ELECTRICAL CONDUCTIVITY AND DIELECTRIC PERMITTIVITY OF COMPOSITE POLYMER MATERIALS BASED ON POLYETHYLENE CONTAINING COPPER NANOPARTICLES

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ABSTRACT

Two types of composite materials containing micro- and nanoparticles of copper in a polyethylene matrix were created and studied. Transmission electron microscopy established that the size of the formed nanoparticles is 13 nm, while X-ray phase analysis indicated that the copper nanoparticles have a "core-shell" structure. The study of the temperature depend-ence of the electrical conductivity of copper microparticles at fixed pressures showed that the oxide shell has a semiconductor nature. The conductivity and static dielectric permittivity of polyethylene containing nano- and microparticles of copper were measured near the percola-tion threshold. It was found that below this threshold, discrepancies between the experimental data and the predictions of modern heterogeneous system theory are observed. It was also es-tablished that in polyethylene-based composites with copper nanoparticles, an additional con-tribution to electrical conductivity and dielectric permittivity is observed in the region below the percolation threshold. The reasons for this effect were analyzed, taking into account the spatial structure of the material within the framework of the model proposed by Balberg and his co-authors for composite systems.

Introduction

Composite materials with nickel-containing nanoparticles embedded in ceramic and heat-resistant polymer matrices were obtained via thermal decomposition of nickel formate. Analysis of the concentration dependence of their electrical conductivity and dielectric permittivity on the volume content of nickel showed that this method allows the formation of nanoparticles in the range of 20–30 nm [1-3]. However, the low solubility of some polymers in organic media creates limitations for the introduction of nanoparticles with a narrow size distribution of about 10 nm. The use of polyethylene as a matrix for stabilizing nanoparticles is of significant interest because it possesses good dielectric properties, chemical stability, availability, and ease of processing into products of any shape. Furthermore, polyethylene is one of the first polymers launched into mass production both globally and in the Republic of Uzbekistan after gaining independence. The use of copper nanoparticles in composites is advantageous due to their potential in medicine, agriculture, catalysis, and sensor technologies [4-5]. Professors S.P. Gubin and I.D. Kosobudsky proposed less labor-intensive methods for obtaining metal nanoparticles in polymer media. In this work, using this method, a series of powdered composite copper-containing nanomaterials based on polyethylene were obtained. Studies using electron microscopy confirmed an average nanoparticle size within 13 nm, and X-ray diffraction analysis showed their uniform distribution within the polymer matrix with a "core-shell" structure.

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The aim of this work is to investigate the concentration dependence of the electrical conductivity and dielectric permittivity of polyethylene-based composites containing nano- and microparticles of copper in the vicinity of the percolation threshold, as well as to analyze the obtained results within the framework of the modern theory of heterogeneous systems, to elucidate the charge carrier transport within them.

Methods

Two types of composites were investigated: one containing copper nanoparticles and the other – PMS 1 grade copper microparticles. The average size of the copper microparticles was 3.5 μm, determined using a BS242E (TESLA) electron microscope (Czechoslovakia, former country). The composite material with copper microparticles was prepared by mixing copper powder with low-density polyethylene (LDPE) in an agate ball mill for 7 hours.
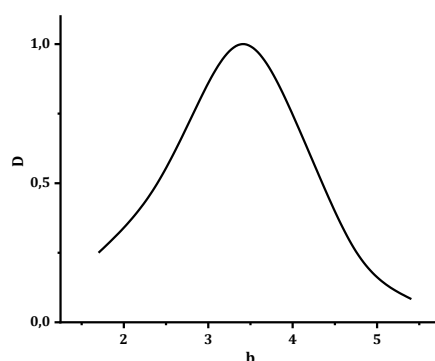
Figure 1. Distribution diagram of microdispersed Cu particles.

The synthesis of copper nanoparticles was carried out via thermal decomposition of a metal-containing precursor immobilized in a low-density polyethylene (LDPE) polymer matrix. The resulting material was investigated using a suite of modern physicochemical analysis techniques.

For the synthesis, an aqueous solution of copper(II) acetate was used as the starting metal-containing precursor. To achieve a temperature significantly exceeding the thermal decomposition threshold of $Cu(CH_3COO)_2 \cdot H_2O$, the polymer sample was heated in a reaction vessel immersed in vacuum oil (VM-6) at 350 °C. The experiment was conducted in an argon atmosphere, ensuring efficient and rapid removal of ligands and residual solvent.

The calculated volume of copper diacetate solution was gradually introduced into the molten polymer. The systematic addition of this compound to the polyethylene melt, which contained mineral oil, was carried out at a temperature of 350°C with active dynamic stirring. This approach ensured the rapid evaporation of the solvent, the removal of water, and the dissociation of acetate ligands. The primary crystalline structures of the metallic phase formed directly within the nanoreactor cavity, without the need for external addition of additional reagents.

A series of copper-containing composite nanomaterials, obtained in the form of brown-colored powder, was characterized by varying mass concentrations of the metallic phase (3, 5, 10, 20, 30, 40, 50, and 60%). Sample preparation included the extraction of residual oil using hexane in a Soxhlet apparatus, followed by vacuum drying and storage under controlled atmospheric conditions until the start of experimental studies. The determination of the sizes of metal-containing nanoparticles was carried out using transmission electron microscopy (TEM) with a JEOL JEM-1011 microscope (accelerating voltage of 100 kV). Sample preparation involved dispersing the nanoparticles in hexane using ultrasonic treatment, followed by depositing the suspension onto a copper substrate coated with a Formvar and carbon film. The research was conducted at Lomonosov Moscow State University and also utilized the Debye-Scherrer method for crystallite size calculations [6].

The composition of the synthesized nanoparticles was studied using X-ray phase analysis. X-ray diffraction measurements were carried out with a Rigaku TTRAX III diffractometer (CuKα radiation, λ = 1.54056 Å, graphite monochromator, 16 kV voltage) at the Weizmann Institute of Science laboratory. The diffraction data were compared to the PDF-2 reference database from the JCPDS International Committee (2004 version) to identify the phase composition.

The study of electrophysical properties was conducted on block-shaped samples with a tablet geometry (diameter 15 mm, height ~2 mm). The samples were molded by hot pressing, a method involving heating the press powder to a viscous-flow state. For polyethylene-based composites containing micro- and nanodispersed copper particles, the heating temperature during hot pressing was set to 230 °C.

The electrical resistance of the samples was measured to determine their electrical conductivity. Metal electrodes with a diameter of 13 mm were applied to the sample surfaces using the vacuum deposition method. Measurements were performed using two ohmmeters: E6-13A (Russia) for the resistance range of 10^1–10^{13} Ω and B7-30 (Russia) for the range of 10^3–10^{17} Ω. The measurement error for conductivity was within 1–7%.

To determine the static dielectric permittivity, the method of extrapolating the frequency dependence of dielectric permittivity to zero frequency was used. The capacitance of the samples was measured in the frequency range of 20–200 Hz. The dielectric permittivity was calculated using the following expression:

$$\varepsilon(\omega) = \frac{C(\omega)h}{\varepsilon_0 S} \qquad (1)$$

where $\varepsilon(\omega)$ – dielectric permittivity at a given frequency; $C(\omega)$ – measured capacitance of the sample; h – its thickness; S – the surface area of the electrodes applied to the flat faces of the sample; ε_0 – the vacuum permittivity (dielectric constant of free space).

The capacitance of the samples was measured using a measurement complex consisting of an E8-2 capacitance bridge (Russia), a G3-33 sinusoidal signal generator (Russia), and an F510 null indicator (Russia). The measurement error of the static dielectric permittivity did not exceed 2%.

Results and discussion

X-ray phase analysis of copper-containing composite polymer materials based on polyethylene revealed that the copper nanoparticles exhibit a 'core-shell' structure. Therefore, to clarify the charge carrier transport mechanism in such systems, it is necessary to investigate the properties of the shell — the copper oxide film. To address this task, a compact autonomous chamber with stabilized pressure, described in reference [7], was employed.

Figure 2 shows the experimental dependence of the conductivity of microdispersed copper powder on the magnitude of pressure.
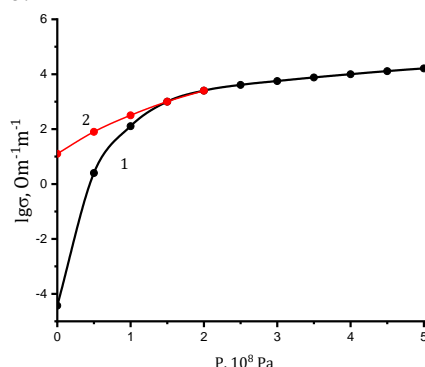
Figure 2 Dependence of the electrical conductivity s of microdispersed Cu particles on the applied pressure P. 1 - increasing pressure, 2 - decreasing pressure.

When the pressure increases to $1,5 \cdot 10^2$ MPa, σ (conductivity) sharply increases. Further increase in P (pressure) leads to a monotonic increase in the electrical conductivity of the copper particles. The sharp increase in σ when P increases to $1,5 \cdot 10^2$ MPa can be explained by an increase in the contact area between the copper particles due to powder compaction. The increase in pressure (P) promotes the expansion of the contact area. At the same time, a decrease in P provokes hysteresis in σ, caused by the adhesion of copper particles to the surface. To determine the type of oxide film, we studied the temperature dependence of σ of copper particles at fixed pressures, in a vacuum of 10^{-3} Torr (Figure 3).
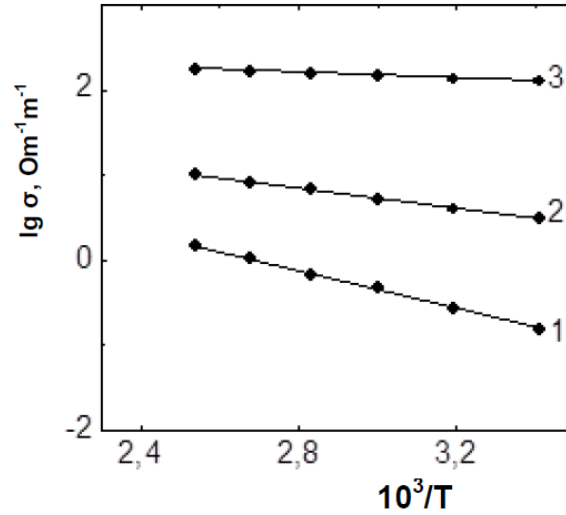
Figure 3. Temperature dependence of the electrical conductivity s of microdispersed Cu particles at fixed pressures (MPa), respectively: 1 = 12.5; 2 = 50; 3 = 100;

As seen in Fig. 3, with an increase in P from 12.5 MPa to 100 MPa, the activation energy decreases from 0.21 eV to 0.03 eV due to the reduction in oxide layer thickness during powder densification, as well as an increase in the probability of charge carrier tunneling between metal particles. These results indicate that the copper oxide film exhibits semiconductor properties.

Figure 4 presents the experimental dependencies of the sample's electrical conductivity on the volume fraction of copper nano- and microparticles (V_1), along with theoretical curves calculated within the framework of percolation theory using the expressions provided below.
The electrical conductivity σ of systems containing a dispersed metallic phase immobilized in a dielectric matrix is described within the framework of percolation theory [8-12] by the following equations:

$$\sigma(V_1) = \sigma_1 (V_1 - V_c)^t \text{ at } V_1 \geq V_c, (2)$$
$$\sigma(V_1) = \sigma_2 (V_c - V_1)^{-q} \text{ at } V_1 < V_c, (3)$$

Where σ_1 - electrical conductivity of the metallic phase (particles). σ_2- electrical conductivity of the dielectric matrix (surrounding medium). V_c -Critical concentration, also known as the percolation threshold.
The formation of a conductive cluster percolating the entire volume of the material occurs when the critical concentration of filler particles is reached. This phenomenon corresponds to the percolation threshold and is characterized by critical indices t and q, which describe the system's behavior in the vicinity of the phase transition point.

For subsequent analysis, taking into account the boundary conditions $V_1 = 0$ and $V_1 = 1$, and applying equations (2) and (3), the original expression is reduced to the following form:

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$$\sigma(V_1) = \sigma_1 \left(\frac{V_1 - V_c}{1 - V_c}\right)^t \text{ at } V_1 \geq V_c, (4)$$

$$\sigma(V_1) = \sigma_2 \left(\frac{V_c - V_1}{V_c}\right)^{-q} \text{ at } V_1 < V_c, (5)$$

For the studied composite materials, the critical volume fraction V_c of copper particles was determined by differentiating with respect to V_1. The critical exponent t was calculated based on the experimental data, plotted in the coordinates $lg\sigma - lg[(V_1 - V_c)/(1 - V_c)]$. The value of t corresponded to the slope of the resulting linear plot. The parameters σ_1 and σ_2 were determined by extrapolating the graph to $V_1 = 1$ and $V_1 = 0$, respectively. It was found that V_c is 0.105 and $t = 2.20$ for composites with nickel nanoparticles, whereas for materials with microdispersed nickel particles, V_c is 0.210 and $t = 1.78$. The critical exponent q was assumed to be 1, which is characteristic of three-dimensional systems [8].

Analysis of the data presented in Figure 4 shows that theoretical predictions and experimental results match for $V_1 > V_c$. In the range $V_1 < V_c$, agreement is observed only for composites containing copper microparticles. In the case of materials with copper nanoparticles, deviations were found in the region below V_c. These discrepancies are explained by the conductivity model for composite systems proposed in studies [10-12]. This model postulates the presence of electrical connections between all metallic particles in composites characterized by a random distribution of the metallic phase in the dielectric matrix.

Charge transport in the studied composite systems occurs via a charge carrier tunneling mechanism, which can take place both between neighboring particles and over distances exceeding interatomic scales. The percolation regime is established when the contribution of tunneling between spatially separated particles to macroscopic conductivity becomes negligible. This condition is satisfied when the particle radius b significantly exceeds the parameter d, which characterizes the localization region of tunneling carriers (or the spatial decay parameter of the tunneling current). In cases where b and d are comparable, tunneling between non-adjacent particles contributes to macroscopic conductivity alongside tunneling between neighboring particles. Under these conditions, the concentration dependence of macroscopic conductivity exhibits deviations from the classical percolation model.

The obtained results demonstrate a deviation from the established trends described in studies [10-12] for systems such as carbon nanotubes in polymer matrices and Ni–SiO₂ metal-ceramic composites. Unlike these studies, the present research reveals variability in the conductivity behavior of composites with identical compositions, attributed to differences in the size of metal-containing particles.
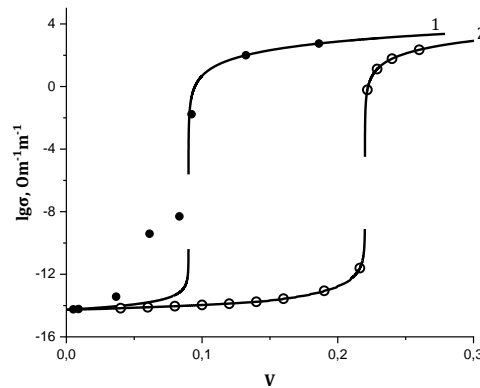
Figure 4. Comparison of experimental (dots/circles) and theoretical (solid lines) values of electrical conductivity as a function of the concentration of copper particles (nanoparticles - dots/line 1, microparticles - line 2) in polyethylene.

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According to the research data [10-12], composite systems with a tunneling charge transport mechanism between non-adjacent particles are characterized by the presence of two percolation thresholds. The first threshold (V_c) corresponds to high filler concentrations and represents the classical percolation transition. The second threshold (V_{cd}) appears at low concentrations of metallic particles and reflects the critical concentration at which the first infinite cluster structure of tunnel-connected conductive elements is formed. By approximating the initial section of the experimental curve ($V_1 < V_c$) for the polymer with copper nanoparticles (Figure 4) to the theoretical dependence described by equation (4) (assuming V_{cd} as the threshold and t' as the critical exponent), the values obtained were $V_{cd} = 0.04$ and $t' = 3.4$.

The results of the study on the frequency dispersion of the dielectric permittivity of composite materials based on polyethylene and copper nanoparticles (Figure 5) indicate the presence of two characteristic frequency regions, in which the dielectric permittivity exhibits different behavior. In the low-frequency range (20–200 Hz), a significant decrease in dielectric permittivity is observed with increasing frequency, which is explained by the Maxwell-Wagner mechanism [13]. This mechanism is caused by polarization at the phase interface due to the difference in electrical conductivity between the polymer matrix and the copper nanoparticles. With a further increase in frequency (200–10^3 Hz), the dielectric permittivity stabilizes, which is associated with a reduction in the contribution of interfacial polarization.

The experimental data characterizing the dependence of the static dielectric permittivity ε on the volume concentration of nanoparticles V_1 in the studied composite materials are presented in Figure 6. This figure also includes the results of a theoretical analysis performed within the framework of percolation theory using the following equation [8]:

$$\varepsilon(V) = \varepsilon_d \left(\frac{V_c - V_1}{V_c}\right)^{-q}, \ V_1 < V_c \qquad (6)$$

where ε_d is the dielectric permittivity of the polyethylene matrix, the value of which was taken as 2.26. The parameter V_c, corresponding to the percolation threshold, was determined based on experimental data on electrical conductivity and was found to be 0.220 for composites with microdisperse copper particles and 0.09 for composites with copper nanoparticles. The value of the critical index q was chosen to be 1, corresponding to a three-dimensional distribution of the filler.

Analysis of Figure 5 shows that for composites containing copper microparticles, the experimentally obtained dependence of ε on V_1 corresponds to the model described by equation (6). At the same time, deviations from the calculated values are observed for samples with copper nanoparticles: at V_1 values not exceeding the threshold $V_c = 0.09$, an increase in ε is recorded.
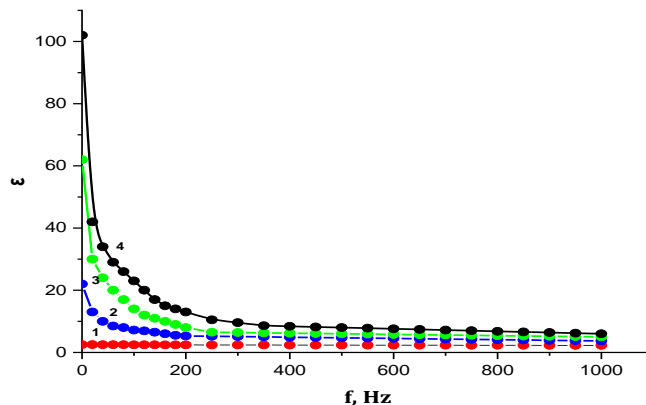
Figure 5. Frequency dependences of the dielectric permittivity of polyethylene composites with copper nanoparticles:
1 – pure polyethylene; 2–4 – composite materials with volume fractions of copper nanoparticles of 0.037, 0.061, and 0.092, respectively.

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The assumption of an additional percolation threshold for the electrical conductivity of polyethylene composites with copper nanoparticles was proposed in [10]. According to the model in [12], the existence of this threshold, with a calculated value of 0.04, is associated with the formation of a continuous chain of tunnel-connected conductors, where tunneling occurs both between neighboring particles and over longer distances. This feature is characteristic of nanocomposites, as nearby particles do not shield interactions with distant ones.
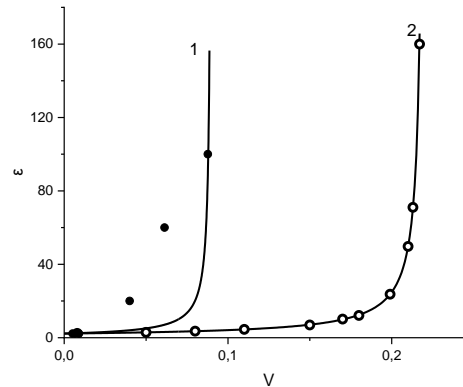
Figure 6. Comparison of the dielectric permittivity of polyethylene/copper composites (nano- and microparticles) as a function of filler concentration (V). Experimental data (points/circles) and theoretical calculations using formula (6) (solid lines).

Thus, Figure 6 confirms a well-known result [8]: at $V_{cd} = 0.04$, corresponding to the "dielectric–conductor" transition, a sharp ("giant") increase in the static dielectric permittivity ε of the nanocomposites is observed, along with the emergence and gradual rise of electrical conductivity σ. Consequently, the dependence of ε on V for composites with copper microparticles further supports the existence of the percolation threshold $V_{cd} = 0.04$ for the electrical conductivity of polyethylene composites with copper nanoparticles.

Conclusions

1. Two types of composite materials were developed and studied, differing in the size of copper particles embedded in the polyethylene matrix: microparticles and nanoparticles. Transmission electron microscopy determined that the obtained nanoparticles have a size of 13 nm. X-ray phase analysis revealed that the copper nanoparticles have a core-shell structure. The study of the temperature dependence of the electrical conductivity of copper microparticles under fixed pressures showed that the oxide shell has a semiconductor-like nature.
2. The conductivity and static dielectric permittivity of polyethylene composites containing copper micro- and nanoparticles were measured near the percolation threshold and analyzed within the framework of modern heterogeneous system theory. It was found that, for the studied composite materials, agreement between the theoretically calculated and experimentally measured values of electrical conductivity and static dielectric permittivity is achieved at filler concentrations above the percolation threshold.
3. Charge transport in composite materials with copper nanoparticles, in accordance with Balberg's model, is explained by the formation of a continuous network of tunnel-connected conductive elements. The percolation threshold V_{cd} corresponds to the formation of the first infinite cluster of such conductors. In this system, tunneling occurs not only between neighboring particles but also between particles separated by significant distances. This mechanism is characteristic of nanocomposites, where nanosized filler particles are not shielded by their immediate surroundings, allowing them to interact with distant "neighbors."

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4. Understanding the charge carrier transport process in such materials opens up broad opportunities for the development of new composites with tailored electrical properties, in particular:

Thermal sensors (detectors) based on polymer composites with enhanced sensitivity, designed to activate at approximately **60°C**.

Due to their unique **core-shell structure**, nanoparticles can be used in the development of **"smart" materials** [14].

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