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STUDY OF THE EFFECT OF PHOTO QUENCHING OF ELECTRICAL CONDUCTIVITY UNDER THE ACTION OF LIGHT IN POLYMER-FERROCENE COMPOSITES

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Abstract. This study, the effect of photo quenching of electrical conductivity under the action of light was observed in composite samples containing a polymer and ferrocene. As a polymer matrix, polymer matrices containing halogens (PVDF, F42, F1, F3) and polyolefins (HDPE, LDPE, PP) are used. During the study, a voltage of 100 V was applied to the sample. The surface of the sample was exposed to light with intensity 400 mWt/cm2 in the field of view.

Keywords: *Electro photo quenching, ferrocene polyolefin, halogen polymers, electrical conductivity.*

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1. Introduction

The essence of the negative internal photoelectric effect is to reduce the electrical conductivity of a photosensitive material or a composite with a photosensitive component due to exposure to electromagnetic or corpuscular rays (Vannikov, 2001; Mehdiyeva, 2015). This effect is less noticeable than the usual internal photoelectric effect, which is an increase in the electrical conductivity of a substance under the influence of light. It should be noted that quantum optical effects are used in more advanced areas of technology in modern times (Gochuyeva, 2022; 2023). This part (department) of modern physics and electronics ensures the development of more efficient technologies for new light-sensitive materials and the resulting photovoltaic materials have photoelectric, photo resistive, photoelectret and negative electrical conductivity (Gochuyeva *et al.*, 2018; Hadiyeva *et al.*, 2023; Bagirzade *et al.*, 2022). Currently, various photosensitive polymers (Kurbanov *et al.*, 2011; Gochuyeva *et al.*, 2023), organic semiconductors (Rustamova *et al.*, 2023; Gochuyeva & Hashimov, 2023; Mammadova *et al.*, 2014) and composites consisting of organic and photosensitive inorganic materials (Kerimov *et al.*, 2012) are being developed for optoelectronic applications. Ferrocene is also used as a chemical in pharmaceuticals (Takhumova *et al.*, 2023; Gafarov, 2023; Jafarov *et al.*, 2023). The development of new light-sensitive polymer composites and the synthesis of their individual components (for example, organometallic compounds, various transition metal complexes) is a very urgent task, since the ability of these components to form

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composites with polymers with different properties ensures the creation of active materials with new optical and electrical properties (Mehdiyeva *et al.*, 2021; Quliyeva & Mehdiyeva, 2022). A new material with negative photoelectric conductivity and interesting for optoelectronics was obtained on the basis of polymer-ferrocene composite, which is the material we obtained. The posistor effect observed in polymer-ferrocene type composites can ensure their application as non-contact relays in electronics, electrical engineering and radio engineering (Rustamova *et al.*, 2023; Mehdiyeva *et al.*, 2022). Particular importance is our first proposed polymer-ferrocene (an organometallic compound of the di $-\pi-$ cyclopentadienyliron $(\pi - C_5H_5)_2Fe$ composite with a negative photoelectric property. First, let's take a quick look at the properties of the ferrocene we are using. At a constant value of the electric voltage (or electric field) applied to the photo semiconductor, the presence of a negative photoelectric effect in the direction of the photocurrent is observed - this direction is opposite to the direction of the normal photoelectric current and therefore the current (the sum of the dark and photocurrent) in the exposed crystal (or composite) is less than the current through unexposed photographic material. The purpose of the case used in this article is to; obtaining composites consisting of polymer-di-cyclopentadienylorgano-organometallic components; experimental observation of the effect of photoquenching of electrical conductivity in a polymer composite (Suleymanov *et al.*, 2017). To achieve the goals set, the following issues were resolved; study of the effect of photoquenching of electrical conductivity in composites with polyvinylidene fluoride (PVDF, polar), high-density polyethylene (YSPE, non-polar) and light-sensitive dicyclopentadienylirone (ferrocene) components; study of the effect of the volume share of ferrocene in composites on the R_{ph}/R_0 index, where R_{ph} and R_0 are the resistance of the composite under light exposure and in a dark environment, respectively and influence of light intensity on the durability of the polymer-ferrocene composite.

In our studies, a negative internal photoelectric effect was observed in the polymer-ferrocene composite.

2. Research objects and methods

The first stage of the composites production technology is the press-rubbing of the components, their size fractionation, magnetic sintering, surface cleaning and thermal treatment of the 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 in a ball mill from the scraps of the selected components (diameter ≤50 mkm) (stirring was carried out at room temperature); the volume of components in the mixture varies depending on the issue; Samples with a size of mm were obtained from a homogeneous mixture in the temperature range (413-483 K) and a pressure of 15 MPa by hot pressing. The photocurrent, photoresistance and photoelectric charges were measured with an electrometric voltmeter (B7-30, U5-11). The light intensity was varied within (200-400) mWt/cm^2. The voltage applied to the composite element is assumed to be 100 V. An electrode system of two designs was used: 1) the distance between the concentric round electrodes was 5 mm; 2) placed between two glasses with transparent metal electrodes on a composite sample. The main component of the homogeneous mixture is polymer and ferrocene. Another component of the composite is a photosensitive semiconductor. Thermoplastic polymers were used as the polymer phase: polyolefin 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. 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 20000-40000, 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 is a photosensitive semiconductor with high (≤ 3.6eV) photoelectric properties and band gap. Ferrocene is sandwich-shaped, symmetrical, consisting of two cyclopentadienyl rings and a ferrium atom. Its density is 1.49 g/cm^3. The size of the ferrocene particles used in the experiment is approximately 50 mkm. Ferrocene is non-polar, F – C bond is covalent. It has a reversible oxidation property.

The choice of CdS as a photosensitive dispersant in the indicated composites is related to the fact that when CdS particles are introduced into PVDF, it is possible to significantly change both the dark current and the photocurrent of the obtained composite. This effect, in turn, allows us to determine the role of electric charge carriers generated in the PVDF – CdS – Ferrocene composite in the quenching of electrical conductivity under the influence of light.

3. Results and discussion

One of the main approaches to the study of composites is to study the dependence of their properties on the volume share of individual phases. To do this, we first consider the dependence of the ratio R_{ph}/R_0 on the volume share of the ferrocene phase in the composite (Figure 1).

A voltage of 100V was applied to the sample containing ferrocene. The surface of the sample is exposed to light with intensity E_{ph}=400 mWt/cm^2 in the field of view. The results obtained show that PVDF - $(C_5H_5)_2$ Fe and HDPE - $(C_5H_5)_2$ Fe composites have a negative effect of photoconductivity - photo absorption. The dependence of the parameter R_{ph}/R_0 of polymer-ferrocene composites on the volume share of the ferrocene phase changes non-linearly and grows faster than the linear dependence (Kurbanov *et al.*, 2011). The results obtained show that the dependence $R_{ph}/R_0=f(\Phi)$ varies depending on the polymer phase of the composite.

The effect of weakening the electrical conductivity under the action of light is observed mainly in composites with a polyolefin matrix (HDPE, LDPE, PP).

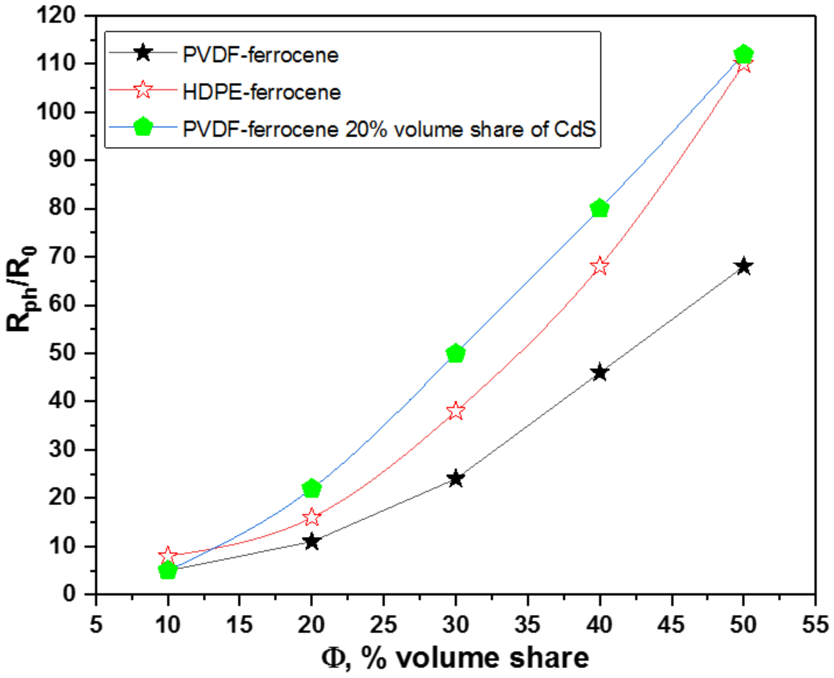

Figure 1. Dependence of R_{ph}/R_0 ratio on the volume share of ferrocene Φ, % composite phase. 1. PVDF – ferrocene; 2. HDPE - ferrocene; 3. PVDF - ferrocene - 20% volume share of CdS; U=100 V; E_{ph}=400 mWt/cm^2

The effect of electrical conductivity photoquenching in composites with a halogen-containing polymer matrix (PVDF, F42, F1, F3) is relatively less than the similar effect of composites with a polyolefin matrix (Table 1).

Table 1. Dependence of R_{ph}/R_0 ratio of polymer-ferrocene composites on the polymer phase of the composite (Φ = 50 % volume share)

Composites	R_{ph} / R_0
HDPE – ferrocene	108
LDPE – ferrocene	120
PVDF – ferrocene	67
PP – ferrocene	120
PVX – ferrocene	36
F1 – ferrocene	100
F3 – ferrocene	50
F42 – ferrocene	86

For example, in high-density polyethylene-ferrocene composites, the surface of which was exposed to light with an intensity of 400 mWt/cm^2, the resistance of the composite increases by a factor of 10–108 when the volume share of ferrocene changes from 10 % to 50 %. That is, the conductivity of the photographic material decreases (Figure 1, curve 2). Similar studies were carried out for PVDF–ferrocene composites (Figure 1, curve 1). Under conditions of stability of the applied voltage (U=100 V) and incident light intensity (400 mWt/cm^2), when the volume share of the ferrocene phase in the composite varied from 10 to 50%, the R_{ph}/R_0 ratio was observed at the level of an increase of 6–67 times in PVDF matrix composites. The results obtained clearly show that the effect of light-induced conductivity dimming is more pronounced in composites with a nonpolar matrix. It should be noted that the effect of photoconductivity quenching strongly depends on the intensity of the incident light. The practical significance of this effect is great. For this, the dependence of HDPE composites (volume share 80 %) - ferrocene (volume share 20 %) on the intensity of the incident light was studied (Figure 2).

$$tg\alpha = \frac{\Delta R_{ph}}{\Delta E} = 18.85 \times 10^5 \frac{Om \cdot m^2}{W}$$

Here, the factor is the ratio of the change in the intensity of the incident light to the resistance of the composite under the action of light. It can be seen from Figure 2 that the resistance of the specific volume of the studied composite depends significantly on the intensity of the incident light and the resistance value increases nonlinearly depending on the light intensity (Kurbanov *et al.*, 2011).

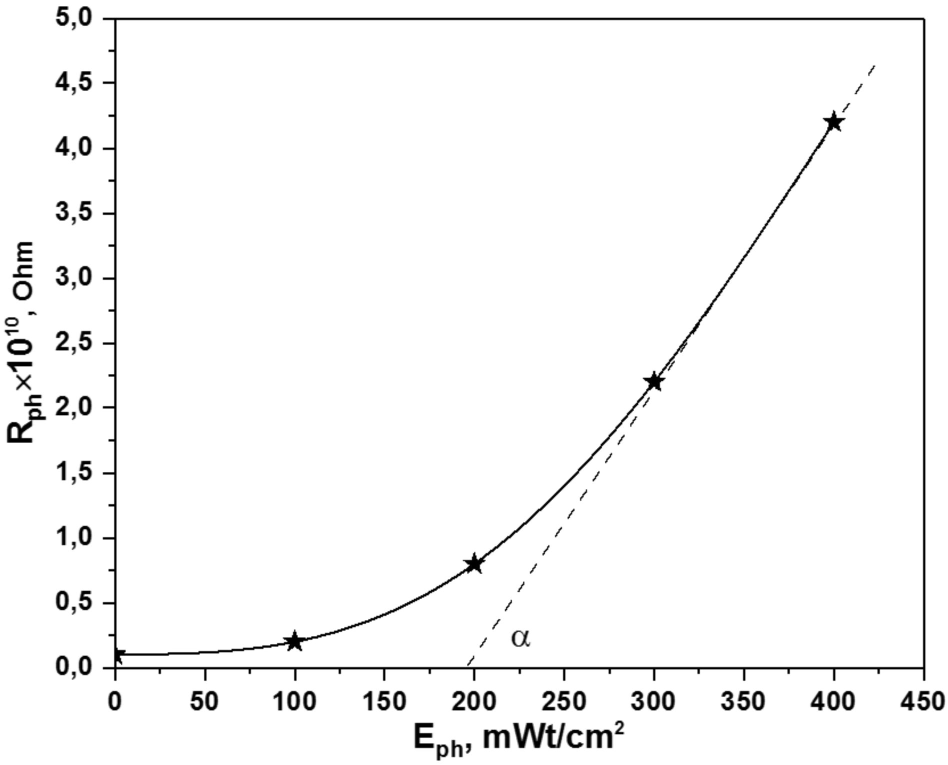

Figure 2. Dependence of the photo resistance of the HDPE-ferrocene compositeon the intensity of the incident light in the visible light region. U=100V, ferrocene volume shares 20% and HDPE volume share 80%

To determine the role of ferrocene in photoquenching in the composite, the dependence of the photocurrent on the wavelength of incident light in different volume share of ferrocene was presented. Studies show that, regardless of the volume share of ferrocene, the minimum value of the photocurrent corresponds to a light wavelength of 600 nm (Figure 3).

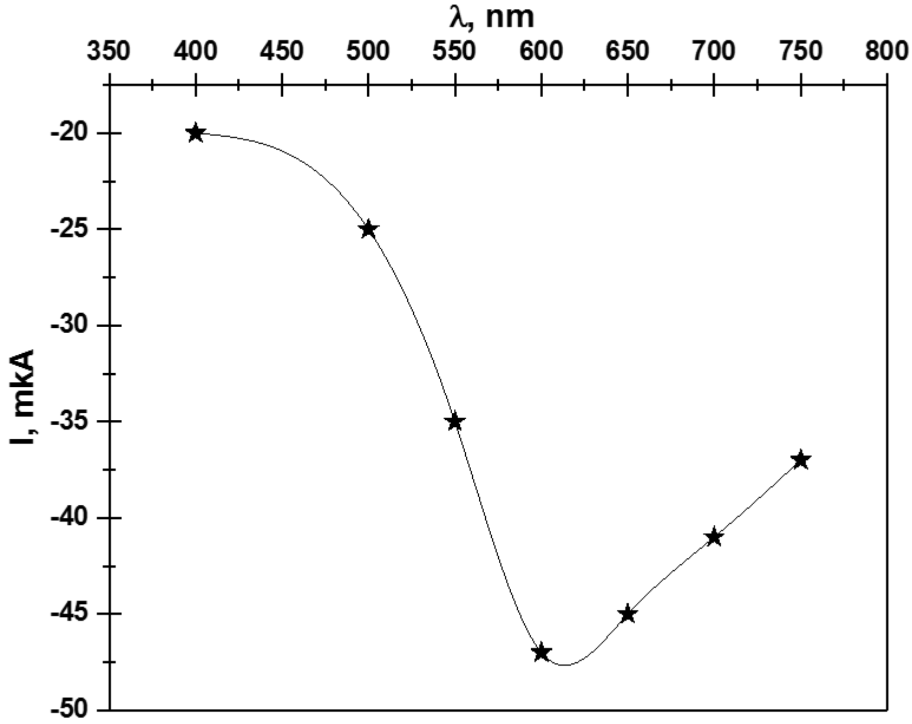

Figure 3. Typical dependence of photocurrent on the wavelength of incident light for ferrocene-HDPE composites. Ferrocene - volume share 40%, U=100 V and E_{ph}=400 mWt/cm^2

4. Conclusions

The main reason for the formation of the effect of photo quenching of rotational electrical conductivity in polyolefin-ferrocene composites is the generation of multiply charged centers and a dipole moment in the ferrocene phase under the action of light, resulting in the formation of a local electric field directed in the direction opposite to the external field. The results tell us that the photoquenching effect of electrical conductivity in halogen-containing polymer matrix composites (PVDF, F42, F1, F3) is relatively less than that of polyolefin matrix composites (HDPE, LDPE, PP). The results show that, regardless of the volume fraction of ferrocene, the minimum value of the photocurrent corresponds to a light wavelength of 600 nm. The results also show that the volume resistivity of the composite depends significantly on the intensity of the incident light and the resistance value increases nonlinearly depending on the light intensity.

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