 600 nm as a function of temperature for heating (triangles) and cooling (circles) (b).