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Photoelectric effects in polymer – (CdS) – ferrocene composites

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In our work, we investigated the photoelectric effects arising in composites consisting of polar (fluorine-containing) and non-polar (polyolefin) polymers—such as high-density polyethylene (HDPE), PVDF, F42 — and an inorganic phase composed of $A^{II}B^{VI}$ (CdS, ZnS) and ferrocene. In addition, the processes occurring in these composites during the creation of these effects have been studied. It was found that the parameters of the formation of the posistor effect in the polymer-ferrocene composite are related to the presence of an interphase potential barrier, which is determined by the geometric dimensions of the interphase transition layer, dielectric permeability, electric charge state, and the difference in ionization potentials of ferrocene and the transition layer. The main reason for the formation of the photoquenching effect of the rotational conductivity in polyolefin-ferrocene composites is the formation of a local electric field directed opposite to the external field as a result of the formation of multi-charged centers and dipole moments in the ferrocene phase under the influence of light.

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1. Introduction

Previously, polymeric materials were mainly considered as substances with dielectric properties. However, in recent times, the discovery of high electrical conductivity in these materials has led to a radical change in the existing views on their physical properties. Thus, doped polymers with a conductivity 10^{12} times higher than that of classical polymers have been prepared and the mechanisms of transfer of electrical charge carriers in these materials have been studied. In these polymers showing conductive properties, the movement of charge carriers is considered to occur mainly by the hopping mechanism and the factors affecting this process and their nature have been studied in detail. Previously, it was assumed that since the internal structure of polymers is at a high level, charge transfer based on the tunneling effect, as in metals, is difficult to implement. However, in recent years, advances in polymer production technologies have created conditions for creating a certain order in their structure and thus enabling the movement of charge carriers by the tunneling mechanism. To clarify the photoelectric effects in composites, the photoelectric properties of their individual components and the factors that can significantly affect them were first considered. It is known that the generation of electric charge carriers in polymers, their transfer and the influence of local levels existing in the quasi-forbidden zone of the polymer on the transfer of electric charges are of particular importance in studying the mechanisms of photoelectric effects in composite materials. As in all solid dielectrics, any change in the chemical and physical structures of polymers results in the formation of local levels in their quasi-forbidden zone. Therefore, by appropriately changing the chemical and physical structures of macromolecules, the density and nature of local levels can be regulated. At the macroscopic level, this means that chemical and spectral sensitization of the conductivity of polymers allows them to be used as various photomaterials [1-3]. Undoubtedly, a deep study of the photoexcitation of polymers and their composites is of great importance in determining the mechanisms of photoelectric effects (photoconductivity, photovoltaic, photoelectret and negative photoconductivity) in them. In organic semiconductor materials, conductivity through the transfer

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of π- electrons from molecule to molecule is of particular importance. Gradually, it was established that the complexity of the chemical structures of macromolecules and the sharp change in the energetic structure closely related to this became a new direction in polymer physics.

Due to the high electrical conductivity of polymers, it is possible to study various effects when they are made into composites with CdS and ferrocene dispersants. Such effects include piezo-, pyro, photoelectric, photovoltaic, photoelectret, electroluminescence, posistor, varistor, piezoresistive and negative photoconductivity. Our article examines the TSD current spectrum, photoelectret potential difference, etc. of CdS composites with various polar and non-polar polymers, polymer-CdS-ferrocene composites [4-8]. 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 magneto photosensitive material by purchasing a composite in the future [9-12]

In our research, photoresistive, photovoltaic and photoelectret effects were determined in composites consisting of halogen-containing polar polymers (PVDF, F42), non-polar polyolefins (HDPE) and CdS photosensitive semiconductor phases. Also, the photoquenching effect of electrical conductivity was determined in composites consisting of halogen-containing polar polymers (PVDF, F42), non-polar polyolefins (HDPE) and photosensitive ferrocene (metal-containing compound).

2. Experimental part

In this work, polar (fluorine-containing) and non-polar (polyolefins) polymers were used as the polymer matrix: high-density polyethylene (HDPE), PVDF and F42. CdS ($A^{II}B^{VI}$) and ferrocene were used as dispersants. We obtain a homogeneous system from the polymer and the used dispersant particles by mechanical mixing. The viscosity and plasticity of the polymer phase of the photocomposites flow between the particles of the inorganic phases under the influence of the given pressure and flow to fill the mold. The shape, size and construction of the sample are one of the main factors for choosing the pressing pressure. During the experimental study, the optimal pressure for obtaining photocomposites 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. Concentric circular electrodes with a distance of 5 mm between them are attached to the obtained sample by pressing.

3. Results and discussion

The composite material we propose has positive properties in terms of negative electrical conductivity compared to existing polymers and inorganic materials with similar properties due to a number of properties:

- high photo extinction coefficient of electrical conductivity;
- simplicity of the production technology;
- the possibility of creating the photo materials we have studied based on various polymer matrices.

Initial studies of photoinduced effects show that light can induce an internal electric field in the composites we studied, creating internal optoelectrical effects: photoelectric and photovoltaic. The formation of the indicated effects in composites is observed with the creation of an internal electric field in them under the influence of light. The direction of the created internal electric field is opposite to the direction of the external electric field applied to the sample. At the same time, light releases electric charge carriers moving under the influence of the internal electric field in the donor centers and, as a result, they are localized at the interphase boundaries and defects. Photoinduced space charges, creating an electric field, create photo extinction in the polymer-ferrocene composite. It should be noted that this phenomenon does not depend on the properties of the structure and the nature of chemical bonds in different classes of materials. For example, photoinduced effects in polymer composites. In the first approach, the photoinduction effect can be expressed as the result of three processes:

- phototransfer of electric charge carriers (without strong changes in the structure of the material);
- photoinduced reversible change of the charge structure of the ferrocene molecule;
- photoinduced phase transitions (photo structural change of the material).

The initial mechanism of the photoquenching effect of electrical conductivity in polymer-ferrocene composites can be imagined as follows:

- the presence of intensive recombination between the main electric charge carriers that determine the dark current and the electric charge carriers that arise under the influence of light;
- local fields arise as a result of the formation of polycharge centers under the influence of light; the electric field intensity of the formed local fields exceeds the electric field intensity applied to the sample from the outside and is opposite in sign to each other, resulting in a sharp decrease in the total electric field of the composite;
- multi-charged centers form on the imperfections (defects) of the composite and, when the composite sample is illuminated, create volume and surface polarization in it, forming a photoelectret effect in the polymer-ferrocene system;
- the electric charge state of ferrocene changes under the influence of light and the formation of rotating traps;

The following experiments were conducted to clarify the role of the mechanisms we proposed in the photoquenching effect. To clarify the role of recombination and conductivity in the formation of the photoquenching effect, we switched from a two-phase system to a three-phase system: polymer – CdS – ferrocene. As the third phase, we took a photosensitive semiconductor of the $A^{II}B^{VI}$ class. By adding CdS to the polymer as the third phase, we ensure the occurrence of the following processes:

1) the formation of non-equilibrium free charges in the composite due to the internal photo effect in CdS;
2) the formation of additional traps that can affect the conductivity.

In the polymer-ferrocene-CdS composite, free electric charge carriers are formed under the influence of the internal photo effect. The main electric charge carriers that create the dark current are recombined more than under the influence of photocharges. Figure 1 shows the dependence of the R_f/R_0 ratio on the volume fraction of the ferrocene phase of the composite Ф, %. These results show that the increase in recombination and the decrease in conductivity can be the leading factors in the formation of the photoquenching effect of electrical conductivity in polymer-ferrocene composites. Thus, the addition of the third phase (CdS) to the composite once again significantly enhances the photoquenching effect [13-15].

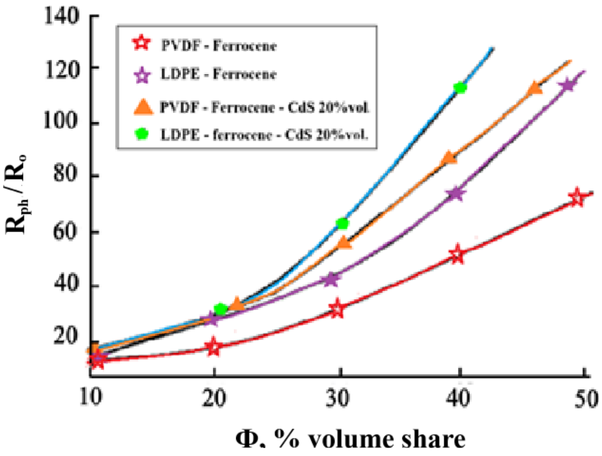

Fig. 1. Dependence of the ratio R_f/R_0 on the volume fraction of the ferrocene phase of the composite Ф, % 1. PVDF – ferrocene; 2. LDPE – ferrocene; 3. PVDF – ferrocene – CdS 20% volume; 4. LDPE – ferrocene – CdS 20% volume; U=100 V; E=400 mW/cm^2.

It is known that when the electret effect and photoelectret effects are formed in dielectric materials, an internal electric field is created in them. If the direction of the electret field, that is, the difference in electret potentials, can compensate for the field applied externally to the sample, then the dependence of the photoconductivity quenching effect on the electret state of the material is of interest. Figure 2 shows the dependence of the electret potential difference of composites consisting of polar, non-polar and ferrocene on the volume fraction of the ferrocene phase. The results given show that as a result of electrophotopolarization, a sufficiently high and time-stable photoelectret is formed in the composite. The result confirming this effect is the formation of electric charge carriers during electrophotopolarization in the composite.

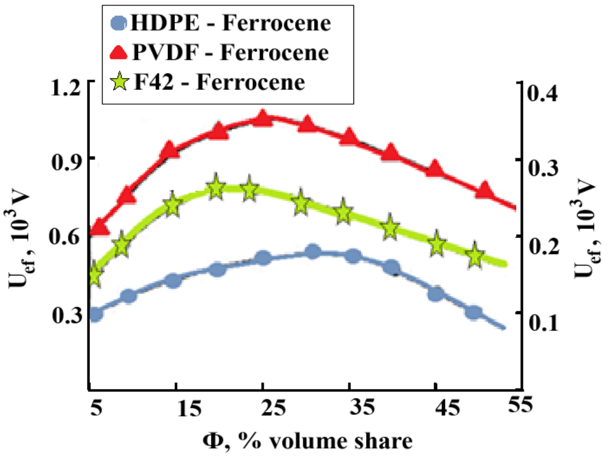

Fig. 2. Dependence of the photoelectret potential difference U_e of composites on the volume fraction (Φ) of the photosensitive phase. 1. HDPE – ferrocene; 2. PVDF – ferrocene; 3. F42 – ferrocene; $E_p=0.4\cdot10^4$ V/m; $E_i=400$ mW/cm^2; $t_p=0.25$ hours; $T_p=293K$; U_e – measured immediately after polarization.

In addition, to further confirm the formation of a photoelectret state in ferrocene-containing composites, the TSD current spectrum of the composite was obtained. Figure 3 shows the TSD current spectrum of the pure polymer (spectrum 1) and HDPE-ferrocene (spectrum 2) as a result of photoelectretization.

As can be seen, the TSD current spectrum of the pure polymer is different from the TSD current spectrum of the polymer phase dispersed with ferrocene particles. These results indicate the presence of an electrophotoelectret state in the polymer-ferrocene composite. At the same time, it is confirmed that the resulting photoelectret potential difference can be reduced by an external field applied to the sample.

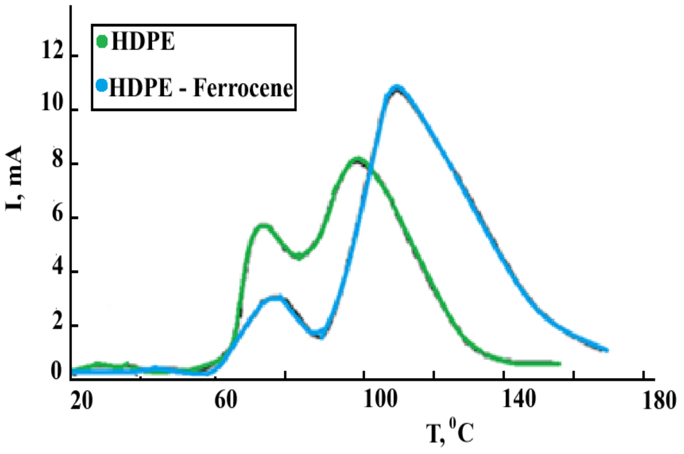

Fig. 3. TSD current spectrum of HDPE (spectrum 1) and HDPE – ferrocene (spectrum 2). $E_p=0.2\cdot10^4$ V/m; $E_i=400$ mW/cm^2; $t_p=0.25$ h; $T_p=293K$; Φ=30% volume fraction (ferrocene).

One of the decisive factors is the formation of the posistor effect as a result of thermal expansion of the polymer phase at the molecular level under the combined action of light and an electric field. As can be seen from Figure 4, the temperature dependence of the resistance initially behaves like a semiconductor, and then the resistance increases anomalous with temperature changes. That is, the electrical conductivity decreases sharply. This indicates that the posistor effect exists in ferrocene-containing composites and may be a decisive factor in the photoquenching effect.

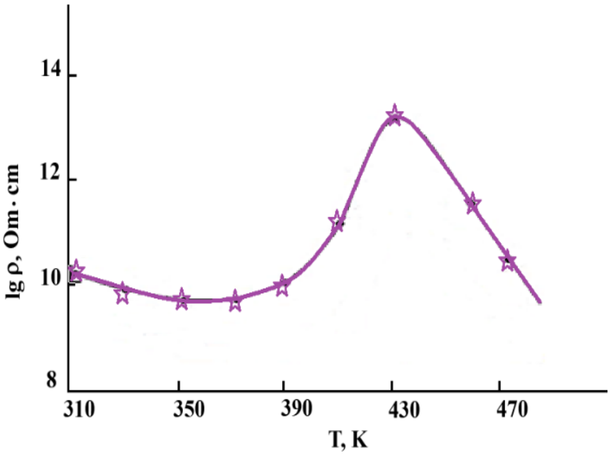

Fig. 4. Temperature dependence of the specific volume resistivity of a composite with 30% volume of HDPE - ferrocene. U=100V; E_i=400 mW/cm^2.

One of the more important and rather complicated factors is the elucidation of the mechanism of localization of photoelectric charge carriers in ferrocene phase composites under the influence of light. This issue requires an explanation of the effect of intensive delocalization of photoelectric charge carriers after the effect of light is stopped. The presence of a photoquenching effect of rotational electrical conductivity in ferrocene-containing composites under the influence of light indicates that the delocalization of photoelectric charge carriers after the effect of light is most likely due to the presence of rotational photochanges in the ferrocene molecule. That is, the complete transition of the photodislocation of the ferrocene molecule to its previous state after the effect of light is stopped.

In the composites we have studied, it can be assumed that the photoquenching effect of electrical conductivity in addition to the possible mechanisms indicated above has a place in other mechanisms in polymer-ferrocene composites, for example: the pyroelectric effect arising under the influence of light, electric field and changing thermal energy. The probability of the presence of a pyroelectric effect in composites based on organic materials (polymers) and organometallic compounds (ferrocenes) is very high. If we assume that organic and organometallic compounds have a very flexible structure, then we can say that reorientation (residual, stable) polarization is formed in the composites based on them. At the same time, it should be noted that the reorientation polarization has a very short relaxation time, and the electric field generated during such reorientation polarization is directed opposite to the external field and provides its sharp decrease. The photoquenching effect of electrical conductivity in polymer composites has more complex and diverse properties than in inorganic materials [14]. The main reasons for this are the following effects:

- electron distribution between π – and σ – bonds;
- reversible grouping of radicals under the influence of light;
- chemical bond cleavage;
- polymerization and dimerization reactions;

- formation of an interphase layer with a different structure at the polymer-ferrocene interface.

When choosing ferrocene as a photosensitive phase, the following factors were taken into account:

- unlike CdS and ZnS (inorganic), $(C_5H_5)_2$ Fe is an organometallic compound;
- the use of photochemical and electrochemical properties of ferrocene is based on the reversibility of its one-electron oxidation and reduction processes;
- unlike CdS (E_g = 2.58 eV) and ZnS (E_g = 3.68 eV), the width of the forbidden band of ferrocene (E_g = 6.72 eV) is close to the corresponding parameter of the polymer;
- the height of the potential barrier formed at the phase boundary of the ferrocene (E_g = 6.72 eV) – polymer (E_g = 10 eV) composite is smaller than the corresponding parameter of CdS (ZnS) – polymer composites;
- ferrocene is an organic iron compound and in its molecule the Fe atom is simultaneously bonded to ten carbon atoms;
- the Fe atom is located in the middle of two five-membered rings with high symmetry and all Fe – C chemical bonds are identical;
- ferrocene is a multicenter system, which can be activated under the influence of light and play the role of highly reversible traps for electric charge carriers;
- the stability of ferrocene and the highly reversible change of its structure under the influence of light;
- the ferrocene molecule has a certain dipole moment under the influence of light and turns into a reversible trap for electric charge carriers.

As mentioned above, the anomalous effect in the polymer-ferrocene composite can be explained by the capture of electric charge carriers by local levels formed in both the polymer phase and ferrocene at the interphase boundary. This indicates that a structurally new interphase layer is formed at the polymer-ferrocene boundary and localizes electric charge carriers that can play a leading role in the conductivity of the composite in the quasi-forbidden zone of the polymer phase in the layer. The thickness of the transition layer formed at the interphase contact usually depends on the polarity of the ferrocene and polymer phases. The greater the thickness of the transition layer, the smaller the difference between the polarity of the phases (polymer and ferrocene), that is, the smaller the difference between the cohesion energies of the components. This results in the formation of such a layer in the composite and the emergence of certain restrictions on the formation of the polymer supramolecular structure in the immediate vicinity of this layer [16-19]. Under the influence of an applied external electric field, photogenerated electric charge carriers move both through the volume of the phases and through the transition layer. As a result of the change in the electronic and chemical structure of the polymer and ferrocene in the transition layer, the phases become more sensitive to the effects of light and electric field. Therefore, more favorable conditions are created for the formation of additional boundary centers, which provide rotational stabilization of electric charge carriers under the combined action of an electric field and light. As we have mentioned above, the main reason for using ferrocene to create photosensitive composites with various properties is the rotational nature of its electrochemical and photochemical characteristics. In ferrocene, both the reversibility of one-electron oxidation and reduction reactions under the influence of light and their low activation energy are also important conditions. The rotational physical and chemical effects occurring in the ferrocene phase located in the polymer matrix under the combined action of light and electric field and the formation of an interphase transition layer make the polymer-ferrocene composite an interesting object as a photosensitive material. The photoquenching effect of electrical conductivity, which can be directly explained by the increase in the thickness of the transition layer in the polymer-ferrocene composite, ensures its use in technology as elements with a high negative electrical conductivity of composite materials [16-19].

Thus, the study of the photoextinction of electrical conductivity of composites containing various polymer matrices and ferrocene allows us to state the following:

- the electronegative photoconductivity effect detected in polymer - ferrocene and polymer - CdS - ferrocene two- and three-phase matrix systems is associated with the formation of a local electric field as a result of the stabilization of electric charges in the interphase boundary traps (at local levels) in the composite and the compensation of the applied external electric field;

- the electric field created by the volume charges provides the formation of the photoextinction effect of electrical conductivity in the indicated composites by sufficiently compensating the applied external electric field;
- CdS and ferrocene are photogeneration phases of electric charge carriers, providing photogeneration under the combined action of an electric field and light;
- the phase providing the rotational localization of electric charge carriers in the composite is ferrocene;
- the interphase transition layer formed as a result of the dissolution of polymer macromolecule segments, their end groups, and the ferrocene molecule can play the role of a phase for the rotational stabilization of electrical charge carriers.

4. Conclusion

These results indicate that the increase in recombination and the decrease in mobility may be the leading factors in the formation of the photoquenching effect of electrical conductivity in polymer-ferrocene composites. Thus, the addition of the third phase (CdS, ZnS) to the composite significantly enhances the photoquenching effect. The main reason for the formation of the photoquenching effect of rotational electrical conductivity in such composites is the formation of a local electric field directed opposite to the external field as a result of the formation of multi-charged centers and dipole moments in the ferrocene phase under the influence of light.

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