JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 5 No 3, 03052(6pp) (2013)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 5 № 3, 03052(6cc) (2013)

Features of Charge Transfer in the Polyethylene Glycol / Carbon Nanotubes System

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

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

(Received 17 June 2013; published online 17 October 2013)

The study of the electrical properties of the systems based on polyethylene glycol and carbon nanotubes nearby the percolation threshold is done using the method of impedance spectroscopy. It is established that the percolation threshold for these systems is 0.5% and critical index $t = 1.17$. It is discovered that non-conducting polymer film appears between separate nanotubes. The thickness of the film which is 7-8 Å and its contact resistance which is $3 \cdot 10^5$ Ohm were derived using the theoretical models. This explains the difference in conductivity of pure nanotubes and probed system after the percolation threshold.

Keywords: Percolation behavior, Polymer nanocomposites, Conductivity, Tunneling, Carbon nanotubes.

PACS numbers: 73.63.Fg, 74.50. + r

1. INTRODUCTION

Use of polymer nanocomposites is important for those fields of application where high specific values of the electrical and mechanical characteristics of materials are necessary. Carbon nanotubes (CNT) dispersed into non-conducting polymer matrix considerably increase the electrical conduction of such nanocomposites. Electrical conduction of a composite significantly depends on the content of nanotubes, morphology, conducting percolation grid and number of contacts between CNT. Other factors such as the size, geometric shape and hardness of electrically conducting nanofillers, their distribution, properties of a polymer matrix, and methods of nanocomposite preparation also influence the electrical conduction and percolation process [1-6]. At a certain content of nanotubes due to the formation of percolation grid of CNT, non-conducting polymer matrix starts to conduct an electrical current. Such process is called the percolation one and critical concentration of filler – the percolation threshold.

However, formation of a percolation grid of nanotubes does not imply a high electrical conduction of the system due to the existence of contact resistance, i.e. resistance which appears in the point of contact of two CNT. For the study and description of the contact resistance phenomenon for the systems containing CNT, the authors have performed many investigations. According to the work [7], theoretical calculations have shown that contact resistance between nanotubes is varied in the range from 100 kOhm to 3.4 MOhm and strongly depends on the atomic structure of contact areas and structural relaxation of nanotubes. Describing theoretically the experimental results obtained by other researchers, the authors of [8] have established that contact resistance between CNT in nanocomposites is about 10^{13} Ohm. They have also suggested that such high resistance appears due to the tunnel mechanism of charge transfer between nanotubes which form percolation cluster. The authors of [9] relying on own experimental data have derived a simple relation between electrical conduction of nanocomposite, which can be experimentally defined, and content of filler for the concentration range higher than the percolation one. Using the given relation one can calculate the contact resistance between nanotubes inside polymer matrix which cannot be directly measured through the influence of complex electrical conduction of the system.

Contact resistance can appear with the formation of non-conducting polymer film between points of contact between two nanotubes due to their wetting by polymer. Formation of such non-conducting polymer layer was suggested by the authors of [10] when describing the electrical properties of the polyamide/CNT system. Polymer film which covers nanotubes leads to the decrease in the system conduction, and charges between CNT move by the tunneling mechanism [11]. Thus, contact resistance in percolation systems is one of the determining factors of high electrical conduction; therefore, its study is very topical. The given work is devoted to the investigation of the features of charge transfer and contact resistance of model nanofilled systems based on polyethylene glycol (PEG) and CNT.

2. EXPERIMENTAL PART

2.1 Description of the investigation materials

Nanocomposites based on PEG and CNT were used for the investigations.

PEG $M_w = 400$ of the Aldrich Corp. production was chosen by polymer matrix. Multilayer CNT of the “Spetsmash” production (Ukraine) are manufactured by the chemical vapor deposition (CVD) method at the content of mineral impurities of 0.1%. Specific surface is equal to 190 m^2/g, external diameter – 20 nm, length – 5-10 μm [12]. Conductivity σ of pressed CNT (at the pressure of 15 TPa) along the contraction axis is equal to 10 S/cm.

Before use PEG was deprived of water by heating in vacuum during 2-6 hours at 80-100 °C and the residual pressure of 300 Pa. Nanocomposites were produced by the method of supersonic mixing at normal conditions using ultrasonic disperser UZN 22/44. Content of filler was equal to 0.1-1.5 mass% (% below).

---

[*] ealisenkov@mail.ru

2.2 Investigation techniques

Study of the electrical and dielectric properties was carried out using the method of impedance spectroscopy realized on the basis of impedance meter Z-2000 (Russia). Sample was placed between cell electrodes, and its real (Z') and imaginary (Z'') parts of the impedance were measured. Electrical conduction at the direct current $\sigma_{dc} = d/SR_{dc}$, where S is the sample area; d is the sample thickness, was defined from the dependences of complex impedance using the technique described in [13]. Measurements were performed at room temperature in the frequency range of 1 Hz-2 MHz. Constant gap between electrodes was equal to 0.11 mm.

3. RESULTS AND DISCUSSION

Polymer systems filled with CNT which have properties of the electrical conduction due to flexibility and nanosizes of nanotubes are characterized by very low critical percolation concentration (percolation threshold). Dielectric/conductor transition is partly described by the percolation theory which is usually used for the establishment of relationships between microstructure of the given systems and their physical properties [14-16]. In accordance with the percolation theory, in systems after percolation threshold the relation between conduction and content of conducting nanofiller is described by the following scaling law [15]:

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

where σ is the system conduction; p is the weight fraction of conducting nanofiller; p_c is the critical weight fraction of nanofiller at the percolation transition (percolation threshold); t is the exponent, critical conduction index which mainly depends on the topological dimension of the system and does not depend on the structure of particles, which form clusters, and on their interaction.

On the other hand, system conduction before percolation threshold can be described by another scaling law which is written as [16]

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

where s is the critical index.

In Fig. 1 we present the dependence of the electrical conduction at direct current on the content of filler for the studied PEG/CNT systems.

Stepwise change in the conduction connected with the percolation process is observed in the concentration range of 0.4-0.7%. At the CNT content of 0.8% electrical conduction of the system is more than one order of magnitude higher than the conduction before percolation threshold.

Applying the least squares method and equation (1) for the description of the experimental data (Fig. 1), we have defined the value of the percolation threshold p_c and critical index t which characterizes the structural organization of nanofiller in composite and structure of clusters. Percolation threshold (p_c) for PEG/CNT system is 0.5% and $t = 1.17 \pm 0.08$ that indicates the formation of three-dimensional spatial percolation grid of nanotube clusters [14]. Low value of the percolation threshold for the given system is explained by high anisotropy of CNT shape (length/diameter ratio is about 100-200) [17].

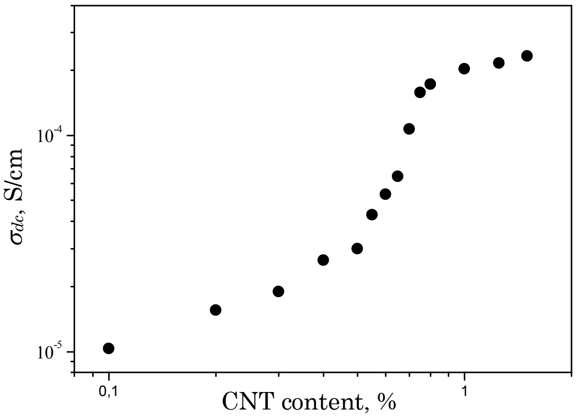

Fig. 1 – Dependence of the electrical conduction at direct current of PEG/CNT system on the content of nanotubes at $T = 293$ K

Value of the critical index t is significantly lower than the theoretical value $t \approx 2$. According to [14], value $t \approx 2$ provides the statistical distribution of conducting particles in dielectric medium. Such low values of t are very close to the values obtained for polyepokside/CNT ($t = 1.2$) [18] and polypropylene glycol/CNT ($t = 1.43$) [6] systems. In our case, low value of the critical index t does not imply the decrease in the system dimension, and, obviously, is explained by the processes of CNT aggregation after preparation of the given systems. To our opinion, formation of conducting grid due to strong attraction (aggregation) between individual CNT is not a statistical percolation process which provides uniform distribution of nanofiller particles.

In accordance with the percolation theory, by using the experimental data for electrical conduction before percolation threshold and equation (2), one can define the critical index s. The value of $s = 0.63 \pm 0.07$ was obtained by the least-squares method. The value of s is very close to that obtained for the polypropylene glycol/CNT systems [6]. According to [14], s characterizes the average number of CNT in any cluster. From this comparison one can conclude that processes of the percolation cluster formation in systems based on polyethers of different topology, but the same molecular mass, have similar behavior.

After reaching percolation threshold, system conduction increases to the value of $2 \cdot 10^{-4}$ S/cm (0.8% of CNT) and is not almost changed with further increase in the CNT content. However, reached conduction of the nanocomposite is much lower than conduction of pure CNT ($\sigma_{CNT} = 10$ S/cm). Such difference in the conductions is explained by the fact that nanotubes dispersed into a polymer matrix do not form direct contacts between each other; a thin polymer film is formed due to wetting between neighboring CNT that leads to the decrease in conduction. In the case, when nanotubes are separated by a polymer film and there are no direct contacts between them, charge transfer can occur according to two mechanisms: hopping mechanism and tunneling mechanism. The first one consists in the electron jumps from one nanotube to another neighboring and is similar to thermal electron emission. Such mechanism takes place only at the thickness of polymer film between CNT of about some nanometers and is realized if electrons have considerable kinetic energy, i.e. at relatively high temperatures. When thickness of non-conducting film between CNT is less than 5 nm, then according to the laws of quantum mechanics there is a non-zero probability to reveal an electron on the other side of the film, therefore, electrons can pass this non-conducting barrier even without sufficient energy. Such mechanism of the charge transfer is called the tunneling.

At uniform distribution of a filler in non-conducting polymer matrix, conduction at the given temperature is realized mainly by the tunneling mechanism, and the potential barrier width is determined as $\omega \propto p^{-1/3}$. The authors of [19] have proposed the identification method of tunneling mechanism in filled systems. According to this approach, at tunneling electrical conduction of the system after percolation threshold versus the filler content is changed as

$$\log \sigma \propto p^{-1/3} . \tag{3}$$

In Fig. 2 we illustrate the dependence of the conduction of the studied systems on the CNT content in coordinates of equation (3). It is seen from Fig. 2 that experimental data is described in the framework of the dependence (3) that implies the presence of tunneling mechanism in the given systems.

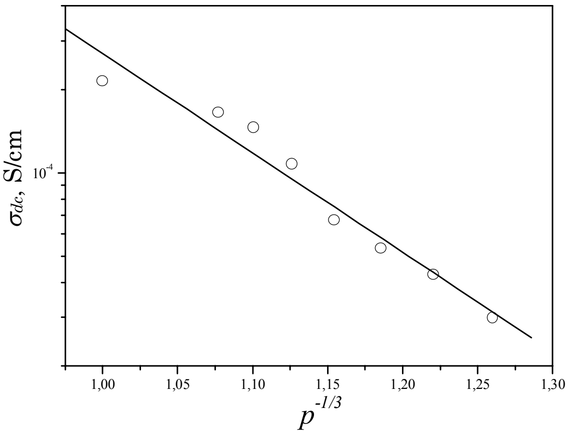

Fig. 2 – Dependence of the electrical conduction at direct current (in logarithmic scale) on $p^{-1/3}$ for PEG/CNT system. Straight line is the linear approximation

For the description of the charge transfer process in accordance with tunneling mechanism and determination of the thickness of non-conducting film between CNT, the following model was proposed in the works [20, 21]. Nanocomposite system is represented in the form of the set of layers. Resistance of a single layer is the set of resistors in parallel. Each resistor has some resistance which is denoted $R_{contact}$ and represents a contact resistance between CNT and polymer matrix in the direction along some segment of nanotube between two contacts as it is schematically shown in Fig. 3.

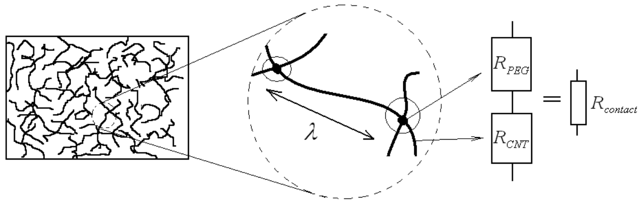

Fig. 3 – Schematic representation of the model from work [20]

Thickness λ of a single layer is equal to the distance between contacts (see Fig. 3). The studied sample of the thickness e is the set of e/λ layers. Electrical resistance of the system is defined as

$$R = \frac{e}{\lambda}\frac{R_{contact}}{N} , \tag{4}$$

where N is the number of contacts in one layer. We accept that area of the investigated sample is equal to S, then electrical conduction is determined by the following formula:

$$\sigma = \frac{1}{R}\frac{e}{S} = \frac{\lambda}{e}\frac{n\lambda S}{R_{contact}}\frac{e}{S} = \frac{n\lambda^2}{R_{contact}} , \tag{5}$$

where n is the number of contacts in the volume unit. For three-dimensional random grid of fibers, n will be defined as [20, 21]

$$n = 4\varphi^2 / \pi d^3 , \tag{6}$$

where φ is the volume fraction of nanotubes in the system; d is their diameter.

For three-dimensional random grid of fibers, distance λ between contacts is determined as [20, 21]

$$\lambda = \pi d / 8\varphi . \tag{7}$$

Finally, electrical conduction of the nanofilled system will be expressed by the formula

$$\sigma = \frac{\pi}{16d}\frac{1}{R_{contact}} . \tag{8}$$

Two assumptions were done in the given model: in each layer grid of nanotubes is three-dimensional and all contacts and channels participate in the conduction (aggregation and abrupted channels are not taken into account); all resistors have the same resistance (distribution over CNT radiuses and change in the thickness of polymer layer are not taken into consideration) [20].

Contact resistance is the sum of R_{PEG} – resistance of polyethylene glycol film of the thickness s and surface area which is equal to the area of contact between two nanotubes, and R_{CNT} – resistance of the region of CNT between two contacts,

$$R_{contact} = R_{PEG} + R_{CNT} . \tag{9}$$

Complexity of the contact surface is not also taken into account in the model, as well as the assumption that area of the contact surface is proportional to the square of diameter of a nanotube $S_{contact} = d^2$. This means that all nanotubes intersect with each other at the right angle and also thickness of polymer film along the CNT region remains constant. Then

$$R_{PEG} = \rho_{tunnel} / d^2 , \tag{10}$$

where ρ_{tunnel} is the resistance at tunneling for polymer film.

Resistance of the CNT region between two contacts is determined as

$$R_{CNT}=\frac{1}{\sigma_{CNT}}\frac{4\lambda}{\pi d^2}=\frac{1}{\sigma_{CNT}}\frac{1}{2d\varphi}\,. \qquad (11)$$

Taking into account equations (8)-(11), one can derive the expression for electrical conduction of composite

$$\sigma=\frac{\pi}{16d}\frac{1}{\rho_{tunnel}/d^2+1/2d\varphi\sigma_{CNT}}=\frac{\pi d\varphi\sigma_{CNT}}{16\varphi\rho_{tunnel}\sigma_{CNT}+8d}\,. \qquad (12)$$

To find ρ_{tunnel}, the authors of [22, 23] have used the models, whose basis are the quantum-mechanical ideas.

For systems, to which small stresses are applied, tunneling resistance can be calculated by Holm model [22]

$$\rho_{tunnel}=\frac{10^{-22}}{2}\frac{X^2}{1+XY}e^{XY}\,, \qquad (13)$$

where $X=7{,}32\cdot 10^5\left(s-\frac{7{,}2}{\psi_0}\right)$; $Y=1{,}265\cdot 10^{-6}\left(\psi_0-\frac{10}{s\varepsilon_{PEG}}\right)$; s is the thickness of polymer film between CNT; ψ_0 is the working function for CNT; ε_{PEG} is the permittivity of polymer.

Simmons in [23] has updated the Holm model by the determination of the real potential shape in contrast to the Holm potential of parabolic shape and obtained the following expression for the calculation of the current density J at tunneling:

$$J=\frac{6{,}2\cdot 10^{10}}{s^2}\left\{\psi\cdot\exp\left(-1{,}025s\psi^{\frac{1}{2}}\right)-\right.$$
$$\left.-(\psi+U_i)\cdot\exp\left(-1{,}025s(\psi+U_i)^{\frac{1}{2}}\right)\right\}, \qquad (14)$$

where $\psi=\psi_0-\left(\frac{U_i}{2s}\right)(s_1+s_2)-\frac{5{,}75}{\varepsilon_{PEG}\Delta s}\ln\left(\frac{s_2(s-s_1)}{s_1(s-s_2)}\right)$,

$$\Delta s=s_2-s_1\,, \qquad (15)$$

$$s_1=\frac{6}{\psi_0\varepsilon_{PEG}}\,, \qquad (16)$$

$$s_2=s\left(1-\frac{46}{3s\psi_0\varepsilon_{PEG}+20-2U_is\varepsilon_{PEG}}\right)+\frac{6}{\psi_0\varepsilon_{PEG}} \qquad (17)$$

where s is the thickness of tunneling layer. Voltage U_i is determined by taking into account one transfer of the elementary electron charge e through the potential barrier of the thickness s, surface area $S_{contact}$ and electrical capacity C:

$$U_i=\frac{e}{C}=\frac{es}{\varepsilon_0\varepsilon_{PEG}S_{contact}}\,. \qquad (18)$$

Having determined the parameters of equations (13)-(18), one can obtain formula for the calculation of tunneling resistance

$$\rho_{tunnel}=U_i/J\,. \qquad (19)$$

The following parameters were used for calculation of tunneling resistance by using both models: $\varepsilon_{PEG}\approx 11$, $d = 40$ nm, $\psi_0\approx 4.95$ [24].

To determine the thickness of tunneling layer the authors of [20, 21] have assumed that thickness of polymer film between CNT depends on the volume content of nanotubes by the following power low:

$$s=K\varphi^{\beta}\,, \qquad (20)$$

where K and β are the adjustable parameters.

In Fig. 4 we present the dependence of the thickness of non-conducting polymer film between nanotubes on the CNT content. As seen from Fig. 4, film thickness is decreased with the increase in the CNT concentration in the system. The values of thickness obtained by using the Simmons model are less than the values calculated according to the Holm model. Difference in thickness is less than 1 Å. This difference is explained by the fact that both models use different shapes of potentials for the calculations. However, in spite of the distinctions, tendency of the dependence of the polymer film thickness on the content of nanotubes remains similar. The values of the thickness of non-conducting film for PEG/CNT system are equal to 7-8 Å. Based on the data of [25], the persistent length of PEG macromolecule is 3,8 Å and the value of statistical segment – 7,6 Å. Thus, distance between two nanotubes dispersed into PEG matrix is equal to one statistical segment of PEG macromolecule.

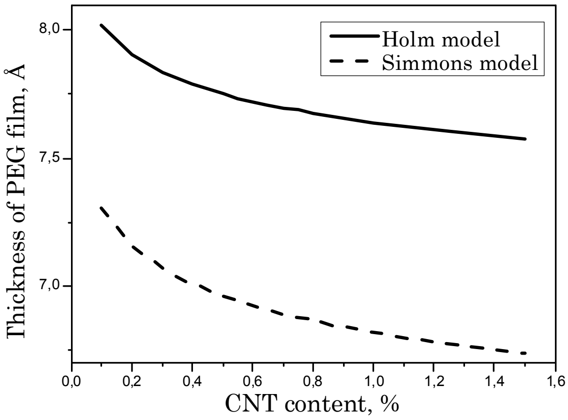

Fig. 4 – Dependence of the thickness of polymer film between nanotubes on the CNT content for the system based on PEG

The values of the film thickness of 7-8 Å are much less than the values obtained in the works [2] (≈ 18 Å) and [20] (12-20 Å). Such difference is explained by the fact that nanotubes were dispersed into different polymer matrices with different values of viscosity, density, and surface tension coefficient that leads to different wetting of CNT by polymers.

For determination of the value of contact resistance between nanotubes in the PEG/CNT system one can use the model proposed in [9]. The given model describes the electrical properties of uniformly dispersed stationary solid particles of cylindrical shape. While connecting, these particles form a grid of n parallel channels which pass through the sample. Channels, in turn, consist of m bars and m contacts. A number of parallel channels is defined by the following equation:

$$n=\frac{\rho_{matrix}\cdot\varphi}{\rho_{all}}\cdot\frac{V_{sample}}{m\cdot V_{one}}\,, \qquad (21)$$

where V_{sample} is the sample volume; V_{one} is the particle volume; φ is the weight fraction of CNT in the system; ρ_{matrix} and ρ_{all} are the densities of polymer matrix and particle, respectively. In accordance with [9], particle-to-matrix density ratio for polymer/CNT system is equal to 2 : 1. A number of particles and contacts between them in one channel is determined as

$$m = \frac{t}{l} \cdot \frac{1}{\varphi^{x}}, \tag{22}$$

where t is the sample thickness; l is the particle length. Expression (22) describes the case when all particles, which experimentally form abrupted channels (separate clusters), are theoretically built into percolation (continuous) clusters and make them longer and more ramified. Probability of the formation of separate clusters is high for low concentrations of filler, therefore, t increases with the decrease in the CNT content in the system. By using equations for parallel (eq. (21)) and series (eq. (22)) connection of particles, which have their own resistance, the authors of the work [9] have proposed the following expression:

$$\sigma \approx \frac{l}{2\pi r^{2}} \cdot \frac{\varphi^{2x+1}}{R + R_{C}}, \tag{23}$$

where r and R are the radius and resistance of separate particle, respectively; R_C is the contact resistance between two particles.

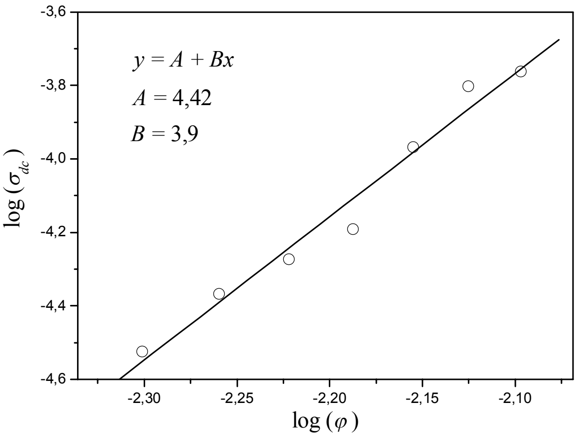

Fig. 5 – Dependence of the logarithm of electrical conduction on the logarithm of weight fraction of nanotubes in PEG/CNT system. Straight line is the linear approximation whose results are represented in the figure

Having built the dependence of log(σ) on log(φ) after percolation threshold, one can theoretically calculate the values of contact resistance R_C. In Fig. 5 we show the dependence of the electrical conduction of the system on the CNT concentration in coordinates of equation (23). Having defined from Fig. 5 such parameters of equation (23) as $2x + 1 = 3.9$ and taking into account that $r = 10$ nm, $l = 5$ μm, $R = 0.1$ Ohm [12], one can calculate R_C. For PEG/CNT system R_C is equal to $3 \cdot 10^5$ Ohm. The obtained value of contact resistance belongs to the resistance range theoretically calculated in the work [7]. Also, the value of contact resistance found in the given work correlates well with the data obtained in the work [26] for polycarbonate/CNT system ($R_C = 10^5$ Ohm) and work [9] for polyepoxide/CNT system ($R_C = 10^5$ Ohm).

However, the model proposed in the work [9] has a number of restrictions: the value of particle agglomeration, degree of wetting of CNT and their real shape are not taken into account. Therefore, the value of R_C for PEG/CNT system requires more precise definitions. Updating of the values of contact resistance and polymer film thickness between nanotubes will be the subject of our further publications.

4. CONCLUSIONS

As a result of the performed investigations, the percolation properties of the systems based on PEG and CNT were studied and analyzed using the percolation theory and scaling approach. Percolation threshold of the given systems which is equal to 0.5% was determined in the issue of the investigation of conduction. Using the scaling approach, critical index $t = 1.17 \pm 0.08$ was defined that implies the formation of three-dimensional spatial percolation grid of nanotubes clusters and considerable aggregation of CNT after preparation of the sample. It is established that non-conducting polymer film is formed in PEG/CNT systems due to wetting. As a result, besides charge transport through direct contacts between nanotubes, an additional tunneling mechanism is realized. Using the Holm and Simmons theoretical models, thickness of polymer film between CNT is calculated. Distance between two nanotubes dispersed into PEG matrix is 7-8 Å and correponds to one statistical segment of PEG macromolecule. Using the theoretical model, the value of contact resistance between nanotubes is calculated. Contact resistance of PEG/CNT system is $3 \cdot 10^5$ Ohm and larger than PEG resistance. Presence of contact resistance and its relatively large value explains the fact that conduction of PEG/CNT system after percolation threshold is significantly lower than the conduction of nanotubes in a free state.

REFERENCES

1. R. Strumpler, J. Glatz-Reichenbach, *J. Electroceram.* **3** No4, 329 (1999).
2. Q. Li, Q. Xue, L. Hao, X. Gao, Q. Zheng, *Compos. Sci. Techn.* **68**, 2290 (2008).
3. Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotisa, *Prog. Polym. Sci.* **35**, 357 (2010).
4. N.I. Lebovka, E.A. Lysenkov, A.I. Goncharuk, Yu.P. Gomza, V.V. Klepko, Yu.P. Boiko, *J. Compos. Mater.* **45**, 2555 (2011).
5. E.A. Lysenkov, N.I. Lebovka, Y.V. Yakovlev, V.V. Klepko, N.S. Pivovarova, *Compos. Sci. Techn.* **72**, 1191 (2012).
6. E.A. Lysenkov, Y.V. Yakovlev, V.V. Klepko, *Ukr. Phys. J.* **58** No4, 378 (2013).
7. A. Buldum, P.L. Jian, *Phys. Rev. B* **63**, 161403 (2001).
8. M. Foygel, R.D. Morris, D. Anez, S. French, V.L. Sobolev, *Phys. Rev. B* **71**, 104201 (2005).
9. J.Z. Kovacs, B.S. Velagala, K. Schulte, W. Bauhofer, *Compos. Sci. Techn.* **67**, 922 (2007).
10. E. Logakis, C. Pandis, V. Peoglos, P. Pissis, et al., *J. Polym. Sci. B: Polym. Phys.* **47**, 764 (2009).
11. B.E. Kilbride, J.N. Coleman, J. Fraysse, *J. Appl. Phys.* **92**,

4024 (2002).

12. E.A. Lysenkov, Yu.P. Gomza, V.V. Klepko, Yu.A. Kunytskiy, *FKhTT* **11** No2, 361 (2010).
13. A. Kyritsis, P. Pissis, J. Grammatikakis, *J. Polymer. Sci.: Part B: Polym. Phys.* **33**, 1737 (1995).
14. D. Stauffer, A. Aharony, *Introduction to percolation theory* (London: Taylor and Francis: 1994).
15. S. Kirkpatrick, *Phys. Rev. Lett.* **27**, 1722 (1971).
16. I. Webman, J. Jortner, M.H. Cohen, *Phys. Rev. B* **16**, 2593 (1977).
17. J. Zhang, M. Mine, D. Zhu, M. Matsuo, *Carbon* **47**, 1311 (2009).
18. J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, *Polymer* **44**, 5893 (2003).
19. M.T. Connor, S. Roy, T.A. Ezquerra, F.J. Balta Calleja, *Phys. Rev. B* **57**, 2286 (1998).
20. A. Allaoui, S.V. Hoa, M.D. Pugh, *Compos. Sci. Techn.* **68**, 410 (2008).
21. M. Mohiuddin, S.V. Hoa, *Compos. Sci. Techn.* **79**, 42 (2013).
22. R. Holm, *Electric contacts: theory and application* (New York: Springer-Verlag: 1967).
23. J.G. Simmons, *J. Appl. Phys.* **34**, 1793 (1963).
24. M. Shiraishi, M. Ata, *Carbon* **39**, 1913 (2001).
25. H. Lee, R.M. Venable, A.D. MacKerell, R.W. Pastor, *Biophys. J.* **95**, 1590 (2008).
26. P. Poetschke, S.M. Dudkin, I. Alig, *Polymer* **44**, 5023 (2003).