Diagnostics of atomic- molecular interactions in nano-compositions organics-inorganics by means of infrared spectroscopy

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Abstract. This paper prolongs our studies of the formation and properties of the organic-inorganic scintillating compositions from activated polystyrene and inorganic nanoparticles from cesium iodide and sulfate. The compositions from the solution of polystyrene in benzene and nano- or micro-particles of cesium iodide were solidified in the form of thin films. Then some of the films were subjected to rolling. The variations of the infrared transmission spectra of the compositions were measured either during their solidification or after the solidification and rolling. The new absorption band was revealed in the process of the solidification and disappeared after it. The fractal-like structures of parallel rows were formed in the films. Quasi-periodical oscillations of the transmission spectra were found in several infrared regions ascribed to the interaction of the infrared radiation with the fractal super-structure of the films. The modifications of the absorption spectra found in our experiments are attributed to the interactions of polystyrene molecules with benzene molecules and nanoparticles of cesium iodide.

1. Introduction
This paper is devoted to development and studies of compositions from nano- and micro-particles of cesium iodide immersed into solid matrices from polystyrene. This work is a part of highly actual studies of physics and technology of composites organics-inorganics. The actuality of these studies is determined by quickly expanding applications of these materials in new trends of micro-electronics, photonics, generation and storage of energy, bio-medicine, etc. [1.2]. On the other hand various hybrids from nano-dimensional organic and inorganic components are of great interest for fundamental research of new features of condensed matters because the amount of the atoms placed at the interfaces between the regions with structures and properties differing significantly from each other is comparable with their total amount. So it is natural to expect revealing of qualitatively new kinds of intermediate substances with unusual properties. Our previous publications devoted to the development and studies of new scintillators composed from nanoparticles of heavy inorganic materials and matrices from scintillating polymer phosphors confirm the reality of these expectations [3 - 7]. It is worth to emphasize that rather promising organic-inorganic composites were obtained when biological polymers like proteins etc. were used as the organic components [8]. As usual any successful kind of composite materials should...
connect advantages of the initial constituents and eliminate their disadvantages. Our composites scintillators got from inorganic nanoparticles their high density and corresponding stopping power for ionizing radiation combined with good radiation hardness. On the other hand organic phosphors gave excellent temporal resolution and high light yield of scintillations. This work prolongs our RD on composite nano-materials organic-inorganic with record sets of scintillation parameters. We have obtained the composite films with new kinds of the internal morphology and unusual optical properties which are presented below. For example the composite films with polystyrene matrices and fillers from nano-particles of cesium iodide acquired complicated fractal-like internal morphology and interesting peculiarities of optical properties resulting from this morphology. The structural transformations of the composites were produced by solidification of the solutions of polystyrene in benzene or toluene with cesium iodide particles inserted into the solution as well as by plastic deformation of the solid composite films with the help of rolling. The fractal-like super-structures observed in our samples are attributed to self-organized crazing and deformation processes taking place in polymers subjected to severe deviations from equilibrium \[9 \text{ – } 12\]. The main portion of the information about modifications of atomic-molecular bonds induced by these structural transformations was obtained by means of Fourier Transformed Infrared Spectroscopy technique \[13,14,15\] which is well known and effective method to reveal these modifications due to high sensitivity of atomic and molecular vibrations to structural disturbances.

2. Experimental materials and methods
The samples of polystyrene-cesium iodide composites were prepared in the form of films with the thicknesses from 300 to 600 micrometers. These films were formed by means of pouring of the solutions of polystyrene in benzene onto the substrates from glass-slides and plates of potassium chloride single crystals. The fillers from the particles of cesium iodide were inserted into the solution before its solidification. The content of the filler was regulated from 0 to 30 volume percentage. The particles of cesium iodide were prepared by 3 techniques: milling of the bulk crystals in the ball mill with steel or zirconia balls, chemical synthesis by condensation of cesium iodide from water solutions and laser evaporation of the powders of cesium iodide \[16\]. The first two methods produced microparticles with dimensions of grains from 10 to 50 micrometers, whereas the particles obtained by the laser evaporation had nanoscopic dimensions from 30 to 200 nanometers. Some films were subjected to plastic deformation by rolling in the jewelry rolls either in one or in two mutually perpendicular directions at temperatures about 70°C. The internal structures of the films were investigated by means of polarization optical microscopy and scanning electron microscopy (electron microscope Supra 50 VP with microanalysis system INCA Energy + ). Infrared spectra were measured by means of Fourier spectrometer Vertex 80 v with infrared microscope Hyperion. The measurements of the infrared transmission were made in the spectral range from 350 to 7000 cm\(^{-1}\) with the spectral resolution 2 cm\(^{-1}\). These measurements were made in the infrared microscope Hyperion with the spatial resolution of about 50 micrometers. To determine the normalized transmission spectra, the results of the transmission measurements were divided by the results of the analogous measurements of the transmission of the plate from single crystalline potassium chloride.

3. Experimental results and discussion
Fig.1 presents the scanning electron microscopy of the composite films of polystyrene with microparticles of CsI subjected to rolling in the direction making up the angle about 45° with the horizontal line. The range of the magnification at these figures is varied by about 40 times from Fig. 1a to Fig. 1c.

It is worth to emphasize that in spite of the significant variations of the scales the appearances of the systems of the parallel rows observed at these photos look likely. The invariance of
Figure 1. The sequence of electron-microscopy photos of internal morphologies of the composite films polystyrene – cesium iodide with varied magnifications manifesting their fractal-like structure.

Figure 2. The optical microscopy photos of the polystyrene film solidified from the solution of polystyrene in benzene. The magnification at the left picture is 8 times higher than at the right one

the spatial distributions of the structural elements being independent on the scales of the observations of a given structure is appropriate to fractal structures [17]. Various structures of fractal types are formed in condensed matter subjected to any severe deviations from equilibrium conditions [17,18]. The transformations of the matters producing structures close to fractal kinds can be attributed to a wide variety of self-organization processes [19]. We have found that the severe plastic deformation by rolling or other methods is not the only way to obtain fractal-like structures in polystyrene films. It turned out that the process of the solidification of the solution of polystyrene in benzene proceeds with distinct signs of self-organization and formation of fractal-like internal structures. This is confirmed by the photos of the polystyrene film obtained by this way made with various magnifications (Fig. 2).

The difference in magnifications of Fig. 2a and 2b is about 8 times. But nevertheless the sets of the distances between the parallel rows, created by coagulation of structural defects formed in the film during its solidification are close to each other. The formation of regular systems of structural defects during the solidification of polymers is well known as crazing [10]. The observations of the fractal-like behavior of these defects delivers additional information useful for further development of technologies of polymer systems and their practical applications.

It turned out that the fractal-like superstructures in the polystyrene films studied in this paper produce several new features of the infrared spectra of these samples. The influence of the structural non-homogeneities described above is influenced essentially by the residual
Figure 3. Dynamics of variations of the transmission spectra in various IR ranges of the polystyrene film during its solidification from the solution of polystyrene in benzene.

benzene which is conserved inside the films for rather a long period of time (not less than for one week). The dynamics of the evaporation of benzene molecules from the solidified solution of polystyrene was studied by means of the Fourier spectroscopy via the microscope Hyperion. The duration of one measurement of the FTIR spectrum in the full range from 350 to 7000 cm\(^{-1}\) did not exceed 30 seconds. The intervals in the sequence of these measurements was about 10 minutes. The results of these measurements for various spectral ranges are presented at Fig.3. The total duration of the measurements was about 60 minutes. The control polystyrene film for comparison of the spectra at various moments of the solidification was obtained by the same technique 7 days before this experiment.

Comparison of the “dynamic” spectra at Figs. 3 with the spectrum of the control film induced the conclusion that in spite of relatively fast evaporation of the solvent residual benzene was present inside the films even after 7 days from the creation of the film. This conclusion is proved by the residual picks of the infrared absorption observed at the well-known benzene frequencies (674, 1030, 1180, 1480, 1815, 1959 cm\(^{-1}\)). We assume that this residual benzene was accumulated inside the nano-scopic cracks (crazers [10]) produced during the process of the solidification of polystyrene. The spectrum in the range 600 – 680 cm\(^{-1}\) (right at the bottom)
presents one more new spectral absorption band which has been induced during the solidification (the band at about 665.99 cm$^{-1}$, the blue curve). The particularity of this band is connected with its dynamics: it was absent at the beginning of the process, then it began to appear after 10 minutes of the solidification (a weak kink at about 665.99 cm$^{-1}$, green curve). Up to the 20-th minute this kink was transformed to a quite distinct Lorentz-like band at 665-665.99 cm$^{-1}$ (the blue curve). But then the sequence of the curves measured after 60 minutes and 23 hours from the beginning demonstrated almost complete elimination of this band. This non-monotonous behavior of the new band at 665.99 cm$^{-1}$ makes us to assume that its existence is induced by the interaction between the molecules of benzene and polystyrene. The necessary conditions for this interaction includes the existence of the optimal distances between these molecules. Just at the beginning the concentration of polystyrene in the solution does not exceed 15 %. So the distances between these molecules are too large for the active inter molecular interaction. After 20 minutes of the evaporation of benzene the concentration of the solution becomes close to the optimum resulting in active interaction between these molecules. Later the concentration of benzene becomes too low interrupting this cooperative process. The additional argument for the validity of this assumption is connected with the values of the resonance frequencies of polystyrene and benzene close to 665.99 cm$^{-1}$. One of the resonance frequencies of the bending vibrations of the benzene rings is 674 cm$^{-1}$ [20]. One of the frequencies of the vibrations of polystyrene is 670 cm$^{-1}$ [20]. In the first approximation the interaction of the polystyrene and benzene oscillators placed close enough to each other arranges various combinations of these frequencies. Up to now we do not know any possible details of this interaction, but one of these combinations (the “mirror” reflection of 674 cm$^{-1}$ with respect to 670 cm$^{-1}$) gives 665.99 cm$^{-1}$ quite exactly.

It is well known that the propagation of electromagnetic waves through 3-D fractal structures produces spatial, temporal and spectral oscillations of the distribution of their intensity [21]. Using the infrared microscope for the measurements of the transmission of the infrared radiation through the films with fractal-like internal super-structure we have observed indeed the quasi-periodical spectral oscillations in various parts of the spectrum. The oscillations were observed the most clearly at the long wavelength edge with the approximate periods about 20 – 25 cm$^{-1}$ (Figs. 4a, 4b). In the interval 350 – 500 cm$^{-1}$ these oscillations demonstrate distinct sinus-like character. These oscillations are observed the most clearly for the films rolled in one direction. In the longer interval (600 – 700 cm$^{-1}$) the oscillations are observed as quasi-periodical distribution of kinks at the transmission curves. At higher wave vectors these oscillations return sometimes to the sinus-like character (Figs. 5a, b, c). These oscillations are observed with relatively small amplitudes for the films subjected to the rolling in one direction – for the films either with or without CsI fillers. For the films rolled in two mutually perpendicular directions these oscillations are much weaker. At the wave-vectors higher than 4000 cm$^{-1}$ these oscillations were not noticed.

It is worth to emphasize that the one-dimensional rolling of the polystyrene films doped with cesium iodide particles results in splitting of the particles to nano- dimensions. The electron microscopy of one these films is presented at Fig. 6a and its transmission spectrum presented at Fig. 6b.

It turned out that the combined action of the doping and the one-directional rolling resulted in severe enhancement of the absorption band with the center at about 540 cm$^{-1}$. This band of polystyrene is attributed to vibrations of its phenyl-groups (modified benzene rings). Usually it is connected with symmetrical vibrations, so the probability of its presence in the infrared spectra is low [13, 20]. Its appearance in this spectrum can be attributed to local disturbances of the symmetry of the vibrations of the phenyl groups. Hence the introduction of the cesium iodide particles combined with the one-directional rolling should enhance these disturbances. For example this process can take place when one of the edges of the phenyl
Figure 4. Quasi-periodical oscillations of the infrared transmission spectra of the composite films from polystyrene and particles of cesium iodide in the spectral range 350-680 cm$^{-1}$

Figure 5. The oscillations of the transmission spectra of the composite films from polystyrene and cesium iodide particles in the spectral range from 2200 to 3950 cm$^{-1}$

Figure 6. The electron microscopy image of the composite film from polystyrene and cesium iodide particles (6a, left) and its transmission spectra in the range 520 – 680 cm$^{-1}$
group becomes attached to the surface of the particle. In order to get the information about the asymmetry of the internal structure of the rolled films we studied the transmission spectra for two polarizations of the infrared radiation: parallel and perpendicular to the direction of the rolling and corresponding rows of the structural defects produced by this rolling. But the spectra at Fig. 6b did not reveal any polarization anisotropy in the region around 540 cm$^{-1}$. From the first impression this fact is in the direct contradiction with quite clear structural anisotropy of the films rolled in one direction shown at Fig. 1. But the electron microscopy with higher spatial resolution of the same film (Fig. 6a) helps to resolve this misunderstanding. The cesium iodide particles are splitted by the rolling to nanoparticles with mean dimensions less than 100 nm. The local compression applied to the films during the rolling provides effective mixing of these nanoparticles and polystyrene molecules. In this situation wrapping of cesium iodide nanoparticles with polystyrene molecules becomes probable. So the asymmetrical disturbances of the rings of the phenyl groups proceed in a wide set of angles. The local asymmetrical disturbances for selected rings are present but the integration along the polystyrene chain wrapped around the nanoparticle eliminates this asymmetry. It is worth noting that the local asymmetry of the contacts of definite phenyl rings can be found for example by polarized excitation of the luminescence combined with analysis of the polarization anisotropy of the corresponding photoluminescence.

Conclusions

It was found that organic-inorganic compositions from polystyrene, benzene and particles of cesium iodide subjected to severe deviations from equilibrium conditions by solidification and plastic deformation demonstrate essential transformations of their atomic-molecular structure and morphology.

Regular systems of internal non-homogeneities with fractal-like behavior are formed inside the films from polystyrene and filling particles of cesium iodide.

The new band in the infrared absorption spectrum of polystyrene films appears during the formation of the films and disappears up to the finishing of the solidification of polystyrene. It is explained by the activation of the quasi-resonance interaction of the benzene rings of the solvent and the phenyl rings of polystyrene when the concentrations of these organic molecules become comparable.

Quasi-periodical oscillations of the spectra of the infrared transmission spectra of the composite films from polystyrene and cesium iodide are observed in several spectral regions. They are explained by the interaction of the infrared radiation propagating through the films with their fractal-like internal structure.

Significant enhancement of the absorption band of polystyrene at 540 cm$^{-1}$ is found in the films of polystyrene with cesium iodide fillers subjected to unidirectional plastic deformation by rolling. This enhancement is explained by the activation of asymmetrical interactions of the polystyrene phenyl rings with the nanoparticle of cesium iodide. The absence of the polarization anisotropy of this enhanced band is explained by the circular wrapping of the nanoparticles by polystyrene molecules.

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