



# Investigation of Surface Structure and Thermostimulated Depolarization Effect of Composite Materials with Aluminum Nano-particles

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**Abstract:** To investigate the effect of semiconductor filler - compounds and aluminum nanoparticles: topography and the nature of the spectra of thermally stimulated depolarization (TSD) of composite materials PE+xvl.%TlInSe<sub>2</sub>, PE+xvl.%TlInSe<sub>2</sub><Al>. A technology of producing composite materials studied by atomic force microscopy, the surface microrelief. The polarization of the films was carried out at a constant voltage of 6 kV in 5 min, according to the method of corona discharge. To study the spectra of the TSD used conventional techniques. Analysis of histograms AFM showed that the surface uniformity of the samples varies between 25 nm and in the boundary layer of the compositions there are some roughness caused by the fact that the destruction of the binding forces remain on the surface of individual atoms, and their groups - clusters.

**Keywords:** Aluminum Nano-additive, Fourier Spectra, Composites PE+xvl.%TlInSe<sub>2</sub>, PE+xvl.%TlInSe<sub>2</sub><Al>, Thermally Stimulated Depolarization

## 1. Introduction

In recent years, investigation in the field of creation of materials with special and the almost important electrophysical properties on the basis of polymer structures is of great interest [1-8]. It should be noted that depending on the nature, size, shape, nature of the distribution of the filler the polymer composition may be electroconductive [9], anti-static or dielectric. By these reasons, the findings of various authors differ concerning about nature of occurrence of various electroactive properties of composites when filling polyolefinola different fillings [10-14]. For obtaining new composite materials are used fillers of organic and inorganic nature. In relatively new papers [10, 14, 15], terpolymers semiconductor compounds TlInSe<sub>2</sub>, TlGaSe<sub>2</sub> and the solid

solution TlIn<sub>0,98</sub>Ce<sub>0,02</sub>Se<sub>2</sub> serve as filler. The investigations show that the compositions LDPE+TlInSe<sub>2</sub> where LDPE is a lower density polyethylene are superfine electrets materials with lifetime by 5÷13 times exceeding pure polymers [10, 15]. In [10] microrelief of the surface of compositions LDPE+xvol.%TlInSe<sub>2</sub> and yvol.%Al was studied by the methods of atomic force microscope. At the same time, the scanning probe microscopy is one of the powerful up-to-date methods for studying morphology and local properties of a solid with higher spatial resolution. For the last 10 years, the method available to limited number of research groups became a widespread and successfully used tool for studying the properties of a surface. Today none of the works in the field of physics of surface and thin-film technologies manage without the methods of scanning probe

microscopy. Development of the scanning probe microscopy served also for development of new methods of nanotechnologies, the technologies for creating structures with nanometer scales. In [1, 14] the microrelief of the surface of compositions  $LDPE + TlInSe_2$  was studied by the methods of atomic force microscope.

It is known that for detailed study of the mechanism of relaxation processes proceeding in polymers and composite systems, various dielectric methods belonging to relaxation spectrometry, various dielectric methods are used. However, for the frequencies  $\leq 10^{-1} Hz$  direct measuring of dielectric losses are connected with great difficulties, therefore by studying molecular mobility in polymers by the dielectric method in frequency range  $10^{-5} - 10^{-1}$  the direct current method is used. To this end, it is reasonable to use the data on temperature dependences of currents of thermostimulated depolarization  $I$ , depolarization function  $\psi$  and other parameters dependent on steady leakage current.

In this connection, the goal of the paper is to study the spectra of thermostimulated depolarization of new composite materials  $PE + TlInSe_2$  and  $PE + Al$  where  $PE$  is polyethylene.

By analyzing the currents of thermostimulated depolarization (TSD) of films on the basis of samples of compositions  $PE + TlInSe_2$ ,  $PE + Al$  crystallized at tempering conditions, it was revealed that on TSD curves, the observed depolarization peaks belong to release of charges from a trap connected as separate components  $PE, TlInSe_2$  and  $Al$ .

## 2. Techniques of Experiment

Composition materials  $PE + TlInSe_2$  with participation of aluminum nano-particle were obtained by the following technology the power of the polymer is mixed with powder  $TlInSe_2$ . Mixing was realized at the laboratory mill at room temperature, and then by hot pressing under pressure  $10^7 Pa$  the samples of dispersity  $50 \mu m$  were obtained. From the obtained mixture, different thickness films, at melting temperature of polymer matrix and pressure  $10 - 15 MPa$  are extruded between aluminum foil. The samples with foil are quickly cooled in water and then the foil is removed [3].

The samples obtained in such a way are suitable for studying the structure and properties. The films  $PE + x vol\% TlInSe_2$  with participation of nano-particles were obtained in the same way.

The size of the aluminum nano-particle used in the experiment was  $50 nm$ . We investigated the relief of the surface of compositions  $LDPE + x vol\% TlInSe_2$  and  $y vol\% Al$  by AFM method [14, 15]. The thermostimulated depolarization (TSD) spectra were studied by the scheme indicated in fig 1.

The installation consists of a shielding (8) a heater built therein (2), a camera (1) located between two electrodes (3), thermocouples in the lower hole of the electrode (4). Heating

is carried out by a system consisting of three LATR (5).

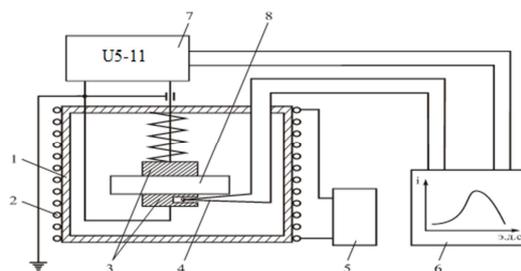


Fig. 1. Apparatus for measuring the thermally stimulated depolarization currents.

Thermodepolarization current from the upper electrode located above the sample, through special high-resistance cable flows to the entry of electrometric amplifier (U5-11) (7). From the output of the amplifier, the signal is submitted to the entry of the recording device (6).

According to the spectra of thermally activated current one can define power and concentration parameters of dipoles, electronic or ionic centers of the capture of charge carriers. Activation energy  $E_a$ , frequency factor  $\omega$  and concentration of carriers  $n$  belong to these parameters. Most simply these parameters are determined by the curves of the current of TSD. In particular, they may be determined by temperature condition of maximums of the current of TSD by the method of variation of heating velocity, by typical points of the curve of TSD and so on [14]. However, in all of these methods for calculating the activation energy, only separate points of experimental curve are used. This reduces to loss of a part of information and increase of error of measurement of parameters. More precise and although bulky are the methods where all experimental curve is used. Let us in short consider the methods for defining above parameters according to spectra of TSD.

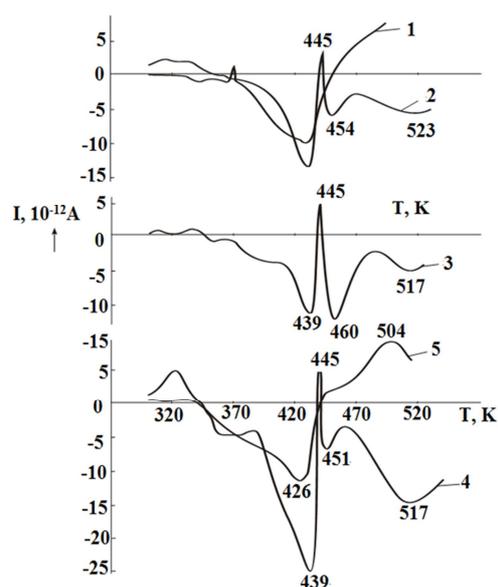


Fig. 2. The spectra of thermally stimulated depolarization compositions  $PE + x vol\% TlInSe_2$ ; 1-x=0; 2-x=1; 3-x=3; 4-x=5; 5-x=10.

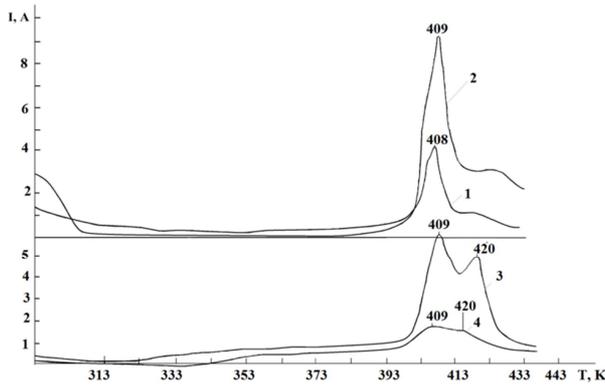


Fig. 3. The spectra of thermally stimulated depolarization compositions  $PE + x \text{ vol. \% } TlInSe_2 + y \text{ vol. \% } A$ ; 1 -  $x=7, y=3$ ; 2 -  $x=5, y=5$ ; 3 -  $x=3, y=7$ ; 4 -  $x=10, y=10$ .

Heating of the sample happened strictly linearly by means of three LATR system with constant speed  $2^{\circ}C/\text{min}$ , therefore the two-coordinate self-recording device 6 in which change of current depending on temperature in the coordinates  $x - y$  was written.

### 3. Results and Discussion

As a result we obtained planar images of the surface of composites  $LDPE + x \text{ vol. \% } TlInSe_2$  (where  $x = 1; 3; 5; 10$ ) of size  $1,6 \cdot 10^3 \times 1,6 \cdot 10^3$ .

The analysis of the histogram of the AFM images showed that the homogeneity of the surface varies from 25 nm. However, in the boundary layer compositions remain some roughness is probably due to the fact that at fracture of tractions not separate atoms but their groups, i.e. clusters remain on the surface. It also shows the results of a Fourier analysis of the surface obtained by the AFM. The concentration at the center of the spectrum shows that the surface particles have approximately the same dimensions i.e. they are comparable.

Investigation of the TSD phenomenon was carried out in temperature ranges 293-543K at linear growth of temperature of samples by the method described in the papers [1-7].

The results of investigation of TSD spectra of composite materials with semi-conduction additive are in fig. 2, where the spectra of TSD for PE (curve 1) and for the samples  $LDPE + TlInSe_2$  with different content of filler (curves 2, 3, 4, 5). Typical for these spectra is that on the curves of TSD samples of compositions with content of filler 1, 3, 5 vol. % we observe clear inversion narrow peak at temperature 445 K. Furthermore, we observe high-temperature wide peak in the domain of temperature  $500 \div 520K$ . These structures have three identical maxima. Temperature location of the first maximum corresponds to  $432 \div 439K$ , of the second one to  $450 \div 460K$ , of the third one to  $517 \div 523K$ . The samples of composite containing  $10 \text{ vol \% } TlInSe_2$ , have two maxima with opposite signs of the accumulated charge. The first maximum of  $426K$  corresponds in temperature to the first maximum of other composites and the base polymer, the second maximum in temperature to the third maximum of composites.

Analyzing the spectra of TSD we can note that introduction of the filler  $1 \div 5 \text{ vol \%}$  into the polymer reduces to appearance of deeper center of capture of carriers. Herewith, the number of injected charges at corona discharge (increase of intensity and area of appropriate maximum) and the depth of their occurrence increases (temperature position shifts in the high temperature area).

The nature of occurrence of the observed inversion peak at temperature 445 K on the background of the large main peak in the  $432 \div 455 K$  may be explained in the following way. At electrets in the process of action of the corona charge it is formed a space charge, and in the field of space charges (SC), on the boundaries of the particles of  $TlInSe_2$  and of a polymer an interfacial polarization (IP) is formed [5]. Direction of this polarization is opposite to the field of space charges. In this case, at depolarization in the spectra of TSD we observe inversion current caused by IP. Explanation of inversion current formation agrees in some sense with the Maxwell-Wagner effect where it is considered that accumulation of charges on homogeneous materials (in our case on composites) is due to difference of conductivity in amorphous and crystalline phases. At electrification of such a material, the carrier will gather near the given interfacial boundary, or vice versa will be away from it depending on which of two currents has great conductivity. Difference in local currents of conductivity reduces also to dissipation of charges when removing the currents of TSD, as in this case currents flow already in opposite direction. It should be noted that the given maximum in great degree is related with relaxation of charges on the surfaces of particles of  $TlInSe_2$  as with increasing the content of the filler in compositions, the quantity of the peak increases.

Effects of inversion of the sign of the current of TSD were observed also for other electrically active dielectrics, electrets and polymer composites [4]. But interpretation of these phenomena remains discussible. Depending on temperature condition of the inversion current, the state of the surface, nature of a polymeric matrix and filler, nature of polarization and other factors, the observed currents with the inverse sign on the curves of TSD are connected also with reorientation of dipoles existing in a polymer. To our mind, the maxima at temperature  $432 \div 439K$  and  $450 \div 460K$  have the same nature, i.e. both of these maxima are a part of one and the same maximum related to  $\alpha$ -relaxation in PE. The observed inversion in narrow range of temperature is the result of reduction of conductivity of  $TlInSe_2$  at polarization of spaces charges in IP in the field of SC. We can suppose that the volume content of  $TlInSe_2$  in the composite may influence on temperature position of  $\alpha$ -relaxation process.

The third high-temperature maximum for  $517 \div 523K$  may be connected with increase of intrinsic conductivity of a filler as the quantity of the peak increases with increasing the filler's content in the composition. For quantitative estimation of the thickness of interfacial layer in heterogeneous polymeric compositions, in a number of cases we use the representation on formation of a double layer (such a point of view is widely held in extrinsic semiconductors, where difference in conductivity reduces to

formation of double layer).

In polymeric mixtures and composites, the thickness of interfacial layer may be estimated by the formula of [16].

$$d_m^2 = \frac{2\varepsilon_1\varepsilon_2\varepsilon_0kT}{n \cdot e^2}$$

where  $\varepsilon_1$  and  $\varepsilon_2$  are dielectric permeabilities of each phase,  $\varepsilon_0$  is a dielectric constant,  $n$  is the concentration of carriers of charge (for polymeric dielectrics  $n = 10^{21} m^{-3}$  is the charge of the electrode,  $k$  is the Boltzmann constant,  $T$  is absolute temperature. Calculations of values of  $d_m$  by the given formula show that they make up about 0,4 ÷ 1,2  $\mu m$ .

The results of investigations of properties of the sample of compositions *LDPE+TlInSe<sub>2</sub>* crystallized at hardening conditions at 273 K are given in fig. 2. The analysis of the obtained results shows that on the curves of TSD we observe a number of depolarization peaks in certain temperature fields. These peaks belong to release of charges from traps connected both separate components (PE and *TlInSe<sub>2</sub>*) and shaped interfacial polarization in the field of space charges. At temperature 445 K on the curves of TSD of the samples of compositions we observe inversion peak with semi-length 3 ÷ 5 K. In the spectra of TSD, on electret compositions with *TlInSe<sub>2</sub>* at temperatures 515 ÷ 520 K we find depolarization peak connected with a new center (of traps) of stabilization of electrets charges.

The fillers *TlInSe<sub>2</sub>* with  $p$ -conductivity and dispersity 50 ÷ 63  $\mu m$  in competitions with a polyethylene play the role of structurant observed in the increase of the degree of crystallinity and change of supramolecular structure of a polymer.

The results of investigations of spectra of TSD of compositions with aluminum nanoparticles are given in fig. 3. The composites 3% *Al*, 5% *Al*, 7% *Al*, 10% *Al* were studied. From fig. 3 it follows that for the composite 3% *Al* on the spectrum  $I(t)$  we observe one strongly marked maximum at temperature 408 K, weak minimum at 413 K. At wide temperature range 298-393 K the current remains constant, then harshly increases to 4,2 A, and in the same way converges to zero. On the spectrum of TSD of the composite 5% *Al* we also observe a strongly marked maximum at temperature 409 K. At this temperature the current achieves to 9,5 A and with further increase of temperature, it decreases. For 415 K we observe weak minimum and decrease of current for this composite. It was revealed that at temperature range 273-397 K the current about 0,5 A remains constant. On the spectrum TSD 7% *Al* we observe two bright maxima at temperatures 409 K current 6,2 A and 42K current 4,9 A. Between these maxima at 413 K it was revealed a deep minimum of the current 3,5 A. Note that also for this composite at temperature range 273-400 K the current 0,4 A remains constant. For the composite 10% *Al* on the curve  $I(t)$  we observe a diffuse maximum at temperature range 405-416 K and for this composite in the wide range 273-403 K the current remains constant.

## 4. Conclusion

By investigating the three-dimensional image of the microrelief of the surface of composites it was revealed that at boundary layer of compositions the roughness of the surface decreases, smoothens. It was revealed that putting a filler into a polymeric matrix reduces to occurrence of deep centers of capturer of carriers at corona and the occurrence depth. Under the influence of aluminum nanoparticles the current of TSD is stabilized to melting temperature of the composite's matrix.

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