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Analysis of Percolation Behavior of Electrical Conductivity of the Systems Based on Polyethers and Carbon Nanotubes

E.A. Lysenkov[1,*], V.V. Klepko[2]

[1] *Mykolayiv National University named after V.O. Sukhomlynskiy, 24, Nikolska St., 54030 Mykolayiv, Ukraine*
[2] *Institute of Macromolecular Chemistry NAS of Ukraine, 48, Kharkivske Ave., 02160 Kyiv, Ukraine*

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The basic theoretical models of electrical conductivity of polymer nanocomposites and their accordance to experimental results are analyzed for the systems based on polyethers and carbon nanotubes using the methods of mathematical simulation. It is established that models which are based on the effective medium approximation do not take into account existence of percolation threshold and cannot be used for exact definition of experimental data. It is discovered that the Fourier model demonstrates a good accordance with an experiment, however it is applicable only for the systems in which a large increase of conductivity under reaching the percolation threshold is observed, that is the systems with low intrinsic conductivity. It is set that the best accordance to experimental data was shown by the Kirkpatrick model and the generalized McLachlan model, which, except for the percolation threshold, take into account the structural description of clusters formed from carbon nanotubes.

Keywords: Percolation behavior, Polymer nanocomposites, Electrical conductivity, Carbon nanotubes, Theoretical models of conductivity.

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1. INTRODUCTION

Polymer composites containing electrically conductive nanoscale filler particles are the subject of intense study in the last decade due to the unique properties and a wide range of applications [1]. Carbon nanotubes (CNT) [2, 3] are one of the most promising materials used as fillers for polymer nanocomposites. Numerous investigations were devoted to the utilization of nanotubes as fillers for preparing various polymer nanocomposites of targeted applications. CNT as amplifying components in composites modify the polymer matrix and generate new properties due to the extraordinary mechanical strength, electrical and thermal conductivity, thermal stability [4, 5]. The use of CNT as filler creates great opportunities for developing new multifunctional materials with a wide range of applications in industry [6, 7].

The formation of an electrically conductive grid in a non-conducting matrix depends on both the characteristics of a conductive filler (content, distribution uniformity, shape, size, aspect ratio, surface treatment, and orientation) and the properties of a polymer matrix (viscosity, crystallinity, polarization, and mixing technique). All these characteristics of both a polymer matrix and electrically conductive fillers significantly influence the formation of a continuous conductive grid composed of the filler particles, percolation threshold, and electrical conductivity of the system. It is established that non-uniform distribution of a filler leads to high values of the percolation thresholds in the system, while improvement of the dispersion level of a filler substantially decreases it [8]. It is also important to note that the formation of a conductive grid created by aggregates of the filler particles does not always occur through the direct contacts between particles. Therefore, in some cases, interaction of two particles, which are located at a distance less than 10 nm can be considered equivalent to the direct contact between them, since this small enough distance can be easily overcome by charge carriers (electrons) due to the jumping or tunneling mechanisms [9, 10]. The contact resistance between the particles is the key factor which determines the electrical conductivity of a composite.

Thus, prediction of electrical conductivity of polymer nanocomposites filled with CNT is a very difficult process. There are many theoretical models by which one can describe the concentration dependence of the electrical conductivity of the system, but each of them takes into account separate characteristics of the matrix or filler. Selection of the optimal model will allow to predict the functional properties of polymer nanocomposite materials filled with CNT. Therefore, the aim of the present work was to analyze the main theoretical models of electrical conductivity of polymer nanocomposites and their application for the description of the experimental data on an example of model systems based on polyethers and CNT.

2. BASIC MODELS OF ELECTRICAL CONDUCTIVITY OF POLYMER COMPOSITES

2.1 The modified Bruggeman model

To describe the concentration dependence of electrical conductivity of filled heterogeneous composite systems, one can use the basic approaches of the effective medium theory and symmetrical Bruggeman formula [11]

$$(1-p)\frac{(\sigma_{DC}-\sigma_m)}{2\sigma_{DC}+\sigma_m}+p\frac{(\sigma_{DC}-\sigma_f)}{2\sigma_{DC}+\sigma_f}=0, \qquad (1)$$

where σ_f, σ_m, and σ_{DC} are the electrical conductivities of the filler, polymer matrix, and composite, respectively.

This equation can be solved by determining σ_{DC}, and then we obtain [12]

* ealisenkov@mail.ru

$$\sigma_{DC} = \frac{1}{4}\left[\delta + (\delta^2 + 8\sigma_m\sigma_f)^{\frac{1}{2}}\right], \qquad (2)$$

where $\delta = (3p-1)\sigma_m + (2-3p)\sigma_f$.

In fact, due to the nonzero probability of quantum-mechanical electron tunneling through a non-conducting medium between the filler particles [9], the system passes from the non-conducting state into the conducting one even under the condition when the filler particles do not have direct physical contacts with each other. This means that the existence of quantum-mechanical tunneling increases the effective volume content of the filler particles. Xue [13] has suggested the existence of two types of the volume content of the filler particles, namely, the real (p_0) and the effective (p). The relation between p_0 and p is written as

$$p = \alpha p_0, \qquad (3)$$

where α is the increasing factor and at that $\alpha > 1$. This factor depends on the polymer and filler nature, on the particles shape and sizes, the volume content and their space distribution.

Taking the Bruggeman equation as the basis, Xue has suggested that electrical conductivities of the filler and matrix depend on the filler content. Assuming that all particles in a composite have a spherical shape, based on the Maxwell-Garnett theory, and correlation between two distinct topological structures (the symmetrical and asymmetrical) [14], electrical conductivities of the filler and matrix can be represented as [13]

$$\sigma_f^b = \frac{2p}{3-p}\sigma_f, \ \sigma_m^b = \frac{2(1-p)}{2+p}\sigma_m. \qquad (4)$$

Substituting (3) and (4) into (1), Xue has obtained the equation for the calculation of the effective electrical conductivity of composite systems

$$(1-\alpha p_0)\frac{\left(\sigma_{DC}-\sigma_m^b\right)}{2\sigma_{DC}+\sigma_m^b} + \alpha p_0 \frac{\left(\sigma_{DC}-\sigma_f^b\right)}{2\sigma_{DC}+\sigma_f^b} = 0. \qquad (5)$$

Equation (5) allows to describe the percolation properties of the conductor-dielectric composites, such as the electrical conductivity, thermal conductivity, dielectric permittivity, etc.

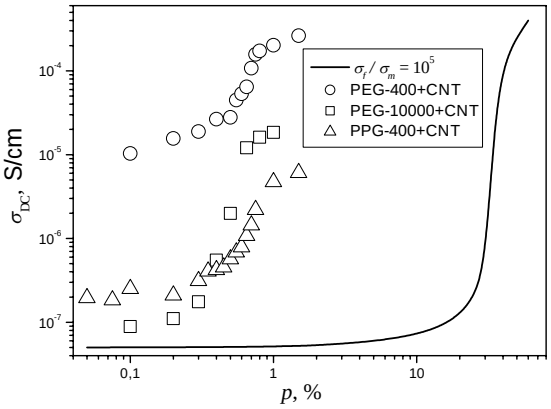

Fig. 1 – Dependence of the electrical conductivity of the polyether-CNT systems on the content of nanotubes. Solid line is the Bruggeman model

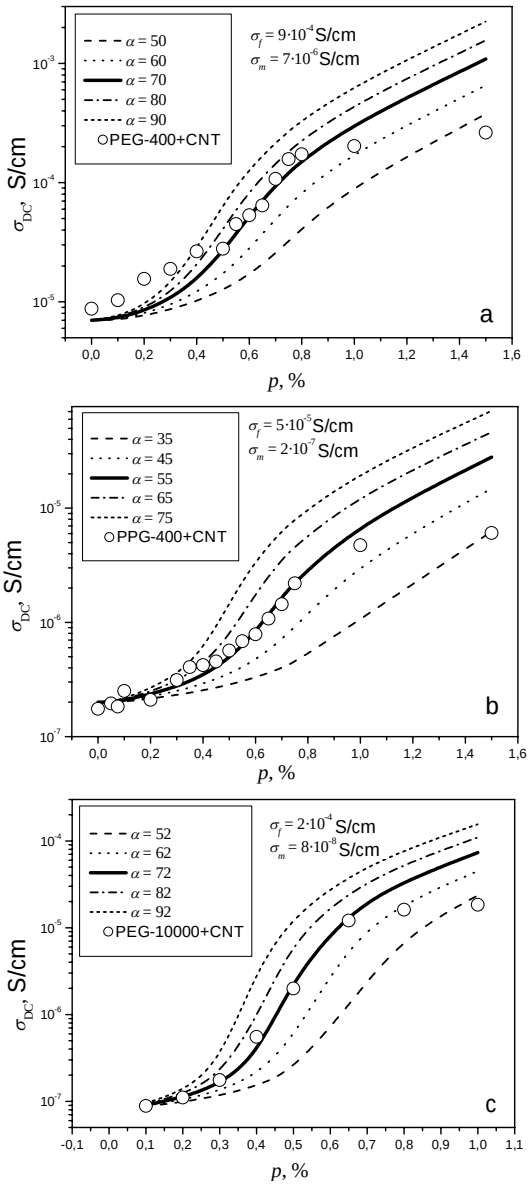

Fig. 2 – The experimental data simulated using equation (5) for nanofilled systems based on PEG-400 (a), PPG-400 (b), and PEG-10000 (c). Solid lines are the modified Bruggeman model

2.2 The Fourier model

In [15], Fourier, et al. have proposed the analytical model, which is based on the Fermi-Dirac distribution and describes the dielectric-conductor transition.

The basic equation of this model is written as

$$\log(\sigma_{DC}) = \log(\sigma_f) + \frac{\log(\sigma_m) - \log(\sigma_f)}{1+\exp\left[b\left(p-p_c\right)\right]}, \qquad (6)$$

where σ_{DC}, σ_f, σ_m are the electrical conductivities of the composite, filler, and polymer matrix, respectively, p is the filler content, b is the empirical parameter, which leads to the change in the electrical conductivity of the system when reaching the percolation threshold p_c.

In general, the Fourier model is very similar to the sigmoidal model [16] by both the "S"-like shape, which qualitatively corresponds to a typical percolation curve, and the influence of most parameters on the value of

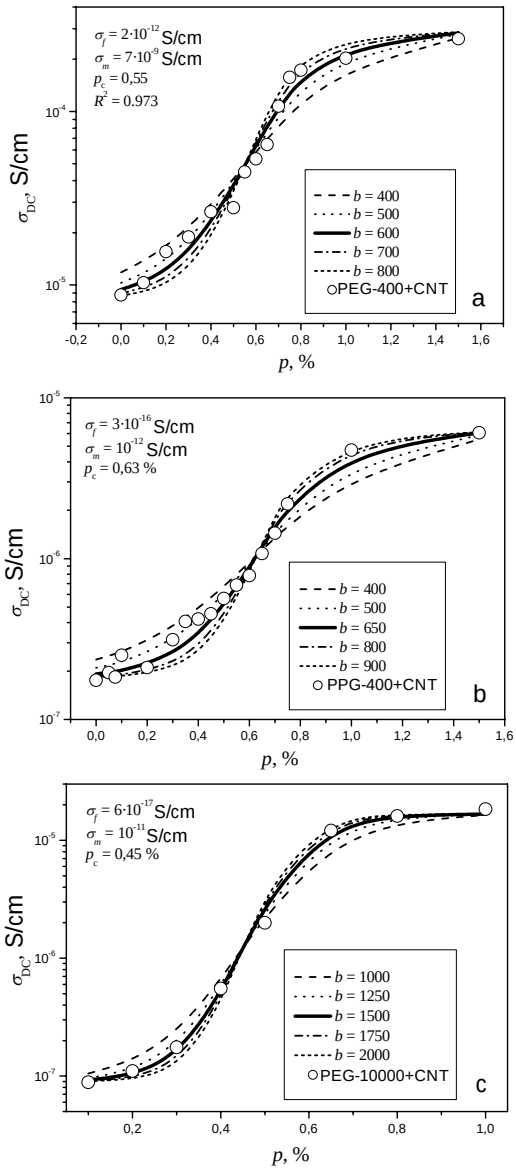

Fig. 3 – The experimental data simulated using equation (6) for nanofilled systems based on PEG-400 (a), PPG-400 (b), and PEG-10000 (c). Solid lines are the Fourier model

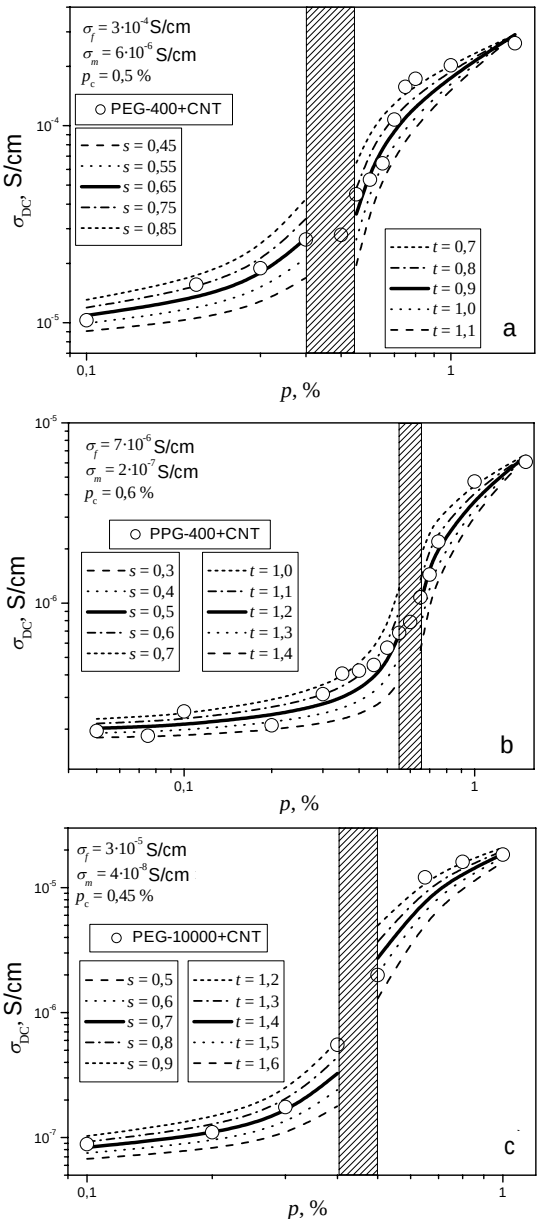

Fig. 4 – The experimental data simulated using equation (6) for nanofilled systems based on PEG-400 (a), PPG-400 (b), and PEG-10000 (c). Shaded area is the percolation threshold region and lines are the Kirkpatrick model

the total electrical conductivity of the system. The main variable parameter of the Fourier model is the parameter *b*, which changes the shape of the curve.

2.3 The Kirkpatrick model (scaling approach)

The Kirkpatrick model assumes that the appearance of high electrical conductivity is explained by the probability of formation of the contact between the filler particles within the composite [17, 18]. The basic equation of this model is the power law, which is written as

$$\sigma_{DC} \infty (p - p_c)^t , \qquad (7)$$

where σ_{DC} is the electrical conductivity of the nanocomposite, p is the filler volume fraction, p_c is the percolation threshold, i.e. the minimum filler content, at which a continuous cluster of particles is formed, *t* is the power, the critical electrical conductivity index, which mainly depends on the topological dimension of the system and does not depend on the structure of particles, which form clusters, and their interaction (the theoretical value of *t* for a three-dimensional system belongs to the range from 1.6 to 2.06 [19, 20])

However, the Kirkpatrick model allows to define the electrical conductivity only after the percolation threshold. To expand the application range of this model, Efros and Shklovskii have proposed to use not one Kirkpatrick equation, but the system of equations of the type [21]

$$\sigma_{DC} = \begin{cases} \sigma_m (p - p_c)^t \text{ at } p > p_c, \\ \sigma_f (p_c - p)^{-s} \text{ at } p < p_c, \end{cases} \qquad (8)$$

where σ_{DC}, σ_m, σ_f are the electrical conductivities of the composite, matrix, and filler, respectively, *s* is the critical electrical conductivity index characterizing the number of particles, which form the percolation cluster (the theo-

retical value of *s* for a three-dimensional system is about ≈ 0.73 [20]). This system of equations is a universal one and allows to describe the electrical conductivity of the filled polymer systems in the vicinity of the percolation transition with a high degree of accuracy.

2.4 The generalized McLachlan model

Using the above mentioned effective medium theory, it is possible to describe the electrical conductivity of systems for the whole range of filler concentrations, but it does not take into account the probabilistic effects, such as, for example, the formation of the percolation microstructure. Percolation models describe with high accuracy the change in the electrical conductivity only in the vicinity of the percolation transition. Further attempts in the modeling of the electrical conductivity of nanocomposites are aimed at combining these two approaches.

For a more complete and correct description of the percolation transition in the nanofilled polymer systems, the following McLachlan equation is used [22]:

$$(1-p)\frac{\sigma_m^{1/s}-\sigma_{DC}^{1/s}}{\sigma_m^{1/s}+A\sigma_{DC}^{1/s}}+p\frac{\sigma_f^{1/t}-\sigma_{DC}^{1/t}}{\sigma_f^{1/t}+A\sigma_{DC}^{1/t}}=0\,. \qquad (9)$$

This equation is the phenomenological relationship between σ_f, σ_m, and σ_{DC}, which are the conductivities of the nanofiller, polymer matrix, and nanocomposite, respectively. We should note that equation (9) can contain both the complex values of σ_{DC}, σ_f, and σ_m and their real parts. The value of the volume fraction p is in the range from 0 to 1; the medium is non-conducting ($\sigma_{DC} = \sigma_m$) at $p = 0$ and it becomes conducting ($\sigma_{DC} = \sigma_f$) at $p = 1$. The critical volume fraction p_c or the percolation threshold characterizes the transition from the non-conducting state into the conducting one and defines the coefficient $A = (1 - p_c)/p_c$. At $s = t = 1$ this equation is transformed into the Bruggeman equation (1) for the symmetrical medium. Equation (9) has two solutions, namely

$$|\sigma_f| \to \infty:\ \sigma_{DC} = \sigma_m\left(\frac{p_c}{(p_c-p)}\right)^s,\ p < p_c\,, \qquad (10)$$

$$|\sigma_m| \to 0:\ \sigma_{DC} = \sigma_f\left(\frac{p-p_c}{(1-p_c)}\right)^t,\ p > p_c\,, \qquad (11)$$

where *s* and *t* are the critical indexes. Equations (10) and (11) are the reduced percolation equations.

3. MODELING RESULTS

The experimental results of the concentration dependence of the electrical conductivity for PEG-400–CNT [10], PPG-400–CNT [23], PEG-10000–CNT [24] systems were used to establish the correspondence between the theoretical models and the experiment.

In Fig. 1 we present a general view of the function of the Bruggeman model, which is seemingly similar to the typical percolation curve. As seen from the analysis of the Bruggeman model and Fig. 1, although the self-consistent field approximation describes almost the entire range of filler concentrations, providing a good coincidence of the numerical calculations and the experiment at very large filler concentrations, but it does not entirely

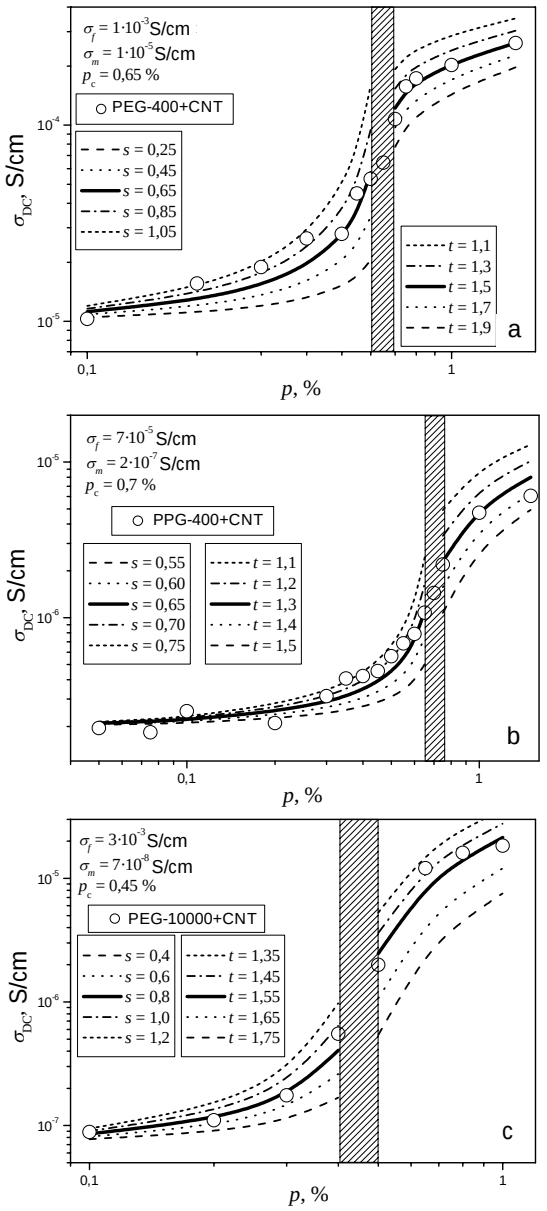

Fig. 5 – The experimental data simulated using equation (9) for nanofilled systems based on PEG-400 (a), PPG-400 (b), and PEG-10000 (c). Shaded area is the percolation threshold region and lines are the generalized McLachlan model

describe the change in the electrical conductivity near the percolation transition in the polyether-CNT systems. The Bruggeman model provides a sharp change in electrical conductivity when certain filler content is reached, but the value of this concentration is fixed and equal to 1/3 of the volume fraction. This model gives only a qualitative description of the behavior of electrical conductivity for such transitions.

The main disadvantages of the Bruggeman model were eliminated in the work of Xue, which has proposed the modified Bruggeman model. As seen from the analysis of the results of simulation of the electrical conductivity for the polyether-CNT systems using the modified Bruggeman model represented in Fig. 2, the modified Bruggeman model provides a good match between the numerical calculations and the experiment at low filler concentrations. Introduction to the model of the increa-

sing factor α gives the possibility to shift the region of a sharp change in the electrical conductivity towards lower concentrations (much less than 1/3 for the original Bruggeman model). This, in fact, allows to compensate the absence of the percolation threshold in this model. However, the modified Bruggeman model describes poorly the change in the electrical conductivity at concentrations higher than the percolation threshold.

In Fig. 3 we show the modeling of the experimental data for the polyether-CNT system by using the Fourier model. The shape of the Fourier model curve depends significantly on its parameters. Thus, by gradually varying the percolation threshold, the electrical conductivity is changed at lower filler concentrations, and the maximum value of the system electrical conductivity can be achieved for any value of p_c. Therefore, the value of p_c substantially influences the maximum electrical conductivity of the nanocomposite. The value of the filler electrical conductivity also impacts the maximum electrical conductivity of the system. The system conductivity increases with increasing filler conductivity.

This model describes well enough the experimental data on the electrical conductivity of the polyether-CNT systems (see Fig. 3). However, to fit the function (6), the values of the parameters σ_f and σ_m were substantially lower compared with the intrinsic electrical conductivities of the CNT and polyether matrix. This significantly decreases the accuracy of the model and limits its application. Such a discrepancy is explained by a small jump of the electrical conductivity when passing through the percolation threshold in the polyether-CNT systems. The authors of the given model described the results of the electrical conductivity for the systems, in which the leap of the electrical conductivity, equal to 10-11 orders of magnitude, was observed [15].

In Fig. 4 we illustrate the simulation of the experimental data for the polyether-CNT system by using the Kirkpatrick model. As seen from the analysis of functions (8) (see Fig. 4), the electrical conductivity of the system increases with decreasing critical index *t*, and a decrease in the critical index *s* leads to the decrease in the system electrical conductivity. After analyzing the system of equations (8), we can say that change in the value of the critical index *t* does not lead to the change in the maximum electrical conductivity of the polymer composite, which is specified only by the filler electrical conductivity. The change in the percolation threshold of the filler in the composite does not result in the change of the system electrical conductivity.

The Kirkpatrick model demonstrates good correspondence with the experimental data of the electrical conductivity for the polyether-CNT systems (Fig. 4). This model assumes that the electrical conductivity critical indexes are universe for the systems with the same dimensions. However, the critical indexes differ from the theoretical values for the studied polyether-CNT systems. This fact does not indicate the decrease in the system dimension, and, probably, is the consequence of a large degree of aggregation of nanotubes in the system [8].

In Fig. 5 we present the modeling of the experimental data for the polyether-CNT system using the generalized McLachlan model. As seen from the analysis of function (9) (see Fig. 5), the electrical conductivity of the system decreases with increasing critical index *t*, and a decrease in the critical index *s* leads to the decrease in the system electrical conductivity. After analyzing the function (9), we can say that the change in the critical index *t* leads to the change in the maximum electrical conductivity of the polymer composite. The value of the percolation threshold also influences the maximum electrical conductivity of the system and with increasing p_c the maximum electrical conductivity decreases.

In general, the McLachlan model describes well enough the experimental data. The values of the critical indexes *t* and *s* determined within the McLachlan approach were found to be higher than within the scaling approach and closer to the theoretical values. Due to the fact that the McLachlan model combines elements of the effective medium theory and percolation theory, it is more universal and can be used for the description of the experimental results of the electrical conductivity of nanocomposites based on polymer matrixes with different intrinsic electrical conductivity.

4. CONCLUSIONS

As a result of this work, we have analyzed the basic theoretical models of electrical conductivity of polymer nanocomposites and their application for the description of the experimental data on an example of model systems on the basis of polyethers and CNT. It is established that the models based on the provisions of the effective medium theory describe poorly the experimental data. This is explained by the fact that these models (Bruggeman and Xue) do not take into account the presence of the percolation threshold. It is revealed that the Fourier model, whose graph is the classical logistic sigmoidal function, describes well enough the experimental data of electrical conductivity of the polyether-CNT systems. However, this model is not suitable for describing systems on the basis of polymer matrixes with high intrinsic electrical conductivity because of a low (1-2 orders) jump of electrical conductivity in the percolation transition. It is shown that the Kirkpatrick model, which is based on the scaling approach for describing properties of the structurally nonuniform systems, demonstrates a good correspondence with the experimental data. This model accounts the presence of the percolation threshold, at which the functions have discontinuity at infinity. The advantage of this model is the accounting of the structural features of the percolation cluster formation which are expressed through the universal critical indexes *t* and *s*. However, the critical indexes defined using the Kirkpatrick model for the polyether-CNT systems were found to be lower than the theoretical ones that is associated with a high degree of aggregation of CNT.

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