JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **9** No 5, 05021(6pp) (2017)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **9** № 5, 05021(6cc) (2017)

Features of Microstructure and Percolation Behavior of Polypropylene Glycol, Filled by Multiwalled Carbon Nanotubes

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(Received 30 May 2017; revised manuscript received 01 September 2017; published online 16 October 2017)

The research of the microstructure features, percolation behavior and impedance of systems based on polypropylene glycol and multiwalled carbon nanotubes (MWCNTs) is conducted using the methods of optical microscopy and impedance spectroscopy. It is set that in the investigated systems the typical percolation transition is observed at some threshold MWCNTs concentration (0.45 %). The fractal behavior of those systems was revealed. Using the method of impedance spectroscopy the corresponding percolation threshold of 0.45 % was found. The critical index of conductivity $t = 1.3$ was determined in the framework of McLachlan equation. The processes of charge transfer in the systems concerned were found to be described well by the proposed equivalent circuit.

Keywords: Percolation behavior, Impedance spectroscopy research, Carbon nanotubes, Microstructure, Equivalent circuit.

DOI: 10.21272/jnep.9(5).05021 PACS numbers: 73.63.Fg, 74.50.+ r

1. INTRODUCTION

The heterogeneous systems, such as polymer nanocomposite materials (NC), are widely utillized in different spheres of industry. Unique properties of NC provided their distribution in an engineering, building, optics [1]. Electric properties of NC served basis for development of numerous devices, utillized in the electrical engineering and electronics [2]. Particular interest NC are presented for production of microsensors [3].

Carbon nanotubes (CNTs) dispersed in an insulation polymeric matrix lead to the considerably increasion of conductivity of such NC. Conductivity of NC considerably depends on nanotubes' content, morphology of conducting percolation network and number of contacts between CNTs. Other factors, such as a size, geometrical form and hardness of conducting fillers, their distributing, properties of polymeric matrix and preparation methods of NC also influence on conductivity and process of percolation [4-6]. At some CNTs content, due to formation of percolation network, an insulation polymeric matrix begins to conduct an electric current. Such insulator-conductor transition called percolation, and critical concentration of the filler is the percolation threshold.

An important factor, determining the operating descriptions of NC, including high sensitiveness of conductivity to external influences, is their structure. Thus conductivity of NC depends both on the atomic-crystalline (molecular) structure of phases, constituents a system and from a topology (spatial) structure, determining distributing of dispersible phase in a dispersion environment (in the matrix) [7]. Impedance spectroscopy is one of effective methods of determination of structure and electrophysics descriptions both: actually NC and phases, entering in the complement of NC [8].

This study discusses microstructure, percolation effects and features of charges transfer in polypropylene glycol, filled by multiwalled CNTs, studied by impedance spectroscopy and optical microscopy.

2. EXPERIMENTAL PART

2.1 Materials

Polypropylene glycol (PPG-400) HO[-CH_2-CH(CH_3)-O-]$_n$H ($n \approx 9$) with a molecular mass of $M_w = 400$ (Aldrich) was used as a fluidic polymer matrix. Its density at $T = 293$ K was $\rho_n = 1010$ kg/m^3. PPG 400 is an oily viscous liquid and it has a pour point of ≈ 236 K. Before using PPG-400 was dewatered by heating in vacuum (2 mm) at residual pressure $p = 270$ Pa and temperature $T = 363$-383 K during 5 hours.

Multi-walled CNTs («Specmash» Ltd., Ukraine) is made by method of CVD (chemical vapour deposition) with FeAlMo as a catalyst [9]. MWCNTs were further treated by alkaline and acidic solutions and washed by distilled water until reaching the distilled water pH values in the filtrate. The typical outer diameter d of MWCNTs was ≈ 30-50 nm [4], their length l was ≈ 5-10 μm and mean aspect ratio was $a = l/d \approx 100$-300. The specific surface area of the powders determined by N_2 adsorption was $S = 130 \pm 5$ m^2/g. The electrical conductivity, σ, of the powder of MWCNTs compressed at 15 TPa was about 10 S/cm along the axis of compression. The density of the MWCNTs was assumed to be the same as the density of pure graphite, 2045 kg/m^3. The MWCNTs content in polymer nanocomposites is varied from 0.02 % to 3 %.

2.2 Preparation of composite materials

The composites were obtained by adding the appropriate weights of filler (MWCNTs) to PPG-400 at $T = 323$ K (viscosity is 30 mPa·s) with subsequent 5

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min sonication of the mixture using a UZDN-2T ultrasonic disperser at frequency of 22 kHz and the output power of 150 W. The series of samples with content of MWCNTs within 0.05-1.5 wt.% (in further %) were investigated.

2.3 Testing and characterization

Electric properties of nanocomposites are investigated by the method of impedance spectroscopy, realized on a base of impedancemeter Z-2000 (Russia). A sample is placed between electrodes of cell and measured its real (Z') and imaginary (Z'') parts of impedance. From the frequency dependence of complex impedance after a method, described in [10], determined a direct current (DC) conductivity $\sigma_{dc} = \frac{d}{SR_{dc}}$, where S is an area of sample, d is a thickness of sample. Measurings carried out at a room temperature in a frequency range 1 Hz-2 MHz.

Transmittance microphotographs of nanocomposites are got using the optical XY-B2 microscope (China), equipped with the ICM 532 digital video eyepiece and by the AMCAP/VIDCAP (Microsoft) system of image treatment. The probed samples are placed in a glass cell with thickness of 100 μm.

3. RESULTS AND DISCUSSION

3.1 Microstructure

For most polymeric NC, filled by MWCNTs, with the increase of nanofiller content, interaction between individual nanotubes become stronger than polymer-MWCNTs interaction. As a result, in such systems, during some threshold concentration of MWCNTs there is a typical percolation transition from the insulation in conducting state. Thus MWCNTs or their aggregates, form a network which pierces all of volume of the probed material. The microscopic images of NC based on PPG with the different concentrations of MWCNTs in a range from 0.075 % to 0.75 % at $T = 393$ K are presented on Fig. 1.

As we can see from Fig. 1, when the concentration of MWCNTs are lower than the percolation threshold ($C_{MWCNTs} = 0.1$-0.3 %), nanotubes form single clusters which do not unite between itself. When the concentration of MWCNTs are very close to the percolation threshold ($C_{MWCNTs} = C^c_{MWCNTs} \approx 0.45$ %), nanotubes begin to form large agglomerates. At achievement of percolation concentration, a continuous percolation cluster appears. When the concentration of MWCNTs are higher than the percolation threshold ($C_{MWCNTs} = 0.5$-0.75 %) C^c_{BHT}, the clusters of MWCNTs begin to grow, forming more continuous conducting channels (percolation network). Such low value of the percolation threshold is typical for the polymer-MWCNTs systems and can be explained by extremely high aspect ratio ($a = l/d$) of MWCNTs ($a \approx 100$-1000) [4, 11].

From microscopic images it is possible to estimate the fractal dimension (d_f), which represents morphology of clusters from MWCNTs in the 2D projection.

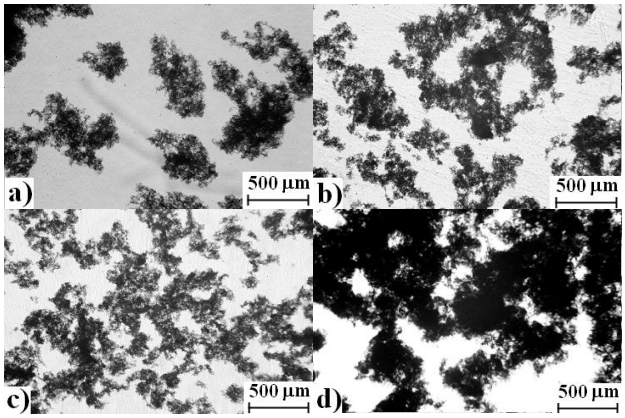

Fig. 1 – The microscopic images of the system based on PPG and MWCNTs. MWCNTs content: a) 0.1 %; b) 0.3 %; c) 0.45 %; d) 0.75 %

The images were analysed using the box-counting method, with the help of the image analysis software ImageJ v1.41. The 'capacity' fractal dimension was obtained from the dependence of the number of boxes necessary to cover the boundary of an aggregate N versus the box size L [12]:

$$N \propto L^{d_f} . \quad (1)$$

For the estimation of fractal dimension all of images translated into a binary format. The dependence of fractal dimension on MWCNTs content in the system is presented in Fig. 2. Unmonotonous growth of d_f with the increase of MWCNTs in the system are observed in Fig. 2. Such behavior also observed for the different types of the systems, filled by MWCNTs, for example, for binary liquid mixtures water – 1-Cyclohexyl-2-pyrrolidone – MWCNTs [13] and glycerol-MWCNTs [14] . The value of d_f lies in the range from 1 (case of linear aggregates) and 2 (case of dense aggregates). For calculation the fractal dimension of three-dimensional aggregates it is possible to use an equation [12]:

$$d_f^3 = d_f^2 + 1 , \quad (2)$$

where d_f^3 is a fractal dimension of $3D$ aggregates, d_f^2 is a fractal $2D$ aggregates.

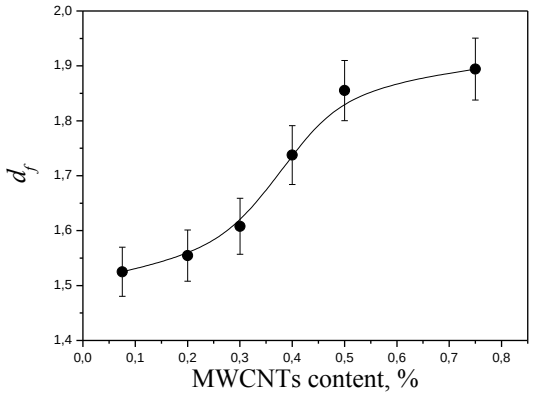

Fig. 2 – Dependence of fractal dimension on MWCNTs content

We can see from Fig. 2, that the most intensive growth of fractal dimension is observed in the area of percolation threshold for the PPG-MWCNTs system. A percolation cluster appears at the concentration equal 0.45 %. At the increase of MWCNTs content in the system, percolation clusters become more dense and the value of d_f grows to 1.8. Thus the surface of MWCNTs aggregates changes from smooth to winding and rough.

3.2. Percolation behaviour

In Fig. 3, the dependence of the dc conductivity on the filler content for the examined PPG-MWCNTs 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.

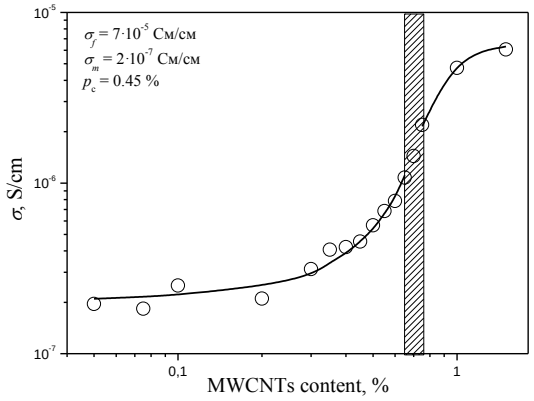

Fig. 3 – Dependence of conductivity on MWCNTs content. Circles indicate an experimental data, solid line is the McLachlan model, dashed area is the area of the percolation threshold

Polymer systems filled with electrically conducting MWCNTs, owing to the flexibility and nano-dimensions of nanotubes, are characterized by a very low 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 [15]. According to the percolation theory, the relation between the electric conductivity and the content of a conducting nanofiller in systems is described by the McLachlan equation [16]:

$$\frac{(1-\phi)\left(\sigma_l^{1/s}-\sigma_m^{1/s}\right)}{\sigma_l^{1/s}+A\sigma_m^{1/s}}+\frac{\phi\left(\sigma_c^{1/t}-\sigma_m^{1/t}\right)}{\sigma_c^{1/t}+A\sigma_m^{1/t}}=0. \qquad (3)$$

This equation is a phenomenological relation between σ_c, σ_l and σ_m, which are conductivity of nanofiller, polymeric matrix and NC accordingly. The value of volume concentration of MWCNTs ϕ lies in the range from 0 to 1, at $\phi = 0$ an environment is insulating ($\sigma_m = \sigma_l$), and at $\phi = 1$ an environment becomes conducting ($\sigma_m = \sigma_c$). A critical volume concentration ϕ_c characterizes a transition from insulating to the conducting state and determines a coefficient $A = (1-\phi_c)/\phi_c$. At $s = t = 1$ this equation grows into classical Bruggeman's equation for a symmetric environment. Equation (3) has two solutions:

$$|\sigma_l| \to 0 \ : \ \sigma_m = \sigma_c \left(\frac{\phi - \phi_c}{(1-\phi_c)} \right)^t, \quad \phi > \phi_c, \qquad (4)$$

$$|\sigma_c| \to \infty \ : \ \sigma_m = \sigma_l \left(\frac{\phi_c}{(\phi_c - \phi)} \right)^s, \ \phi < \phi_c, \qquad (5)$$

where the power exponents t and s are the critical exponents of conductivity.

The exponent t 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. The exponent s characterizes the cluster's structure. Equations (4) and (5) are harmonized percolation equations.

By applying the least-squares method and Eq. (4) for the description of experimental data (Fig. 3), we determined the percolation threshold ϕ_c and the critical exponent t. The results of approximation are shown in Fig. 3. For the PPG-MWCNTs systems, we obtained $\phi_c = 0.45$ % and $t = 1.3 \pm 0.05$. Using the experimental data for the electric conductivity below the percolation threshold and Eq. (5), we can determine the critical index s. The least-squares method gave the value $s = 0.65 \pm 0.07$, which is very close to the relevant theoretical value ($s = 0.73$) [15]. In percolation theory, the quantity s is coupled with the dimensions of electric channels consisting of cluster-composing MWCNTs. Such value of s indicates to the formation of fluffed clusters from MWCNTs [15].

The value of critical exponent t is much smaller than the relevant theoretical value, $t \approx 2$. According to work [15], the value $t = 2$ corresponds to the uniform distribution of electrically conducting particles in a dielectric medium. Such small values of t are very close to the values obtained for similar oligoether-MWCNTs systems ($t = 1.17 \div 1.46$) [17].

The analysis of publications devoted to the study of electric properties of polymer composites with MWCNTs shows that the critical exponent t can considerably differ from its theoretical value, and, in the majority of systems, it takes values within the limits $1.2 < t < 3$ [18]. The deviation of the exponent t in dependence (4) from the value $t = 2$ testifies to a more complicated mechanism of charge transfer in the corresponding systems and can be associated with the features of the cluster formation near the percolation threshold in polymer systems. In particular, in the absence of direct electric contacts between filler particles, the conductivity can take place due to tunnelling effects [19, 20]. In this case, because of different distances between the particles in a conducting cluster, expression (4) loses its universal character. In work [21], a model was proposed that suggested another possible reason for a deviation of the exponent t from

the value inherent to systems with the average statistical distribution of the conducting phase. It was postulated that some fraction of the electrically conducting filler is attached to the percolation cluster in the form of dangling chains ("dead ends"); i.e. they are connected to the cluster by only one of their ends and do not make any contribution to the conductivity of a continuous cluster. It was shown that, in the framework of this model, $t = 1.6 \div 1.8$ [21].

Fogel et. al. assumed that deviation of value of critical exponent t from universal was investigation of large anisometry of the form of conducting filler [22]. According to the theoretical calculations they estimate, that for MWCNTs with an aspect ratio more than 500, the value of t is equal 1.2-1.4. So, the value of t is very close to the value, calculated by Fogel et. al. In our opinion, the formation of an electrically conducting network owing to the strong attraction between separate MWCNTs and hidh aspect ratio is not a statistical percolation process corresponding to the uniform distribution of filler nanoparticles.

3.2 Features of charges transfer

The further analysis of the data obtained was carried out by simulating the impedance spectra f the PPG-MWCNTs system using the equivalent circuit method and applying the EIS Spectrum Analyser software. This allowed us to quickly and simply attain the complete understanding of charge transfer processes in the system.

The dependence of actual part of impedance on imaginary for the PPG-MWCNTs systems is presented on Fig. 4. Impedance spectrums for the probed systems based on PPG in the concentration range of MWCNTs (area of percolation transition) consist of two arcs (half-circles) and one linear area. Each of areas of impedance spectrum correspond to the phase or mechanism of charges transfer.

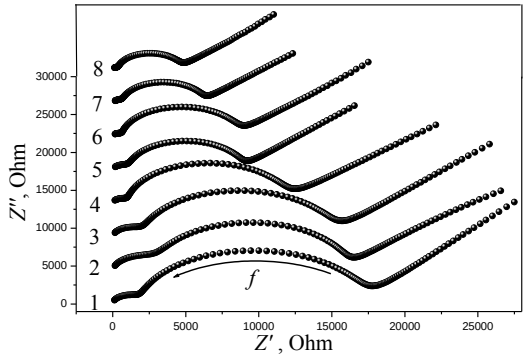

Fig. 4 – Nyquist plots ($Z'(Z'')$ dependences) for the PPG–MWCNTs systems, where the MWCNTs content is: 1 – 0.35 %; 2 – 0.4 %; 3 – 0.45 %; 4 – 0.5 %; 5 – 0.55 %; 6 – 0.6 %; 7 – 0.65 %; 8 – 0.7 %

The impedance of a polymeric material is often modelled as a resistor and a capacitor connected in parallel. However, for the nanofilled systems such equivalent circuit isn't correct [4]. In our model, the constant phase element (CPE) is used to compensate inhomogeneities of fractal structure in the investigated system [23]. CPE is a generalized universal means for simulating the impedance in a wide class of electrochemical systems. This element can reflect both the exponential distribution of parameters in the given electrochemical reaction, which is connected with the overcoming of an energy barrier at the charge and mass transfer, and the impedance behavior associated with the fractal structure of the surface of an examined specimen. The impedance of CPE is determined by the following empirical formula:

$$Z_{CPE} = A(j\omega)^{-n}, \qquad (6)$$

where A is a proportionality factor, and n is the power exponent, which characterizes the phase deviation.

Based on the results of the dielectric spectrums simulation it is possible to offer the model of structure of probed NC. In accordance with this model, the charges transport takes a place in two phases: in the volume and surface. The equivalent circuit described these processes are presented on Fig. 5. This circuit consists of two blocks. The first block which consists of CPE_1 element and capacitance-resistance elements united parallel describes the impedance of PPG volume phase.

On Fig. 4, where the Nyquist plots for the PPG–MWCNTs systems are presented, the linear and half-circle part of the plots in the area of low frequencies and large resistances are responsible for the impedance of volume phase. In the first block of the equivalent circuit, the consistently united elements C_1 and R_1 are responsible for charges motion in the volume of material, and the CPE_1 element is responsible for the contact phenomena. In this case, the contact phenomena can show up both at a contact between separate nanotubes or their aggregates (tunnelling) and at interaction between an electrode and NC. The second block which consists of united parallel CPE_2 element and resistor R_2 describes the impedance of surface layer on the polymer-filler boundary.

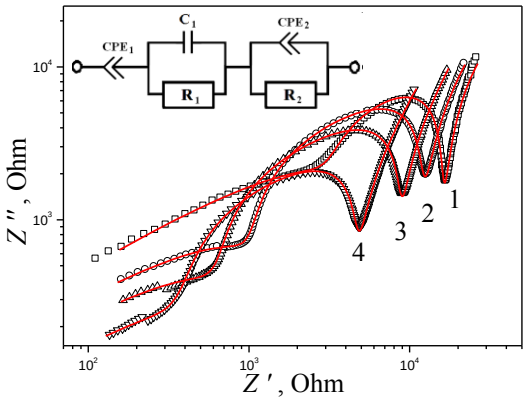

Fig. 5 – Z'-Z'' diagrams for the systems based on PPG, which filled by MWCNTs: 1 – 0.4 %; 2 – 0.5 %; 3 – 0.6 %; 4 – 0.7 %. Empty symbols are the experimental data, a solid line is a model

According to the equivalent circuit, presented on Fig. 5, the complete impedance of the system will be written as:

$$Z = (i\omega)^{\alpha_1} C + \frac{1}{i\omega C_1 + \frac{1}{R_1}} + \frac{1}{(i\omega)^{\alpha_2} C_2 + \frac{1}{R_2}}, \qquad (7)$$

where C is a capacity constituent of CPE_1; C_2 is a capacity constituent of CPE_2; $\alpha = \varphi_{CPE} / 90°$, φ_{CPE} it is a shift of phases, which does not depend on frequency and exponent (α) also does not depend on frequency. The phase φ_{CPE} almost always less than 90° and α is less than 1. At $\alpha = 1$, CPE becomes a condenser.

Impedance spectrums for the systems based on PPG–MWCNTs simulated using the proposed equivalent circuit are presented on Fig. 5. The results with of the simulation using the proposed equivalent circuit fully describe the experimental data that testifies to accuracy and authenticity of the proposed model.

Usually CPE are used for indemnification of heterogeneities on the boundary of phases and in some models it is suggested to describe the impedance behavior within the framework of fractal approach [24]. One of such theories, the theory of electrode with a fractal surface sets relationship between α and an effective fractal dimension (D_f) [24]:

$$\alpha = \frac{1}{D_f - 1}. \quad (8)$$

In this case, a surface of the phases distribution is not absolutely smooth. For a heterogeneous surface, fractal dimension changed in the range $2 < D_f < 3$. At such values of D_f the system is ramified in all of space directions. A fractal behavior is observed while $\alpha \neq 1$. Values of α_2 for surface layers on the boundary between PPG and MWCNTs were got from the results of the simulation (Fig. 5). Calculated, using the eq. (8) value of D_f are presented on Fig. 6.

As we can see from Fig. 6, the fractal dimension of boundary layers increases with the increase of the MWCNTs content in the system. A value of D_f lies in the range 2.65-2.9. These value of D_f well correlate with the results of fractal analysis of microphotographs of the PPG–MWCNTs system, where d_f^2 (fractal dimension of 2D aggregates), in this concentration area, increases from 1.7 to 1.9. Calculating the 3D fractal dimension of aggregates from d_f^2, using eq. (2) will get very similar values of d_f^3 (fractal dimension of 3D aggregates) from 2.7 to 2.9. The increase of D_f of boundary layers testifies to the greater filling of space by nanotubes

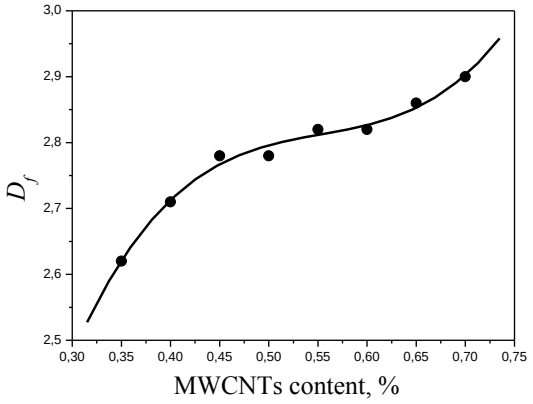

Fig. 6 – A value of fractal dimension of boundary layers for the PPG–MWCNTs systems, calculated using eq. (8)

and their aggregates. With the increase of MWCNTs content, the general area of the boundary layer which has a considerable influence on the processes of charges transfers in the PPG–MWCNTs systems increases.

4. CONCLUSIONS

The microstructure, percolation behavior and impedance of systems based on PPG and MWCNTs have been studied. 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 McLachlan equation, the critical index $t = 1.3$ is found, which testifies to the formation of a three-dimensional spatial percolation network composed of the particles with high aspect ratio and great contact resistance, and to a considerable aggregation of MWCNTs 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 MWCNTs cluster is formed at a MWCNTs content of 0.45%. The impedance of the systems based on PPG was studied, and also an equivalent circuit for impedance spectrum simulation was proposed. It is shown that boundary layers have a considerable influence on the processes of charges transfer in the probed systems. It is discovered that these systems show a fractal behavior.

Особенности микроструктуры и перколяционное поведение полипропиленгликоля, наполненного многослойными углеродными нанотрубками

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Используя метод импедансной спектроскопии и оптической микроскопии, проведено исследование микроструктуры, перколяционного поведения и импеданса систем на основе полипропиленгликоля и многослойных углеродных нанотрубок (УНТ). Показано, что для исследованных систем при некоторой пороговой концентрации УНТ (0,45 %) наблюдается типичный перколяционный переход. Используя

метод импедансной спектроскопии, был определен порог перколяции электропроводности, который равен 0,45 %. Используя уравнение МакЛачлана был определен критический индекс электропроводности $t = 1.3$. Предложена эквивалентная схема, при помощи которой можно идентифицировать процессы переноса зарядов в системе.

Ключевые слова: Перколяционное поведение, Импедансная спектроскопия, Углеродные нанотрубки, Микроструктура, Эквивалентная схема.

Особливості мікроструктури та перколяційна поведінка поліпропіленгліколю, наповненого багатошаровими вуглецевими нанотрубками

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Використовуючи метод імпедансної спектроскопії та оптичної мікроскопії проведено дослідження мікроструктури, перколяційної поведінки та імпедансу систем на основі поліпропіленгліколю та багатошарових вуглецевих нанотрубок (ВНТ). Показано, що для досліджених систем при деякій пороговій концентрації ВНТ (0,45 %) спостерігається типовий перколяційний перехід. Використовуючи метод імпедансної спектроскопії був визначений поріг перколяції електропровідності, який становить 0,45 %. Використовуючи рівняння МакЛачлана був визначений критичний індекс електропровідності $t = 1.3$. Запропонована еквівалентна схема, за допомогою якої можна ідентифікувати процеси перенесення зарядів у системі.

Ключові слова: Перколяційна поведінка, Імпедансна спектроскопія, Вуглецеві нанотрубки, Мікроструктура, Еквівалентна схема.

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