

ELECTRIC CONDUCTIVITY OF PTCR POLYETHYLENE–GRAPHITE COMPOSITES

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The paper presents the results of investigations of polyethylene-graphite composites which imply that the decisive contribution to the total conductivity belongs to the electron transfer through a polyethylene layer between graphite particles. It is shown that the model of electron tunneling with the participation of localized states in the polyethylene layer, which takes the layer expansion with increase in temperature into account, satisfactorily describes the static current-voltage characteristics of such composite materials.

1. Introduction

Polyethylene-graphite composites are inhomogeneous systems consisting of statistically distributed graphite particles (about $\sim 1 \mu\text{m}$ in size) within a polyethylene matrix. In recent years, they have been used as materials for the PTCR (positive temperature coefficient of resistance) elements [1] and renewable fuses [2,3]. It is believed that the key factor responsible for the appearance of the PTCR effect in such systems is the thermal expansion of polyethylene layers between graphite particles [1]. For this reason, when studying the charge transfer processes, the main attention has been concentrated on the properties related to the structural inhomogeneity of the composites [4,5], rather than on the mechanisms of electron transport through the layers, which remain poorly studied hitherto.

This paper presents the results of investigations of electron processes and the analysis of the mechanisms of electric transfer through the potential barriers formed by the dielectric matrix in such composites.

2. Experimental Results

A low-density polyethylene (15803–020) [6] and graphite with particles $\sim 1 \mu\text{m}$ in size were used as starting materials for the composite fabrication. The graphite concentration p_V varied from 40 to 44 vol. percents. The size of graphite particles was determined by the optical microscopy methods. To fabricate the composite, polyethylene was melted and carefully mixed with

powdered graphite. The procedure of mechanical mixing lasted 20 min at a temperature of 540°C . Then the mixture was cooled down to room temperature with a rate of $\sim 20 \text{ K/min}$. To improve homogeneity, the composite obtained after cooling was ground into a powder with particle dimensions of $0.3\text{--}0.5 \text{ mm}$. The pellet-shaped specimens were prepared from the powder under a pressure of 30 atm. The thickness of specimens varied from 2 to 5 mm. To perform electric measurements, the copper electrodes were fused into the specimens.

Static current-voltage characteristics (CVC) were measured with the use of commercial digital voltmeters. To perform impulse measurements, a characterograph was used. The current-voltage characteristics obtained experimentally for the composite specimens are shown in Figs. 1 and 2.

The static CVC show the PTCR effect. At the initial stage of each curve, the current density j grows with increase in the electric field E . Then, upon the achievement of a certain E , whose value depends on the graphite content, the current stabilizes. The further increase in E leads to a reduction in j . Electric conductivity rises with growth in the graphite volume fraction.

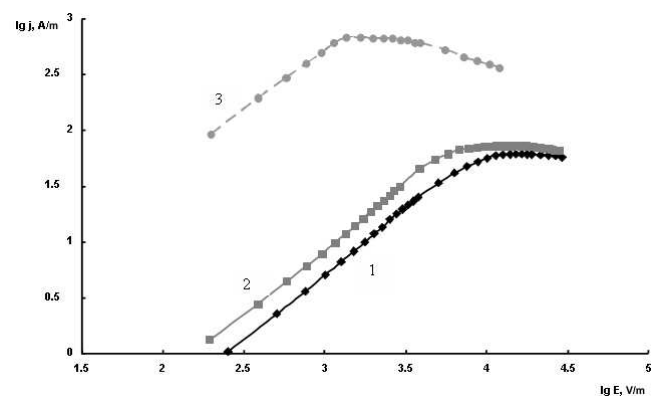


Fig. 1. Static current-voltage characteristics for the polyethylene-graphite composites with the different volume fractions of graphite (%): 1 – 40; 2 – 42; 3 – 44

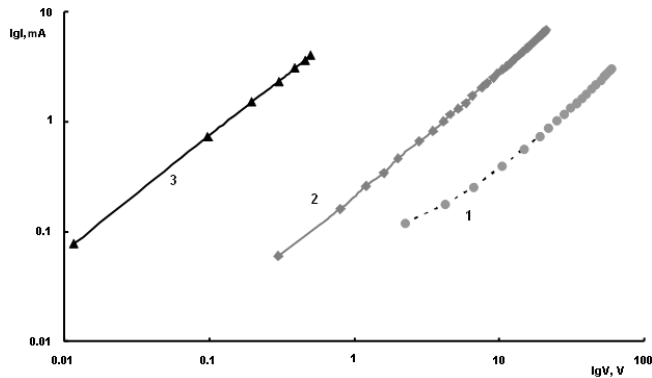


Fig. 2. Impulse current-voltage characteristics for the polyethylene-graphite composites with the different volume fractions of graphite (%): 1 – 40; 2 – 42; 3 – 44

As for the impulse measurements of CVC, the PTCR effect was not observed (see Fig. 2). The electric conductivity also increases with the content of graphite.

3. Discussion of Results

The results obtained are in compliance with the general ideas of the PTCR effect mechanism in the composites under consideration. The electric current passing through a specimen gives rise to the increase in the specimen temperature due to the Joule heating. The temperature coefficient of linear expansion for polyethylene $((2.1 \div 5.5) \times 10^{-4} \text{ K}^{-1}$ [6]) is far greater than that for graphite $((3.5 \div 8) \times 10^{-6} \text{ K}^{-1}$ [7]). Thus, the heating leads to the creation of breaks in the conducting channels between conducting particles, which results in the increase in the total resistance.

To understand the mechanisms of electron transfer through the barriers formed by the layers of the matrix phase between graphite particles, one should take the following remarks concerning the layer thickness into account. The known mechanisms of electron transfer through the potential barriers (tunneling, thermoelectronic emission), developed for such high-concentration systems as zinc-oxide ceramics, seem to be inapplicable to the case under consideration. First, such peculiar features as a strong nonlinearity of current-voltage characteristics (with the nonlinearity coefficient up to 50) and the field dependence of capacity [8] are not characteristic of the materials under study. Second, the graphite volume fraction, p_V , which in our case doesn't exceed 0.5, is not sufficiently high to form the tunnel-transparent layer between conducting particles.

It is noteworthy that, in the case of the highly homogeneous composites, the graphite particles are

arranged at the same distance from one another and, thus, the thickness of the dielectric layer can be calculated. Consider a situation where a cubic graphite particle with edge a is inside a dielectric cube with edge b . Then, the volume fraction of graphite in polyethylene is

$$p_V = V_{gr}/V_c = a^3/b^3,$$

where V_{gr} is the volume occupied by graphite, and V_c is the composite volume. Since the distances between particles is assumed to be identical, the thickness of the polyethylene layer is

$$\Delta = b - a = a/\sqrt[3]{p_V} - a = a \left(\frac{1}{\sqrt[3]{p_V}} - 1 \right).$$

Given $a = 1 \mu\text{m}$ and $p = 40\%$, we obtain $b \approx 1.5 \times 10^{-6} \text{ m}$ and $\Delta \approx 3 \times 10^{-7} \text{ m}$.

In the inhomogeneous systems with a statistical distribution of components, the critical potential barriers (in terms of percolation theory [9]) which govern the carrier transfer should have different thicknesses. A change in the thickness, even within the minor limits (for example, by 1.5 – 2 times), has to result in a substantial change in the conductivity of the potential barriers of a critical subnet [10], which is not observed in experiment. As follows from the dielectric measurements [11], the thickness of the dielectric region, which surrounds a graphite particle and contains a “space” charge induced by polarization, is of the order of a linear size of the particle ($\sim 1 \mu\text{m}$).

In view of the aforesaid, the most probable mechanism of charge transfer through a dielectric barrier consists in the transfer of electrons between localized states of the dielectric matrix located between two graphite particles.

4. Modeling of Static CVC

It is seen from the above-presented results that the barrier thickness, which should be overcome by an electron, is sufficiently great. Thus, the conductivity mechanism related to the transitions between local centers is most probable. The probability that an electron passes from one particle to another one is greatest along the field direction. The difference of the oppositely directed flows of charge carriers between the neighboring (donor) levels located in the planes of a unit area, cut parallel to the electrodes, determines the density of the stationary current through the structure under consideration.

As follows from the values of conductivity we observed in the experiment, the dielectric layer between two graphite particles contains several centers, the distance between which doesn't exceed 10^{-7} m.

We assume for simplicity that there are only 2 such centers and they are on the same energy level (Fig. 3). To construct a mathematical model, we should take the transitions from the graphite particle to a center and the reverse transitions into account.

Accounting for this and basing on the results of work [12], the following system for the stationary current density through a specimen can be written:

$$\begin{cases} i = eN[C_{m,1}(1-f_1)n_m - C_{1,m}f_1], \\ i = eN[C_{2,m}f_2 - C_{m,2}n_m(1-f_2)], \\ i = eN^2[C_{1,2}f_1(1-f_2) - C_{2,1}f_2(1-f_1)]. \end{cases} \quad (1)$$

Here, e is the electron charge; N is the concentration of local centers; $C_{m,i}$ and $C_{i,m}$ are the kinetic coefficients which characterize the probabilities of the electron transitions from a graphite particle to a local center i along the field direction and backwards, respectively; $C_{i,j}$ ($i, j = 1, 2$) are the probabilities of the electron transitions between the local centers i and j , respectively; f_i is the electron filling function at the trapping centers in the plane i ; and n_m is the electron concentration in the graphite.

The relation between the kinetic coefficients without applied external field and with it reads [13]

$$\begin{aligned} C_{m,1} &= C_{m,1}^0 f(V) = C_m^0 f(V), \\ C_{1,m} &= C_m^0 M n_m f(V) \exp\left(\frac{eV \Delta}{kT d}\right), \\ C_{1,2} &= C_{1,2}^0 f(V), \\ C_{2,1} &= C_{1,2}^0 f(V) \exp\left(\frac{eV \Delta}{kT d}\right), \\ C_{2,m} &= C_{2,m}^0 f(V) = C_m^0 M n_m f(V), \\ C_{m,2} &= C_m^0 f(V) \exp\left(\frac{eV \Delta}{kT d}\right), \end{aligned} \quad (2)$$

where k is the Boltzmann constant; $M = \exp((\epsilon_i - \epsilon_F)/kT)$; ϵ_i and ϵ_F are the energies of the local level and the Fermi level, respectively; T is the temperature of the environment; $f(V)$ is a function of the voltage which characterizes the process of electron tunneling and has the form

$$f(V) = \exp\left\{-\frac{4}{3} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{d}{eV}\right\}$$

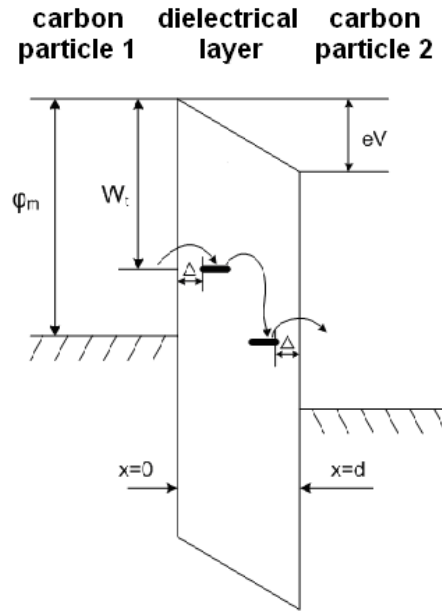


Fig. 3. Energy-band picture for the structure "graphite particle - polyethylene layer - graphite particle"

$$\times \left[W_t^{3/2} - \left(W_t - \frac{eV \Delta}{d} \right)^{3/2} \right] \}, \quad (3)$$

where m^* is the electron effective mass, \hbar is the Planck's constant, d is the distance between the graphite particles, Δ is the distance between the local centers, W_t is the energy depth of the local centers, and V is the voltage applied to the barrier.

It should be noted that there is the interrelation between f_1 and f_2 :

$$f_2 = \frac{1 + \exp\left(\frac{eV}{kT} \cdot \frac{\Delta}{d}\right)}{M + \exp\left(\frac{eV}{kT} \cdot \frac{\Delta}{d}\right)} - f_1 \frac{1 + M \exp\left(\frac{eV}{kT} \cdot \frac{\Delta}{d}\right)}{M + \exp\left(\frac{eV}{kT} \cdot \frac{\Delta}{d}\right)}. \quad (4)$$

Substituting expressions (2) and (3) into the system of equations (1) with regard for Eq. (4), we obtain the equation

$$a_2 f_1^2 + a_1 f_1 + a_0 = 0, \quad (5)$$

where

$$a_0 = C_m^0 n_m + N C_{1,2}^0 e^A \frac{1 + e^A}{M + e^A},$$

$$a_2 = N C_{1,2}^0 (e^A - 1) \frac{1 + M e^A}{M + e^A},$$

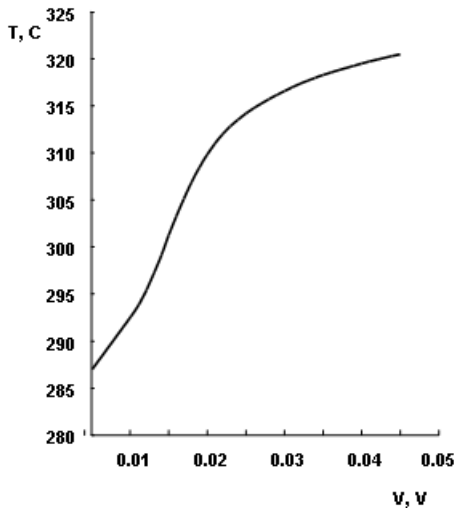


Fig. 4. Temperature of a polyethylene layer as a function of the voltage applied to the structure

$$a_1 = C_{1,2}^0 N \left[1 + e^A \frac{1 + Me^A}{M + e^A} + (e^A - 1) \frac{1 + e^A}{M + e^A} \right] +$$

$$+ C_m^0 n_m (1 + Me^A),$$

$$A = \frac{eV \Delta}{kT d}.$$

A solution of Eq. (5) provides the following form for the current-voltage characteristics for the material under investigation:

$$j = N^2 e C_{1,2} \left[f_1(1 - f_2) - f_2(1 - f_1) \times \exp\left(\frac{eV \Delta}{kT d}\right) \right] e^{f(V)}. \quad (6)$$

The current passing through the composite leads to the specimen warming and an increase in its thickness. Thus, we should account for the fact that the thickness depends on temperature and consider the corresponding quantities in formulas (3)–(5) as the functions of temperature: $d = d(T)$ and $\Delta = \Delta(T)$.

To find the temperature of the layer phase, we use the equation of thermal balance for a stationary state:

$$I(V, T)V - \alpha(T - T_0) = 0, \quad (7)$$

where α is the heat transfer coefficient, V is the voltage applied to the interparticle phase, T_0 is the temperature

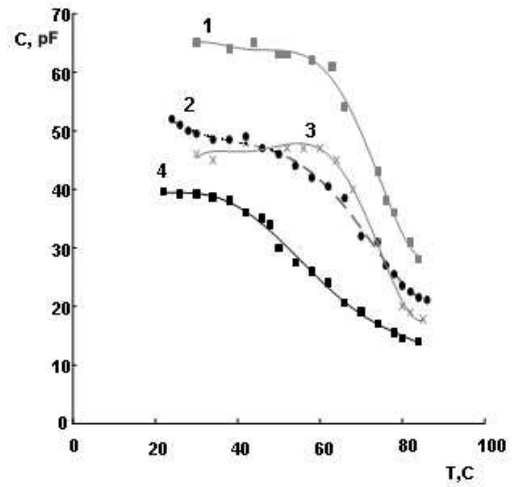


Fig. 5. Experimental temperature dependences of the polyethylene capacity at frequencies of 1 kHz (1, 2) and 10 kHz (3, 4). The graphite volume fraction equals 42% (1, 3) and 40% (2, 4)

of the environment, $I(V, T)$ is the current passing through the specimen, and $T(t)$ is the temperature of the material at the time moment t .

A numerical solution of Eq. (7) [14] at various voltages V applied to the interparticle phase gives rise to the $T(V)$ dependence shown in Fig. 4.

The temperature dependence of the layer thickness was experimentally found from the temperature dependence of the polyethylene capacity at several frequencies (Fig. 5) by using the known formula

$$C(T) = \varepsilon \varepsilon_0 S / d(T),$$

where ε is the permittivity of dielectric material (polyethylene), $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $d(T)$ is the temperature dependent thickness of a sample, and S is the electrode area.

At calculations, we accounted for the fact that, within the temperature and frequency ranges under consideration, the polyethylene permittivity almost doesn't change and is approximately equal to 2.3. The temperature dependence of d calculated in such a way can be fitted with high precision by a polynomial

$$d(T) = d_0 [b_3 \tau^3 + b_2 \tau^2 + b_1 \tau + 1],$$

where $b_1 = 2.85$, $b_2 = -43.91$, $b_3 = 276.98$, $\tau = (T - T_0)/T_0$; and $T_0 = 287$ K.

The temperature dependence of the effective (corresponding to the energy location of a local center

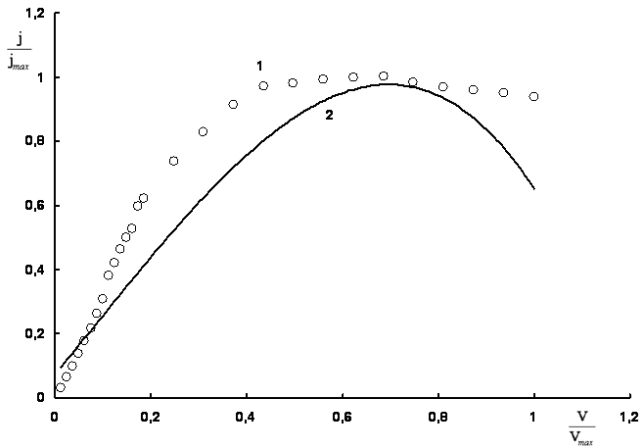


Fig. 6. 1 – experimental static current-voltage characteristics for the polyethylene-graphite composite; 2 – calculated current-voltage characteristics for the structure “graphite particle – polyethylene layer – graphite particle”

level) electron concentration in graphite can be written in the form (see work [15])

$$n(\epsilon_i, T) = \frac{4\pi}{h^3} (2\pi m^*)^{3/2} \epsilon_i^{1/2} \frac{kT}{1 + \exp((\epsilon_i - \epsilon_F)/kT)}, \quad (8)$$

where $\epsilon_i = \epsilon_F + \Delta\epsilon_0 - eV$ is the energy of the local center, and $\Delta\epsilon_0$ is the difference between the energy of the local center and the Fermi level.

Expression (8) and the temperature dependence of the layer thickness were taken into account in calculations of the current-voltage characteristics according to formula (6). The results obtained are shown in Fig. 6, where j_{\max} is the maximal value of the current density, and V_{\max} is the voltage corresponding to j_{\max} .

As is seen from the figure, the calculated current-voltage curve displays a PTCR region, whose character agrees with the experimental data. The broadening of the experimental curve in comparison with the calculated one can be associated with the structural inhomogeneity of the PTCR material under investigation.

5. Conclusions

The absence of both the PTCR effect and a pronounced nonlinearity in the impulse current-voltage characteristics obtained experimentally, as well as the peculiar compositional features (the graphite volume fraction doesn't exceed 50%) of the polyethylene-graphite composites imply that the decisive role in the total conductivity is played by the electron

transfer through the polyethylene layer between graphite particles.

The model of electron tunneling with the participation of localized states in the polyethylene layer, which takes into account the layer expansion with increase in temperature, allows the satisfactory description of the static current-voltage characteristics of such composite materials.

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ЕЛЕКТРОПРОВІДНІСТЬ ПОЗИСТОРНИХ КОМПОЗИТІВ ПОЛІЕТИЛЕН-ГРАФІТ

А.В. Дегтярьов, О.С. Тонкошкур

Резюме

Наведено результати дослідження композитів поліетилен-графіт, які свідчать про визначальний вплив на їхню електропровідність проходження електронів крізь поліетиленовий прошарок між графітовими зернами. Показано, що модель тунельного електропереносу за участі локалізованих станів у зазначеному прошарку, яка враховує його розширення з ростом температури, дозволяє задовільно описати статичну вольт-амперну характеристику таких композитних матеріалів.