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Optical recording in spiropyran and polymer composite films

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The optical properties of spiropyran-polymers and spiropyran-chalcogenide-As_2S_3 composition are reported. A composite preparation method is proposed, in which polyvinylacetate, polymethylmetacrylate and copolymer of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) are used as host polymers. The transmission spectra of composites were measured before and after illumination by 248 nm, 325 nm, 375 nm and 532 nm laser beam light. The dependence of optical transmission changes for merocianine form of composite films on the intensity of exciting 532 nm laser beam is shown. The holographic recording of diffraction gratings was performed by 325 nm and 532 nm laser beam lines. During recording, the diffraction efficiency in transmission mode was measured. The profiles of the grating areas were analyzed by AFM.

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1. Introduction

Recently, a great number of publications have been devoted to studying the optical recording media for holography and processing of information. Among many kinds of photosensitive materials, the organic photochromic compounds are given much attention because of their potential abilities to be used in various photoactive devices. Spiropyrans are well-known photochromic compounds, which undergo the ring opening and transformation from spiropyran form to their corresponding merocyanine form via irradiation by UV light and vice versa by visible light or heat [1, 2]. In order to improve the stability of photochromism in a polymer with spiropyran, a photocrosslink can be induced under the same UV light that is usually employed for photochromism [3, 4]. These media possess a high photosensitivity, therefore spiropyran and organic polymer composites can be interesting from the viewpoint of holographic recording and nanometer-scale surface relief formation.

In our previous work we reported the possibility of direct relief formation by action of laser illumination on composite films [5]. It was shown that the depth of relief depends on the presence of photochromes in composites of arsenic sulfide and organic polymers. In the mentioned work, Disperse Red 1 (DR1) dye was used as photochrome whose photochromic properties can be explained by cis-trans-isomerisation in relation to the N=N bond. It is supposed that the relief formation in polymer-photochrome compositions can be initiated by difference in the values of dipole moments of cis- and trans-photochrome forms [6]. Therefore, the laser-beam-induced difference in the dipole moments of photochromic molecules causes their movement along the direction of laser beam electric field gradient from dark to bright areas of the film or vice versa. According to [5], for the relief formation high values of exposure are required. Nevertheless, photochromic transition of DR1 occurs at rather low values of the exposure [7]. It was instructive to study the kinetics of cis-trans-transition of spiropyran in polymeric matrix, because this material has the greatest – among the accessible photochromic materials – distinction between the dipole moments of isomeric forms [6].

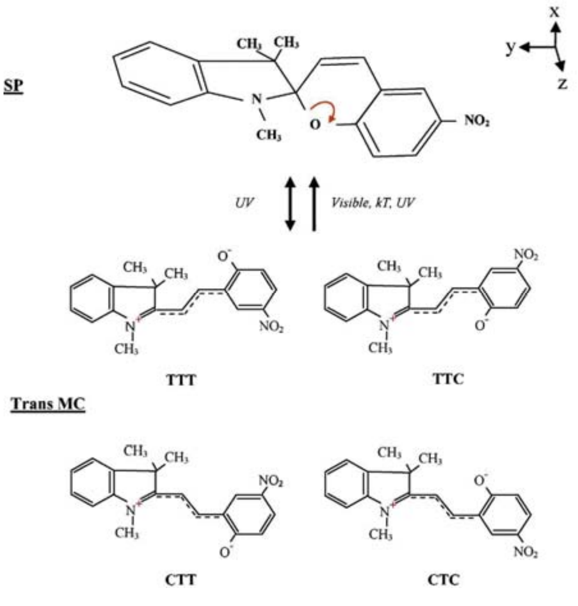

Fig. 1. Chemical structures and isomerisation reaction between a photochromic spiropyran molecule and its stable isomeric forms of merocianines [10].

The spiropyran in polymers was studied earlier [8-11], by methods of holographic recording included [12], however the majority of works describe composites on the polyacrylates base. In this work we have studied various polymers as matrix of composites, and compared the optical properties of these materials. The diffraction efficiency of holographic recording was taken as one of the kinetic indicators of photochromic processes.

The photoinduced isomerisation mechanism of spiropyran is presented in Fig.1. As is seen from this scheme, under the influence of irradiation a rupture of the heterocyclic link C-O occurs, which is followed by the formation of molecules with various spatial configurations. Thus, during a holographic recording a phase diffraction grating with various structures of isomers in the area of the maximum and minimum light intensity is produced. The photoisomerization process is reversible, and it is possible to write a positive or a negative diffraction grating by preliminary illumination of recording media with the light of required wavelength.

It would also be instructive to record a holographic grating if arsenic sulphide is present in a composite. By analogy [5], we can suggest that a combination of photochrome and chalcogenide in the composite would essentially change the optical properties of the films.

2. Experimental

The spiropyran (CAS 1498-88-0) was dissolved in chloroform at room temperature. A 5 wt % solution of spiropyran was mixed with poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) M_w= 50 000 ÷ 80 000 (GPC) (CAS 27360-07-2), poly(vinyl acetate) M_w= 500 000 (CAS 9003-20-7) and poly(methyl methacrylate) M_w=350 000 (CAS 9011-14-7) dissolved in chloroform. The solutions were mixed in such proportion that after drying the mixtures on a substrate the concentration of spiropyran in the polymer would make 5 % wt. Also, to the solution with spiropyran and poly(vinyl acetate) there was added 10% As_2S_3 solution in organic solvents (as described in [5]), in such a proportion that after drying the mixtures on a substrate the concentration of arsenic sulphide in the composite would be 1% wt. For studying the transmission spectra of composite in the UV region in more detail, a composition with a 1% wt. spiropyran concentration in poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) was prepared (all reactants being purchased from Aldrich).

The films from composite solutions were produced using a BYK Gardner GmbH Co. applicator; the initial thickness of liquid layer was 30 μm. As the substrate, glass and quartz plates were used. The films were dried in oven at the temperature 423 K for 30 min. The thickness of dried films was 4-9 μm (measured by a Veeco Dektak 150 surface profiler).

For all the films (including a film of pure polymer), the transmission spectra were measured by an Ocean Optic HR4000CG spectrometer, with a quartz substrate used. The optical transmission spectra of composite films were measured before and after irradiation by laser light with wavelength 248 nm, 325 nm and 375 nm, the total exposition being 0.36 J/cm^2.

For studying the kinetics of reversible photoisomerization, a composite film containing 5% of spiropyran in poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) was irradiated by laser beam with wavelength 375 nm (intensity 0.01 W/cm^2) for 5 min. After that, the sample was illuminated by a laser beam with wavelength 532 nm, with the time fixed for 50% optical transmission of the film in dependence on the laser beam intensity.

The holographic gratings with a period of Λ = 1 μm were recorded by two symmetrically laser beams of equal intensity with linear horizontal polarization (p-p), using 325 nm (beam intensity 2 x $1.8 \cdot 10^{-4}$ W/cm^2) and 532 nm (beam intensity 2 x $1.4 \cdot 10^{-3}$ – 2 x $4.2 \cdot 10^{-2}$ W/cm^2) lasers. The readout of transmission diffraction efficiency was made at Bragg's angle using a 640 nm semiconductor laser beam (for the 325 nm recording laser) at the 2nd order maximum of recording beam (for the 532 nm recording laser). Immediately before recording by the 532 nm laser, the samples were illuminated by a 375 nm laser beam (intensity 0.01 W/cm^2) for 5 min.

After recording, the surface relief of samples was analyzed using Atomic Force Microscope (AFM).

3. Results and discussion

Fig. 2 shows transmission spectra of the composite films containing 5 % of spiropyran in different polymers. The spectra of spiropyran in various polymeric matrixes have been examined; however, it was of interest for us to study the influence of polymers on the absorption spectra of meracionine forms. In Fig. 2 it is seen that the influence of a polymeric matrix of the used polymers on the spectra is insignificant. For more detailed research of spectral changes under the influence of UV radiation, we tried reducing the spiropyran concentration or the film thickness. Figure 3 shows the spectra of ~ 3 μm thick composite films. At the presence of arsenic sulphide in the composite a spectral shift towards the red region is observed.

Fig. 4 displays the changes in optical transmission spectra for a composite containing 1 % of spiropyran in poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) under the influence of 248 nm, 325 nm and 375 nm lasers. The absorption peak observed in the region of 475–650 nm is characteristic for the appearance of an open form of spiropyran (different merocianine isomers). It is seen that spiropyran transfer in the merocianine form in the composite occurs more vigorously at the irradiation light of 325 nm.

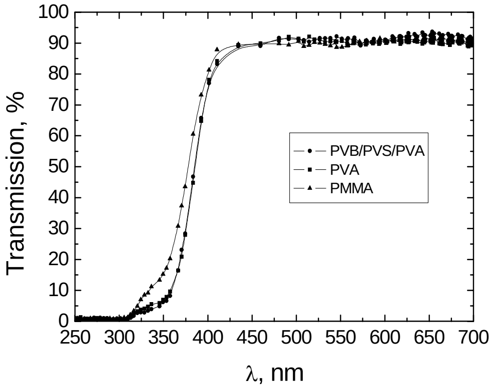

Fig. 2. Transmission spectra of spiropyran-polymer composites. Film thickness 6-9 μm.

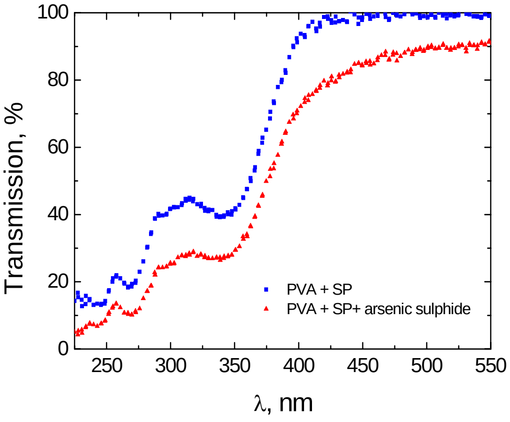

Fig. 3. Transmission spectra of spiropyran-PVA and spiropyran-As_2S_3-PVA composites. Film thickness ~3 μm.

The kinetics of reversible isomerisation was studied by measuring the optical transmission changes for the 532 nm spectral line. The sample (previously converted into the merocianine form by irradiation of the 375 nm laser light) was illuminated by a 532 nm laser beam of different intensity. Figure 5 shows the temporal dependence of 50% transmission changes on the intensity of a 532 nm laser beam.

The diffraction gratings were recorded on this composition using for the grating formation the direct and reversible isomerizations of spiropyran. The direct recording was performed by the 325 nm laser, with the readout of diffraction efficiency made by a 640 nm diode laser. The dependence of transmission diffraction efficiency on the exposure is presented in Fig. 6, where strong influence of the host polymer matrix on the diffraction efficiency of gratings can be observed. The thickness of composite layers on the polyvinylacetate and PMMA bases is 4.50±0.50 μm, and the difference of diffraction efficiency, as is seen from the graph, is two times.

Fig. 7 shows the dependence of diffraction efficiency maxima on the intensity of 532 nm recording beams for holographic recording on the merocianine form of photochrome in three (different) composites. The character of curves is the same, but the presence of arsenic sulphide increases the diffraction efficiency.

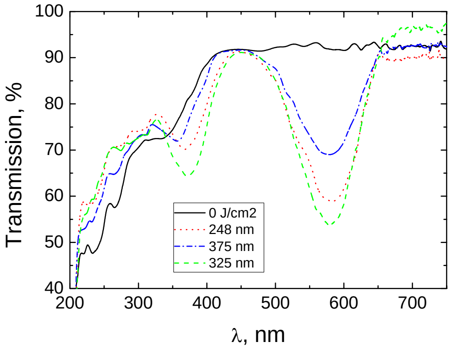

Fig. 4. Transmission spectra of spiropyran-poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) composite before and after illumination by different UV - lasers (E=0.36 J/cm^2).

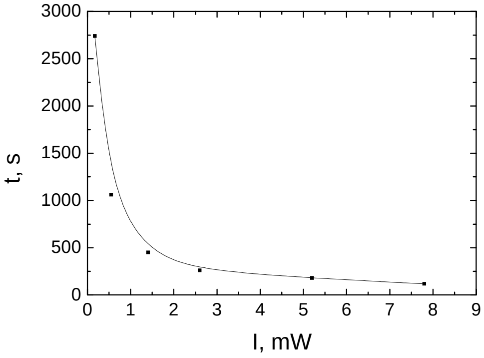

Fig. 5. Temporal dependence of 50% transmission changes (spectral line 532 nm) on the 532 nm laser beam intensity.

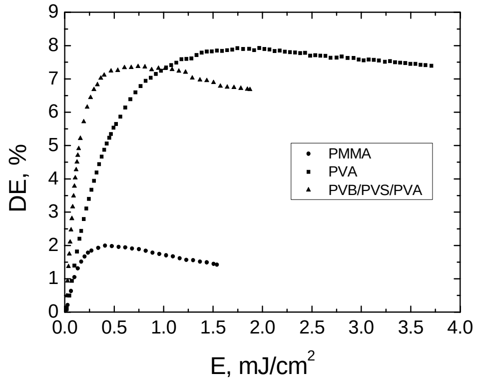

Fig. 6. Dependence of transmission diffraction efficiency on the exposure (recording laser 325 nm, reading laser 640 nm).

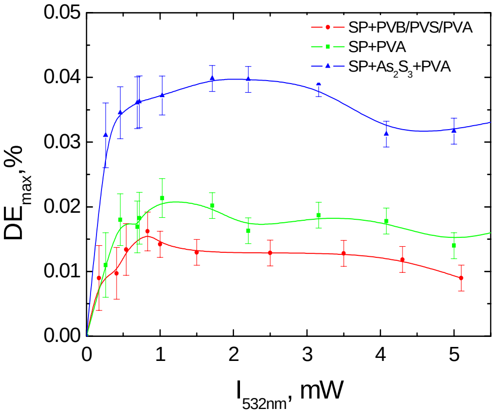

Fig.7. Dependence of transmission diffraction efficiency maxima on the recording beam intensity (recording and reading lasers 532 nm).

Examination of samples by AFM has not revealed the presence of any periodical surface relief after holographic recording. This means that photoisomerization processes during holographic recording in the studied spiropyran films do not lead to a matter transport in the films as it is observed in azobenzene containing polymer films [5]. Thus the holographic recording in spiropyran containing organic films is based on refractive index changes due to photoinduced izomerization processes.

4. Conclusion

In our work we have obtained composites with various concentration of spiropyran, with and without presence of arsenic sulphide in various polymers (polyvinylacetate, polymethylmetacrylate and copolymer of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate).

The studies of the initial transmission spectra of composites and their changes induced by lasers of wavelengths of 248, 325 and 375 nm revealed an appearance of absorption band in the spectral region of 475 – 650 nm with maximum at 580 nm. The holographic recording of transmission gratings with diffraction efficiency of 8 % was performed. It was shown that diffraction efficiency depends on the composite host polymer and increases in the presence of arsenic sulfide.

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