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**K. Grytsenko[1], O. Navozenko[1], Yu. Kolomzarov[1],
A. Kryuchin[2], O. Tolmachev[3], Yu. Slominsky[3],
V. Kurdukov[3], V. Ksianzou[4], S. Schrader[4]**
[1]Institute of Semiconductor Physics
41 Prospect Nauki, 03650 Kyiv, Ukraine
[2] Institute for Information Recording
2 Shpak Str., 02113 Kyiv, Ukraine
[3] Institute of Organic Chemistry
5 Murmanska Str., 02660 Kyiv 94, Ukraine
[4] University of Applied Sciences
Bahnhofstrasse, 15745 Wildau, Germany

Optical Properties of Dye-Filled Polymer Films Deposited in Vacuum

The results of investigating properties of polytetrafluoroethylene (PTFE) and polyparaphenylene sulphide (PPS) films filled with dye molecules by co-deposition in vacuum are given. Thin polymer films filled with different polymethine dyes with various dye concentration are investigated. Film properties at room temperature and during heating were studied using optical absorption spectroscopy. It is shown that the polymer matrix prevented dye molecules aggregation, particularly the PTFE matrix prevented aggregation more strongly than the PPS matrix. During heating the PTFE matrix keeps the dye molecules in non-aggregated state up to dye decomposition temperature.

Key words: *dye, PTFE, PPS, composite, thin film, optical spectra, heating.*

Introduction

Thin dye- and metal-filled polymer films [1–4] were used as optical media for laser information recording long ago. Composite materials have the sum of the properties of the components, therefore a thin film of the composite material has the characteristics absent in natural materials. Recent developments in superhigh density optical carriers include thermolitography method [5]. The optical media for using this method must have strong threshold properties to obtain marks with diameter much smaller than diameter of a laser beam. In most cases the novel developments use hybrid organic-based materials [6–9]. The dye in the polymer matrix can unite threshold parameters of the both materials. Polymer materials have no melting and evaporation temperature like nature materials and small organic molecules (dyes). They are characterized by viscosity and decomposition rate as a function (usually nonlinear) of heating temperature. Depending on the chemical structure of polymer these parameters can be quite different. From this viewpoint, the polytetrafluoroethylene (PTFE), which has temperature of softening almost equal to its decomposition temperature, seems to be a promising material for superhigh density optical carriers. Polyparaphenylene sulphide (PPS) represents another stable novel polymer with the chemical structure and thermal properties different from those for PTFE.

Previous studies of the dye-filled PTFE films revealed additional positive properties. First, various aggregation states of dyes in the PTFE matrix were detected depending on the dye chemical structure and concentration [10]. The extreme stability of the dyes in the PTFE matrix to action of external factors was detected [11, 12].

The aim of this work is to study the behaviour of the various dyes in the different type polymer matrices during heating. The influence of the type of polymer matrix on the optical properties of the dye-filler is to be established.

Experimental details

The structure and spectral properties in toluene of the various dyes used for solid film production are presented in the Table. Dye 1 is the monomethinecyanine's base; 2 — merocyanine; 3 — hydroxystyryl's base; 4 — bis-dimethylaminostyryl derivative of dimethylpyrazine; 5 and 6 are squaraine dyes.

Chemical structure and UV/Vis spectral characteristics of the dyes

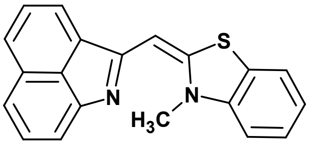
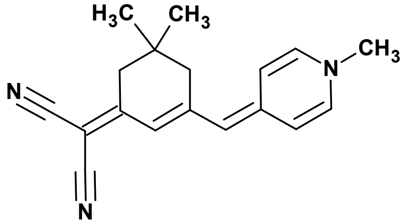
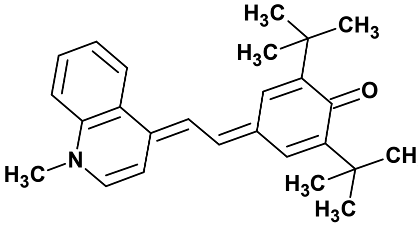
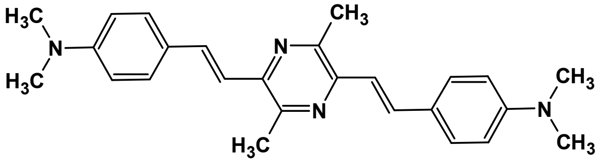
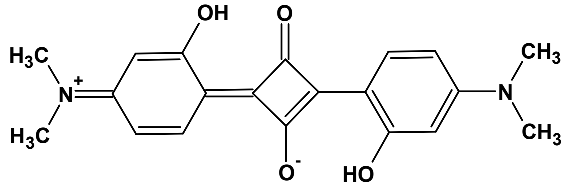
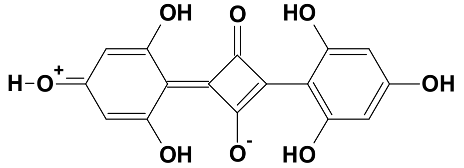
№	Structure	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$, L / mol·cm) in toluene
1.		527(2.5)
2.		564 (4.75); 600 (5.70)
3.		571 (5.04); 606 (5.39); 660 (2.83)

Table to be continued

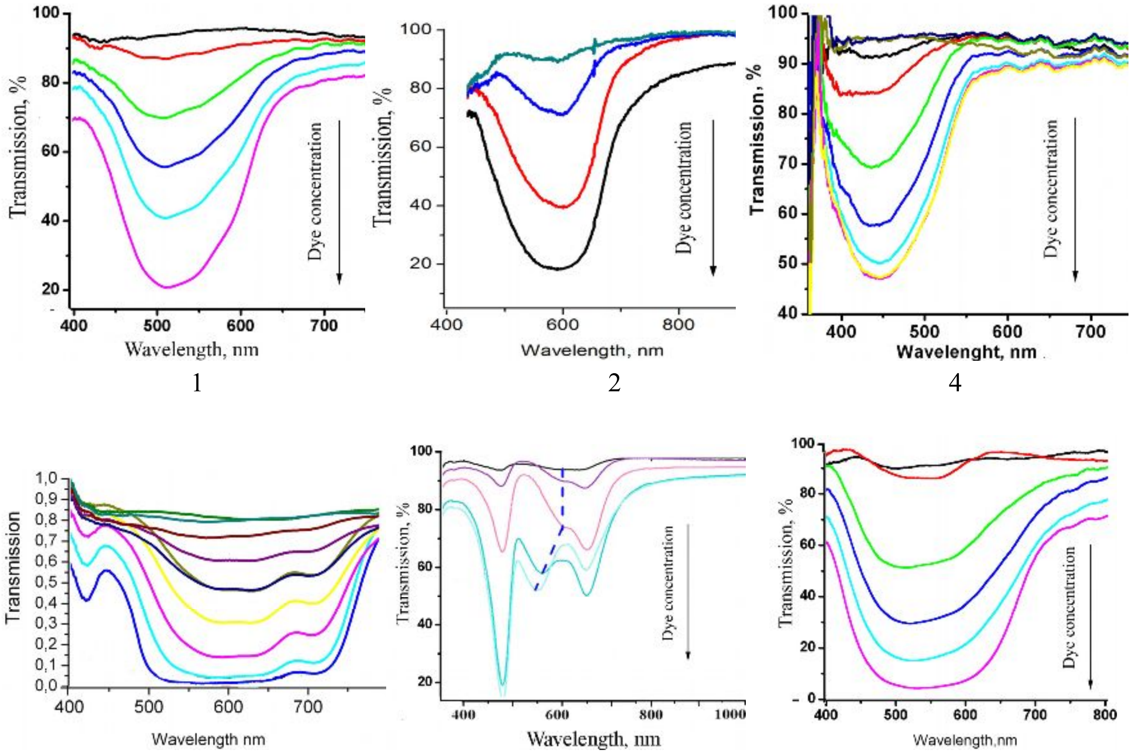
4.		446 (4.8)
5.		636 (–)
6.		574 (–)

Films were deposited using UVN-74 vacuum installation equipped with the computerised control system, including Pfeiffer pressure meter and four channel Sigma quartz thickness monitor. Starting pressure in the chamber was 10^{-3} Pa. Polymer films were deposited by two methods: 1 — thermal decomposition of PPS powder; 2 — decomposition of the bulk PTFE pellets and activation of the gases with cloud of accelerated electrons. The dye was evaporated from the thermally heated crucible. Glass substrates were used. Details can be found in [13, 14]. The spectra of the as-deposited composite thin films were measured using Polytec optical spectrometer. The same spectrometer was also used for spectra recording ***in situ*** during film heating in air in the home-made oven up to 280 °C. The spectra were recorded using an one-beam scheme.

Results and discussion

The first stage of the research was the deposition of thin dye solid films. Several types of dyes led to formation of smooth and uniform films, but mostly the films consisted of large grains or even were not continuous [15]. The smaller dye molecule, the stronger inclination to formation of micrometer size solid aggregates like bricks, but not a film at all. This means that standard dyes with absorption maximum nearby 400 nm are not able to produce a smooth film by themselves. For example, the dye 4 produced a solid film with grain size of about 0.2 micrometers, while azo-dyes mostly produced separate islands up to film thickness of about 0.5 micrometers [15]. One way is the dye combination with the polymer matrix, which prevents dye molecules from strong aggregation. Dye-filled PTFE and PPS films were deposited on glass substrates with dye concentration ranged from 5 to 70 vol. %. Depending on dye concentration and film thickness, the film transmission was ranged from 80 to 50 %. Investigation of the rows of various types of dyes showed that some dyes have the optical spectrum in the polymer matrix almost the same as a solid film of the net dye, but in many cases the spectra were different.

Fig. 1 shows the spectra of dye-filled PTFE films. The PTFE films filled with dye 1 showed the same absorption maximum as for dye in solvent, which was not changed with dye concentration variation, instead of a pure dye film on glass, which formed large aggregates with red band in the spectrum [10]. The PTFE films filled with dye 2 and dye 4 also showed no changes in the optical spectra with dye concentration variations. The dye 3 in the PTFE matrix showed blue shift for the short wavelength band 571 nm → 550 nm and red shift of the long wavelength band 660 nm → 720 nm. The optical spectra of squaraines in the PTFE matrix were dependent on the dye chemical structure. The dye 6 in the PTFE matrix showed broadened band being the same as in solution, which was not changed with dye concentration variation. Hydroxy-squaraine 5 exhibited strong optical changes when dye concentration was varied. A new strong band was formed at 480 nm, the shoulder splitting (603 nm and 660 nm) at low dye concentration was smaller than for a pure dye film. The splitting was grown as dye concentration was increased. The appearance of the new short wavelength band can be explained by aggregation of squaraine dye at medium concentration in the polymer matrix. The correct measurement of the squaraine's absorption in solution was not done due to low dye solubility.

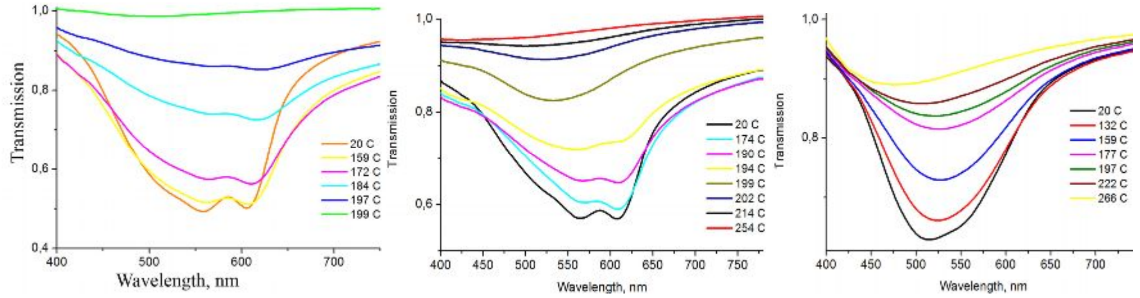


1 2 4

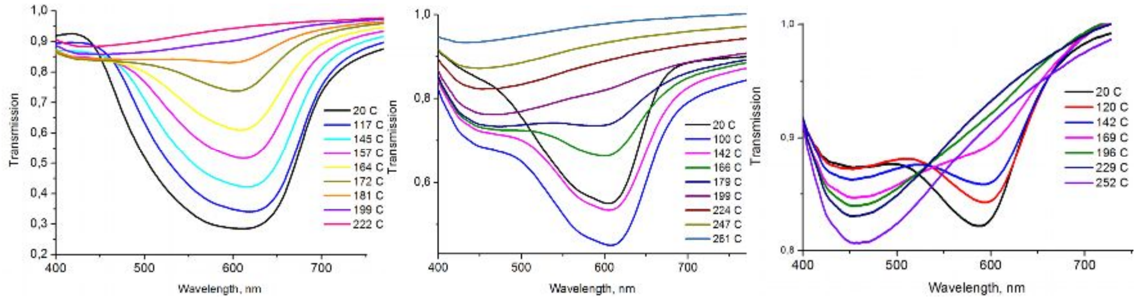
3 5 6

Fig. 1. The spectra of PTFE films filled with different dyes with various concentrations

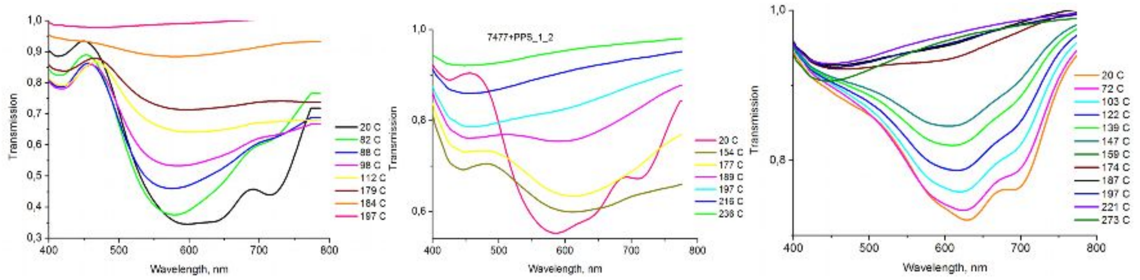
Fig. 2 presents spectra evolution of dye-filled polymer films with dye concentration in the range 10–15 vol. % during heating. The effect of the polymer matrices on the film optical properties changes during heating is clearly seen. It should be mentioned that dye optical band splitting or widening in as-deposited PPS matrix are stronger than in as-deposited PTFE matrix. The dye molecules aggregation in PPS matrix decomposed at the temperature close to dye decomposition itself. At the temperature at which dye-filled PPS films became transparent, dye-filled PTFE films still revealed some optical absorption. The PTFE film filled with dye 2 exhibited change of 600 nm band into 460 nm band. The film was not transparent up to 260 ºC. The same behaviour showed dye 5 in the PTFE matrix. The effect can be explained by partial dye molecule decomposition, the decomposition products were kept in the PTFE matrix.



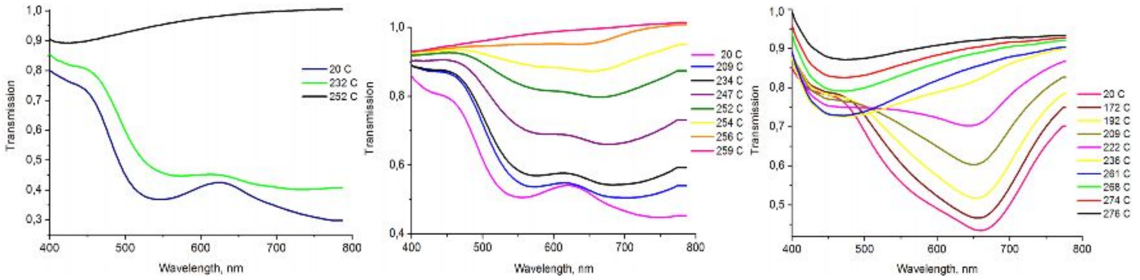
1 in PPS in PTFE



2 in PPS in PTFE



3 in PPS in PTFE



5 in PPS in PTFE

Fig. 2. Evolution of the optical spectra of dye-filled polymer films during heating

The transformation of the film optical absorption during heating is the important matter for the design of recording media for thermolithographic method of information recording. The temperature of dye decomposition should not be smaller than temperature of the polymer matrix softening.

Conclusions

1. PTFE and PPS films filled with various dyes were deposited by co-evaporation in vacuum.
2. The PTFE matrix prevents aggregation of the molecules of the dye-filler better than the PPS matrix and keeps molecules from aggregation during heating up to the dye decomposition temperature.

Acknowledgments

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