

## Photoelectret effect in polymer-A<sup>II</sup>B<sup>VI</sup> (CdS, ZnS) composites of photosensitive semiconductors

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The photoelectret effect in composite heterostructures consisting of polar (fluorine-containing) and non-polar (polyolefins) polymers - high density polyethylene (HDPE), low density polyethylene (LDPE), F42, F2-ME and the inorganic phase A<sup>II</sup>B<sup>VI</sup> (CdS, ZnS) has been studied. It has been established that the difference in photoelectret potentials in a given volume share of the inorganic phase mainly depends on the polarity of the polymer matrix. A possible mechanism of the photoelectret effect formed under the combined action of a strong electric field and light in these composites. It has been experimentally established that the potential barrier formed at the polymer- A<sup>II</sup>B<sup>VI</sup> semiconductor interface separates the electric charge carriers formed as a result of the internal photoelectric effect and ensures the formation of an electret potential difference. The electret charge state of polymer- A<sup>II</sup>B<sup>VI</sup> composites was studied using the spectrum of thermally stimulated current.

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### 1. Introduction

One of the main issues raised in our research is the study of the photoelectret effect in polymer-light-sensitive semiconductor composites. For this, macroscopic parameters were determined, which are indicators of the electret state in composites consisting of various photoelectric dispersants (CdS, ZnS) and thermoplastic polymers. A possible model of composite photoelectrets is determined and, on its basis, the mechanisms of formation of the photoelectret effect in polymer-CdS and polymer-ZnS composites under the action of an electric field, temperature, and light are presented. The obtained experimental results show that under the conditions of the combined action of light, electric field and temperature in these composites, it is possible to obtain photoelectrets with different characteristics and applications [1,2]. The photopolarization process is based on the generation of nonequilibrium electric charge carriers in composites under the action of light and an electric field and their placement in traps with different activation energies. Chemically active oxidation centers and physical defects should be considered as surface traps. Chemically active mixtures adsorbed on the surface of small- and large-molecular compounds of electronegative origin also play an important role in the formation of surface traps. A factor of great interest in the role of surface traps for electric charge carriers is the difference in the arrangement of macromolecules on the surface and in the bulk, i.e., the difference in the supramolecular structure of macromolecules on the surface and in the bulk. Thus, in the surface and near-surface volumes of polymer samples, microphases and interphase boundaries are formed that differ from each other in physical structure [3,4]. Sufficient traps for photoelectric charge carriers are created at such interfacial microboundaries. The formation of volume traps is associated with the following effects:

- with the presence of mixtures and defects in the size of the monomers;
- inconsistency in the chain of the polymer macromolecule;
- with the unevenness of the formed crystallites and the presence of free volumes;
- with the presence of an interfacial (polymer and semiconductor) boundary.

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## 2. Research objects and methods

Polar (fluorine-containing) and non-polar (polyolefins) polymers were used as matrices - high density polyethylene (HDPE), low density polyethylene (LDPE), F42 and F2-ME. Semiconductors CdS, ZnS ( $A^{IV}B^{VI}$ ) were used as dispersants. We obtain a homogeneous system of polymer and particles of the used dispersant by mechanical mixing. Viscosity and plasticity of the polymer phase of photo composites (rotational deformation ability) flows between the particles of inorganic phases and fills the mold. The main factors in choosing the pressing pressure are the shape, size and design of the sample. Experimentally, the optimal pressure for obtaining photo composites with a diameter of 10–40 mm and a thickness of  $200 \cdot 10^{-3}$  mm was determined in the range of 10–30 MPa. The current spectrum of thermally activated depolarization (TSD) of photoelectrets, photoelectric potential difference and photoelectric methods were used as research methods. In general, the method of thermal activation depolarization spectroscopy is widely used to create various types of electrets and study the mechanisms of their formation. Using this method, it is possible to determine the concentration of electric charge carriers, the activation energy and the lifetime in the process of depolarization of electrets. Regardless of the polarization method, the method of thermal activation spectroscopy can be widely used with the same probability in the study of photoelectrets. The essence of the method for studying the photoelectret effect in composites is to determine the concentration and relaxation time of electric charge carriers created in the composite under conditions of light exposure to photosensitive composites [5]. The relaxation time of the electric charge of the photoelectret composite is taken as the time corresponding to the subsequent decrease in electric charges arising directly during illumination to "e".

## 3. Analysis and discussion of the experimental results

One of the important results of our work is the dependence of the photoelectret potential difference  $U_e$  on the volume share of the photosensitive inorganic phase of the composite, i.e.  $U_e=f(\Phi)$ , fig. 1 and 2. The extreme nature of these dependences has the following reasons. Firstly, during mechanical mixing of components, oxidation of the polymer matrix during pressing under the combined influence of temperature and pressure (mechano-thermal destruction and thermal oxidation), generation of polar groups that form a heteroelectric charge. Secondly, during photoinjection, a change in the probability of formation of a quasi-neutral system due to stabilized homocharges and heterocharges at the interface and a decrease in the electret charge  $\Delta Q_e = Q_r - Q_{het}$  or the electret potential difference, defined as a superposition of homo- and heterocharges. Third, with an increase in the volume share of the photosensitive phase, the specific photoconductivity of the composite can increase and the relaxation of the homoelectric charge can be enhanced. Fourth, with an increase in the volume share of CdS and ZnS in the composite, the mass of the polymer phase, which plays the main role in electretization, decreases. Indeed, in the studied composites (polymer - photosensitive CdS and ZnS), as a result of phase interaction, the crystal structure of the polymer and the electronic structure of CdS and ZnS change, and these effects increase with increasing volume share of the photosensitive semiconductor phase [6].

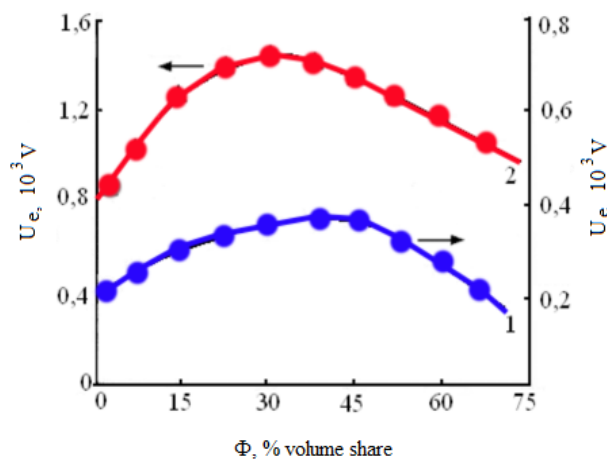


Fig. 1. Dependence of the difference of photoelectret potentials of composites  $U_e$  on the volume share ( $\Phi$ ) of the photosensitive phase. 1. ASPE - CdS; 2. F42 - ZnS;  $E_p=0.4 \cdot 10^4$  V/m;  $t_p=0.25$  hours;  $E_i=400$  mWt/cm<sup>2</sup>;  $T_p=293$ K;  $U_e$  - measured immediately after polarization.

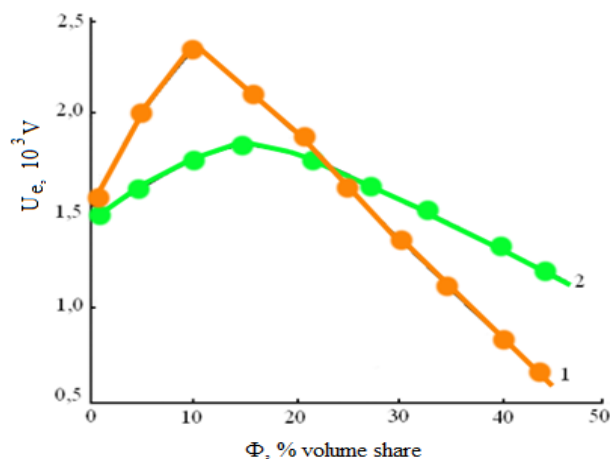


Fig. 2. Dependence of the photoelectric potential difference ( $U_e$ ) of composites on the volume share of the photosensitive phase. 1. F42 - ZnS; 2. F42 - CdS.  $E_p=0.4 \cdot 10^4$  V/m;  $t_p=0.25$  hours;  $E_i=400$  mWt/cm<sup>2</sup>;  $T_p=393$ K.

Therefore, the maxima on the dependences  $U_e=f(\Phi)$ , shown in figures 1 and 2, depend on the dielectric (electric charge) of the polymer matrix under the conditions  $\Phi=\text{const}$ , the optical properties of CdS or ZnS. It should be noted that in composites with a polymer matrix, it is the polymer phase that has more opportunities for modifying components. In our work, we used an electric gas discharge plasma to modify the polymer phase. We exposed polar or non-polar polymers to electrical gas discharge plasma at various temperatures [7].

In nondisperse polymeric photoelectrets, the TSD spectrum has one maximum (fig. 3, curve 1). The TSD spectrum of photoelectrets based on dispersed polyolefins (with ZnS particles) exhibits two maxima (fig. 3, curve 2). The first maximum at  $\sim 80^\circ\text{C}$  and the second maximum at  $\sim 110^\circ\text{C}$  were recorded for the LDPE-ZnS photoelectret composite. On fig. 4 shows the results of similar experiments for the HDPE-ZnS photoelectret composite. It can be seen from the spectrum that the observed maxima shifted towards relatively high temperatures: the first maximum was recorded at  $\sim 95^\circ\text{C}$ , the second - at  $\sim (120-130^\circ\text{C})$ . The activation energies corresponding to the maxima in the TSD spectra differ by about 1.6 times. Depending on the parameters of electrophotopolarization ( $E_p$ ,  $T_p$ ,  $t_p$ ,  $E_i$ ), the activation energies vary within 0.6-0.82 and 0.9-1.5 eV, according to the first and second maxima of the TSD of the polyolefin - ZnS composite. It has

been established that with an increase in the volume share of the light-sensitive semiconductor phase in the composite, the amplitude and half-width of the second maximum in the TSD spectrum increase; the corresponding parameters of the first maximum decrease. The main reason for this effect is an increase in the area of the interface with an increase in the volume share of the inorganic and light-sensitive phases.

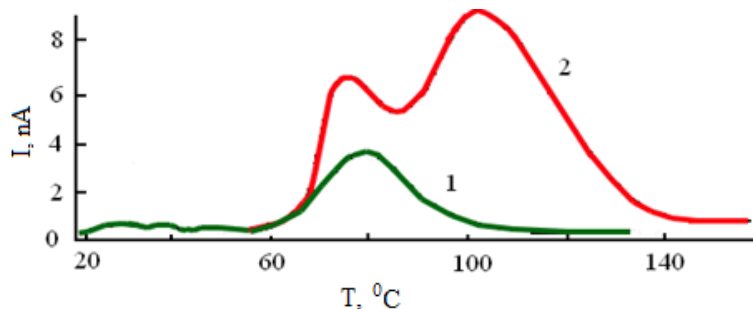


Fig. 3. TSD current spectrum of non-dispersed polyethylene (curve 1) and low-density polyethylene dispersed with ZnS particles (curve 2): 1. LDPE; 2. LDPE - volume share of ZnS 30%.  $E_p=0.2 \cdot 10^4$  V/m;  $t_p=0.25$  hours;  $E_i=400$  mWt/cm<sup>2</sup>;  $T_p=293$ K.

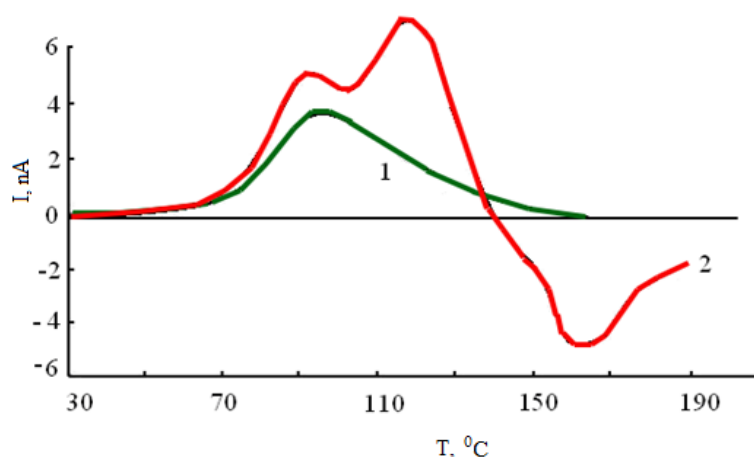


Fig. 4. TSD current spectrum of non-dispersed polyethylene (curve 1) and high-density polyethylene dispersed with ZnS particles (curve 2): 1. HDPE; 2. HDPE - volume share of ZnS 30%.  $E_p=0.2 \cdot 10^4$  V/m;  $t_p=0.25$  hours;  $E_i=400$  mWt/cm<sup>2</sup>;  $T_p=293$ K.

A preliminary analysis of photoelectric effects in composites based on polar and nonpolar polymers and photosensitive materials allows us to conclude that these composites can be used as highly efficient photoelectric materials. Therefore, the goal of our work is to study the photoelectret effect in a polymer matrix and composites with CdS, ZnS phases. On fig. 5 shows the dependence of the photoelectric charge on the volume share of the photosensitive phase for composites consisting of polyethylene, fluorine-containing polymers and CdS [8-11]. The results show that the photoelectric charge relaxation time and value of various polymer matrix composites strongly depend on the polarity of the matrix and the volume share of the photosensitive phase. F42 - CdS composite is more efficient as a photoelectret material. One of the notable results shown in the figure is that the optimal value of the photosensitive inorganic phase depends on the polymer matrix. In our opinion, the main reason why the optimal volume share of the inorganic phase in the composite depends on the chemical structure of the polymer matrix is related to the differences in the mechanisms of the transfer of photoelectric charge carriers and electron-ion processes at the interface. On fig. 6 shows the dependence of the relaxation time of the photoelectric charge of the F2ME-ZnS composite on the volume share of the photosensitive phase

(ZnS). The results show that the relaxation time of the photoelectret charge of the F2ME – ZnS composite depends to a lesser extent on the volume share of ZnS.

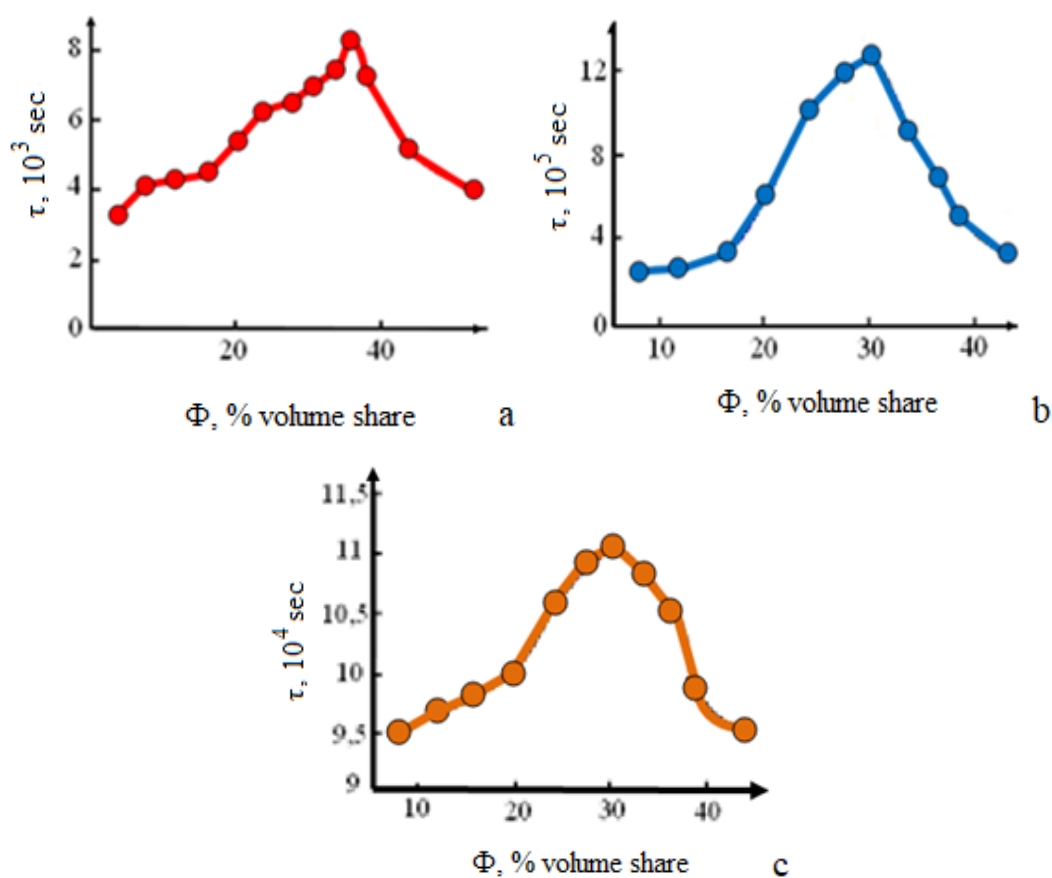


Fig. 5. Dependence of the relaxation time of the photoelectret charge of various polymers and composites based on CdS on the volume share of CdS. a) HDPE - CdS;

b) F2ME - CdS; c) F42 - CdS;  $E_p = 0,2 \cdot 10^4 \frac{V}{m}$ ;  $t_p = 0.25$  hours.

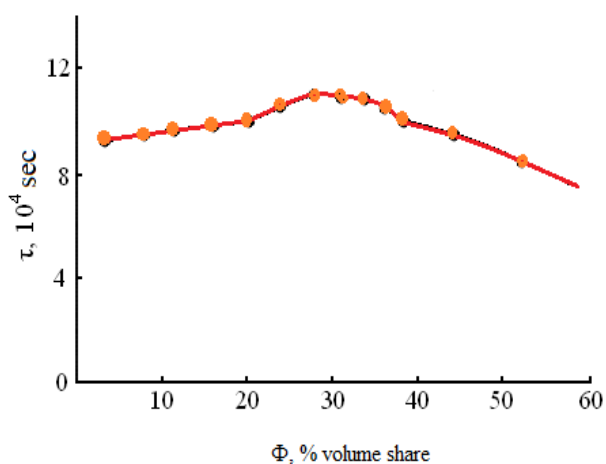


Fig. 6. Dependence of the relaxation time of the photoelectret charge of the F2ME-ZnS composite on the volume share of the photosensitive phase (ZnS).  $E_p = 0.2 \cdot 10^4 \frac{V}{m}$ ;  $t_p = 0.25$  hours.

In the process of electro-optical polarization, the separation of electric charges (i.e., the absence of recombination) can be formed both due to an external field and due to an internal field due to electron exchange at the polymer-semiconductor interface. The experimental results obtained show that the internal field formed at the interface plays an important role in the process of polarization of photoelectrets. Thus, the choice of polymers with polar and nonpolar structures as the polymer matrix and the choice of semiconductors with different surface-electronic properties as the semiconductor phase makes it possible to determine the mechanism of the photoelectret effect in polymer-CdS and polymer-ZnS composites. These results clarify the role of electron-ion effects in the process of polarization at the polymer-photosensitive semiconductor interface as a result of the combined action of light and electric fields [12-17].

#### 4. Conclusions

The main reason for the formation of the photoelectret effect under the action of a strong electric field and light in composites with polymer-  $A^{\text{II}}B^{\text{VI}}$  components is the formation of a potential barrier at the polymer- $A^{\text{II}}B^{\text{VI}}$  interface and the gradual separation of electric charge carriers created due to the internal photoelectric effect.

#### References

- [1] M. A. Kurbanov, G. Z. Suleymanov, A. F. Gochuyeva, N. A. Safarov, Z. M. Mamedova, I. N. Orujov, *Semiconductors*, 45(4), 510-517 (2011); <https://doi.org/10.1134/S1063782611040130>
- [2] A. F. Gochuyeva, M. A. Kurbanov, B. H. Khudayarov, A. M. Aliyeva, *Digest Journal of Nanomaterials and Biostructures*, 13(1), 185-191 (2018).
- [3] A. V. Vannikov, *Russian Chemical Journal*, XLV(5-6), 41-50 (2001).
- [4] M. F. Galikhanov, A. H. Borisova, R. Y. Deberdeev, *Russian Journal of Applied Chemistry*, 78(5), 836 - 839 (2005); <https://doi.org/10.1007/s11167-005-0400-2>
- [5] M. K. Kerimov, M. A. Kurbanov, A. A. Bayramov, G. Z. Suleymanov, N. A. Safarov, A. F. Gochuyeva, Z. M. Mamedova, S. H. Aliyeva, 11th International Symposium on Ferroic Domains and Micro-to Nanoscopic Structures, Ekaterinburg, Russia, 117 (2012).
- [6] M. K. Kerimov, M. A. Kurbanov, A. A. Bayramov, N. A. Safarov, A. F. Gochuyeva, *J. Scientific Israel - Technological Advantages, Materials and environmental engineering*, 14(4), 9-15(2012).
- [7] P. N. Kovalskiy, A. D. Shneyder, "Photoelectret effect in semiconductors" Lvov: High school, 210, 1977.
- [8] M. K. Kerimov, M. A. Kurbanov, A. F. Gochuyeva, I. N. Orujov, *Report NASA*, LXIII(3), 33-37 (2007).
- [9] M. K. Kerimov, M. A. Kurbanov, N. A. Safarov, A. F. Gochuyeva, I. N. Orujov, *Report NASA*, LXV(5), 33-39 (2009).
- [10] A. F. Gochuyeva, M. A. Kurbanov, A. A. Bayramov, N. A. Safarov, I. N. Orujov, *Materials of International Symposium "Nanomaterials for Industrial and Underground Constructions Protection" and XIth International Conference "Solid - State Physics" (SSP - XI)*, Ust - Kamenogorsk, 29 - 33 (2010).
- [11] Z. M. Mammadova, M. A. Gurbanov, A. F. Gochuyeva, G. Z. Suleymanov, D. B. Taghiyev, *European Applied Sciences, Chemistry*, No. 11, Section 13, 108-109 (2014).
- [12] G. Z. Suleymanov, A.F. Gochuyeva, M. A. Kurbanov, F. S. Ibrahimova, O. A. Aliyev, S. Ch. Aliyeva, *Azerbaijan Journal of Physics*, XXII(4), 10-12 (2016).

- [13] G. Z. Suleymanov, A. F. Gochuyeva, M. A. Gurbanov., B. H. Chudayarov, Z. M.Mamedova, Azerbaijan Journal of Physics, XXI(2), 6-10 (2015).
- [14] A.F. Gochuyeva, Modern Physics Letters B, 36(2), 2150542 (2022).
- [15] A.F. Gochuyeva, D.A. Mamedov, F.F. Yaxyayev, AJP FİZİKA section C: Conference L.M. Imanov, 21-22 September, 74-78 (2022).
- [16] A.F. Gochuyeva, F.F. Yaxyayev, AJP FİZİKA section C: Conference M.H. Shahtakhtinski, 19-20 Oktober, 33-36 (2022).
- [17] A.F. Gochuyeva, Power Engineering Problems, №3, 57-60 (2022).