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PERCOLATION PROPERTIES OF SYSTEMS BASED ON POLYPROPYLENE GLYCOL AND CARBON NANOTUBES

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Impedance spectroscopy researches have been carried out for the electric and dielectric properties of systems based on polypropylene glycol and carbon nanotubes. The fractal behavior of those systems was revealed. The corresponding percolation threshold of 0.45% was found. The critical index of conductivity $t = 1.43$ was determined in the framework of the scaling approach. The processes of charge transfer in the systems concerned were found to be described well by the intercluster polarization model.

K e y w o r d s: impedance spectroscopy research, percolation threshold, carbon nanotubes.

1. Introduction

Critical phenomena compose one of the important domains in fundamental physics. They are mainly observed at phase transitions of the second kind, when large fluctuations characterized by the infinite correlation length manifest themselves. The system is nonlinear at that. Percolation is an analog of critical phenomena. In contrast to temperature-induced phase transitions, where the transition between two phases occurs at a certain critical temperature, the percolation transition is a geometric phase transition. The percolation threshold, or the critical concentration, divides two phases: clusters are of a certain length in one phase and infinite in the other [1].

In connection with a rapid progress in nanotechnologies, the attention of many scientists is focused on nanofilled systems. As a filling agent in such systems, metal oxides, layered silicates, aerosil, and so forth are used. Carbon nanotubes (CNTs) are one of the promising filling agents. CNTs and nanofibers attract the enhanced attention of scientists because of an opportunity of their application in various domains of science and engineering. The semiconductor properties of CNTs allow them to be applied in emission displays, facilities for information storage, and other electric devices [2]. In addition, CNTs are characterized by considerable elasticity and hardness, which allows them to be used as a component in various nanocomposites. The addition of a relatively small amount of CNTs to a polymer substance substantially changes some of its properties (electric conductivity, thermal conductivity, mechanical strength), which is connected with the formation of a continuous (percolation) cluster [3].

There is a large number of publications devoted to the study of polymer systems filled with CNTs. For instance, in work [4], the authors introduced multiwalled CNTs into an epoxy polymer using the ultrasonic mixing technique. The percolation threshold was detected at a nanotube content of 0.05%. In work [5], systems on the basis of high-density polyethylene and single-walled CNTs were prepared by the hot pressing method to obtain a percolation threshold value of 0.25%. The authors of work [6] showed that the percolation threshold for the polyethylene

oxide–CNTs systems amounts to 0.45%. However, the majority of the works on this topic have a utilitarian materials science character. Therefore, this work aimed at studying the percolation phenomenon in nanofilled systems from the fundamental viewpoint in the framework of percolation theory and scaling approach.

2. Experimental Part

In our researches, we used model systems prepared on the basis of polypropylene glycol (PPG) and electrically conducting anisometric nanofillers (carbon nanotubes). Polypropylene glycol with M_w = = 400 (Aldrich) was selected as a polymeric matrix. Multi-walled CNTs (public corporation "Spetsmash", Ukraine) were fabricated with the use of the method of vapor chemical deposition, provided the content of mineral impurities equaled 0.1% [7]. The specific surface of nanotubes was 190 m^2/g, the external diameter 40 nm, and the length varied from 5 to 10 μm.

Before being used, PPG was dehydrated by heating it in vacuum (forevacuum) for 2 to 6 h at 80–100 °C and a residual pressure of 300 Pa. Specimens were fabricated, by using the method of ultrasonic mixing under normal conditions with the help of a UZN 22/44 ultrasonic disperser. The filling agent content was equal to 0.1–1.5 wt.% (below denoted as %).

In order to elucidate the influence of a filling agent on the charge transfer processes, we studied the electric properties of the composite. The researches were carried out with the use of the impedance spectroscopy method implemented on the basis of a Z-2000 impedance meter. A specimen was arranged between cell electrodes, and the real, Z', and imaginary, Z'', parts of its impedance were measured. The obtained dependences $Z''(Z')$ were used to determine the dc resistance of the specimen, $R_{\rm dc}$ [8]. Measurements were carried out in the temperature interval from 0 to 40 °C and the frequency range from 1 Hz to 2 MHz. The constant gap between electrodes was 0.11 mm. To obtain microphotos of the examined systems, an optical microscope (Ningbo Sunny Instruments Co., Ltd, China) was used, which was supplied with a digital camera mounted into the microscope eyepiece and connected to a computer. Specimens to study were placed into a glass cell 50 μm in thickness.

3. Results and Their Discussion

Polymer systems filled with electrically conducting CNTs, owing to the flexibility and nano-dimensions of nanotubes, are characterized by a very low critical percolation concentration (the percolation threshold). The insulator–conductor transition is partially described by the percolation theory, which is used, as a rule, to determine relations between the microstructure of those systems and their physical properties [4–6, 9, 10]. According to the percolation theory, the relation between the electric conductivity σ and the content of a conducting filling nanoagent in systems above the percolation threshold is described by the scaling law [10]

$$\sigma \propto (p - p_c)^t, \tag{1}$$

where p is the mass fraction of a conducting nanofiller, p_c the critical mass fraction of a nanofiller at the percolation transition (the percolation threshold), and the power exponent t is the critical index for electroconductivity. The latter mainly depends on the topological dimension of the system and does not depend on the structure of particles that form clusters, as well as on the interaction between them. Depending on the way of preparation of a system, as well as on the types of the polymer matrix and the filling agent, the critical index t varies from 0.9 [11] to 4.9 [12].

On the other hand, the conductivity in the systems below the percolation threshold can be described with the use of another scaling law, which looks like [9]

$$\sigma \propto (p_c - p)^{-s}, \tag{2}$$

where the critical index s changes from 0.42 [3] to 0.73 [13].

For polymer systems, the dependences $Z''(Z')$, the Nyquist diagrams, are semicircles (in the classical variant) with deviations in the low-frequency region. These deviations results from the surface polarization effects, which become more pronounced, as the segmental mobility in the polymer system increases. At frequencies lower than the frequency corresponding to the minimum of Z'', the surface processes dominate over the bulk ones, and the values of Z' in the Z''-minima corresponds to the bulk resistance of a material, $R_{\rm dc}$. The dependences of the complex impedance were used to determine the dc conductivity by the formula $\sigma_{\rm dc} = d/(SR_{\rm dc})$, where S is the specimen area,

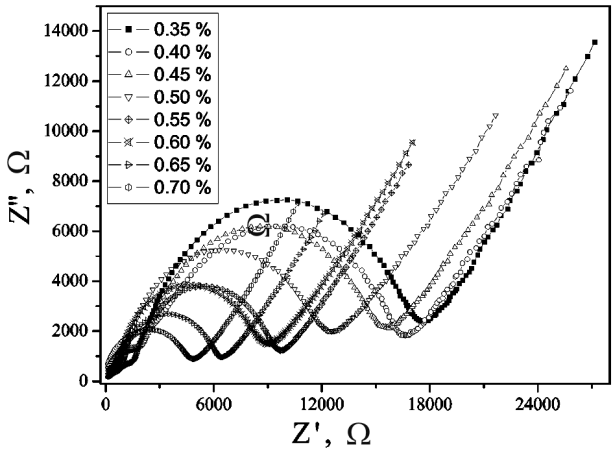

Fig. 1. Dependences $Z'(Z'')$ for the PPG–CNTs systems with various CNT contents

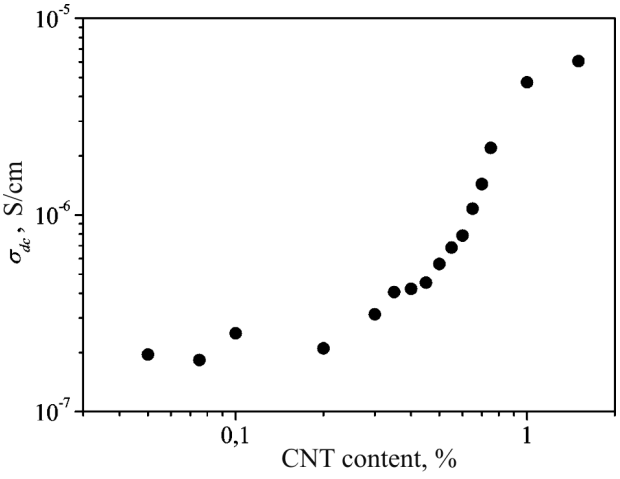

Fig. 2. Dependence of dc conductivity on the CNT content in the PPG–CNTs systems at $T = 293$ K

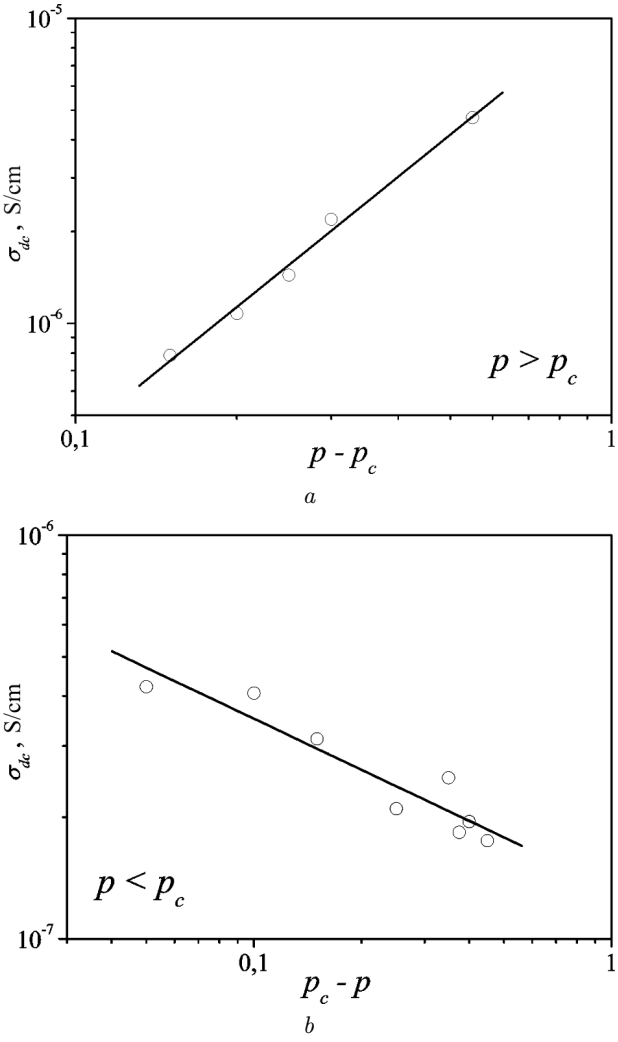

Fig. 3. Dependences of the conductivity in the PPG–CNTs systems on (a) $p - p_c$ and (b) $p_c - p$ in log-log coordinates. Solid curves correspond to the approximation of (a) Eq. (1) and (b) Eq. (2)

and d is the specimen thickness [8]. The Nyquist diagrams for the PPG–CNTs systems with various filler contents are depicted in Fig. 1.

In Fig. 2, the dependence of the dc conductivity $\sigma_{\rm dc}$ on the filler content for the examined PPG–CNTs systems is exhibited. The step-like change of the electroconductivity is associated with the percolation phenomenon and is observed in a concentration interval of 0.4–0.6%. At a CNT content of 0.7%, the dc conductivity of the system is of an order of magnitude higher that its values below the percolation threshold.

By applying the least-squares method and Eq. (1) for the description of experimental data (Fig. 3), we determined the percolation threshold p_c and the critical index t, which characterizes the structural organization of a nanofiller in the composite and the cluster structure. The results of approximation are shown in Fig. 3, *a*. For the PPG–CNTs systems, we obtained $p_c = 0.45\%$ and $t = 1.43 \pm 0.07$, which testifies to the formation of a three-dimensional spatial percolation network composed of CNT clusters [1, 3].

The value of critical index t is much smaller than the relevant theoretical value, $t \approx 2$. According to work [1], the value $t \approx 2$ corresponds to the uniform

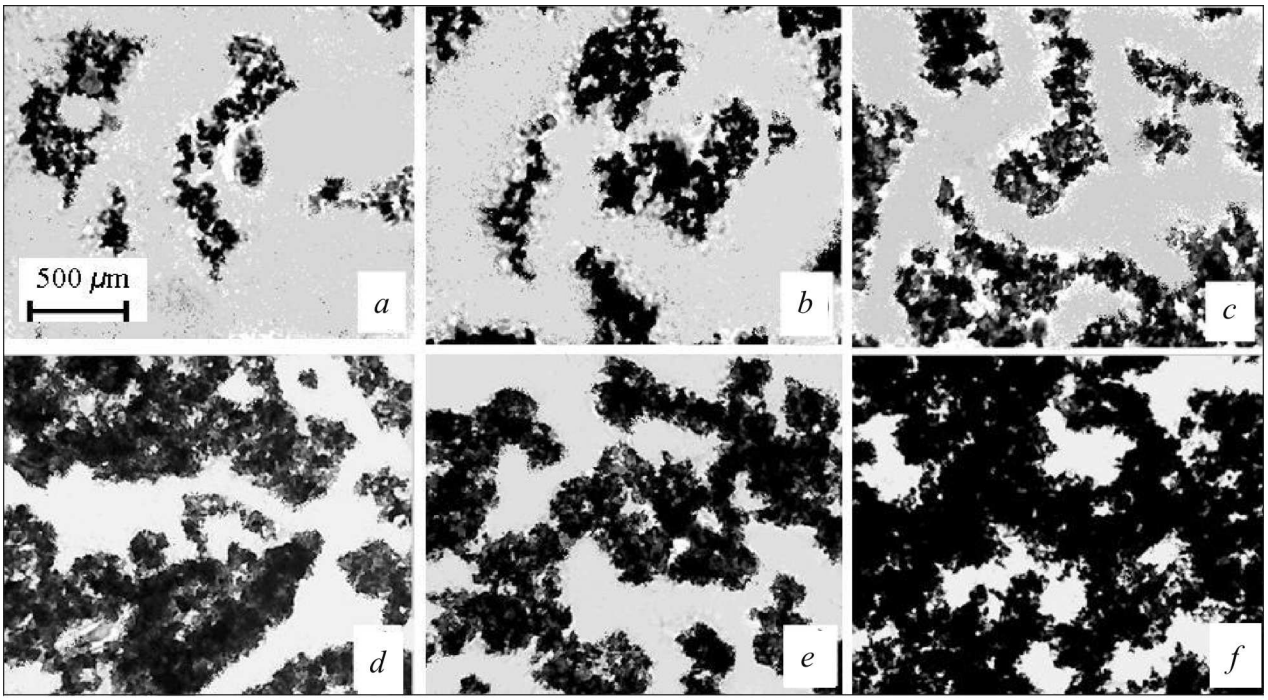

Fig. 4. Microphotos of the PPG–CNTs systems with various CNT contents: (*a*) 0.075, (*b*) 0.1, (*c*) 0.03, (*d*) 0.4, (*e*) 0.5, and (*f*) 0.75

distribution of electrically conducting particles in a dielectric medium. Such small values of t are very close to the values obtained for the polyepoxy–CNTs ($t = 1.2$ [4]) and polyvinyl alcohol–CNTs ($t = 1.36$ systems [14]). In our case, the small value of critical index t does not indicate a reduction in the dimensionality of the system, but can probably be explained by the processes of CNT aggregation occurring after those systems had been prepared. In our opinion, the formation of an electrically conducting network owing to the strong attraction between separate CNTs is not a statistical percolation process corresponding to the uniform distribution of filler nanoparticles.

Using the experimental data for the electric conductivity below the percolation threshold and Eq. (2), we can determine the critical index s. Figure 3,*b* demonstrates the dependence of dc conductivity in systems on the basis of PPG–CNTs in the coordinates of Eq. (2). The least-squares method gave the value $s = 0.44 \pm 0.06$, which is very close to that obtained for the polyvinyl alcohol–CNTs system in work [3] ($s = 0.42$), but is smaller than the values obtained in works [15] ($s = 0.6$) and [13] ($s = 0.73$). This difference can be explained by the different structures of clusters in the filling agents. In percolation theory, the quantity s is coupled with the dimensions of electric channels consisting of cluster-composing CNTs. According to the results of works [1, 16], the value of parameter s characterizes the average number of CNTs in clusters. For clusters with an identical effective volume to be formed, a smaller number of anisometric CNTs with a larger, in comparison with isometric-shaped nanofillers, length-to-diameter ratio should be taken. That is why the value of s for the systems PPG–CNTs is smaller than that for systems containing isometric filling agents.

The value obtained for the percolation threshold in the PPG–CNTs systems is confirmed by microscopic data. In Fig. 4, the microphotos of researched systems are shown. In Figs. 4, *a* to *c* obtained below the threshold CNT content, one can see that the nanotubes form separated clusters that are not in contact with one another. At a concentration near p_c (Fig. 4, *d*), CNTs start to form large agglomerates. When the percolation concentration is achieved, there emerges a continuous cluster, as is shown in Fig. 4, *e*. At concentrations higher than p_c (Fig. 4, *f*), CNT

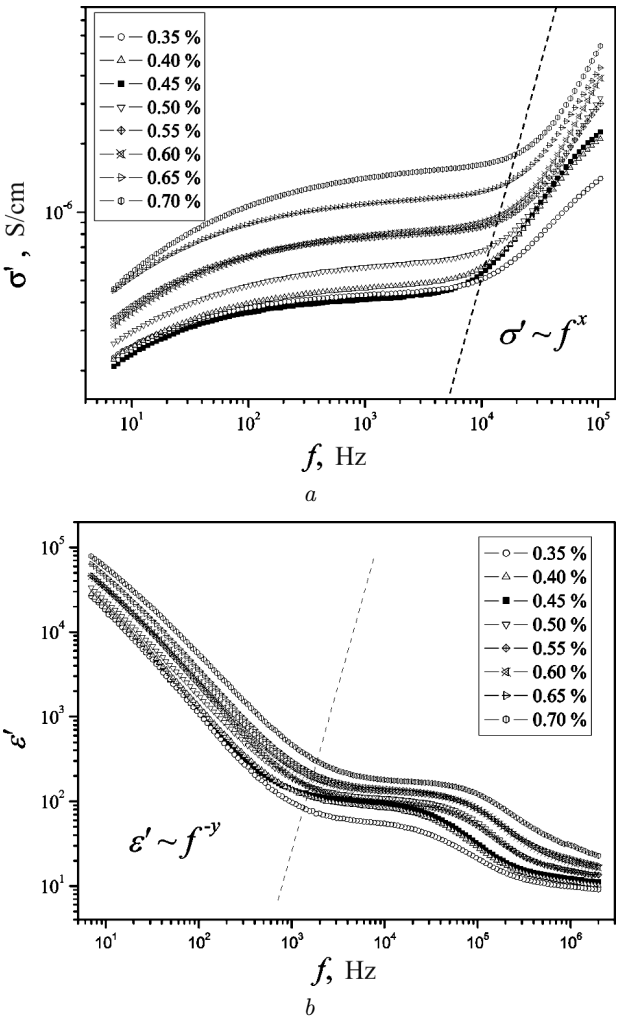

Fig. 5. Frequency dependences of (a) ac conductivity and (b) dielectric permittivity of the PPG–CNTs systems in the interval of the percolation transition for various filler contents

clusters start to grow, with more and more continuous electrically conducting channels (the percolation network) being formed.

The analysis of the ac conductivity in and the dielectric permittivity of substances is used to obtain a more detailed information concerning the microscopic structure of the researched systems in the forms of macroscopic physical parameters. The concentration dependences of the ac conductivity and the dielectric permittivity in a vicinity of the percolation transition in the PPG–CNTs systems are depicted in Fig. 5. Near the percolation threshold ($p \approx p_c$), the frequency dependence of ac conductivity, $\sigma'(f, p_c)$ (Fig. 5, a) and the dielectric permittivity, $\varepsilon'(f, p_c)$ (Fig. 5, b), can be described using the power laws [16]

$$\sigma'(f, p_c) \backsim f^x, \tag{3}$$

$$\varepsilon'(f, p_c) \backsim f^{-y}. \tag{4}$$

The critical indices x and y satisfy the relation $x + y = 1$. The frequency dependences of ac conductivity and dielectric permittivity for studied systems can be described in the framework of either two existing models [17], namely, the model of intercluster polarization [10, 18] and the model of anomalous diffusion in clusters [16]. The both are based on percolation theory.

The essence of the intercluster polarization model consists in the description of the electric conductivity in nanofilled systems in the framework of an equivalent resistance–capacitance circuit. In this model, the resistance and the capacitance are equivalents of all conducting clusters and intercluster gaps, respectively. By a CNT cluster, we mean a set of the nearest single nanotubes contacting with one another. CNTs with specific anisometric shapes–i.e. a large value of length-to-diameter ratio–are capable of contacting with one another to form a three-dimensional continuous percolation network. At concentrations much higher than p_c ($p \gg p_c$), the total conductivity in the system is mainly governed by the contribution of CNTs owing to the emergence of a large number of continuous percolation channels. In this case, the contribution made by the capacitance of intercluster gaps is insignificant. On the other hand, if the CNT concentration is near the percolation threshold, the number of continuous clusters is insignificant, and, therefore, the contribution of intercluster capacitance becomes very substantial.

If only the intercluster polarization effects are taken into consideration, the analysis brings about the following relations [10, 15]:

$$x = \frac{t}{t+s}, \quad y = \frac{s}{t+s}. \tag{5}$$

However, the system with a conducting filling agent also manifests effects associated, e.g., with an anomalous diffusion in fractal-like clusters [16]. The model of anomalous diffusion is based on the assumption that the conducting clusters are fractal-like on the length scale of quantities lying between the period of

crystal lattice a and the percolation correlation length ξ. In systems with a high conductivity ($p \gg p_c$), electrons can freely pass through the emerged infinite clusters. However, in systems, where the filler content is close to the percolation threshold ($p \approx p_c$), there appear a small number of electrically conducting ways composed of percolation clusters. Therefore, the motion of electrons in confined clusters plays a crucial role. At a certain frequency f, electrons pass the distance r_f for half a period. According to the model of anomalous diffusion, if $r_f < \xi$, it is evident that the conductivity should grow with the frequency. As the content of a filling agent in the system decreases, the number of conducting ways formed by percolation clusters diminishes, and the charge carriers start to spend more time to move along them; therefore, the anomalous diffusion begins at lower frequencies. Provided that $p < p_c$, the infinite cluster is not formed, and the charge carriers move only in confined clusters. According to the model of anomalous diffusion, the following relations are obeyed [16]:

$$x = \frac{t}{\nu(2+\theta)}, \quad y = \frac{2\nu - \beta}{\nu(2+\theta)}. \tag{6}$$

Here, ν, β, and θ are critical indices depending mainly on the dimensionality of a percolation system. The indices defined by Eqs. (5) and (6) satisfy the major scaling relation $x + y = 1$.

According to the procedure described in work [3], Eq. (3) and the data obtained experimentally for the frequency dependence of the ac conductivity can be used to determine the critical index x. For the threshold concentration in the PPG–CNTs systems, we obtain $x = 0.71 \pm 0.03$.

Analogously, with the use of the procedure described in work [3] and Eq. (4) for the PPG–CNTs systems at the threshold concentration (0.45%), the frequency dependences of the dielectric permittivity at high frequencies can be used to determine the critical index y. Having approximated the experimental data by the least-squares method, we obtained the value $y = 0.18 \pm 0.02$.

Substituting the values of t and s calculated from the experimental data in Eq. (5), we obtain $x \approx 0.77$ and $y \approx 0.23$. On the other hand, substituting the known values for ν, β, and θ calculated in works [16, 19] (for a three-dimensional system, $d = 3$, $\theta \approx 1.5$, $\nu \approx 0.9$, and $2\nu - \beta \approx 1.3$) in Eq. (6), we obtain $x \approx 0.58$ and $y \approx 0.42$. Our researches using the experimental data and Eqs. (3) and (4) gave the values for the critical indices $x \approx 0.71 \pm 0.03$ and $y \approx 0.18 \pm 0.02$. The latter values are much closer to those calculated in the framework of the intercluster polarization model than to the values obtained, by using the model of anomalous diffusion. Hence, the model of intercluster polarization better describes the percolation behavior of the PPG–CNTs systems. The difference between the critical indices obtained from the experimental data and calculated according to the model of anomalous diffusion is explained by the fact that this model does not consider the tunnel transitions between separated CNT clusters, as well as other transport effects, such as the charge capture by clusters and the charge hopping between them [20, 21].

4. Conclusions

The percolation properties of systems on the basis of PPG and CNTs have been studied and analyzed with the use of the percolation theory and the scaling approach. The examined nanofilled systems are found to be characterized by a fractal structure. By studying the conductivity in the systems concerned, the corresponding percolation threshold was determined to be 0.45%. In the framework of the scaling approach, the critical index $t = 1.43 \pm 0.07$ is found, which testifies to the formation of a three-dimensional spatial percolation network composed of nanotube clusters and to a considerable aggregation of CNTs after the preparation of a specimen. The results of microscopic researches confirmed the percolation threshold value obtained from the results of impedance measurements. The continuous CNT cluster is formed at a CNT content of 0.45%. The processes of charge transfer in the studied systems are described well in the framework of the intercluster polarization model. This fact testifies to a considerable contribution made by gaps between percolation clusters to the conductivity of the system.

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ПЕРКОЛЯЦІЙНІ ВЛАСТИВОСТІ СИСТЕМ НА ОСНОВІ ПОЛІПРОПІЛЕНГЛІКОЛЮ ТА ВУГЛЕЦЕВИХ НАНОТРУБОК

Р е з ю м е

Методом імпедансної спектроскопії досліджено електричні та діелектричні властивості систем на основі поліпропіленгліколю та вуглецевих нанотрубок. Виявлено, що дані системи проявляють фрактальну поведінку. Визначено поріг перколяції для досліджуваних систем, який становить 0,45%. Із використанням скейлінгового підходу було визначено критичний індекс провідності $t = 1{,}43$. Встановлено, що процеси переносу зарядів добре описуються в рамках моделі міжкластерної поляризації.