Local Energy of Activation of Conductivity of Phenylene-Based Composite Materials Containing Nickel Nanoparticles

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By measuring the dependence of conductivity on temperature and analyzing this dependence within the framework of the reduced conductivity activation energy, it was found that in composite polymer materials containing Nickel nanoparticles in the region below the classical percolation threshold in the studied temperature range, there are three regions with different temperature dependence. The origin of these dependencies is discussed in terms of a spatial-structural hierarchical model.

I. Introduction

In recent years, great interest has been shown in nanomaterials, since they exhibit physical properties that differ from those of the corresponding compact materials \cite{1–3}. In particular, among these materials are composites consisting of metal-containing nanoparticles distributed over the volume of dielectric matrices \cite{4–7}.

Previously, the authors of this work synthesized composite materials based on a phenylene matrix containing two types of Nickel particles: microparticles and nanoparticles, and conducted a study of the electrical conductivity and static permittivity of these composites near the percolation threshold \cite{8, 9}. It was found that below the percolation threshold, the experimentally obtained dependence of conductivity and permittivity on the fraction of Nickel nanoparticles differs from the dependence calculated according to the percolation theory.

This problem is discussed in detail in \cite{8}, where the origin of this discrepancy is considered in terms of a spatially structural hierarchical model, which assumes the formation of a continuous spatial structure from tunneled conductors.

According to this model, all metal particles in composites, in which they are randomly distributed in the dielectric matrix, are electrically connected. The conductivity of these composites is defined by tunneling of charge carriers both between neighboring particles and between particles located at a distance. Percolation behavior is observed when the contribution of tunneling between particles distant from each other to macroscopic conductivity is negligible. This is the case when the radius of the b particles significantly exceeds the tunneling region parameter d (or the tunneling decay parameter). In the case of b ~ d, tunneling of charge carriers between non-neighboring particles contributes to macroscopic conductivity along with tunneling between neighboring particles. The dependence of macroscopic conductivity on the concentration of metal-containing particles differs from that obtained according to the classical percolation theory.

When the classical percolation theory is used in describing the electric properties of such composites, certain problems are encountered. For example, below the percolation threshold, the behavior of the electric conductivity of composites containing nickel grains embedded in a SiO\textsubscript{2} matrix cannot be explained within the framework of the classical theory. This problem is discussed in detail in study \cite{10}, where the cause of this inconsistency is considered in terms of hierarchical spatial-structural model, which supposes formation of a structure of tunnel-coupled conductors. The dependence of the behavior of the electric conductivity on the volume fraction of the filler is described in \cite{10} and shown in \cite{11} for composites containing nickel particles dispersed in an aceramic matrix. In the present paper, we present the results of an investigation of the influence of the filler particle size on the conductivity of metal–polymer composites containing nickel particles localized in a phenylon-based polymer matrix.

As shown in \cite{10}, there are two percolation thresholds in composites where a contribution to electrical conductivity is observed from tunneling of charge carriers between non-neighboring particles. One of them is observed at high \(V_{f1}\) values, which is the percolation threshold \(V_{c1}\) defined above. Another threshold (additional percolation \(V_{c2}\)) is observed at low \(V_{f1}\) values, this is the critical fraction of the volume of metal particles that initiates the first infinite cluster of tunnel-bound conductors. We also established two percolation thresholds in

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composite polymer materials based on phenylene containing Nickel nanoparticles, the values of which were $V_c=0.105$ and $V_{cd}=0.05$ [8].

If the assumption of the authors [12] is correct, the mechanism of charge carrier transport in a constant electric field in such systems should be carried out by tunneling over localized States. For this reason, the temperature dependence of the conductivity in such composites is investigated and this dependence is analyzed within the framework of the local activation energy of the conductivity proposed in the first by A. G. Zabrodsky for doped and compensated semiconductors. This technique has been successfully applied to various systems (pyropolymers, composite materials based on ceramics, etc.) over the past 30 years.

II. The Experimental Part

Two types of composite materials based on phenylene matrices were prepared: the first one contained nickel nanoparticles and the second contained nickel microparticles.

The composite material containing nickel nanoparticles was prepared by the thermal decomposition of nickel formate in phenylene similarly to the synthesis of nanoparticles in polyethylene and polypropylene. Thenickel_formate powder was added to solution of phenylin dimethyl formamide made in the proportion of 4 g ofphenyI on to 100 g of solvent. After thorough stirring, theobtained mixture underwent thermal treatment until the solvent was completely removed. In order to prevent aggregation of the nickel format particles in the process of evaporation, the reaction mixture was treated with ultrasound generated by a UZDN 1 disperser at a vibration frequency of 22 kHz and radiation power of 0.3 W. Themixture obtained on the evaporation of the solution was placed in vacuum and was kept at a temperature of 373 K for 1 h so that the remains of the solution were completely removed. After that, the temperature was raised up to 573 K and the mixture was kept at this temperature for 5 h. The resulting thermal destruction of the nickel format lead to formation of nickel containing Nanoparticles.

The composite containing nickel micro particles was prepared by direct mixing of the nickel micro powder with thephenyl on in a planetary type mill for 7 h. The nickel powder used in the experiment was obtained by thermal decomposition of the nickel formate under vacuum at a temperature of 573 K in the course of 3 h.

In both cases, nickel concentration $V_1$ was calculated from the nickel concentration in the initial metal containing compound.

The size distribution of micro particles and Nanoparticles in the composite materials under study was analyzed and the contribution of individual components was quantitatively determined by the method of small angle Xray scattering. In determining the size of the nickel micro particles, a KRM 1 small angle X ray camera was used. The investigations were conducted on the wavelength $\lambda=0.1542$ nm with the use of the Kati geometry in the wavevector region $0.12 < s < 5.5$ nm$^{-1}$ ($s=4\pi \sin \theta/\lambda$ and $2\theta$ is the angle of scattering). The width of the receiving slit was 200 $\mu$m. The obtained experimental data were normalized to the intensity of the incident beam, after which a correction for collimation distortion was introduced.

The size of the nickel nanoparticles in the samples was determined by the electron microscopy method with the use of a JEOL JEM1011 transmission electron microscope at an 80kV accelerating voltage. Prior to the investigation, the samples were ultrasonically dispersed in ethanol, and the obtained dispersion was deposited on a copper grid coated with layers of formvar and carbon.

The phase composition of nanoparticles was determined by an Xray phase analysis. The diffraction patterns were recorded by a DRON 3 diffractometer (Cu $K\alpha$ radiation, $\lambda=1.54056$ E, a pyrolytic graphite monochromator, a scanning velocity of 2 deg/min).

To conduct the electric measurements, pellets 15 mm in diameter and 2 mm in thickness were prepared by hot pressing the initial powdery samples. The procedure for measuring these samples is described in detail in [11].
To prevent thermal expansion of the composition, measurements of the temperature dependence of electrical conductivity were carried out in a specially developed cell [13] - a small-sized Autonomous chamber of fixed pressure, where the geometric dimensions of samples with increasing temperature remain almost constant. The method of measuring the resistance of samples is described in detail in [11].

III. Results And Discussions
The small angle X-ray scattering method allows their regularities in a substance whose sizes exceed the interatomic distances and are 5–10 to ~10^4 A\(^0\) to be studied[14]. Nickel particle radius \(b\) was calculated with the formula

\[
b = \frac{\lambda}{2\pi N} \sqrt{\frac{d \ln J}{d(2Q)^2}},
\]

(1)

where \(J\) is the intensity of the X-ray beam and \(Q\) is the scattering angle in the coordinates \(2\lambda J - (2Q)^2\). During the investigation of the composite materials obtained by mixing nickel powder with phenylon, it was found that the nickel particle diameter in the material under investigation was 1–3 \(\mu m\) (Fig. 2).
The investigation of the sample whose nickel particles were synthesized by decomposition of nickel formates showed that the average size of the nanoparticles did not exceed 20 nm. This result is in good agreement with the data obtained by the transmission electron microscopy. Figure 1 shows a typical image of nickel nanoparticles ($d \approx 3–4$ nm) that are stabilized in the bulk of phenylon and that are investigated in the present study. Against the dark gray background (phenylon), dark spherical formations stand out, which are nanoparticles that are nearly spherical in shape.

In the diffraction patterns of the composite samples containing both nano and microparticles of nickel, intense reflexes can be observed that are typical of phenylon along with the reflexes that correspond to nickel metal with a cubic structure (JCPDS 040850). The relative intensity of the diffraction signals from the metal containing phase in the samples with nickel microparticles exceeds the intensity of the corresponding signals in the nanocomposite by a factor of more than 100. The analysis of the diffraction patterns, performed with the use of the Rietveld method, showed that the nickel particles have cubic structure $Fm\overline{3}m$ (225) with the parameters $a = b = c = 3.524 \text{ Å}$, $\alpha = \beta = \gamma = 90$, and $V = 43.8$.

Figure 3 shows the experimental dependences of $\log \sigma$ (where $\sigma$ is the electric conductivity of the sample) on concentration of nickel particles $V_f$ for the investigated composites and the dependences calculated within the framework of the percolation theory with the use of the formulas given below. According to the percolation theory [10], electric conductivity $\sigma$ of systems containing metal particles randomly distributed over a dielectric matrix is described by the following formulas:

$$\sigma(V_f) = \sigma_1 (V_f - V_c) \tau \text{ at } V_f \geq V_c, \quad (2)$$
$$\sigma(V_f) = \sigma_2 (V_c - V_f)^{-q} \text{ at } V_f < V_c, \quad (3)$$

Here $\sigma_1$ is the electric conductivity of the metal particles; $\sigma_2$ is the electric conductivity of the dielectric matrix; $V_c$ is the critical concentration (percolation threshold), at which an infinite cluster of filler particles is formed for the first time; and $\tau$ and $q$ are the parameters that are called critical indices. By using the boundary conditions ($V_f = 0$ and $V_f = 1$), formulas (2) and (3) can be reduced to the form

$$\sigma(V_f) = \sigma_1 \left( \frac{V_f - V_c}{1 - V_c} \right)^\tau \text{ at } V_f \geq V_c, \quad (4)$$
$$\sigma(V_f) = \sigma_2 \left( \frac{V_c - V_f}{V_c} \right)^{-q} \text{ at } V_f < V_c, \quad (5)$$
For the composite materials under study, critical volume fraction $V_c$ of the nickel particles was determined by differentiating with respect to $V_1$. In order to find critical index $t$, the experimental data were represented as a plot of $-V_c y (1 - V_c)$. Quantity $t$ is the angle of inclination of the obtained straight line. Quantities $\sigma_1$ and $\sigma_2$ were found by extrapolating this plot to $V_1 = 1$ and $V_1 = 0$, respectively. It was found that $V_c = 0.105$, $t = 2.20$ for the composite material with nanoscale nickel particles and $V_c = 0.210$, $t = 1.78$ for the composite material with microdispersed nickel particles. Critical index $q$ was taken to be unity, which is valid for 3D systems [15].

It can be seen from Fig. 3 that, for both types of composite materials under study, the theoretical and experimental data agree at $V_1 > V_c$. If $V_1 < V_c$, the agreement is observed only for the composite material with microdispersed nickel particles. For the composite material with nanoscale nickel particles, there exist regions below $V_c$. These results can be explained using the composite conductivity model proposed in [10].

According to this model, all metal particles in the composites, in which they are randomly distributed over the dielectric matrix, are electrically coupled. The conductivity of these composites is determined by tunneling of charge carriers between both neighboring particles and particles that are distant from each other. The percolation behavior is observed when the contribution of the tunneling between the non-neighboring particles to the macroscopic conductivity is negligible. This circumstance occurs when particle radius $b$ is considerably greater than the tunneling region parameter (tunneling decay parameter) $d$. If $b \sim d$, the charge carrier tunneling between non-neighboring particles, along with the tunneling between neighboring particles, contributes to the macroscopic conductivity. In this case, the dependence of the macroscopic conductivity on the concentration of metal containing particles differs from the dependence predicted by the classical percolation theory.

The above-described behavior of the conductivity of the composite materials under study agrees with the model predictions, which is demonstrated in [10] with carbon nanotubes localized in polymer composites and with Ni–SiO$_2$ cermets. The particular feature of the results obtained in this study is that different behavior of the conductivity was observed in composites of the same composition, the behavior being dependent on the size of metal-containing particles present in the composite under investigation.

As is known, the temperature dependence of the electrical conductivity $\sigma$ of composite materials based on nanodisperse metals (Ni, RT, Al) in a dielectric matrix (SiO$_2$, Al$_2$O$_3$) when the filler concentration is below the critical one is described by the expression [14]

$$\sigma \approx \exp \left[-\left(\frac{A}{T}\right)^x\right]$$

Fig. 3. Experimental (dots and circles) and theoretical (solid lines) electric conductivities as functions of the concentration of nickel-containing nanoparticles (dots and line 1) and microparticles (dots and curve 2) localized in the bulk of a phenylon-based polymer matrix.
where A=hundredths, x>0. In this case, the charge transfer is carried out by tunneling electrons between isolated metal particles through a dielectric medium. Therefore, the question arises about the exact determination of the exponent x in (6), and ultimately the energy course of the density of localized States

$$g(\varepsilon)=g_0 (\varepsilon-E_F)^n$$

near the Fermi energy $E_F$, since there is a connection [14] $x=(n+1)/(n+d+1)$, where d is the dimension of space. The study of this issue is the material of this work.

To explain the behavior of the $\sigma(T)$ dependence in cerments when metal particles do not contact, a charging (tunneling) model is proposed, in which it is assumed that the electron needs $\Delta E$-tunneling energy from one neutral grain to another to transfer charge. In this case, two oppositely charged grains are formed. Based on this model in [15], based on the inhomogeneous distribution of particle sizes and their spatial distribution in cermet materials, it was shown that three characteristic regions can be observed on the dependence of $\sigma$ on $T$. At high temperatures ($T \geq 300^0 K$), the conductivity associated with the transfer of charges between particles that are spatially closest neighbors dominates. At low temperatures, transitions between particles that are not nearest neighbors dominate, and the dependence of $\sigma$ on $T$ is described by the law (6) with $x \approx 0.5$, and at very low temperatures, $\sigma(T)$ is described by the formula (6) with $x \approx 1/3$. The specific temperature regions in which these dependencies must be observed, as shown in [16], depend on the type of the distance distribution function between the particles.

In [17], the previous transport theories proposed by the authors of [18] for granular metals are modified and the calculated conductivity formula obeying the law (6) with $x \approx 0.5$ is obtained. It was shown that the calculated values of electrical conductivity are in good agreement with the experimental results for Pt-SiO$_2$ systems in a wide temperature range from 40 to 300$^0K$.

It is also known [19, 20] that the low-temperature conductivity of some compensated and amorphous semiconductors in direct current is carried out by carrier jumps over localized states with a variable jump length in the energy band in the vicinity of the Fermi level [21] and is described by the law (1) with $x \approx 0.5$. The authors came to this conclusion by determining and analyzing the local activation energy of the conductivity $\varepsilon_0(T)$ in such systems.

Analysis of the literature data shows that charge carrier transport in heterogeneous materials containing nanodisperse metal inclusions is explained by various models. There is no single method of verification to find out the mechanism of charge carriers transfer in them.

Fig. 4 shows the experimental dependences of the conductivity $\sigma$ in the temperature range from 100 K to 450$^0K$ for samples obtained at $V_{cd} \leq V < V_c$, where $V_c$ is the critical concentration (flow threshold) at which an infinite cluster of metal particles is formed for the first time, $V_{cd}$ is another additional percolation thresholdthis is the critical fraction volume of metal particles that initiates the first infinite cluster of tunneled conductors.

Fig. 4.Temperature dependences of electrical conductivity $\sigma$ of composite polymer materials. The volume fraction of the filler in the composition 1-0.067; 2-0.080 and 3-0.088.1-3 построены в координатах $\lg \sigma-10^3/T$. Данные для образца 2 представлены также в координатах $\lg \sigma-10^{1/4}$, $\lg \sigma-10^{1/3}$ and $\lg \sigma-10^{1/2}$. (6).
The numerical value of the indicator x in (6) was confirmed in [22, 23] by the method of straightening in the pre-selected coordinates $\lg \sigma - T^{-1/4}$. However, our analysis of the data from these studies shows that straightening is possible at other scales with no less accuracy. Also, as can be seen from Fig. 4, the dependence of $\sigma$ on $T$ can be straightened not only in the coordinates $\lg \sigma - T^{-1/2}$, but also in the coordinates $\lg \sigma - T^{-1/3}$ and $\lg \sigma - T^{-1/4}$.

To determine x in equation (6) in composite materials, the method of analyzing the temperature dependence of the reduced activation energy of the conductivity is used. Over the past 30 years, we have used this processing method to analyze the temperature dependence of the conductivity of organic pyropolymers [24], as well as in composite ceramic materials containing Nickel nanoparticles [9]. In the studied samples, the characteristic regions of temperature dependences of conductivity were identical. In [20] it is shown that the equation can be used to determine $x$

$$\lg \omega = B - x \lg T,$$

$$\omega = -\frac{1}{T} \frac{\partial \lg \sigma}{\partial T^{-1}} = \frac{\partial \lg \sigma / \partial \lg T}{T}.$$  

(7)

where $B=\text{const}$, $\omega$ is the reduced activation energy of the conductivity.

For Fig.5 and Fig.6 shows the temperature dependence $\omega$ for samples obtained by graphical differentiation of the curves in Fig. 1 in the coordinates $\lg \sigma - \lg T$ and $\varepsilon_0(T) = \omega / T$ (local conduction activation energy) in coordinates $\varepsilon_0(T)$ from $T^{-1/2}$, respectively.

**Fig. 5.** Temperature dependences of the reduced activation energy of the conductivity $\omega$ of composite polymer materials. Notation, as in Fig. 4.

**Fig. 6.** Temperature dependence of the local activation energy of the conductivity $\varepsilon_0(T)$ of composite materials. Notation, as in Fig. 4.
From these data, it can be seen that in the studied temperature range there are three regions with different temperature dependence-high-(I) and low-temperature (III), separated by a transition region (II).

In the high-temperature region (T\geq T_0 to the right of curve a), there is a region of linear dependence of \( \log \sigma \) on \( \log T \) (figure 5), corresponding to the exponential law \( \sigma(T) \) with \( \approx 1 \)

\[
\sigma = \sigma_0 \exp \left( -\frac{\Delta \varepsilon}{KT} \right)
\]

where \( \Delta \varepsilon \) required energy is tunneled from one neutral grain to another.

This conclusion is supported by the dependence of \( \varepsilon(0) \) on \( T_{1/2} \) in \( T \geq T_0 \) region (Fig. 6).

At relatively low temperatures (\( T \leq T_c \) to the left of the curve C), there is also a region of linear dependence of \( \log \sigma \) on \( \log T \), corresponding to the exponential law \( \sigma(T) \) with \( \approx 0.5 \). This corresponds to a special case of Mott's law [21] for conductivity with variable activation energy of conductivity and equation (6) takes the form

\[
\sigma = \sigma_0' \exp \left[ -\left( \frac{T_0}{T} \right)^{1/2} \right]
\]

In order to understand the nature of the temperature dependence of electrical conductivity in such systems, it is necessary to study their structure. From a physical point of view, the process of forming inhomogeneous composites containing metal nanoparticles can be considered as a consequence of doping of the initial dielectric with metal nanoparticles like doped compensated semiconductors. This means that electronic States similar to impurity levels occur in the forbidden zone of the source material (polymer, ceramics, glass). The increase of the volume content of metal nanoparticles influences not only their concentration but also on their distribution in size. If the above representation is correct, then the nature of the conduction mechanism in such systems is jump-like and can be considered from the point of view of a spatial-structural hierarchical model, in which it is assumed that a continuous spatial structure is formed from tunneled conductors [24].

As can be seen from Fig. 6, the high-temperature region \( \Delta \varepsilon = \varepsilon(0) \) is constant. This means that in the \( T \geq T_0 \) region, the contribution to electrical conductivity mainly gives tunneled charge carriers between non-neighboring compared to neighboring particles with a constant conduction activation energy, i.e. in this temperature region, the jump length remains constant. At relatively low temperatures in the region \( T \leq T_c \) in such systems, the conductivity is characterized by the so-called "sliding" activation energy, i.e. the jump length (r) increases with a decrease in temperature according to the law \( r \sim T^{-1/2} \) [24].

The linear dependence of \( \varepsilon(0) \) on temperature at \( T \leq T_0 \) in coordinates \( \varepsilon(0) \) from \( T_{1/2} \) shows that the number of metal particles involved in electrical conductivity or their density in the energy band in the vicinity of the Fermi level changes in a parabolic way, similar to the behavior of energy levels in compensated and amorphous semiconductors [24]. As can be seen from Fig. 6, the high-temperature region \( \Delta \varepsilon = \varepsilon(0) \) is constant. This means that in the \( T \geq T_0 \) region, the contribution to electrical conductivity mainly gives tunneled charge carriers between non-neighboring compared to neighboring particles with a constant conduction activation energy, i.e. in this temperature region, the jump length remains constant. At relatively low temperatures in the region \( T \leq T_c \) in such systems, the conductivity is characterized by the so-called "sliding" activation energy, i.e. the jump length (r) increases with a decrease in temperature according to the law \( r \sim T^{-1/2} \) [24].

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IV. Conclusion

1. by measuring the dependence of conductivity on temperature and analyzing this dependence within the framework of local conductivity activation energy, it was found that in polymer materials containing Nickel nanoparticles in the region below the classical percolation threshold, in the high-temperature region (\( T \geq T_0 \)), the main contribution to electrical conductivity is provided by tunneled charge carriers between non-neighboring compared to neighboring particles with a constant conduction activation energy. At relatively low temperatures (\( T \leq T_0 \)), electric transfer in such systems is carried out by tunneling charge carriers between non-neighboring compared to neighboring particles, but with a variable activation energy of conductivity. In the transition region, both of these conduction mechanisms smoothly pass from one to the other.

2. the Previous [22,23,25] and present scientific research shows that the method of processing the temperature dependence of electrical conductivity within the local energy of activation of conductivity proposed
by A. G. Zabrodsky can be used as a single method for elucidating the mechanism of charge carrier transport in inhomogeneous materials containing metal nanoparticles.

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