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ELECTRICAL AND MAGNETIC PROPERTIES OF MATERIALS

FEATURES OF INTERPRETATION OF PULSED RADIATION-INDUCED CONDUCTIVITY OF POLYMERS AT LOW TEMPERATURE

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Abstract. The pulsed radiation-induced conductivity of polyethylene and polypropylene was studied at low (about 100 K) temperatures under the influence of electron pulses with an energy of 50 keV and a duration of 1 ms. To explain the results obtained, the Rose-Fowler-Vaisberg model was used. It is shown that when using it, it is necessary to take into account the difference in the shifts of carriers in a unit electric field before the first trapping ($\overline{\mu_0}\,\overline{\tau_0}$) and those moving by recapture along traps ($\mu_0 \tau_0$) appearing in the theoretical Rose–Fowler–Vaisberg model. Both of these parameters were calculated based on the results of experimental results.

Keywords: *electrons with energy 50 keV, numerical calculations, semi-empirical model of radiation electrical conductivity of polymers*

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1. INTRODUCTION

From the mid-70s to the late 80s, the scientific school led by A. P. Tyutnev, V. S. Saenko and E. D. Pozhidaev performed a series of works on the radiation-pulse electrical conductivity (RPEC) of engineering polymers when they are irradiated with pulses of accelerated electrons, usually at room temperature [1–4]. The obtained results were interpreted on the basis of the quasi-zone Rose-Fowler-Weisberg model (RFW) [1, 5] with the involvement of the basic theoretical concepts borrowed from the ion-pair mechanism of radiolysis of liquid hydrocarbons (Onzager theory, Langevin recombination). It is quite obvious that these data relating to the bulk irradiation of polymer films in the small-signal regime most directly characterize the transport of excess charge carriers in polymers. It is found that in the response of polymers it is possible to distinguish the instantaneous and delayed components of the RPEC. The first of them is described by first-order kinetics with a time constant of the order of fractions of a nanosecond. The second one is caused by hopping transport of charge carriers both in the composition of hemin (twin) pairs (the case of low temperatures) and free charges (room temperature).

Currently, the RPEC of polymers under pulse irradiation has been well studied not only at room temperature [3, 4, 6] but also at low temperature [7–9]. It turned out that the RPEC of polymers is also well described by a semiempirical model of RFW based on the multiple capture formalism (most convincingly shown in [8]). This fact is extremely surprising, because at low temperature (77–103 K) the application of the quasi-zone multiple-capture model should encounter serious difficulties, since in this temperature region the dominant position is occupied by the tunneling mechanism of charge carrier transport [10]. This situation required a careful consideration of the situation both from the theoretical point of view and additional experimental studies.

The aim of the present work is to study the RPEC of polyethylene and polypropylene at low temperature (around 100 K), similar to what was done earlier for normal conditions [11] and to give an explanation of the obtained results using a modified RFW model.

The system of equations of the classical RFW model has the following form:

$$
\begin{gathered}
\frac{dN(t)}{dt} = g_0 - k_r N_0(t) N(t) \\
\frac{\partial \rho(E,t)}{\partial t} = k_c N_0(t)\left[\frac{M_0}{E_1}\exp\left(-\frac{E}{E_1}\right) - \rho(E,t)\right] - \\
-\nu_0 \exp\left(-\frac{E}{kT}\right)\rho(E,t) \\
N(t) = N_0(t) + \int_0^{\infty} \rho(E,t)\,dE
\end{gathered}
\tag{1}
$$

By definition, the radiation conductivity

$$\gamma_r(t) = e\mu_0 N_0(t),$$

where $N_0(t)$ is the concentration of the main charge carriers (hereinafter electrons) in the conducting state (in the transfer zone) with microscopic mobility μ_0; $N(t)$ is their total concentration; g_0 is the rate of bulk generation of electrons and holes; k_r is the bulk recombination coefficient of quasi-free electrons with fixed holes acting as recombination centers; k_c is the rate constant of trapping of quasi-free electrons on traps; M_0 is total concentration of biographical traps exponentially distributed in energy ($E > 0$ and counted down from the bottom of the transfer zone); $\tau_0 = (k_c M_0)^{-1}$ is lifetime of quasi-free electrons before capture; $\rho(E,t)$ – density of distribution of trapped electrons on traps of different depth; ν_0 is effective frequency factor of thermal release of trapped electrons from traps; E_1 is a parameter of exponential distribution of traps in energy. The dispersion parameter $\alpha = kT / E_1$, where k is the Boltzmann constant and T is the temperature.

According to the RFW model, ionizing radiation creates pairs of free charges (i.e, charges moving under the action of an external electric field only), of which only electrons are mobile. The holes formed do not participate in the transfer of electric current and serve as recombination centers. Initially, electrons appear in a mobile state with microscopic mobility μ_0, but their motion occurs in the presence of numerous traps, the depth of which is distributed in a wide energy range according to the exponential law.

A distinctive feature of the RFW model is that the parameters μ_0 and τ_0 enter the analytical formulas only as their product [1–4], while α, τ_0, and ν_0 appear in the expression for the transit time even as a triple product $\mu_0\tau_0\nu_0^{\alpha}$ [1, 4, 11]. To determine the frequency factor ν_0, we have proposed a special procedure that uses short pulses of radiation [9, 12].

The recombination rate constant k_r reflects the bimolecular nature of the process, but can be much smaller than its Langevin value (so-called non-Langevin recombination [1]). The RPEC of polymers at low temperatures decreases to the level of the instantaneous component of the radiation conductivity γ_p, which within the framework of the RFW model is equal to $\gamma_p / R_0 = K_p = \eta_0\mu_0\tau_0 e$, where R_0 is the dose rate, K_p is the reduced instantaneous component of the RPEC, and η_0 ($m^{-3}Gr^{-1}$) is the initial concentration of hemin electron-hole pairs formed in the polymer for every 100 eV of absorbed ionizing radiation energy [1, 8, 9]. The parameter K_p under these conditions becomes one of the main experimental quantities characterizing the RPEC and, moreover, the most easily determined by measurements.

It turned out that the value $\mu_0\tau_0$, appearing in K_p, is not always equal to $\mu_0\tau_0$, determined by the RFW model from analyzing the properties of the delayed component $\gamma_{rd} = \gamma_r - \gamma_p$ [4]. To reflect this difference, it is denoted as $\overline{\mu_0}\,\overline{\tau_0}$. Typically $\mu_0\tau_0 = k\overline{\mu_0}\,\overline{\tau_0}$ and $k \le 1$.

The temperature dependence of the RPEC of polymers enters the equations of the RFW model through the parameter η_0 (generally speaking, at nitrogen temperatures, it is a weak dependence) and the frequency factor ν_0, which carries the major part of the activation dependence. Charge carrier transport in disordered solids at low temperature is believed to occur by thermally activated tunnel jumps involving molecular motions of polymer structural units acting as hopping centers [13, 14]. The concept of transport level [15, 16], which has been intensively developed recently, allows us to reduce these theoretical results to the multiple capture equations, on which the RFW model is based. A direct experimental determination of ν_0 appears to be an urgent experimental problem, allowing us to parameterize *a* modified RFW model that distinguishes between the parameters $\mu_0\tau_0$ and $\overline{\mu_0}\,\overline{\tau_0}$.

2. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

2.1 Experimental methodology

To conduct the experiments we used the methodology described in [7]. Films of technical high-pressure polyethylene (HDPE) of domestic production and polypropylene (PP) of “Torayfan” trademark with thicknesses of 20 μm and 12 μm, respectively, were used. Samples of 40 mm diameter

Table 1. Absorbed dose rate for tested polymers (data kindly provided by D. N. Sadovnichiy)

Material	Thickness, μm	Absorbed dose rate (Gy/s) per 1 nA of primary electron current registered by the shutter	
		without PET film	PET film
LDPE	20	2.8	2.1
PP	12	2.3	1.7

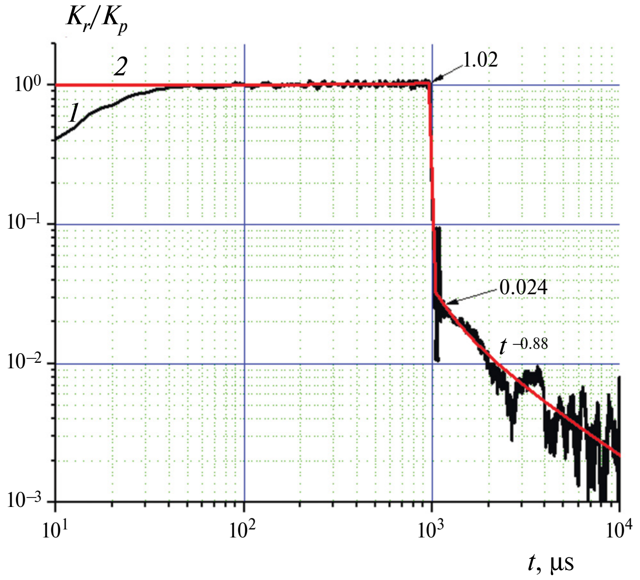

Fig. 1. Experimental (*1*) and calculated (*2*) radiation-pulse electrical conductivity of LDPE at 103 K, dose rate 2.1×10^4 Gy/s

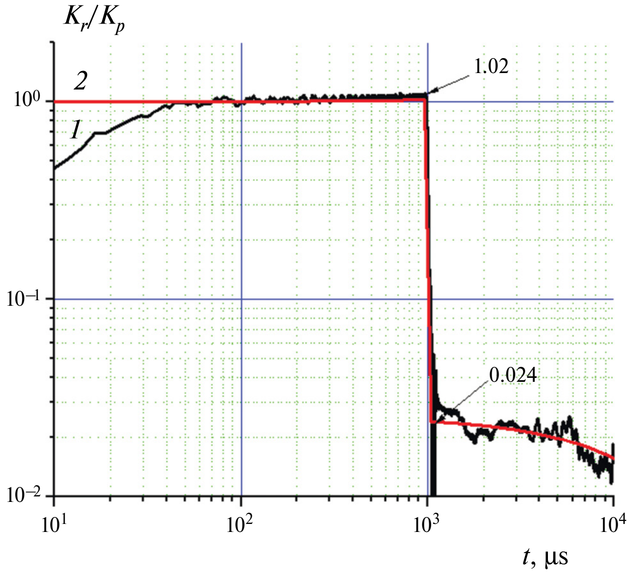

Fig. 2. Experimental (*1*) and numerically obtained (*2*) radiation-pulse electrical conductivity of PP at 103 K, dose rate 1.7×10^4 Gy/s

with sputtered aluminum electrodes of 32 mm diameter were irradiated with monoenergetic electrons with energy of 50 keV at the duration of rectangular irradiation pulses of 1 ms at low (103 K) temperature. All experiments were performed at an electric field strength in the sample of 4×10^7 V/m.

Table 1 shows the calculated values of the absorbed dose rate from the current of 1 nA electrons falling on the flap and registered directly when they flow to the ground. When estimating the averaged dose rate, the depth course of the dose rate calculated by the Monte Carlo method [3] was taken into account. The data are given both in the presence and absence of a 5 μm thick light- and heat-reflecting polyethylene terephthalate (PET) film over the irradiated sample, since the measurements at room temperature were carried out without the PET film.

2.2 Experimental results and their analysis

Figs. 1 and 2 show that in both cases the instantaneous component of the RPEC dominates, and after the end of the radiation pulse the conductivity sharply decreases by more than an order of magnitude. Under low temperature conditions, the concentration of charge carriers cannot change appreciably during the beam turn-off time [8, 9]. Thus, the observed effect is related to the specificity of transport of thermalized electrons.

When working with rectangular radiation pulses in the small signal mode (as in the present work), the transient RPEC current density j_r at any moment of time is proportional to the dose rate, so it is convenient to consider not the current density j_r, but its reduced value $K_r = j_r / R_0$, calculated per unit dose rate. The dimensionality of K_r coincides with the dimensionality of the reduced instantaneous component K_p or its theoretical analog K_p' (see below), which appears in the RFW model.

The procedure for determining k is illustrated on the example of RPEC of LDPE at room temperature (Figs. 3 and 4), since the experimentally recorded drop in conductivity after the end of the pulse

(Fig. 3) is well labeled. These data are based on unpublished results of [4].

Having determined the parameter K_p, we estimate the value of $\overline{\mu_0\tau_0} = \frac{0.1}{3\rho}K_p$ [1], where ρ is the density of the polymer (see Table 2). It is assumed that the absorbed energy of 100 eV leads to the formation of three electron-hole pairs [1].

After that, the dispersion parameter α is determined by the decline of the delayed component after the end of irradiation, represented in logarithmic coordinates $\lg j_{rd} - \lg t$ at $t \geq 3t_p$ ($j_{rd} \propto t^{-1+\alpha}$), where t_p is the duration of the radiation pulse (Fig. 3, curve *1*). The parameter ν_0 can be found by the method given in [12] (see Fig. 4). At $\nu_0 t_p = 4$ the decline curve of the delayed component of the RPEC is transformed into a straight line, at $\nu_0 t_p < 4$ the curve is convex in the sense that the slope of the curve decreases when approaching the end of the pulse from the high time side as in curve *5* in Fig. 4. At $\nu_0 t_p > 4$, the decline curves become convex as in curves *1–3* in Fig. 4. Curve *3* ($\nu_0 = 6.5 \times 10^5$ c^{-1}) allows us to determine the value of this parameter for LDPE at 298 K (Table 2).

After that, it is necessary to determine the experimental value of the delayed component reduced to the unit of dose rate at the moment of pulse termination (K_{d1}) and the dimensionless ratio $\delta_{d1} = K_{d1} / K_p$, equal to 0.28 for curve *1* in Fig. 1. Further, for the found values of α and ν_0 we determine the parameter δ_{d2} by the value of the delayed component of the RPEC at the moment of pulse termination, expressed in units of the instantaneous component of the RFW model $K'_p = \eta_0\mu_0\tau_0 e$ [4, 8], using the MathCad program, as in [11, 12]. In the calculations, it was assumed that both μ_0, and $\overline{\mu_0}$ are equal to 10^{-5} m^2/B · s, and τ_0 and $\overline{\tau_0}$ are chosen so that the product of $\mu_0\tau_0$ retains the required value. Thus, the value of K_{d1} for LDPE at 298 K is 0.28 K_p (curve *1* in Fig. 3), i.e. $\delta_{d1} = 0.28$, and $K_{d2} = 1.7K'_p$ (curve *3* in the same figure) i.e. $\delta_{d2} = 1.7$. In determining k, we proceed from the original relation $K_{d1} = K_p\delta_{d1} = K'_p\delta_{d2}$ and find that $\overline{\mu_0}\,\overline{\tau_0}\delta_{d1} = \mu_0\tau_0\delta_{d2} = k\,\overline{\mu_0}\,\overline{\tau_0}\,\delta_{d2}$. Here each term of the equality is reduced by the common multiplier $\eta_0 e$. Hence we find that $k = \delta_{d1} / \delta_{d2} = 0.28 / 1.7 = 0.165$ (Table 2). The control calculation by the RFW model fully confirmed the correctness of the calculation of the coefficient k.

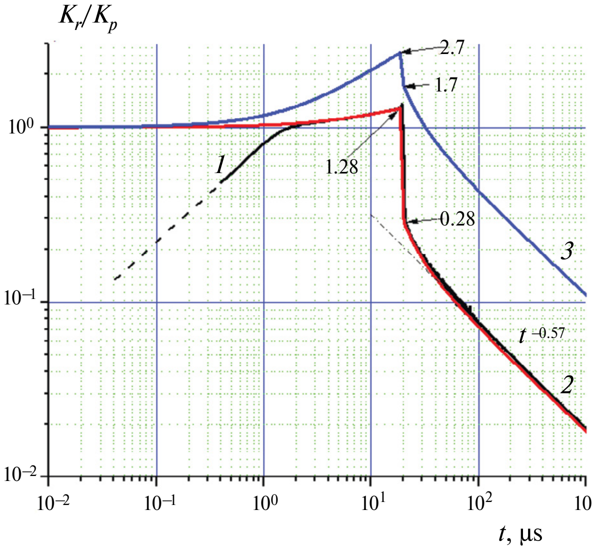

Fig. 3. Experimental (*1*, black, on the ordinate axis the ratio K_r / K_p) and numerically obtained (*2*, on the ordinate axis the ratio K_r / K'_p) RPEC curves of LDPE at 298 K, dose rate 6.2×10^5 Gy/sec. Curve *2* almost coincides with curve *1*, which drops sharply to zero at $t \leq 0.4$ μs (shown in dashed line) due to the influence of methodological factors (measurement time constant, inertia of the electronic system, etc.). The electron pulse duration is 20 μs. The calculated curve (*3*, blue) is calculated for the parameter $\overline{\mu_0\tau_0} = 1.9 \times 10^{-16}$ m^2/V (Table 2)

Table 2. Values $\mu_0\tau_0$ calculated using the described methodology with the necessary parameter values for calculation

Polymer / temperature		$K_p \cdot 10^{15}$, F / (m · Gr)	$\nu_0 \cdot 10^{-3}$, c^{-1}	α	δ_{d1}	δ_{d2}	k	$\overline{\mu_0\tau_0} \cdot 10^{16}$, m^2/B	$\mu_0\tau_0 \cdot 10^{16}$, m^2/B
LDPE	298 K	5.5	600	0.43	0.28	1.7	0.165	1.9	0.31
	103 K	3.5	4	0.12	0.024	0.24	0.1	1.2	0.12
PP	298 K	5.6	20	0.38	0.1	2	0.05	2.0	0.1
	298 K	5.6	4	0.38	0.07	0.7	0.1	2.0	0.2
	103 K	4.7	0.17	0.17	0.024	0.024	1.0	1.7	1.7

Note. The density of LDPE and PP is 0.95 and 0.92 g / cm^3, respectively. The first line for PP at 298 K corresponds to curve 2 and the second line corresponds to curve 3 in Fig. 5

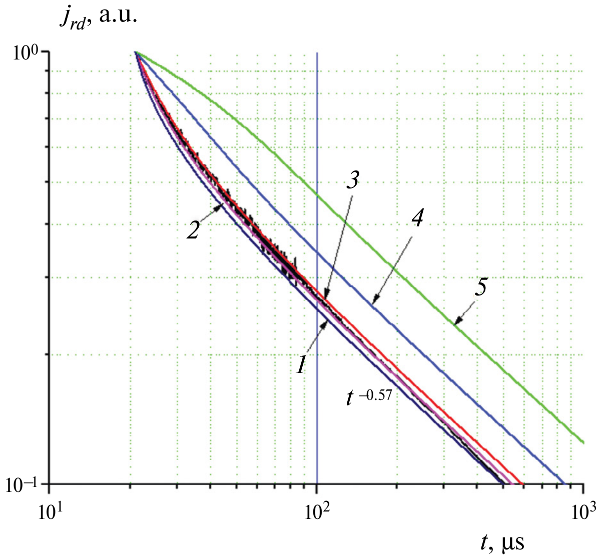

Fig. 4. Experimental (black) and calculated curves (*1–5*) demonstrating the method of frequency factor selection on the example of LDPE (normalized to the value of j_{rd} at the moment of radiation pulse termination). The temperature is room temperature, the pulse duration is 20 µs. The frequency factor values are 10^7 (*1*), $10^{(6)}$ (*2*), 6×10^5 (*3*), 2×10^5 (*4*), and 8×10^4 s^{-1} (*5*)

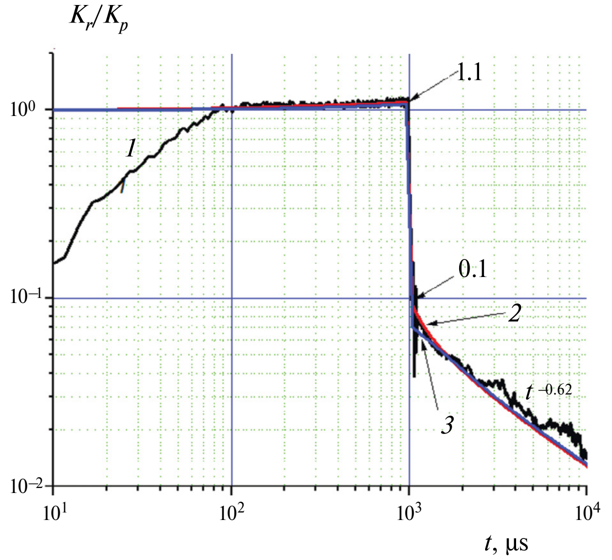

Fig. 5. Experimental (*1*) and numerically calculated (*2, 3*) RPEC curves of PP at 298 K, dose rate 1.7×10^4 Gy/s. For curve *2* the parameter $\delta_{d1} = 0.1$, for curve *3* it is equal to $\delta_{d1} = 0.07$ (shown by arrows)

The table shows the values of $\mu_0\tau_0$, for LDPE and PP at 103 K (for PP and at 298 K), calculated by the above described method with the necessary data for calculation. Let us point out one peculiarity of the above methodology. Fig. 5 shows that the course of the delayed component decline curve allows ambiguity of interpretation at the earliest stage after the end of the pulse. The data of Table 2 refer precisely to the type of the decline curve adopted in the figures (highlighted in red). In the approach used for curve *3* in Fig. 5, the parameter $\delta_{d1} = K_{d1} / K_p$ will decrease to 0.07 at $\nu_0 = 4 \times 10^3$ s^{-1} (the decline curve is a straight line up to the end of the $t_{p\ pulse}$), so that $\mu_0\tau_0$ appears to be $0.2\times10^{-16} m^2/V$ ($k = 0.1$), which is two times the original value. This result emphasizes the importance of determining the exact course of the decay curve of the delayed RPEC component immediately after the end of the radiation pulse.

Table 2 also shows that in PP the parameter $\overline{\mu_0}\,\overline{\tau_0}$ practically does not change at transition from room temperature to 103 K and is within the experimental error± 20%.

One more peculiarity should be noted: k in PP increases with decreasing temperature and approaches unity. In LDPE the opposite effect is observed – the coefficient k, when passing from room temperature to 103 K, decreased. This issue requires serious study and interpretation in the future.

The model used in this work can be applied to analyze the photogeneration of current carriers in organic solar cells at low temperature [17, 18]. Also, this model of an effective homogeneous medium can be applied to study the properties of modern composite materials [19, 20], which are of interest for various fields of science and technology.

3. CONCLUSION

The technique we have described allows us to estimate the parameter $\mu_0\tau_0$ directly from the experiment. Thus, all parameters of the RFW model are estimable from experimental data, although this procedure relies on obtaining accurate data on the decay of the delayed component immediately after the end of the radiation pulse, as demonstrated in Fig. 3 curve *1*, which is not always possible in a real experiment. The modified dispersive transport model can be called a two-parameter model, distinguishing between shifts of carriers in a unit electric field before the first trapping ($\overline{\mu_0}\,\overline{\tau_0}$) and those moving by recapture across traps ($\mu_0\tau_0$). These parameters were determined experimentally for both polymers (see Table 2). Thus, the fundamental difficulty in explaining such a significant drop in the RPEC (up to a factor of ten, as observed in LDPE and PP at 103 K) immediately after the end of the radiation pulse has been eliminated. In [11], this phenomenon was erroneously explained by the influence of hemin recombination.

In the future it is necessary to elucidate the issue related to the temperature dependence of $\mu_0\tau_0$ to explain the different temperature dependence of the shift of thermalized charge carriers in a unit electric field.

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ETHICS DECLARATION

There are no human or animal studies in this paper.

CONFLICT OF INTEREST

The authors of this paper declare that they have no conflicts of interest.

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