

Structural, optical and thermal properties of benzofluoran-based thermochromic composite

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Abstract: *Thermochromic composites, consisting of leuco dye, colour developer and organic solvent indicate reversible thermochromism, with colouration in the solid state and discoloration in the molten state. These functional materials, the so-called smart materials, are of considerable interest in graphic art technology for applications such as temperature sensors, security markers, thermal printing, cutlery and clothing.*

Thermochromic composites of 6'-(diethylamino)-1'-2'-benzofluoran (BF) dye, 2,2-bis(4-hydroxyphenyl)propane (BPA) developer and 1-octadecanol (OD) solvent were investigated in this work. Composites with four different molar ratios of BPA were analysed. The chemical structure, thermal and optical properties of samples were analysed by UV-VIS and FTIR spectroscopy, colorimetric measurements and differential scanning calorimetry. The applied methods enable to study the properties of the material below and above the phase-changes. Much interest was devoted to analyse how different molar ratio of developer influence on the structural, optical and thermal properties of the composites.

Keywords: *thermochromic composites, leuco dye, structural, optical, thermal properties*

Introduction

Thermochromic (TC) composites, consisting of leuco dye, colour developer and high temperature melting organic solvent, change colour due to structural modifications occurring with temperature, i.e. reversible thermochromism, with colour in the solid state and discoloration in the molten state [1–6]. They are suitable for many applications also in graphic art, e.g. temperature sensors, security markers, thermal printing, cutlery and clothing.

We have thoroughly investigated the properties of TC printing inks in the past. The dynamic colorimetric properties of pure [5,7] and mixed inks [8] were analysed. The rheological properties [9] and printability of offset inks were analysed [10]. The light fastness and high-temperature stability of inks were studied as well [11]. After extended research of special properties of TC printing inks we start to investigate the active component, the TC composite [6], which is normally protected in polymer capsules and dispersed in resinous medium. The optimisation of the composite was done according to its colorimetric properties. The current work represents continuation of this research with focus on material research to analyse the changes of chemical structure in both states of the TC composite. Much attention is devoted to the influence of the applied substances on thermal properties of the TC composite.

Thermochromic composites of 6'-(diethylamino)-1'-2'-benzofluoran (BF) dye, 2,2-bis(4-hydroxyphenyl)propane (BPA) developer and 1-octadecanol (OD) solvent were investigated in this work. Four different molar ratios of BPA were applied to study the chemical structure of the composite and its changes. For this purpose, the UV-Vis and IR spectroscopy were applied. In

addition, colorimetric measurements and differential scanning calorimetry (DSC) were applied. The methods were used to study the properties of the material below and above the phase changes. Much interest was devoted to analyse how different molar ratio of developer influence on the structural, optical and thermal properties of the prepared composites.

Theoretical background

BPA influences on the interactions of BPA with BF in the solid and on BPA-OD complexes in the liquid state and consequently on reversibility of colour change. To determine the colour modulation of prepared TC composites, their reflectance spectra were measured in the visible (Vis) spectral region as a function of temperature and used colorimetric calculations. The absorbance spectra of all composites in coloured and discoloured states were measured in UV-Vis spectral region. The vibrational analysis was done applying infrared (IR) measuring technique. Results are supported by differential scanning calorimetry (DSC).

Formation of a positive charge on the spiro-centre carbon happens because of the opening of the lactone ring in the BF dye. This opening brings also changes in carbonyl C=O and C–O bands. They are replaced by the equivalent (or nearly equivalent) C = O bond-and-a-half bonds: symmetric and asymmetric COO⁻ stretch. A conjugated structure is revealed by increase in the C=N (double) bond, which occurs as a result of electron donation through the phenyl rings (Figure 1c). The C=N group is indicated by the C=N stretching band in IR spectra. [12]

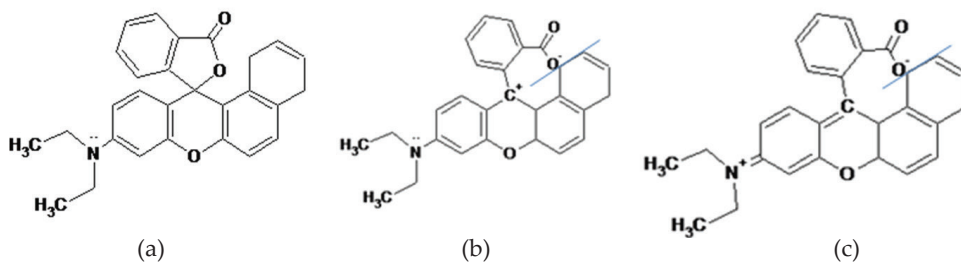


Figure 1: Structure of ring-closed (a) and ring-opened forms (b), and conjugated structure of ring-opened form (c) of the BF dye

Experimental

Four TC composites were prepared applying 0.1 mmol BF (>98.0%, TCI Europe), different amounts of BPA developer (>98.0%, TCI Europe) in a mmole ratio from 0.1 to 0.4 and 30 mmol OD (95%, Sigma Aldrich). The BF and BPA were dissolved in melted OD by mixing at 80 °C for 6 h and then slowly heated to 120 °C. The solution was kept at 120 °C for 2 h, then cooled rapidly by quenching in liquid nitrogen. All composites were milled to the same particle size.

Spectral absorbance was measured by the Lambda 950 UV-Vis-NIR (Perkin Elmer, USA) spectrometer, equipped with integrating sphere (150 mm diameter) in the 200–1000 nm spectral region. The composites were precisely weighted and then compressed in molten state between two fused silica discs (Corning 7980). The samples were placed on the water-thermostatted cell holder (Perkin Elmer, USA) and heated/cooled with the water thermostatic circulator to the fully coloured and totally discoloured states.

Reflectance spectra of prepared TC composites were measured as a function of temperature using the i1 Pro (X-Rite, USA). The KeyWizard software was used for calculating the CIELAB values (D50, 2° standard observer) [13]. A specially designed copper holder with white electrodeposited surface coating, heated/cooled on the water block surface was applied to measure the reflectance spectra in dependence on temperature. The temperature of the measured

composite was supposed to be equal to that of the white-coated holder. Its surface temperature was evaluated by infrared thermometer, combined with thermocouple (Type-K probe, Fluke 561, accuracy ± 2.2 °C) and compared with the temperature of the water circulating inside water block and controlled by thermostatic circulator. TC composites were placed on the white copper holder for 5 min at 20 °C, then slowly heated to 70 °C, and left there for 3 min before cooling. This way a stable shape of the sample inside copper holder was obtained. The average heating and cooling rates were 3.7 ° and 2.0 Cmin⁻¹, respectively.

DSC measurements were obtained with Pyris 1, Perkin Elmer at a scan rate 2 °Cmin⁻¹ in the temperature range 40–62 °C.

IR data were obtained with a BRUKER IFS 66/S spectrometer. BF, BPA and their binary mixtures were dissolved in benzene and placed in thin layer on CsI transmission windows. The spectra were normalized according to the 1630 cm⁻¹ band.

Results and discussion

UV-Vis absorbance spectra

UV-Vis absorbance spectra of TC composites with different molar ratio of BPA have similar UV absorbance spectra at room temperature (RT) and in molten state (at 65 °C) (Figure 2). The spectra depend on the BPA content: all peaks are stronger in composites with more BPA and practically disappear in the sample with the lowest amount (Figure 2a). In the visible region the RT spectra show the coloured state; greater amount of BPA gives stronger absorption. In the liquid state all the spectra practically coincide (Figure 2b). The samples are transparent in molten state giving negligible scattering of light, thus also practically zero baseline in absorbance. This behaviour extends from the visible up to 340 nm where a small UV absorption appears in composites with higher BPA content. Scattering of collimated light beam on crystallites in the solid state of samples gives rise to higher baseline.

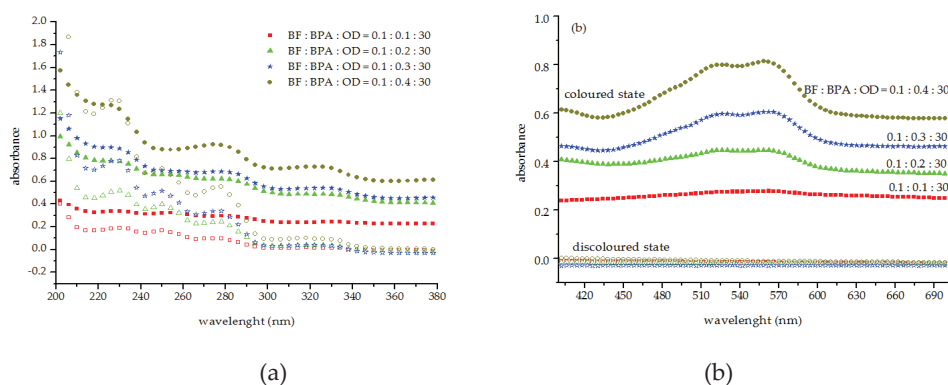


Figure 2: The absorption spectra of TC composites with 0.1 mmol of BF and 30 mmol of OD and different amounts of BPA from 0.1 to 0.4 mmols in UV (a) and visible spectral range (b)

Colorimetric properties

All composites have high C^* values in the solid states and good heating-cooling reversibility, except the sample with the lowest content of BPA. The TC composite BF : BPA : OD = 0.1 : 0.2 : 30 has a 2.1 °C width of the hysteresis loop (Figure 3a). In coloured state the samples have different colour hue whereas in discoloured one they have $a^*=0$ and b^* close to zero (Figure 3b).

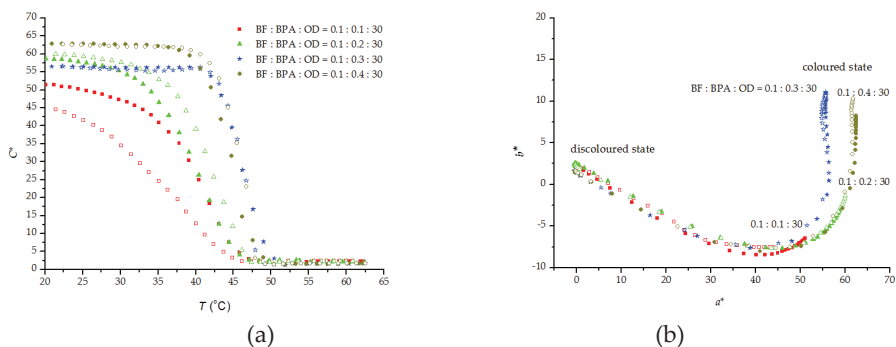


Figure 3: C^* values as a function of temperature (a), and a^* , b^* values (b) of the studied TC composites

DSC analysis

The OD is responsible for phase changes and for basic thermal properties of studied composites. It exhibits the solid-solid (S-S) and liquid-solid (L-S) phase changes, which are overlapped at heating and clearly displaced at cooling [14]. A small amount of BF and BPA practically do not influence on melting temperatures but influence much the transitions at cooling – the liquid-solid (L-S) and solid-solid (S-S) phase changes (Figure 4).

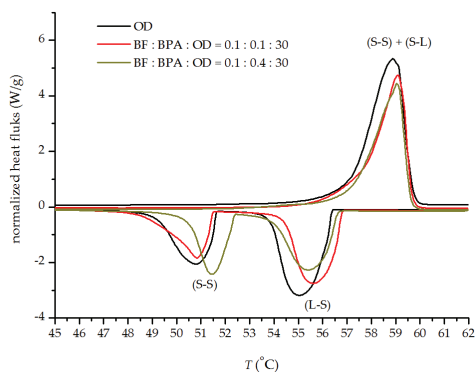


Figure 4: DSC curves of OD and two TC composites

IR absorbance spectra

Binary mixtures of BF and BPA were prepared in the same molar ratio as the ternary composites. Their IR absorbance spectra are shown in Figure 4.

When the C=N group is conjugated to an aromatic system (e.g. Figure 1c), the C=N stretching vibration mode is shifted by the conjugation effect from 1650 to 1600 cm^{-1} [15, pp. 199–201]. In our samples, the peak appears at 1590 cm^{-1} in composites but not in pure compounds, revealing the ring-opened form. This is in accordance with similar TC composites based on fluorane dye where C=N vibration formed in the open ring form was assigned to peaks in the $1520\text{--}1608\text{ cm}^{-1}$ region [16].

Five-member ring esters (γ -lactones) have C=O frequencies at $1790\text{--}1760\text{ cm}^{-1}$ [15, pp. 134–135]. In the IR spectra of BF dye this band is located at 1760 cm^{-1} (Figure 4). It is still present in the

BF : BPA = 0.1 : 0.1 but disappears at higher BPA content. This shows that 0.1 mmol BPA is not enough for complete opening of the lactone ring. In similar binary systems this band was found at 1745 cm^{-1} (crystal violet lactone – lauryl gallate) with similar properties [12]. Increasing the amount of developer to BF : BPA = 0.1 : 0.2 causes opening of the lactone ring. The new band appearing at 1720 cm^{-1} appears in spectra of samples with 0.2, 0.3 and 0.4 mmol of BPA. It is characteristic for hydrogen-bonded carboxyl C=O (but not for dimerized as in alcohol-carbonyl bonding) [15, pp. 139]. This vibration was found in crystal violet lactone – lauryl gallate binary system showing the ring open form at 1710 cm^{-1} [12]. The appearing of this band further confirm the ring-opening form of the BF leuco dye.

With the opening of the lactone ring the peak at 1280 cm^{-1} disappears, corresponding to (O=C)-O stretch in ring closed form of the BF dye.

The symmetric COO⁻ stretching band is usually seen at $1450\text{--}1360\text{ cm}^{-1}$ and the asymmetric one at $1650\text{--}1540\text{ cm}^{-1}$ [15, pp. 141]. In the IR spectra the strong peak at 1548 cm^{-1} belongs to asymmetric carboxylate vibration and the peak at 1373 cm^{-1} is assigned as the symmetric COO⁻ stretch.

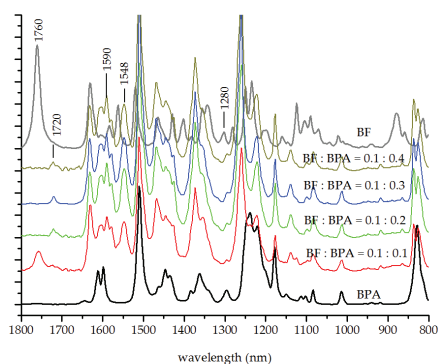


Figure 4: IR spectra of applied BPA developer, BF dye and binary mixtures

Conclusions

The material properties of benzofluorane-based thermochromic composite were investigated. Most attention was devoted to the concentration of the applied developer.

DSC analysis showed that small amounts of BF and BPA do not influence on temperature of the melting point but shift the temperatures of phase changes at freezing: the liquid-solid (L-S) and solid-solid (S-S) transitions.

Increasing the amount of BPA developer results in the stronger absorption in the visible range and large chroma. IR absorption spectra show that molar ration of BF : BPA = 0.1 : 0.1 is not enough for complete opening of the lactone ring in the dye molecules. Larger amount of developer (at least 0.2) is needed for this to occur.

The samples with 0.2 mmol BPA or more approximately reversibly changes the colour during heating-cooling cycle.

The present research gave the optimal molar ratio needed for efficient thermochromic effect to occur in the studied system.

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