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V.V. KLEPKO,<sup>1</sup> E.A. LYSENKOV<sup>2</sup><sup>1</sup>Institute of Macromolecular Chemistry, Nat. Acad. of Sci. of Ukraine  
(148, Kharkivske Road, Kyiv 02160, Ukraine)<sup>2</sup>V.O. Sukhomlynskyi National University of Mykolaiv  
(24, Nikolska Str., Mykolaiv 54030, Ukraine)

## FEATURES OF PERCOLATION TRANSITION IN SYSTEMS ON THE BASIS OF OLIGOGLYCOLS AND CARBON NANOTUBES

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*The results of researches on the electric conductivity in the percolation transition region of the oligoglycol/nanotubes systems are reported. It is shown that the conductivity can be described in the framework of the critical percolation theory. The critical parameters of percolation transition are found to change, by depending on various factors, and to differ from the predictions of the statistical percolation theory. A relationship between the critical conductivity indices and the fractal dimensionality of a conducting cluster is found. It is demonstrated that the application of a scaling function allows the concentration dependences of conductivity to be described with the help of a unique universal function.*

*Key words:* electric conductivity, oligoglycol, nanotubes, percolation transition.

### 1. Introduction

Researches of the structure and properties of nanosystems have been attracting a high interest in the recent years [1]. Such attention to nanosystems is associated, first of all, with a complex of their new unique properties different from those demonstrated by macroscopic systems, which makes their application in novel nanotechnologies very promising [2]. It was found that the properties of substances can substantially change at the transition from macroscopic structures to microscopic ones (the dimensions of the latter lie in the nanometer range, 1–100 nm), because nanoclusters in the condensed state are characterized by properties that are different from those for macrosystems. The results of modern researches [3] testify that the properties of nanosystems are governed not only by the size of nanoparticle clusters, but also by the structure organization in them. The character of the latter in the systems concerned depends on the origin of nanoparticles themselves and on the technology of their fabrication, as well as on the matrix (the medium), in which nanoparticles are distributed. At the same time, the research of specific features of the clustering in nanosystems (nanocomposites) is often not a triv-

ial problem, because the structural effects can manifest themselves at extremely low concentrations of nanoparticles (e.g., 0.001–0.5% if nanoparticles with high anisotropy of their shapes are applied, such as nanotubes, nanofibers, and nanowhiskers). One of the effective methods to study the processes of structure formation in those systems is the method of neutron scattering, which allows various “fine” structural effects in nano-structured systems to be analyzed owing to wide capabilities of the contrast variation. The advantages of the neutron scattering method over other methods were demonstrated, in particular, in works by L.A. Bulavin *et al.* [4–8] devoted to the study of nanosystems on the basis of fullerenes, ferrofluids, and colloids.

Among the nanofilled systems, a special place is occupied by systems on the basis of carbon nanotubes (CNTs). Since CNTs are characterized by a high strength and high electric and heat conductivities, they are very usable for the creation of various composite materials with enhanced parameters. A high shape anisotropy of nanotubes results in a drastic change of composite properties near the percolation transition point, which is observed at filler contents of about 0.1% [9]. For instance, the electric conductivity in the matrix/nanotubes systems grows by several orders of magnitude, which is associated with

the formation of a continuous conducting cluster by the filler.

In the framework of the critical percolation theory, the following scaling relations are used to describe the conductivity near the percolation transition point:

$$\sigma \propto (p - p_c)^t \text{ at } p > p_c, \quad (1)$$

$$\sigma \propto (p_c - p)^{-s} \text{ at } p < p_c, \quad (2)$$

where  $\sigma$  is the conductivity of the system,  $p$  the filler concentration,  $p_c$  the critical filler concentration, and  $t$  and  $s$  are critical exponents for the electric conductivity. In the statistical percolation theory, the latter equal  $t \approx 2$  and  $s \approx 0.73$  [10].

The analysis of publications devoted to the study of electric properties of polymer composites with CNTs 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  $1.2 \leq t \leq 3$  [11]. The deviation of the exponent  $\gamma$  in dependence (1) from the value  $t \approx 2$  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 tunneling effects [12–14]. In this case, because of different distances between the particles in a conducting cluster, expression (1) loses its universal character. In work [15], 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,  $t = 1.6 \div 1.8$  [15].

To analyze the influence of the features in the cluster formation and in the percolation cluster microstructure on the conductivity near the percolation transition point, we carried out the electrophysical researches of some oligoglycols – polyethylene glycol (PEG) and polypropylene glycol (PPG) – filled with multiwalled CNTs.

## 2. Experimental Part

Composite matrices were prepared with the use of PEG with  $M_w = 400$  (Aldrich), PEG with  $M_w = 10000$  (Fluka), and PPG with  $M_w = 400$  (Fluka). Multiwalled CNTs (the content of mineral impurities 0.1%, the specific surface  $190 \text{ m}^2/\text{g}$ , the external diameter 20 nm, and the length  $5 \div 10 \mu\text{m}$ ) were fabricated at the public corporation “Spetzmash” (Ukraine), by using the chemical vapor deposition method [16]. The specific conductivity  $\sigma$  of pressed CNTs (at a pressure of 15 TPa) was  $10 \Omega^{-1} \text{ cm}^{-1}$  along the compression axis.

Before their application, the oligoglycols were dehydrated by heating in the vacuum for 2 h at  $80\text{--}100^\circ\text{C}$  and a residual pressure of 300 Pa. The specimens were prepared, by using the ultrasonic (US) and mechanical mixing under normal conditions. The ultrasonic mixing was performed with the help of a disperser UZDN-2T at an US frequency of 22 kHz and a power of 400 W. The mechanical mixing was executed, by using a mechanical mixer with a screw diameter of 15 mm at a rotation velocity of 300 rpm. The ultrasonic mixing was performed for 0.5, 2.5, 5, and 10 min; the mechanical one for 5 min.

The electrical properties were studied on an impedance meter Z-2000 (Russia), by using the impedance spectroscopy method. A specimen was placed between the cell electrodes, and the real,  $Z'$ , and imaginary,  $Z''$ , parts of its impedance were measured. The complex impedance dependences were used to determine the  $dc$  conductivity  $\sigma_{dc} = \frac{d}{SR_{dc}}$ , where  $S$  and  $d$  are the specimen area and thickness, respectively, by following the technique described in work [17]. The measurements were carried out at room temperature in a frequency interval from 1 Hz to 2 MHz. The constant gap between the electrodes amounted to 0.11 mm. The measurements were carried out in a temperature interval from 20 to  $80^\circ\text{C}$ .

## 3. Research Results

### 3.1. Influence of polymer matrix crystallinity

In Fig. 1, the conductivity dependences on the CNT content are shown for composites on the basis of PEG-400 and PEG-10000. At room temperature, the crystallinity degrees of PEG-400 and PEG-10000 equal 0 and 72%, respectively. A drastic jump of the conductivity (the percolation transition) is observed in the CNT content interval of 0.3–0.6% for both an-

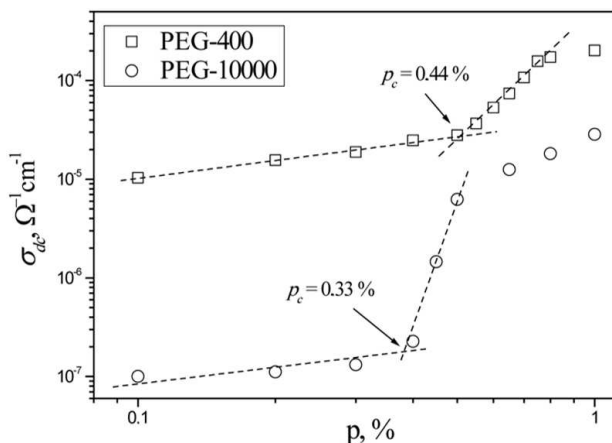


Fig. 1. Conductivity dependences on the CNT content for PEG-400/CNTs and PEG-10000/CNTs systems

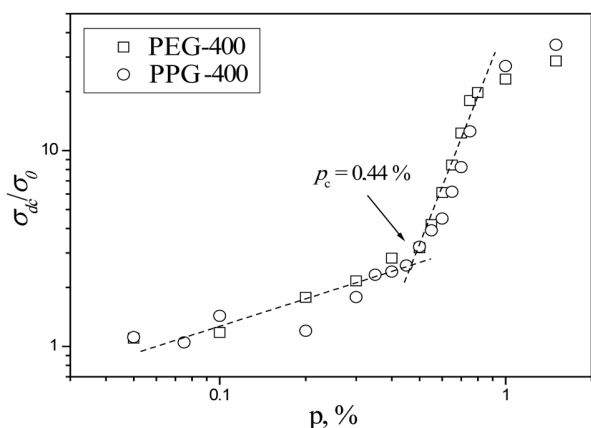


Fig. 2. Conductivity dependences on the CNT content for PEG-400/CNTs and PPG-400/CNTs systems

alyzed systems. From Fig. 1, one can see that the interval of percolation transition for the system on the basis of PEG-400 is much wider than the analogous interval for the system on the basis of PEG-10000. According to the results of work [19], the percolation transition interval width is reciprocal to the crystallinity degree of a polymer matrix.

The values of percolation threshold indicated in Fig. 1 are reciprocal to the crystallinity degree of the polymer matrix. This dependence is explained by the structure of partially crystalline polymers. The structure of crystalline regions in a polymer is highly compact, because their formation is driven by the densest-packing principle. At the same time, the structure of amorphous regions is chaotic and disor-

dered. Therefore, the conducting fillers can accumulate only in the amorphous regions in the course of formation of a nanocomposite: when crystallites grow at the polymer crystallization, nanofiller particles are pushed out into the amorphous regions. As the crystallinity degree of the polymer matrix increases, the fraction of crystalline regions grows. Accordingly, the filler concentration in the amorphous regions increases, and a percolation cluster emerges at a lower CNT content [18]. As a result, the systems on the basis of highly crystalline PEG-10000 have a lower percolation threshold than the systems on the basis of amorphous PEG-400.

### 3.2. Influence of polymer matrix topology

The issue concerning the influence of a polymer matrix topology on the percolation behavior of nanofilled systems is also of importance. For its elucidation, the researches of conductivity were carried out for the systems on the basis of polyethers with the same molecular mass, but with different topological structures: polyethylene glycol, which has no lateral branches, and polypropylene glycol, which has one lateral group in every monomer link. In Fig. 2, the conductivity dependences on the CNT content are depicted for the systems on the basis of PEG and PPG. The dependences were plotted in the coordinates  $(\sigma/\sigma_0, p)$ , which allowed the contribution of the intrinsic conductivity of polymer matrices to be excluded.

From Fig. 2, one can see that the percolation curves for the systems on the basis of PEG and PPG have identical character and identical values of reduced conductivity. The both systems demonstrate a percolation behavior and are characterized by the same percolation threshold. The similar values of percolation thresholds were obtained in works [20, 21] for nanocomposite systems on the basis of PEG and PPG filled with CNTs. The discrepancies between the experimental results obtained for the PEG/CNTs and PPG/CNTs systems and shown in Fig. 2 fall within the experimental error limits. Therefore, by analyzing Fig. 2, a conclusion can be drawn that the polymer matrix topology practically does not affect the percolation behavior and the percolation parameters of nanofilled systems on the basis of polyethers.

### 3.3. Temperature effect

In order to establish the influence of a temperature on the percolation behavior of nanofilled systems, the

dependences of the conductivity of a composite on the CNT content were measured at various temperatures. The corresponding experimental results are exhibited in Fig. 3. One can see that the general view of percolation curves does not change with the temperature. However, the influence of the temperature on the conductivity is substantial. For instance, for a filler content of 0.1%, the temperature growth leads to the conductivity growth by more than an order of magnitude. This fact is associated with the transition of the polymer matrix from the crystalline state into the amorphous melt, which stimulates a considerable increase in the mobility of polymer macromolecules [22].

From Fig. 3, one can see that the percolation thresholds become a little higher if the temperature increases. This effect is explained by the fact that the mobility of polymer macromolecules grows with the temperature. Nanotubes begin to move at that and, owing to strong van der Waals attraction forces, aggregate with one another. Hence, as the temperature grows, the aggregation degree of CNTs increases, which results in higher percolation thresholds.

### 3.4. Influence of mixing regimes

The results of conductivity researches for systems PEG-400/CNTs prepared with the help of US dispersion and mechanical mixing are exhibited in Fig. 4. One can see that the method of CNT dispersion in the oligomer and the mixing time affect both the magnitude of conductivity in the system up to the percolation threshold (it can be a result of different morphologies of aggregates that are formed) and the percolation threshold itself. The smallest values of percolation threshold were observed in the case of US dispersion for 0.5 min. The increase of the US dispersion time resulted in a gradual shift of the percolation threshold toward higher CNT concentrations. If the US dispersion period exceeded 5 min, the percolation threshold practically did not change. At the mechanical mixing, the percolation threshold was maximal and equal to 0.52%.

Hence, the changes in the percolation behavior (the percolation threshold) of the PEG-400/CNTs system and the electric conductivity in it (in the interval before the percolation threshold) depending on the mixing regime result from the features of the nanofiller structuring in the matrix. If the US dispersion is ex-

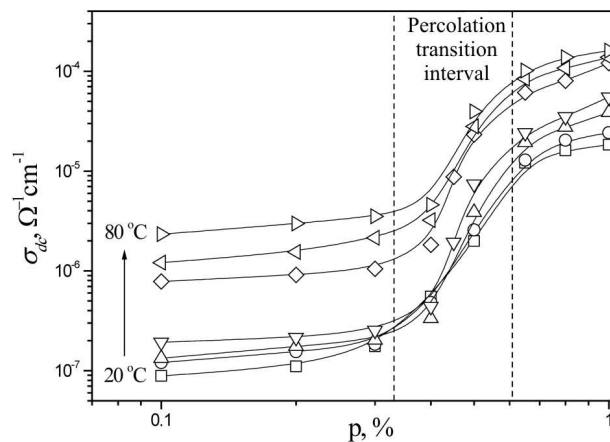


Fig. 3. Conductivity dependences on the CNT content for PEG-10000/CNTs system at various temperatures from 20 to 80°C

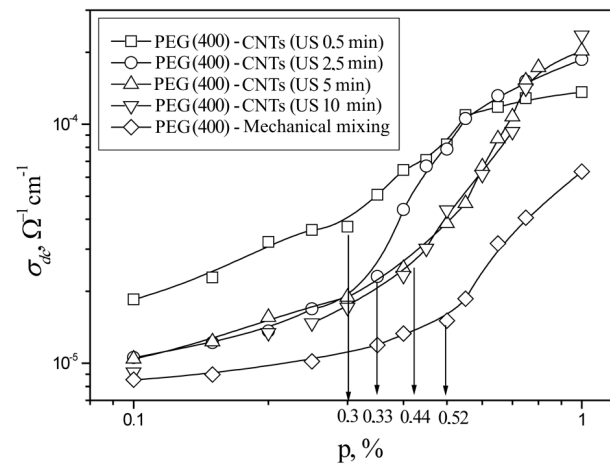
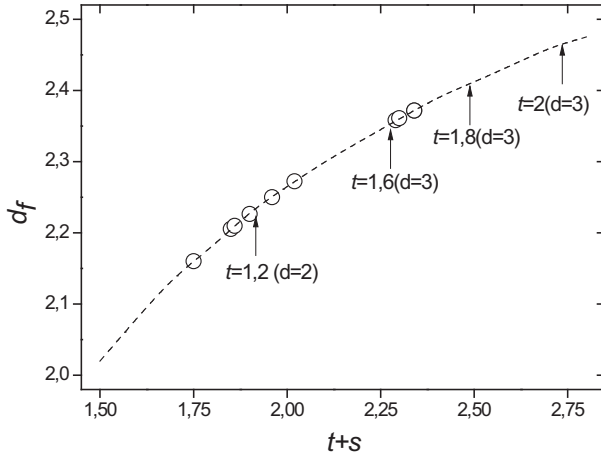
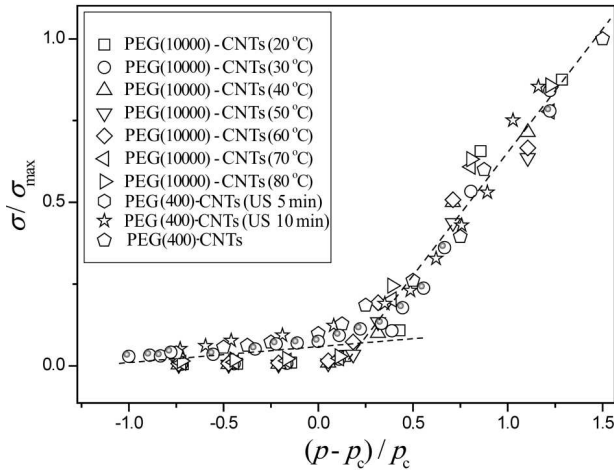


Fig. 4. Conductivity dependences on the CNT content for PEG-400/CNTs system at various mixing regimes

ecuted for 0.5 min, some CNTs become “fluffed” and form a percolation cluster. Nanotubes themselves are not destroyed at that, and a considerable amount of a filler is in the aggregated state and in the form of separate nanotubes, which explains the highest conductivity level in the interval before the percolation threshold. Longer dispersion times results in a shift of the percolation threshold toward higher CNT contents. This fact is associated with the destruction of both aggregates (and, as a consequence, with a reduction of the aspect ratio) and separate nanotubes. Some of the separate CNTs reaggregate, which diminishes the conductivity level in the system



**Fig. 5.** Dependence of the fractal dimensionality on the critical exponents of conductivity for systems PEG-400/CNTs, PPG-400/CNTs, and PEG-10000/CNTs. Arrows mark  $d_f$ -values obtained in various models of the critical percolation theory



**Fig. 6.** Scaled dependence conductivity versus the concentration for systems oligoglycol/nanotubes

before the percolation threshold. At the mechanical mixing, the filler mainly exists in the form of large aggregates. Therefore, the number of contacts between nanotubes is small, which gives rise to an increase of the percolation threshold [23].

#### 4. Analysis of Results

In order to quantitatively analyze the results obtained, let us determine the relationship between the parameters that characterize, on the one hand, the

conductivity of the system (the critical exponents  $t$  and  $s$ ) and, on the other hand, its microstructure (the fractal dimensionality of “the conducting” cluster  $d_f$ ). In work [24], it was shown that the following relation between the fractal dimensionality and the critical exponents of the order parameter,  $P \sim (p - p_c)^\beta$ , and the correlation length,  $\xi \sim (p - p_c)^{-\nu}$ , is satisfied near the percolation transition point:

$$d_f = d - \frac{\beta}{\nu}, \quad (3)$$

where  $d$  is the Euclidean space dimension. Using the scaling approach and the relationships between the critical exponents in Eq. (3) and in Eqs. (1) and (2):

$$t = \theta\nu + \beta, \quad (4)$$

$$s = 2\nu - \beta, \quad (5)$$

where  $\theta$  is the critical exponent, we obtain the expression for the fractal dimensionality of the system in terms of the critical exponents  $t$  and  $s$ :

$$d_f = d - \frac{\beta(2 + \theta)}{t + s}. \quad (6)$$

Using the theoretical values  $\beta = 0.42$  and  $\theta = 1.5$  [25, 26] and Eq. (6), we can calculate the fractal dimensionality of the conducting cluster in the researched systems.

The results of calculations are depicted in Fig. 5. One can see that the upper values of experimental results agree with the calculations of the fractal dimensionality in the framework of the three-dimensional model of critical percolation with “dead ends”:  $t \approx 1.6$  and  $d = 3$  [27]. The lower values of experimental results are close to the results of calculations given by the two-dimensional model of critical percolation:  $t = 1.2$  and  $d = 2$ .

In Fig. 6, the concentration dependences of the composite conductivity are exhibited for all studied systems (Figs. 1–4) in the reduced coordinates  $\sigma/\sigma_{\max}$  versus  $(p - p_c)/p_c$ , where  $\sigma_{\max}$  is the corresponding composite conductivity maximum. One can see that the applied scaling allows all experimental results obtained for the conductivity to be adequately described irrespective of the specific matrix, preparation conditions, and temperature regimes.

Hence, the results of experimental researches of the electric conductivity in systems of the type oligoglycol/nanotubes show that the corresponding critical

parameters can change, by depending on various factors, such as the matrix type, the temperature, the mixing regime, and so forth. Since the process of percolation cluster formation in such systems is not statistical, the critical exponents for the conductivity can differ from their theoretical values. The application of the scaling function for the conductivity eliminates the influence of microstructural factors and allows the behavior of similar systems near the percolation threshold to be described, by using a universal dependence.

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*В.В. Клепко, Е.А. Лисенков*

#### ОСОБЛИВОСТІ ПЕРКОЛЯЦІЙНОГО ПЕРЕХОДУ В СИСТЕМАХ НА ОСНОВІ ОЛІГОГЛІКОЛІВ ТА ВУГЛЕЦЕВИХ НАНОТРУБОК

#### Резюме

Представлено результати досліджень електропровідності в системах типу олігогліколь/нанотрубки в області перколяційного переходу. Показано, що електропровідність може бути описана в рамках теорії критичної перколяції. Встановлено, що критичні параметри перколяційного переходу можуть змінюватись в залежності від різних факторів і відрізняються від передбачень статистичної теорії перколяції. Знайдено зв'язок між критичними індексами провідності та фрактальною розмірністю провідного кластера. Показано, що використання масштабної функції дозволяє описати концентраційні залежності провідності за допомогою єдиної універсальної залежності.