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THERMOCHROME PRINT COMPOSITIONS FOR SMART PACKING

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Abstract

The present study reports the development of novel thermochromic compositions based on carbocyanine (polymetine) dyes and their mixtures. The sensors of the compositions are two types, they have various temperature transitions from 25°C to 40°C and higher (in first type) and from T = -10ºC to 0ºC (in second type). Both types differ in compositions and preparing conditions. The compositions can be used in printing process like inkjet printing and flexographic methods, they can be applied on paper and polymer materials. The advantage of the development of thermochromic compositions is that they have no need of manufacture microencapsulated systems. But just how the microencapsulated ones they can be used for "smart packaging".

Morphology, chemical structure and spectral properties of thermochromic films were investigated by SEM, XPS and reflectance spectroscopy. The mechanism of the thermochromic transitions is based on controlled formation / destruction of organic molecular crystals known in literature as J-aggregates.

Key words: *thermochromic compositions, print, smart packing, cyanine dyes, reflectance spectra SEM, XPS*

INTRODUCTION

The thermochromic systems attracted much attention because of their different industrial applications. The great scientific and practical interest to thermo chromic systems is related to the abilities to protect pharmaceutical and food product, from falsification of securities. There are also quality product inspections for correct temperature control, improving food industry process efficiency, especially in the field of food supply chain management.

The improvement of smart packaging for better food safety directly benefits the end-consumer, but there may also be direct benefits for the food retailers and suppliers with this technology. Sustainability of food supply chains is a topic of considerable political interest and these acts as another driving force for the development of this technology.

It should be noted here that most of known time-temperature indicators of smart packaging are microencapsulated systems. Manufacturing process of such systems is expensive and not efficient due to the complexity of the manufacturing process of the microencapsulated indicators and their large capsule size (5-6 microns when the size of the ink film is 1.5 microns). Therefore, the development and study of new time-temperature indicators including thermo chromic systems are important today

We applied polymethine (cyanine) dyes as novel heat-sensitive compounds of thermochrome compositions. This class of dyes has been object of continuous interest in the scientific community because of their application in the spectral sensitization of photographic emulsion and wideband semiconductors, information recording materials, nonlinear optical materials and as fluorescence indicators in biological systems. A feature of polymethine dye molecules is ability to self-organize so-called J-aggregates (molecular crystals). The degree of dye crystallinity depends on the environments (temperature, humidity), resulting in shift and change of a spectral curve of a visible absorption band (from wide to narrow, and conversely). Phase transition induces a large bathochromic or hypsochromic shift. This effect forms the basis of the principle using polymethine dyes as the main component of the thermochromic sensor [1,2]. Concerning the mechanism of the thermochromic process of the cyanine dyes in layers in the literature there is no consensus.

METHODS

During the experiment as a media was used biaxially oriented polymer films of polyethylene terephthalate (PET) and polypropylene (PP), polymer films for ink jet printing with a modified surface layer, glossy and matt inkjet paper, various types of coated fine paper. SEM-images showing basic types of media can be seen in Fig. 1.

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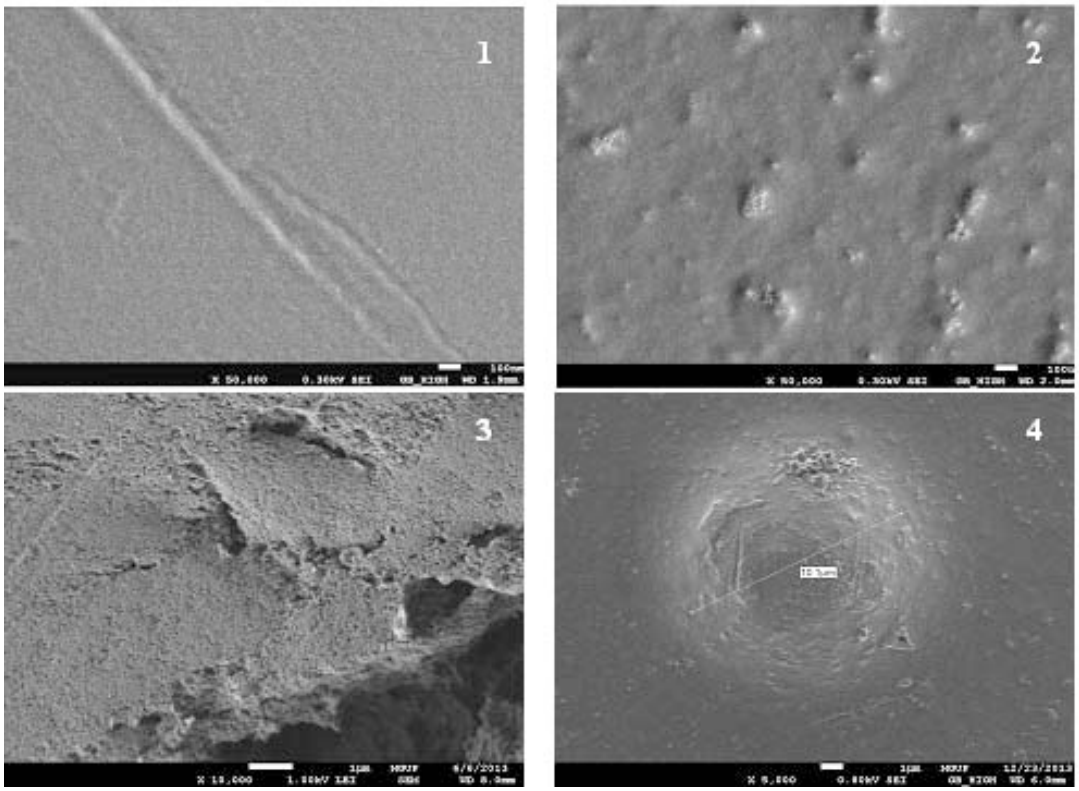


Figure 1

SEM-images of the surface of various types of media , wherein 1 - PET resin film, 2 - PET resin film, corona treated, 3 - inkjet paper, 4 - polymer film for inkjet

As a base of the thermochromic compositions was used following dyes: pyridine salt of 3,3-di-γ-sulfopropyl-9-ethyl-4,5,4',5'-dibenzotiacarbocyaninbetain (D1), three-butilammony salt of 3,3'- di-γ-sulfopropyl-9-ethyl-5-methyl-5'-phenyltiacarbocyaninbetain (D2), three-ethylammony salt of 3,3'- di-γ-sulfopropyl-5,5'-dichlorinetiacyaninbetain (D3) and 3,3'-di(betahydroxiethyl)-5,5'-dimetoxy-9-ethyl-tiathreemethimecyaninchloryde (D4). Polymethine dyes were purchased from Scientific Center of Chemfotoproject and used without further purification.

As a film-formers was used various of hygroscopic polymers. That kind of agents helps also for adjusting the viscosity of the composition to the desired values and helps to correct temperature transitions.

For the preparing of the aqueous and alcoholic thermochromic compositions solutions of dyes at the next step the composition was sonicated, after which are introduced the polymer solutions in various ratios.

After that the compositions were applied to the media by the help of spin-coating, inkjet and flexo printing.

Spectral reflectance and CIELab values were measured by using SpectroEye spectrophotometer (X-Rite), using D65 illuminant and 2ºstandart observer. Standard deviation of the measurements did not exceed 5%.

The surface treatment of polymer films was carried out high-frequency (40 kHz) corona discharge at room temperature. The corona current value were changed from 50 to 100 mA. The distance between the grounded plate electrode with samples and the grid was 0,5-0,7 mm.

The surface morphology was investigated using Jeol JSM 7500F field emission SEM. To avoid destruction of samples was applied low acceleration voltages (from 0,3 to 0,8 kV). Images were obtained in secondary electron detection mode. Chemical structure of surfaces were analyzed by XPS using Jeol JPS-9200 in monochromatic AlK excitation source under a base pressure of 5×10^{-8} Pa. The spectra of C1s, O1s (also N1s and S2p for dyes) lines were recorded. All recorded lines were calibrated to the C1s line at 285eV.

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Thermochromatic effects were estimated by using origin device at temperature intervals from -20 ºC to +80 ºC with at accuracy of measurement ± 3 ºC.

Conditions for the formation of containing polymethine dyes layers with necessary optical properties on a surface of initial and modified substrates are the subject of the study.

RESULTS

As a result of research was developed three compositions with color contrasting thermochromic transitions, two of which appear upon heating in the range of 40 to 70 º C (depending on the composition) and one - upon cooling to approximately -10 º C and the subsequent heating above 0 º C.

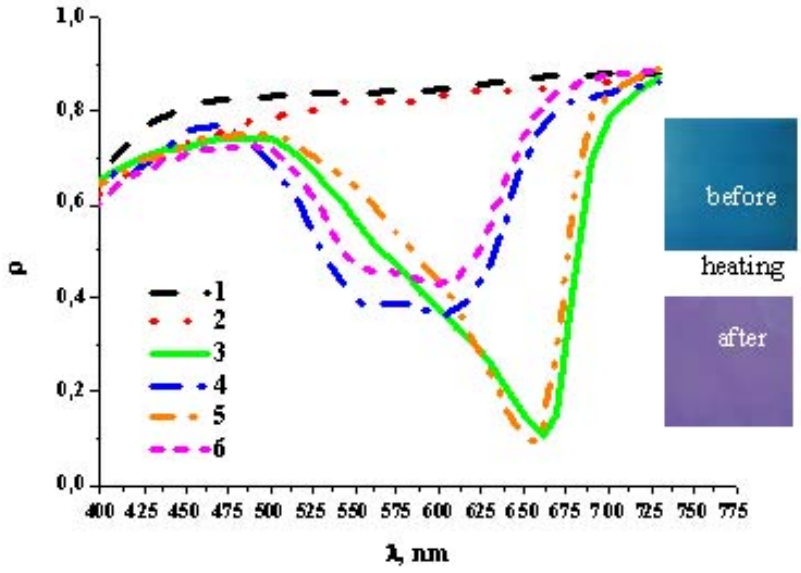


Figure 2

Reflectance spectra (left) and visual images (right) of the D1 films, where 1 –standart, 2 – substrate, 3– dye layer on initial polymer film at room temperature, 4 – dye layer on initial polymer film after heating, 5 – dye layer on modified polymer film at room temperature, 6 – dye layer on modified polymer film after heating

Figure 2 shows reflectance spectra and image of the D1 films on activated by corona discharge and nonactivated PET surface before and after heating. The D1 films have irreversible contrasting color transition after heating at temperature up to 70 ºC from blue to violet color. The as-deposited film is blue in color associated with a J-band located at 660 nm. After heating, the 660-nm band disappears, but violet color appears, indicating that the J-aggregates are destroyed. The color difference value ΔE is 50,3.

According to SEM and XPS studies, we consider that the change of optical properties based on thermally induced structure transitions dye layers (figure 3) and partial destruction of first type dye, presumably due to thermal oxidation (Fig. 4).

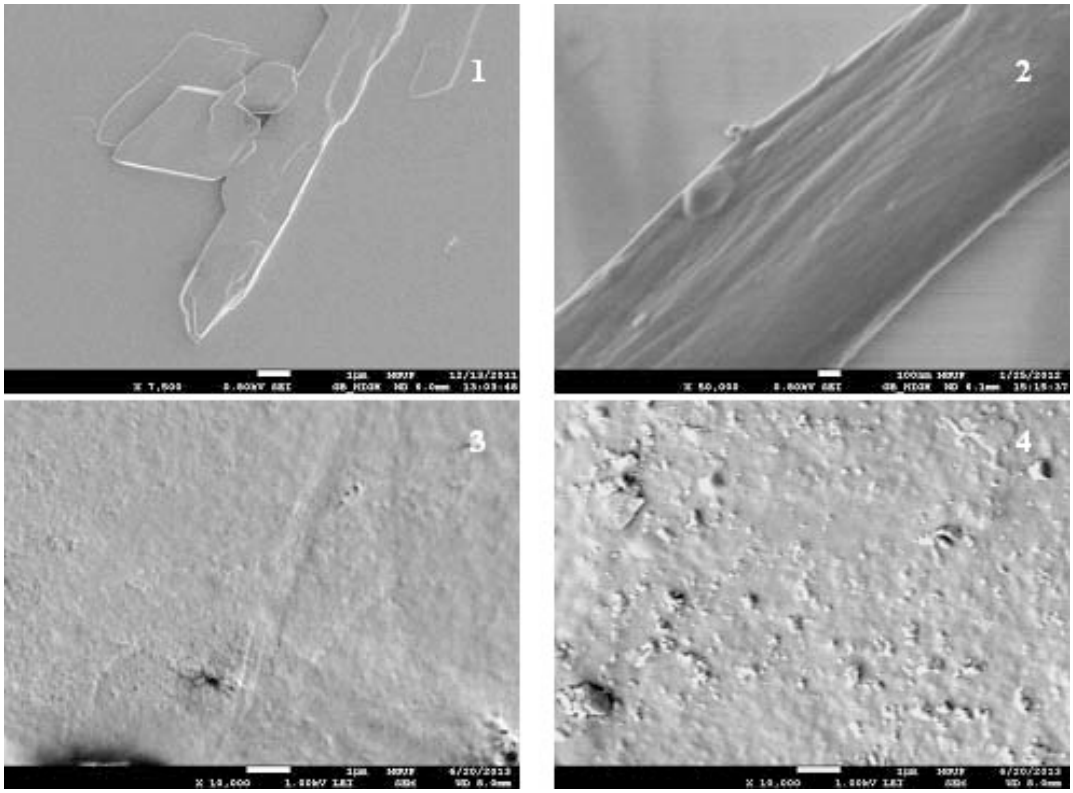


Figure 3

SEM-image of dye (D1) layer, where 1 - on polymer film at room temperature, 2 - on polymer film after heating, 3 – on paper at room temperature, 2 - on paper after heating

Fig. 4, which shows the XPS spectra of the basic powder dye D1 and layers of D1 deposited in a different ways on the PET film, we can see the ratio between the component lines N1s, S2p and O1s, increase in oxygen concentration after the thermal influence in layer K1 and appearance of C1s spectrum of a high energy component with regard ~ 288.6 eV that may be due to partial degradation and possibly thermal oxidation in D1.

At the same time it must be emphasized that the broad spectra of S2p and O1s and unequal ratio of high-and low-energy components of the line of starting powder N1s D1 (curve 1 in Fig. 4) may indicate some degradation of the basic powder dye. Another possible reason for the observed shape of the spectra of S2p and O1s - is differential charging of the surface of the powder dye, however, its effect was eliminated by a special technique.

For to reduce the transition temperature of the composition D1 was administered solutions hygroscopic polymers. Depending on the quantity of the solutions the transition temperature can vary from 70 to about 40 º C. The introduction of these substances do not influence the spectral characteristics of the layers.

These effects were obtained by applying the composition to surfaces of polymer films and surface-modified papers. It should be noted that the deposition of cyanine dyes with the required optical properties, namely, J-aggregate form, typically involves the necessity of preconditioning the surface by applying a so-called counter-substrate (metal ions), polyelectrolytes, amphiphilic substances etc. [2,3,4]

As is known, the surface of the polymeric film as PET and PP is hydrophobic. In this connection, the binding step of printing on such films is modification of the surface in advance, in most cases, by the corona discharge. Determined that such treatment, namely the formation of characteristic sections of the inhomogeneous structure due to the etching of the amorphous phase and surface contamination (Fig. 1) and the formation of additional surface carboxyl and carbonyl groups (data XPS studies), promotes the crystallization of dye that is particularly evident after corona treated.

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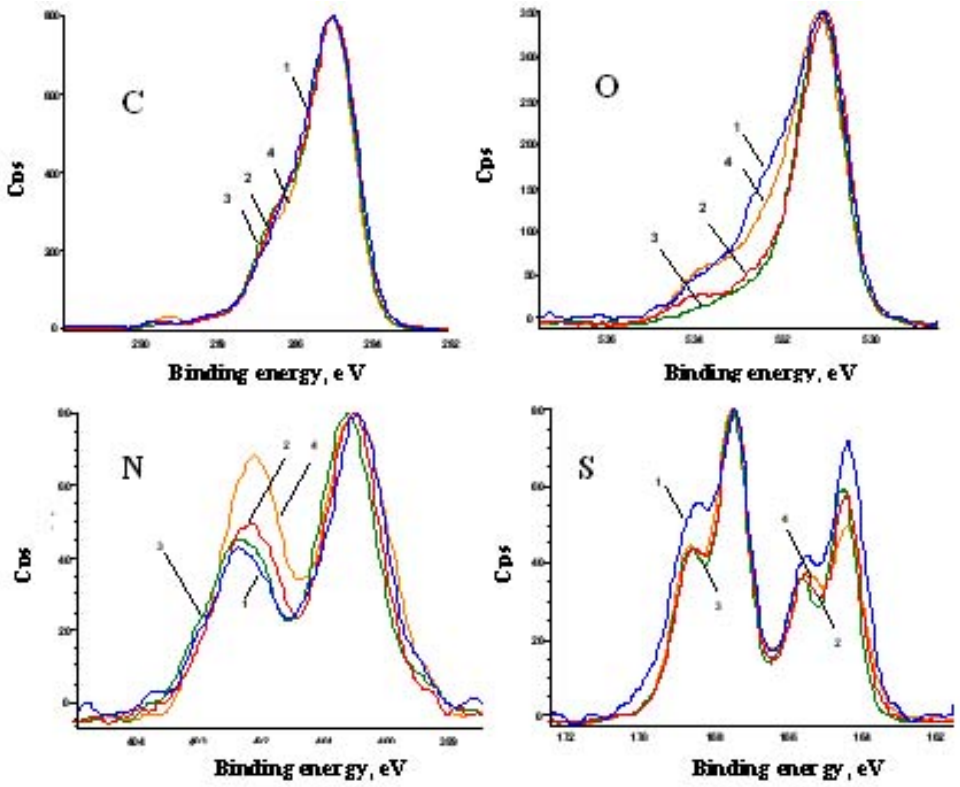


Figure 4

Detailed XPS spectra of D1, where 1 - powder 2 - ink jet, 3 - spin coating, 4 - after thermal treatment on the surface of the PET. Curves are normalized to the maximum intensity curve.

In the case of inflicting of the composition at paper, the formation of layers with the desired spectral characteristics is possible only when using paper is primer precoated. Otherwise, the components of the composition interact with the cellulose of the paper which is followed by bleaching.

The photochemical stability of the compositions during storage at room temperature under artificial lighting characteristics are stable until thermal processing of storage in the light for 2 months to one year if stored in the dark. After heating for 1-2 weeks discoloration occurs layers.

Thermochromic layers without film-formers are weakly resistant to water and humidity above 80%, but there are resistant to some organic solvents, in particular acetone. In the presence of the polymers resistance to external influences, and adhesion to the substrate increased, however, when the film-forming polymer content of more than 30 wt. % thermochromic effect disappears

The basis of the second type is a colorant composition D2. Figure 5 shows reflectance spectra of three-butilammony salt of D2 films. One can observe a reversible double contrasting color transition after coating at T = 20ºC, followed by samples frizzing at the temperature lower T = -20ºC and later heating up to 0ºC and higher with discoloration after 4-5 cycles. Visual color changes from pink to blue at frozen and to violet at heating. The color difference values ΔE are 62,8 and 39,9, recently. The curve 3 of the graphic (figure 2) associates with a J-band of second dye type located at 610 nm.

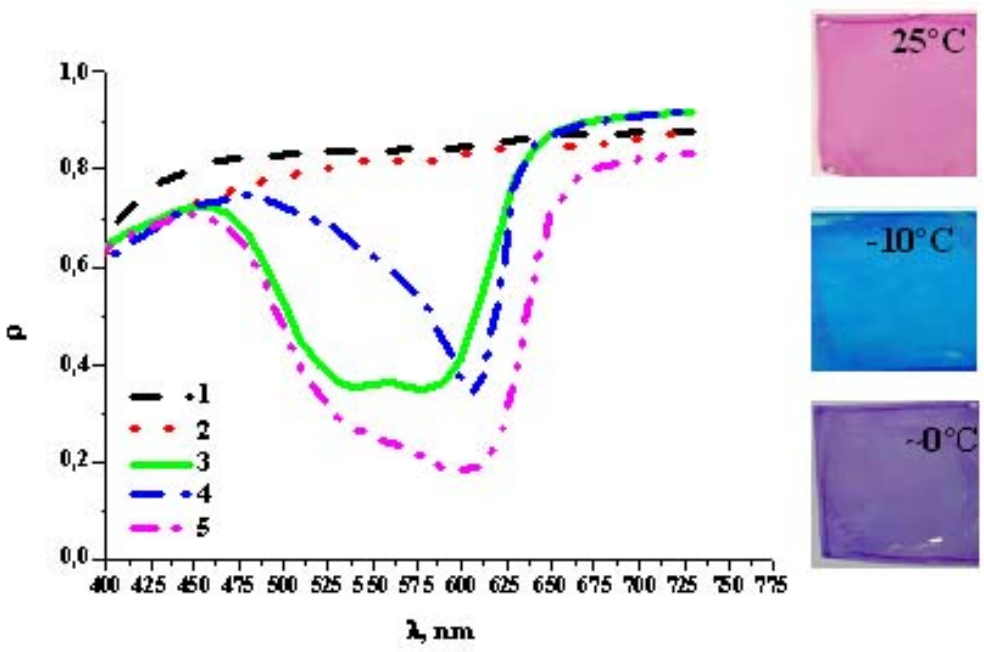


Figure 5

Reflectance spectra (left) and visual images (right) of the D2 films,

where 1 – substrate. 2 – polymer film, 3 – dye layer at room temperature, 4 – dye layer after freezing, 5 – dye layer at above 0ºC

Quasi thermochromic characteristics of D2 are based on the recrystallization due to the partial dissolution of the surface layers of the composition by the moisture which condensed on the surface of the dye when it is heated and then cooled. When excluding the impact of the condensed moisture on the surface layer the thermochromic effect disappears.

As in the previous case, ink composition can be inflicted only on modified surface of polymeric films and papers. However, this condition will not cause technological problems when applying compositions with flexo or inkjet printing methods. When applying layers of thermochromic ink jet expedient to use as a solvent ethyl alcohol, since in this case there is no crystallization of the dye in the solution is not going to clogged the nozzles of an inkjet printer furthermore ethyl alcohol increases the shelf life of the composition.

Layers D2 exhibit photochemical stability for 3 months when stored in the light and more than one year when stored in the dark.

Third type of composition based on using of anion and cation dyes mixture (D3 and D4). Moreover, apparently due to the electrostatic attraction of the molecules they formed new crystal structure (Fig. 6), respectively, with the new spectral properties (Fig. 7).

The colors of the dye layer in case of a separate application are: yellow and magenta for the D3 and D4, whereas, when they are mixed in solution, and at the media they becomes saturated green. When the temperature rises to about 50 ° C formed by two dyes crystal structure (Fig. 6, image 3) breaks (Fig. 6, figure 4), that causes a shift of the spectral curve and sharp color change from green to red (Fig. 7). Transition mechanism in the formation and decay of the crystal structure of two dyes require additional studies.

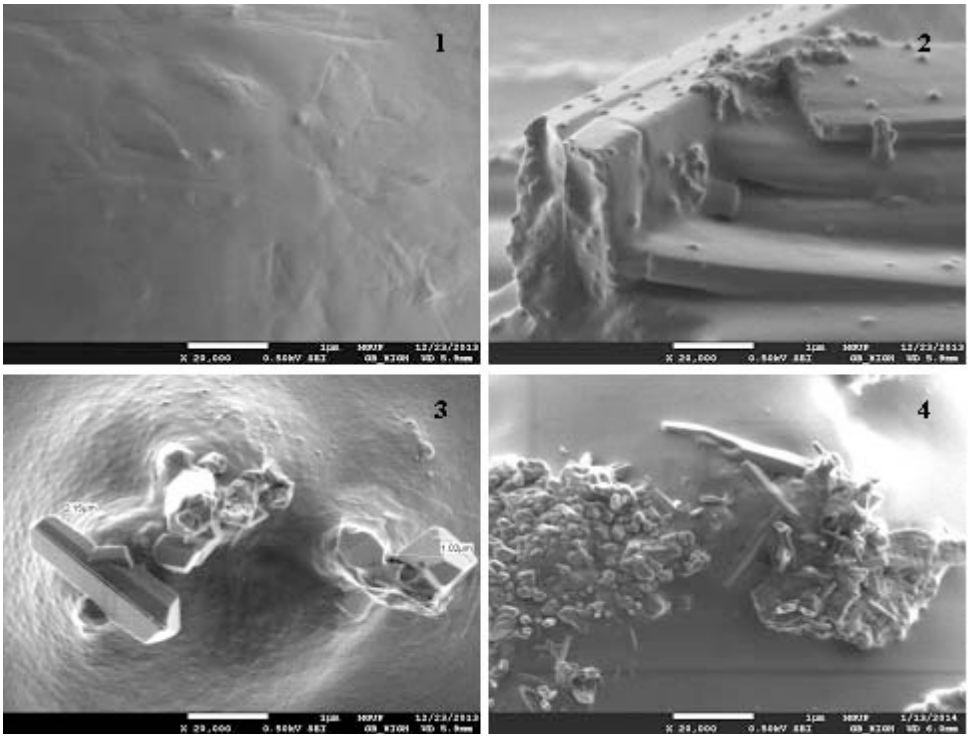


Figure 6

SEM-image of dye layers , where 1 - D3 on polymer film at room temperature, 2 – D4 on polymer film at room temperature, 3 – D3D4 crystals at room temperature, 2 - D3D4 crystals after heating

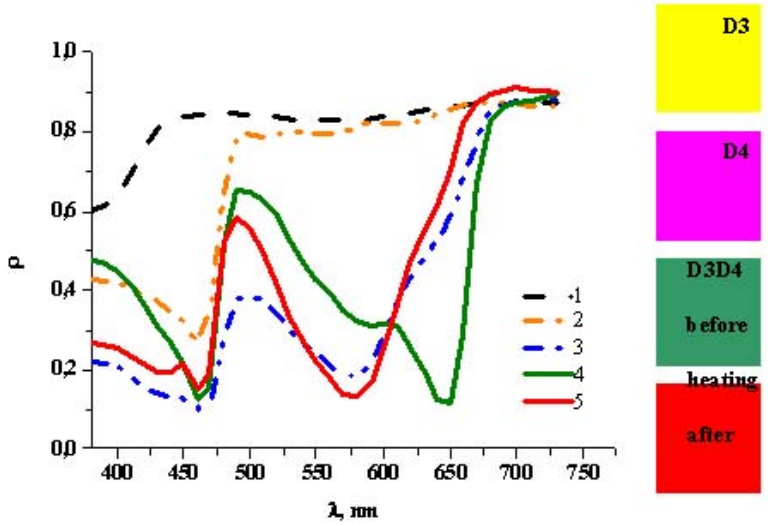


Figure 7

SEM-image of dye layers , where 1 – standard, 2 - D3 on polymer film at room temperature, 3 – D4 on polymer film at room temperature, 4 – D3D4 crystals at room temperature, 5 - D3D4 crystals after heating

Introduction different hygroscopic polymers in the composition solutions reduces the transition temperature to about 40 º C. At the same time their introduction allows controllably alter the spectral characteristics, for example, recorded the appearance of the following color transitions: green - yellow, red - yellow, as well as

double transition green-yellow-red according to the type and amount of the hygroscopic polymer. However, these effects are subject of a separate report and they will not be discussed in this article.

Thermochromic transitions may appear when compositions are applied of the surface of commercial films and papers for ink-jet printing (determined as a result of XPS studies).

Ink layers obtained from the third composition have photochemical stability for more than 4 months when stored in light and over a year if stored in the dark.

CONCLUSIONS

The main aim of this study is to investigate the development of a thermochrome sensor for smart polymer packaging for possible future commercialization.

1. We have developed 3 types of thermochromic systems for different temperature ranges. We have obtained stable thermochromic layers on polymer surface, модифицированной различными способами, в том числе activated by corona discharge and на бумаге с модифицированной поверхностью, в том числе на промышленно выпускаемой бумаге для струйной печати.
2. We have investigated morphological and chemical structure changes of thermochromic layer depending on temperature treatment.

The advantage of the developed thermochromic compositions is no need to manufacture multicomponent microencapsulated systems, as provided for in the existing to data technologies of such indicators production and the possibility of their application to food packaging in-line with packaging equipment.

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