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NEW TECHNOLOGIES OF MATRIX COMPOSITE POLYMER PHOTOVOLTAIC AND PHOTOELECTRET MATERIALS

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Abstract. The main goal of our work is the development of new technologies of photovoltaic and photoelectret effects based on polar and non-polar polymer matrices and CdS, ZnS semiconductors. It was determined from the research that the interfacial effect in photoelectric composites is completely dependent on the size of the particles of the semiconductor phase. The main reason for the formation of photovoltaic, photoelectret effects in polymer, CdS, ZnS composites under the combined effect of light and electric field is the formation of homo and hetero charges that determine the difference in electret potentials at the interphase boundary of the composites in the process of electrophotopolarization.

Keywords: *photovoltaic effect, photoelectret effect, electrophotopolarization.*

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1. Introduction

As with organic and inorganic photosensitive materials, their photoelectric properties (photoconductivity, photovoltaic, photoresistive, photogeneration and stabilization of electric charge carriers) are of particular importance in polymer-CdS and polymer-ZnS composites as a decisive factor in the formation of the photoelectret effect (Kurbanov *et al.*, 2011; Gochuyeva *et al.*, 2018; 2023). Regardless of the type of photosensitive materials of the indicated properties, the initial stages of photoeffects that can occur in them are practically the same: optical excitation of non-equilibrium electrons, internal photoeffect, recombination, increasing the concentration of electric charge carriers, such as electrons, due to the influence of photons, photoconductivity, photovoltaics, photopolarization, photopolarization retention time and photoelectret. The properties of any active composites are directly related to the characteristics of their inorganic phase (ZnS, CdS). Therefore, the initial stage of the study of any effects to be studied in composites, including photoelectric effects, should begin with the selection of an inorganic phase. For the study of photoresistive, photovoltaic and photoelectret effects, which are intended to be studied in our work, it is appropriate to use light-sensitive simple semiconductors (Se, Te) (Jafarova & Orudzhev, 2021), $A^{II}B^{VI}$ and $A^{II}B^{V}$ compounds as the active phase (Jafarova, 2022; 2023). The width of the forbidden zone of these photosensitive materials increases accordingly. ZnS has the largest value in terms of the width of the forbidden zone. Such a choice of the photosensitive phase allows to appropriately change the parameters of the potential barrier formed at the polymer-

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semiconductor boundary in the composite. At present, structurally, thermally, etc. non-ferromagnetic nanoparticles studying the properties of the materials we have taken as objects of research in our work, we will conduct research to acquire any magnetophotosensitive material by purchasing a composite in the future (Gochuyeva, 2022; 2023). Photoconductivity, photovoltaic and photoresistive effects should be studied in parallel in order to determine the formation mechanism of the photoelectret effect in polymer – $A^{II}B^{VI}$ photosensitive materials taken as the object of research. The main parameters of the photoelectret materials (lifetime, photoelectret potential difference, electrical conductivity, spectra of photo- and thermo-depolarization currents) should be optimized by purposeful variation of the photoelectric phenomena that ensure the formation of the indicated effects (Vannikov, 2001; Galikhanov *et al.,* 2005).

2. Research objects and methods

The study of photovoltaic and photoelectret effects in composites was carried out under atmospheric conditions at room temperature in an automated network described in our previous work (Kerimov *et al.,* 2012). The light intensity was in the range of (0.2-2.5) Wt/m^2. The intensity of the external electric field varied in the range of (0.1-1.2)$\cdot 10^4$ V/m. Composites based on low-density polyethylene (LDPE)-CdS and polyvinylideneftoride (PVDF)-CdS, PVDF-ZnS, F42-CdS, F42-ZnS were selected as the studied object. The volume content (Φ) of CdS and ZnS in the composites varied in the range of (20-40)% by volume. Beyond this range, studies are not interesting in terms of photovoltaic and photoresistive effects. We can say the following about the characteristics of the elements that make up the constituent phases of our composite. Low-density polyethylene has a molecular weight of 20.000-40.000, a density of 916-935 kg/m^3, a release coefficient of 4.5, a refractive index of 1.52 and a degree of crystallization of 50-60%. F42 and polyvinylidene fluoride are halogen-containing thermoplastic polymers that are polar and crystallizable linear polymers. F42 specific volume electrical resistance is 10^9–10^{10}, ε=9-11. Density of PVDF 1760 kg/m^3, molecular weight 100·000, crystallization temperature range 141–152^{0}C, melting temperature 171–180 ^{0}C, release coefficient 94, refractive index 1.54, degree of crystallization 40–65%, operating temperature range 120–166 ^{0}C is. CdS and ZnS are photosensitive semiconductors with high (≤ 3.6eV) photoelectric properties and band gap.

The initial stage of the technology of obtaining composites is the purchase of press-rubbing of the components, their separation into fractions according to their sizes, passing through magnetic sintering, surface cleaning and thermal treatment of particles. Their constituent phases (components) are selected according to the requirements placed on the photocomposites to be purchased. A homogeneous mixture is obtained by mixing the selected components in a ball mill. The main component of the homogeneous mixture is the polymer. Another component of the composite is photosensitive semiconductors. Thermoplastic polymers were used as the polymer phase: polyolefins and fluorine-containing polymers. Mixing components and obtaining a homogeneous system based on them is an important stage of the technology used in creating any composite. The characteristics of the obtained composite depend very much on the level of performance of this stage. Obtaining a homogeneous system ensures the smooth distribution of components in the composite and the stability and uniformity (repeatability) of the properties of the obtained material. We pour the obtained homogeneous mixture into a press mold with a diameter of 40 mm and a thickness of $200 \cdot 10^{-3}$ mm, put lead foils on it and place it in the pressing equipment. We provide pressure in the range of 10-30MPa as the optimal pressure. The pressing process is characterized by three main indicators: pressure, temperature and time of keeping under pressure.

3. Results and its discussion

Recently, the photovoltaic effect in polymer-photosensitive semiconductor composites has been widely studied. The main reason for this is the following: -newly created composite type photovoltaic materials are obtained by simple technology; - the possibility of purchasing elements of smaller sizes, homogeneous in terms of physical structure and any shape;- simplicity of appropriate modification technology of the properties of such systems; - the possibility of expanding the range of spectral sensitivity of photo materials and increasing their lifetime. We know that the photovoltaic effect in crystals is the generation of photovoltaic voltage when they are illuminated. At this time, the electrodes drawn on the surface of the crystal are open. If the electrodes drawn on the crystal are closed, then a stationary photovoltaic current will be generated from it under the influence of light. Determining the mechanisms of optical effects (for example, photovoltaic) in dielectrics or composites under the influence of light is an important factor for the creation of photoelectrets (Guangsen *et al.*, 2019, Kerimov *et al.*, 2012). When choosing dielectrics for photoelectrets, the following should be taken into account:

- photosensitive materials with small dark resistance;
- having high photosensitivity, the dark conductivity of the dielectric should be less than $\sigma < 10^{-12} - 10^{-14}$ cm /m;
- in such dielectrics and composites, the effective electret charge (Q_{eff}) should be formed under the influence of both electric field (E_p) and light.
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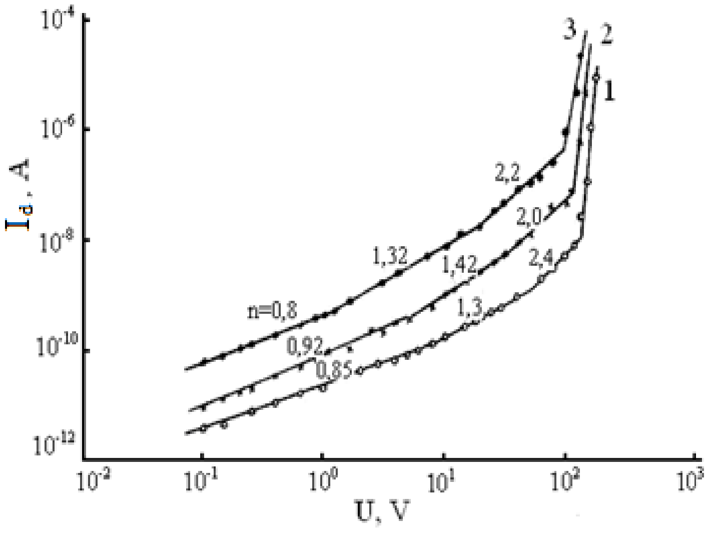

Fig. 1. Volt–ampere characteristic of PVDF–ZnS composite in the dark.
1. PVDF - 20% volume ZnS; 2. PVDF - 40% volume ZnS; 3. PVDF - 60% volume ZnS.

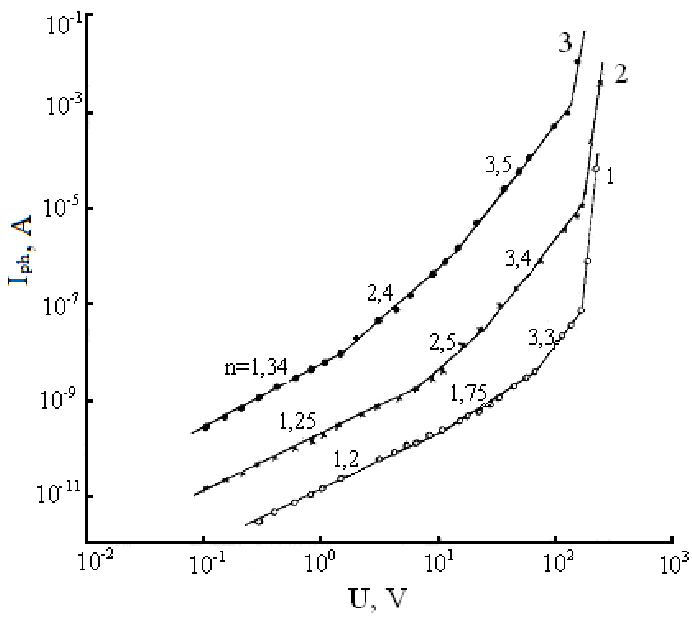

Fig. 2. Volt-ampere characteristic of PVDF-ZnS composite under the influence of light with an intensity of 400 mWt/cm^2.
1. PVDF - 20% volume ZnS;2. PVDF - 40% volume ZnS; 3. PVDF - 60% volume ZnS

As we mentioned earlier, the presence of phases in composite systems that differ from each other and the formation of a new phase at the border as a result of their interaction, create various photoeffects, including photovoltaic effect (Kovalskiy & Shneyder, 1977, Rustamova *et al.,* 2023). The mechanism of this effect is based on the separation and transfer of electric charges. It is rather difficult to clarify the nature of this process. For this purpose, in order to clarify the nature of the photovoltaic effect, the volt-ampere characteristics were studied both under the influence of light and in the dark (Figs. 1 and 2).

One of the main issues in our work is the study of photoelectret effect in polymer-photosensitive semiconductor composites. For this purpose, macroscopic parameters that are indicators of the electret state were determined in the composites consisting of various photoelectric dispersants (CdS, ZnS) and thermoplastic polymers. A possible model of composite photoelectrets has been determined, and based on it, the mechanisms of electret effect formation in polymer-CdS and polymer-ZnS composites under the influence of electric field, temperature and light have been given (Mammadova *et.al.,* 2014; Kosobudskiy *et al.,* 2005; Sen *et al.,* 2007). The obtained experimental results show that it is possible to obtain photoelectrets with different characteristics and fields of application under the conditions of the combined effect of light, electric field and temperature in the above-mentioned composites. The photopolarization process is based on the generation of non-equilibrium electric charge carriers in composites under the influence of light and electric field and their placement in traps with different activation energy. Chemically active oxidation centers and physical defects should be considered as surface traps. Chemically active mixtures, small and large molecular compounds of electronegative origin adsorbed on the surface also play an important role in the formation of surface traps (Mehdiyeva *et al.,* 2022; Rumyantsev *et al.,* 2005). A factor of great interest in the role of surface traps for electric charge carriers is the differences in the arrangement of macromolecules on the surface and in the volume, that is, the difference in the supramolecular structures of macromolecules on the surface and in the volume.

Therefore, microphases and interphase boundaries, different from each other in terms of physical structure, are formed on the surface and near-surface volumes in polymer samples. Sufficient traps for photoelectric charge carriers are created at such interphase microboundaries (Davidenko *et al.*, 2004). The formation of volumetric traps is related to the following effects:

– with the presence of mixtures and monomer size defects;
– non-sequence in the polymer macromolecule chain;
– with the irregularity of the resulting crystallites and the presence of free volumes;
– with the presence of an interphase (polymer and semiconductor) boundary.

It should be noted that one of the main factors that distinguish photosensitive composites is the possibility of extensive modification of its polymer matrix with simple technology, for example, by the effect of electric gas discharge plasma. Fig. 3 shows the dependence of the electret potential difference (U_e) of the polymer matrix modified photoelectret composite under the combined effect of electric gas discharge plasma and temperature on the volume share (Φ) of its photosensitive semiconductor phase.

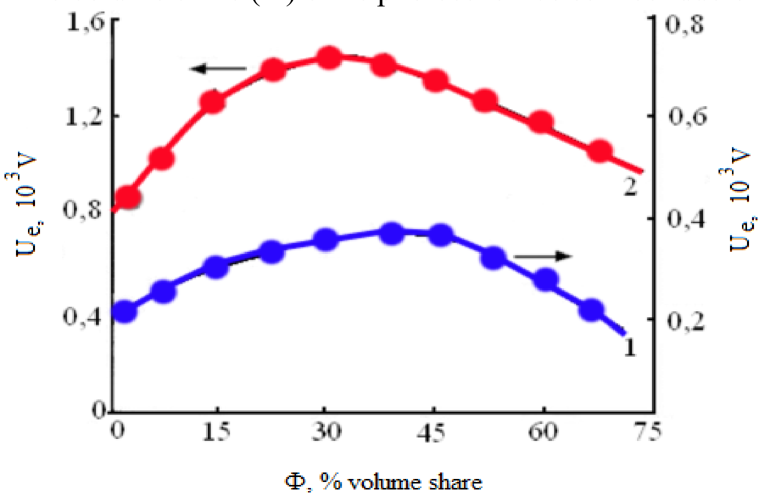

Fig. 3. Dependence of the photoelectret potential difference Ue of the composites on the volume share (Φ) of the photosensitive phase. 1. ASPE – CdS; 2. F42 – ZnS; E_p=0.4·10^4 V/m; t_p=0.25 hours; E_i=400 mWt/cm^2; T_p=293K; U_e – measured immediately after polarization.

The obtained results show that the plasma modification of the polymer matrix strongly affects the parameters and nature of the U_e=f(Φ) dependence. Modification in plasma conditions was carried out in a core with the following parameters. The thickness of the air layer is h=1.5 mm. Sinusoidal voltage applied to the core U_c=15·10^{3}V; The air layer of the core (h=1.5mm) is limited on both sides by a glass plate with a thickness of h=1.5mm. The frequency of the voltage applied to the core is 50 Hs. The modification was carried out in a closed container. In the modification process, the polymer powder (diameter ≤ 60mkm) was frequently stirred and brought to the discharge zone. The obtained experimental results led to the determination of the following regularities: in the photoelectret composites consisting of polymer-photosensitive semiconductors (CdS, ZnS), as the volume share of CdS or ZnS increases, the photoelectret potential difference U_e first increases, reaching a maximum and decreases, that is, the dependence of U_e=f(Φ) has an extreme character (Figs. 3, 4, 5);

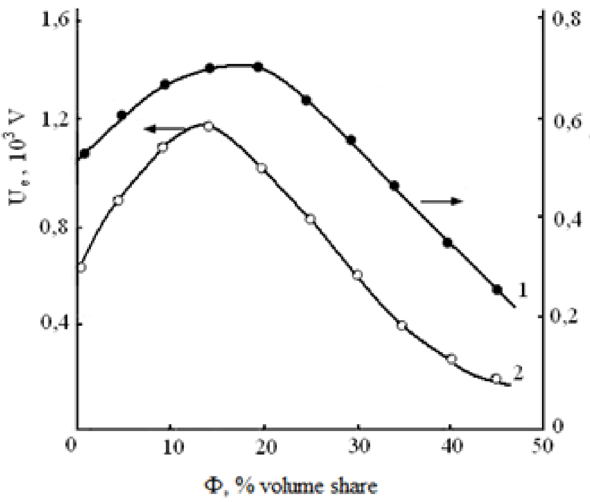

Fig. 4. Dependence of the photoelectret potential difference U_e of the composites on the volume share of the photosensitive phase (CdS) . 1. PVDF – CdS; 2. ASPE – CdS. Ep=$0.4\cdot10^4$ V/m; t_p=0.25 hours; E_i=400 mWt/cm^2; T_p=373K; U_e - measured immediately after polarization.

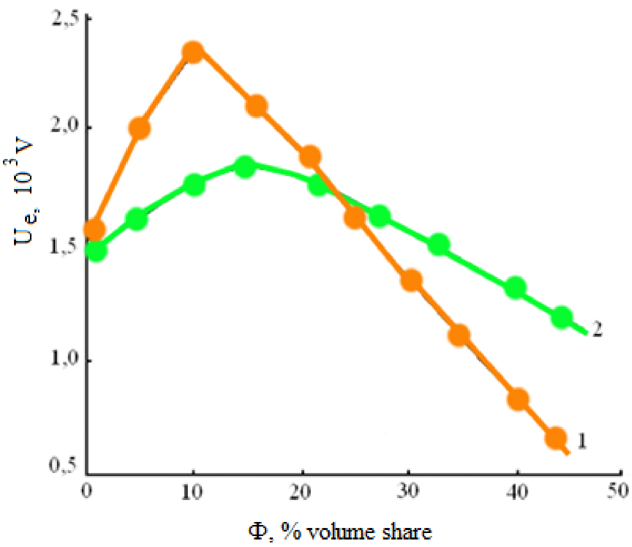

Fig. 5. Dependence of the photoelectret potential difference (Ue) of the composites on the volume share of the photosensitive phase. 1. F42 – ZnS; 2. F42 – CdS. E_p=$0.4\cdot10^4$ V/m; t_p=0.25 hours; E_i=400 mWt/cm^2; T_p=393K.

Composites with different polymer and light-sensitive semiconductor phases are different in terms of the maximum values of dependences of the photoelectric potential difference U_e on the volume share of the light-sensitive inorganic phase; the maximum potential difference in U_e=f(Φ) dependencies of photocomposites with polar polymer matrix is greater than the corresponding parameter of photocomposites with non-polar matrix (Figs. 3, 4, 5).

4. Conclusions

In the composites consisting of polymer (LDPE, PVDF, F42) and CdS, ZnS components, the main reason for the formation of the photoelectret effect under the combined effect of light and electric field is homo and is the formation of heterocharges. The main reason for the formation of the photovoltaic effect in polymer matrix (LDPE, PVDF, F42) and light-sensitive ZnS, CdS phase composites is the gradation of electric charge carriers formed as a result of the internal photoeffect under the influence of the potential created at the interphase boundary.

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