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**ELECTRIC FIELD EFFECT ON THE PERCOLATIVE BEHAVIOR OF SYSTEMS BASED ON POLYETHYLENE GLYCOL AND CARBON NANOTUBES**PACS 61.46.+w, 61.41.+e,  
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*Thermophysical properties and the percolative behavior of systems based on polyethylene glycol and carbon nanotubes formed under normal conditions and the action of a dc electric field have been studied, by using the differential scanning calorimetry and impedance spectroscopy methods. It is shown that the electric field substantially affect the behavior of nanotubes dispersed in the polymer matrix. Nanotubes are supposed to execute three basic types of motion (rotation, translation, and migration) under the field action, and the corresponding characteristic times are calculated. It is found that the percolation threshold decreases from 0.42% to 0.1% if nanofilled systems are formed in the electric field, which testifies to a substantial alignment of nanotubes in the polymer matrix.*

*Keywords:* nanocomposite, percolative behavior, carbon nanotubes, polyethylene glycol, dc electric field.

**1. Introduction**

Polymeric nanocomposite systems filled with carbon nanotubes (CNTs) have attracted a considerable attention of scientists for last two decades. This fact is associated with unique characteristics of CNTs such as their high mechanical strength [1], low density [2], and high electron [3, 4] and thermal [5] conductivities. This specific combination of properties allows CNT-based nanocomposites to be used in nanoelectronic and optoelectronic devices [6] and nanosensors [7], as electroconductive materials and coatings with improved and controllable operational parameters [8].

There are plenty of methods aimed at a modification of polymeric nanocomposites filled with CNTs [9–11]. One of the most promising of them is the introduction of inorganic fillers, for example, montmorillonite [10] or laponite [8, 11], into a nanocompos-

ite composition. However, this method does not provide a sufficient contact between CNTs. Owing to the one-dimensionality inherent to nanotubes, CNT-filled nanocomposites are characterized by anisotropic mechanic, electric, magnetic, and optical properties. In general, the majority of their characteristics are much better if they are measured along the nanotube axis than perpendicularly to it. Therefore, the nanotube alignment in a polymer matrix is one of the ways to improve and to modify polymeric nanocomposites filled with CNTs.

The main methods to create an oriented state of CNTs can be divided into two basic groups: the orientation of nanotubes during the creation of a nanocomposite and the growth of oriented nanotubes. The most widespread methods include the CNT alignment under the action of external physical fields, a considerable shear deformation, a powerful stationary liquid flow, a strong flow of bubbles, and the creation of aligned nanotubes in Langmuir–Blodgett films [12].

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It is known that the tensor of static dielectric susceptibility of CNTs is extremely anisotropic. Therefore, the dielectric susceptibility along the tube axis is much higher than that perpendicularly to this axis [13]. An applied electric field generates large dipole moments that align CNTs along the electric field lines, which results in the appearance of the oriented state of a nanocomposite. The authors of work [14] obtained this effect in a nanocomposite filled with single-walled CNTs by placing the specimen between two gold electrodes separated by a distance of 25  $\mu\text{m}$  and applying the ac electric field with a frequency of 5 MHz and a voltage of 10 V. The authors of work [15] developed an electrophoretic deposition method to align single-walled CNTs in a dc electric field. Nanotubes were dispersed in a mixture of solvents on the basis of tetrahydrofuran and tetraoctylammonium bromide. If the applied voltage exceeded 100 V, nanotubes, which were covered with quaternary ammonium, assembled into stretched bundles oriented normally to the electrode surfaces. Such a technique was successfully applied in order to align CNTs dispersed in a polymer matrix, by improving the functional characteristics of nanocomposites [16].

Another approach used to orient CNTs in the electric field is based on dielectrophoresis, the phenomenon of the motion of a microparticle in a non-uniform electric field stimulated by the interaction between the induced dipole moment of the microparticle and the external electric field [17]. However, despite a considerable number of publications, there is no unique universal method to create the aligned state in nanocomposites. Moreover, the mechanism of action of the electric field on the orientation of nanotubes in the polymer matrix has not been studied in detail. Therefore, this work is aimed at finding the physical regularities in the influence of a dc electric field (dcEF) on the structural features and the percolation behavior of nanocomposites on the basis of polyethylene glycol and carbon nanotubes.

## 2. Experimental Part

In our researches, we used model systems on the basis of polyethylene glycol and carbon nanotubes. Polyethylene glycol (Aldrich) with  $M_w = 1000$  (PEG-1000) was selected as a polymer matrix ( $T_m = 34$  °C; in the molten state,  $\varepsilon = 11$  and  $\eta = 17$  Pa·s). Multi-walled CNTs (JSC Spetsmash, Ukraine) were fabri-

cated with the use of the chemical vapor deposition (CVD) method. The content of mineral impurities was 0.1%, the specific surface 190  $\text{m}^2/\text{g}$ , the outer diameter 20 nm, and the length 5–10  $\mu\text{m}$  [18]. The specific conductance  $\sigma$  of pressed CNTs (at a pressure of 15 TPa) was 10 S/cm along the compression axis. Before the application, PEG was dehydrated by heating it in vacuum for 2–6 h at a temperature of 80–100 °C and a residual pressure of 300 Pa.

To study the influence of the electric field on the percolation behavior, two batches of nanocomposites were fabricated. Specimens in the first batch were produced, by using the method of ultrasonic mixing of components with an ultrasonic disperser UZN 22/44 at 60 °C. Then the mixture was cooled down under normal conditions. The CNT content was varied within the limits 0.2–1 wt.% (below marked as %). Specimens in the second batch, after the mixing in the molten state, were formed in a dc electric field. The specimens were placed between two electrodes separated by a distance of 3 cm; the voltage difference applied to the electrodes equaled about 30 kV. The corresponding strength of the dcEF was about 1 MV/m. Nanocomposites were held under the dcEF action for 1 h and then cooled down in the electric field.

The electric properties of nanocomposites were studied with the help of the impedance spectroscopy method on an impedancemeter Z-2000 (Russia). A specimen was placed between the cell electrodes, and the real,  $Z'$ , and imaginary,  $Z''$ , parts of its impedance were measured. Following the technique described in work [19], the dc conductivity was determined from the complex impedance dependence, by using the formula  $\sigma_{dc} = \frac{d}{SR_{dc}}$ , where  $S$  is the specimen area, and  $d$  its thickness. The measurements were carried out at room temperature in the frequency range from 1 Hz to 2 MHz. The constant gap between the electrodes was 0.11 mm. The electric parameters of nanocomposites formed in the dcEF were measured in the direction of the electric field during the formation of a specimen.

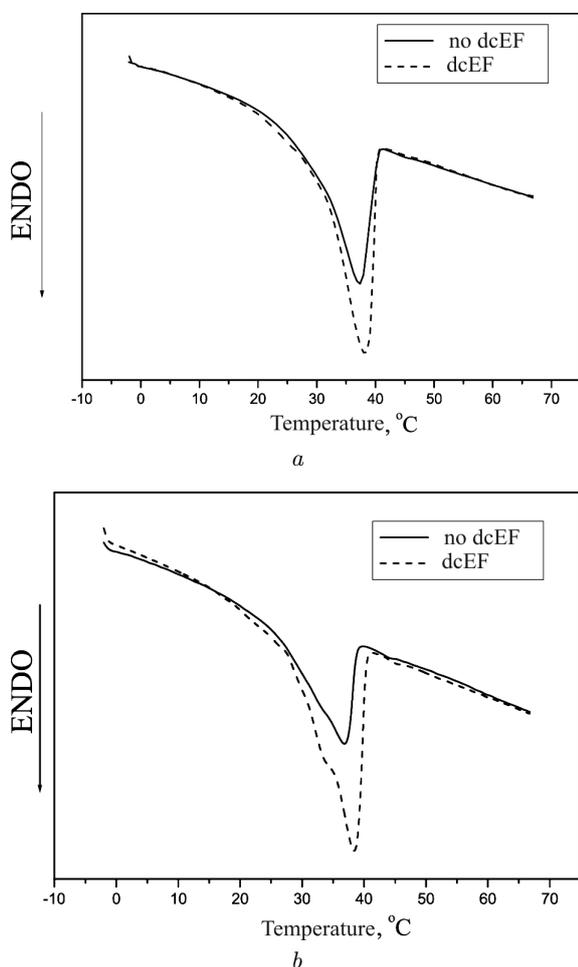
Thermophysical researches were performed with the use of the modulated differential scanning calorimetry (DSC) method on a Perkin Elmer DSC-2 installation (Germany) modernized and equipped with the software IFA Gmb (Ulm). The measurements were carried out in a dry air environment in the temperature range from –5 to 65 °C. The heating rate was 2 °C/min.

### 3. Results and Their Discussion

In order to elucidate the influence of the electric field on the structural features and the percolation behavior of polymeric systems filled with carbon nanotubes, it is necessary to study firstly its influence on both the polymer matrix and nanotubes. We will consider those issues separately.

#### 3.1. Influence of an electric field on the polymer matrix

In order to study the influence of a dc electric field on the thermal characteristics and the degree of crystallinity in the polymer matrix, specimens formed both under the dcEF action and without it were re-



**Fig. 1.** DSC thermograms for PEG-1000 (a) and the systems on the basis of PEG + 0.8% CNTs (b) formed under the action and in the absence of dcEF

searched using the DSC method. In Fig. 1, the results of DSC researches in the temperature interval from  $-5$  to  $65$  °C are shown. This interval was selected as the most informative. Moreover, in it, the melting of the polymer takes place. In Table 1, some thermal parameters of the systems obtained are quoted.

By analyzing Fig. 1 and Table 1, one can see that the electric field substantially affects the thermal characteristics of nanofilled polymeric systems. In particular, specimens formed in the electric field demonstrate an increase in the melting temperature and the melting enthalpy for all CNT concentrations in the composite. This fact testifies to the emergence of crystalline regions that are characterized by larger dimensions in comparison with crystallites in the specimens formed without the field action. The melting of larger crystallites consumes more energy; therefore,  $T_m$  grows.

Using the obtained thermophysical data, we calculated the crystallinity degree in nanocomposites on the basis of PEG-1000 using the formula [20]

$$\chi_c = \frac{\Delta H_m}{\Delta H_{m,c}}, \quad (1)$$

where  $\Delta H_m$  is the experimental value of melting enthalpy, and  $\Delta H_{m,c}$  the melting enthalpy for the 100% crystalline polymer (for poly(ethyl oxide),  $\Delta H_{m,c} = 165.5$  J/g [21]).

The crystallinity degrees calculated by formula (1) for the examined systems are quoted in Table 1. During the formation of the system under the action of dcEF, the degree of its crystallinity increases. Those data correlate well with the results of work [22], in which the authors observed a compression of the electric dipole structure in polymeric systems under the action of external dcEFs 0.5–1 kV/m in strength. In works [22, 23], the growth of domains in the polymer volume under the action of dcEFs 0.03 kV/m in strength was also registered and explained by the effects of coalescence under the field action. For PEG with a molecular mass of 8000, it was found that the application of a dcEF gives rise to the formation of a structure with a pearl-chain-like morphology [23].

Hence, the formation of nanofilled polymeric systems in a dcEF results in a higher ordering of macromolecules at the melt–crystal transition. This influence of dcEF on the polymer matrix can be explained as follows. If a polar polymer is held at a

Table 1. Thermal parameters of nanocomposites on the basis of PEG-1000

Name/parameter	$T_m$ , °C		$\Delta H_m$ , J/g		$\chi$ , %	
	no dcEF	dcEF	no dcEF	dcEF	no dcEF	dcEF
PEG	37.3	38.1	124.8	134.5	75.4	81.3
PEG + 0.2% CNTs	36.2	37.4	121.1	133.7	73.2	80.3
PEG + 0.4% CNTs	36.4	38.4	124.3	135.7	75.1	82.0
PEG + 0.6% CNTs	37.8	38.3	122.9	132.5	74.3	80.1
PEG + 0.8% CNTs	37.0	38.3	122.3	137.9	73.9	79.7
PEG + 1.0% CNTs	37.9	38.2	121.1	131.2	73.2	79.3

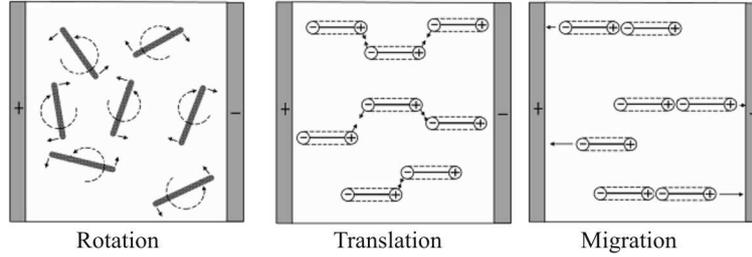
temperature above  $T_m$ , i.e. when it is annealed, the intense thermal motion violates the orientation of the polar groups of macromolecules and their relative fixation. If the intermolecular interaction becomes weaker, some sections in a macromolecule chain change their alignment by means of the self-diffusion process: the macromolecule can accept a more energy-favorable folded conformation. The electric field interferes with this process by stimulating the polarization attraction forces, which increase the cohesion energy. The polarization of a polymer occurs because the links connected in a single chain attempt to be so arranged that their dipole moments and strongly polarized bonds would be aligned in the external field direction. Hence, the influence of the electric field results in hampering the molecular conformation reconstruction and in the fixation of a forced macromolecular conformation in the polymer after the annealing. If the thermal motion becomes more intense (if the annealing is carried out at  $T > T_m$ ), the equilibrium between the numbers of coupled and uncoupled lateral groups shifts toward the increase of the latter. If polymers are annealed in the electric field, this equilibrium is also violated, but the electric field stimulates the appearance of an electric charge in the chain owing to its polarization, and this charge counteracts the chain folding. The considered conformation of chains in the initial (non-annealed) polymer does not undergo substantial modifications if the repulsion forces between separate chain sections increase and is stabilized if the thermal motion becomes less intense, when the polymer is cooled down below its melting temperature  $T_m$ . In other words, the appearance of electric forces increases the potential barrier for the link rotation and reduces the probability of macromolecule

segment transitions from one equilibrium state into the other [24].

Hence, the mechanism of electric field effect on the polymer is reduced to a deceleration of the kinetics of segment translational motion by electric forces, hampering the macromolecular conformation reconstruction, and the transition of the system into a state with the free energy minimum. As a result, the macromolecules mainly stay in a prolate conformation, which facilitates their packing into a crystalline structure.

### 3.2. Influence of electric field on the behavior of CNTs in the polymer matrix

Since the polymer matrix changes under the dcEF action owing to the alignment and the packing of polarized macromolecules, the electroconducting CNTs behave themselves in a similar way: they become oriented in the electric field. In order to confirm theoretically the existence of the aligned state of nanotubes, we may use a simple model [25], which is capable of estimating the ability of CNTs to orient in a given polymer matrix under the action of a dcEF with a certain strength. The orientation degree in the nanofilled system grows owing to the field-induced polarization of nanotubes and due to the attraction and repulsion forces between induced dipole moments [26]. However, in a nanofilled system at temperatures higher than  $T_m$ , besides the dipole interaction, there exists the intense Brownian motion. Therefore, the energy responsible for the dipole interaction has to be higher than the energy of thermal motion. For spherical inclusions, the parameter that demonstrates the energy ratio between the dipole interaction and the



**Fig. 2.** Schematic diagrams for the main types of CNT displacements in the polymer matrix [27]

thermal motion is defined as follows:

$$\lambda = \frac{\pi \varepsilon_0 \varepsilon_1 a^3 (\beta E)^2}{kT}. \quad (2)$$

Here,  $\varepsilon$  is the electric constant ( $8.85 \times 10^{12}$  F/m),  $\varepsilon_1$  the dielectric permittivity of the polymer matrix in the molten state,  $a$  inclusion's radius of inertia,  $E$  the strength of the applied electric field,  $k$  the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K), and  $T$  the absolute temperature. If the nanotube is represented in the form of a rigid cylinder, its radius of inertia, taking into account that  $R \ll L$ , can be calculated as

$$a = R_g = \sqrt{\frac{R^2}{2} + \frac{L^2}{12}} \approx \sqrt{\frac{L^2}{12}}. \quad (3)$$

If the nanofilled polymeric system becomes polarized owing to the difference between the dielectric susceptibilities of the matrix and the filler, the parameter  $\beta$  is defined as

$$\beta = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}, \quad (4)$$

where  $\varepsilon_2$  is the dielectric permittivity of CNTs ( $\varepsilon_2 \approx 10^5$ ). Since this value is much larger than the dielectric permittivity of the polymer matrix in the molten state ( $\varepsilon_1 \approx 10$ ), the parameter  $\beta \approx 1$ . According to the results of work [25], if the parameter  $\lambda$  in Eq. (2) is larger than 1, the nanotubes dispersed in a polymer matrix undergo alignment. Putting  $L = 5 \mu\text{m}$ , formula (3) can be used to calculate nanotube's radius of inertia,  $R_g = 1.4 \mu\text{m}$ . Using the result obtained for the CNT radius of inertia and taking into account that the dcEF strength was 1 MV/m, the alignment parameter  $\lambda$  can be calculated with the help of formula (4). In particular, for the examined system PEG–CNTs,  $\lambda \gg 1$ , which testifies that the energy responsible for the dipole interaction exceeds

the energy of the Brownian thermal motion and provides the nanotube alignment in the polymer matrix.

To elucidate the origin of the nanotube alignment and to determine the mechanism of processes running in the polymer–CNTs system in an external dc electric field, the authors of work [27] suggested the following model representation to be used. The nanotubes are represented in the form of rigid prolate ellipsoids with the small axis  $d$  and the large axis  $l$  that is equal to their diameter. The mass of such nanotube is determined either as the mass of all carbon atoms composing the nanotube or from the density of a graphite structure. The interaction between the nanotube and the liquid medium is described by the laws of classical dynamics. Any chemical interaction and matrix flow are absent. According to this model [27], if an external dcEF is applied to the system concerned, four basic types of CNT motion in the liquid polymer matrix take place: nanotube rotation, translation (chain formation from charged nanotubes), migration, and relaxation.

### 3.2.1. Rotational motion

According to work [28], the electric rotation moment of a nanotube,  $M_{el}$ , which depends on the strength  $E$  of the applied electric field, dipole moment  $p$ , and angle  $\varphi$  between the field lines and the tube axis is defined as

$$M_{el} = [p \times E] = 4\pi\varepsilon_0 (\alpha_{\parallel} - \alpha_{\perp})^2 \sin \varphi \cos \varphi, \quad (5)$$

where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the longitudinal and transverse dielectric susceptibilities, respectively. If we admit that the longitudinal dielectric susceptibility is much higher than the transverse one, Eq. (5) can be rewritten in the form

$$M_{el} = 2\pi\varepsilon_0 \alpha_{\parallel} E^2 \sin 2\varphi. \quad (6)$$

The longitudinal dielectric susceptibility can be expressed in terms of geometric nanotube dimensions [29]:

$$\alpha_{\parallel} = \frac{\varepsilon l^3}{24 \ln\left(\frac{2l}{d}\right) - 1}, \quad (7)$$

where  $\varepsilon$  is the dielectric permittivity of the polymer, and  $d$  and  $l$  are nanotube dimensions. On the other hand, there is a viscous friction between the nanotube and the polymer matrix, for which the rotation moment of CNTs is defined as

$$M_{\text{tr}} = -\eta k \omega, \quad (8)$$

where  $\eta$  is the viscosity of the polymer in the liquid state,  $\omega$  the angular velocity, and

$$k = \frac{\pi l^3}{3 \ln\left(\frac{l}{d}\right)} \quad (9)$$

is the coefficient of rotational friction.

The equation that includes all rotational motions of a CNT looks like  $\mathbf{M}_{\text{el}} + \mathbf{M}_{\text{tr}} = I \mathbf{a}$ , where  $I$  is the moment of inertia for a nanotube represented in the form of an ellipsoid (in this case,  $I = m(d^2 + l^2)/20$ ), and  $a$  is the angular acceleration. Adopting that  $d \ll l$  and substituting  $\omega$  by  $\dot{\varphi}$  and  $a$  by  $\ddot{\varphi}$ , we obtain a differential equation of the second order that describes the nanotube rotation dynamics as a function of nanotube parameters and the properties of the polymer matrix,

$$\frac{1}{20} m l^2 \ddot{\varphi} - \eta k \dot{\varphi} = 2\pi \varepsilon_0 \alpha_{\parallel} E^2 \sin 2\varphi. \quad (10)$$

Making some simplifications and assumptions [27], the solution of this equation can be obtained in the form

$$\varphi(t) = \arctan(\tan \varphi_0 e^{-2At}), \quad (11)$$

where  $\varphi_0$  is the initial angle, and the coefficient  $A$  is defined as follows:

$$A = \frac{2\pi \varepsilon_0 \alpha_{\parallel} E^2}{\eta k}. \quad (12)$$

The time required for the nanotube to attain the angular position  $\varphi$  when deviating from the initial angular position  $\varphi_0$  can be easily obtained from Eq. (11):

$$t(\varphi) = \frac{1}{2A} \ln \left( \frac{\tan \varphi_0}{\tan \varphi} \right). \quad (13)$$

The nanotube becomes completely aligned, when its final rotation angle  $\varphi$  equals zero. In view of this fact and the asymptotic behavior of the function under the condition  $\varphi = 0$ , the CNT rotation time can be written as

$$t_{\text{rot}} = \frac{1}{2A} \ln \left( \frac{\tan \varphi_0}{\tan \Delta} \right), \quad (14)$$

where  $\Delta$  is the infinitesimally small positive number.

### 3.2.2. Translational motion (formation of a chain from charged CNTs)

Since the polarized nanotubes are aligned along the electric field, they try to connect with one another into an electrically conductive cluster, being driven by different charges at their ends [16]. This process is provided by two factors: the electric forces and the translational motion in the viscous state caused by the force of internal friction. To determine the electric force, let us assume that the electric charge concentrating at the opposite nanotube ends can be calculated with the use of the formula for the dipole moment,

$$4\pi \varepsilon_0 \alpha E = ql. \quad (15)$$

Then, the electric force can be written as

$$F_{\text{el}} = \frac{4\pi \varepsilon_0 \alpha^2 E^2}{\varepsilon l^2 x^2}, \quad (16)$$

where  $x$  is the distance between two oppositely charged nanotube ends. Relating the electric and internal friction forces by the formula

$$F_{\text{visc}} = \eta k \dot{x}, \quad (17)$$

where  $k = \frac{3\pi l}{\ln(2l/d) - 0.3}$ , we obtain the differential equation describing the translational motion of nanotubes,

$$m\ddot{x} + \eta k \dot{x} - \frac{4\pi \varepsilon_0 \alpha^2 E^2}{\varepsilon l^2} \frac{1}{x^2} = 0. \quad (18)$$

The solution of this complicated differential equation cannot be written down in the analytical form. However, when evaluating the coefficients of this equation and taking the order of magnitude of the interparticle distance  $x(t)$  into account, we may neglect the term

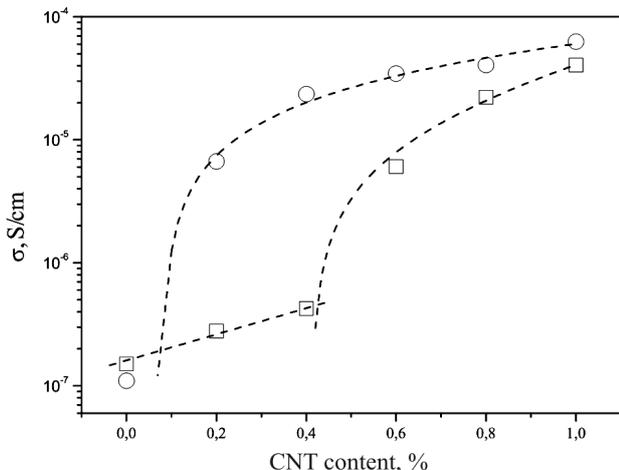


Fig. 3. Dependences of the electric conductivity on the CNT content for PEG–CNTs systems formed without (squares) and under the action (circles) of a dcEF

containing the derivative of the second order. Then, Eq. (18) reads

$$\dot{x} = \frac{C}{x^2}. \tag{19}$$

This equation of the first order can be solved analytically:

$$x(t) = \sqrt[3]{3Ct + x_0^3}, \tag{20}$$

where  $x_0$  stands for the initial distance between two oppositely charged parts of a nanotube, and  $C$  is a coefficient depending on all parameters. In order to establish the influence of various parameters on the time required for the chain of polarized CNTs to be formed, it is possible to write down the equation

$$t_{\text{trans}}(x_0) = \frac{x_0^3}{3C}. \tag{21}$$

According to the data of work [27], the value of  $x_0$  equals 245 nm.

Table 2. Characteristic times for the main types of the motion of CNTs

CNT motion type	Characteristic time, s
Rotation	312
Translation	196
Migration	11641

### 3.2.3. Migrational motion

Polarized nanotubes accumulate charges at their ends; therefore, in an applied dcEF, they are attracted to electrodes. The translational motion of nanotubes toward the electrode with a negative or positive surface charge is governed by the electrophoretic mobility of charged CNTs [30],

$$\mu = \frac{v}{E} = \frac{\varepsilon_0 \varepsilon \zeta}{\eta}, \tag{22}$$

where  $\zeta$  is the zeta-potential of CNTs in the polymer matrix,  $\varepsilon$  the dielectric permittivity, and  $v$  the nanotube motion velocity. From Eq. (14), we can calculate the time requires for a CNT to pass the distance  $\lambda$ :

$$t_{\text{migr}} = \frac{\eta \lambda}{\varepsilon_0 \varepsilon \zeta E}. \tag{23}$$

In our calculations, we adopted  $\lambda = 2$  mm (the specimen thickness) and  $\zeta = 30$  mV [31].

### 3.2.4. Relaxation of CNTs

After the action of an external dcEF terminated, the nanotubes start to relax. This process occurs owing to the Brownian motion of macromolecules in the polymer matrix. In some cases, it can destroy the formed CNT grid. The rate of relaxation of CNTs and its duration depend substantially on the temperature and the macromolecule mobility. Since the experiment was carried out at room temperature, when the polymer matrix was in the crystalline state, which considerably confined the Brownian motion, the CNT relaxation contribution to the general mechanism of alignment of nanotubes can be neglected.

In Table 2, the results of calculations for the characteristic times of the main types of CNT motion in the polymer matrix are presented in the case where a dcEF of 1 MV/m is imposed. One can see that the fastest processes are the rotational and translational CNT motions. The corresponding displacements under the action of the external field take place almost simultaneously within the first 5 min, which is enough for the processes of CNT alignment and nanotube grid formation to terminate. The time of the nanotube migration toward the electrode considerably exceeds the specimen formation duration in the dcEF in the described experiment. Therefore, the formed clusters and some polarized CNTs have no time to

reach electrodes and do not destroy the electrically conducting grid. Hence, from the results of model calculations, one can see that if an external dcEF is applied to carbon nanotubes dispersed in a polymer matrix in the liquid state, three basic types of the nanotube displacement take place. During the specimen formation time, the nanotubes become aligned, being driven by their polarization, rotation, and the formation of chains from charged CNTs. However, the migrational CNT motion, which would impede the electrically conducting grid formation, almost does not take place within this time interval.

### 3.3. Influence of electric field on the percolation behavior of PEG–CNTs nanocomposites

The electric field considerably affects the percolation behavior of the analyzed systems. In Fig. 3, the dependences  $\sigma(p)$  obtained for the PEG–CNTs systems formed in the dcEF and without it are exhibited. The plots demonstrate that the examined composites reveal a percolation behavior. In accordance with the percolation theory, the relationship between the electric conductivity and the content of electrically conducting nanofiller above the percolation threshold is described by the scaling law [32]

$$\sigma \propto (p - p_c)^t \text{ at } p > p_c, \quad (24)$$

where  $\sigma$  is the conductivity of the system,  $p$  the mass fraction of an electrically conducting nanofiller,  $p_c$  the critical value of parameter  $p$  at the percolation transition (the percolation threshold), and  $t$  the power exponent (the critical index of the electric conductivity) mainly depending on the topologic dimensionality of the system and not depending on the structure of particles that form clusters, as well as on their interaction. Analyzing the experimental data (see Fig. 3) with the use of the least-squares method and Eq. (24), we calculated the percolation threshold  $p_c$  and the critical index  $t$ , which characterizes both the structural organization of a nanofiller in the composite and the cluster structure. For the PEG–CNTs system formed without the action of a dcEF, we obtained  $p_c = 0.42\%$  and  $t = 1.93 \pm 0.1$ , which testifies to the formation of a three-dimensional spatial percolation grid from nanotube clusters [33]. While approximating the experimental dependences  $\sigma(p)$  measured for PEG–CNTs systems formed in a dcEF, we obtained  $p_c = 0.1\%$  and  $t = 1.25 \pm 0.07$ . From the results of

calculations, one can see that if the system concerned is formed in the dcEF, the electrically conducting percolation cluster is formed at a much lower concentration of CNTs than in the field absence. This happens owing to the alignment of CNTs and their clusters in the electric field. The alignment of and the structure change in the clusters are testified by the values of corresponding critical electroconductivity index. In the field absence, one may talk about a three-dimensional structure of clusters and a uniform distribution of CNTs. At the same time, under the action of an electric field, the two-dimensional structure of aggregated clusters is formed [33]. From Fig. 3, one can also see that, above the percolation threshold, the conductivity in the specimens formed in the dcEF is higher than that in the specimens formed without the field application. This fact testifies that, in the course of percolation grid formation from nanotubes, the latter create more direct contacts, which reduces the electric energy dissipation at the charge transfer and provides a higher conductivity.

### 4. Conclusions

The results of our researches bring us to a conclusion that the electric field substantially affects the structure and the properties of nanofilled polymeric systems. It is found that the formation of polymeric nanocomposites in external dcEFs increases the degree of crystallinity in the polymer matrix. This phenomenon occurs owing to the kinetic deceleration of the translational motion of macromolecule segments by electric forces, and the impediment to the conformation reconstruction (folding) of macromolecules and the transition of the system into the state with the free energy minimum. As a result, the macromolecules mainly exist in a prolate conformation, which facilitates their packing into a crystalline structure. It is shown that the electric field affects the behavior of CNTs dispersed in a polymer matrix, when the latter is in the liquid state. An assumption is made that three basic types of the motion of nanotubes are realized if a dcEF is applied to the system. Within the time interval of the formation of a specimen, the nanotubes become aligned as a result of their polarization and rotation, and the chains are formed from charged CNTs. However, almost no migrational motion of CNTs, which would impede the creation of an electrically conducting grid, occurs during its formation. It is found that the formation of

nanofilled systems under the action of a dcEF gives rise to a four-fold reduction of the percolation threshold. This fact makes it possible to use the described method of alignment of CNTs for the production of electrically conducting polymeric nanocomposites with a reduced percolation threshold.

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ВПЛИВ ЕЛЕКТРИЧНОГО ПОЛЯ  
НА ПЕРКОЛЯЦІЙНУ ПОВЕДІНКУ СИСТЕМ  
НА ОСНОВІ ПОЛІЕТИЛЕНГЛІКОЛЮ  
ТА ВУГЛЕЦЕВИХ НАНОТРУБОК

Резюме

Методами диференціальної сканувальної калориметрії та імпедансної спектроскопії досліджено теплофізичні властивості й перколяційну поведінку систем на основі поліетиленоксиду й вуглецевих нанотрубок, сформованих за нормальних умов і під дією постійного електричного поля. Показано, що електричне поле суттєво впливає на поведінку нанотрубок, диспергованих у полімерній матриці. Зроблено припущення, що при накладанні поля здійснюються три основних типи руху нанотрубок (обертальний, трансляційний та міграційний) і обчислено характеристичний час для кожного типу. Виявлено, що при формуванні нанооповнених систем в електричному полі поріг перколяції знижується від 0,42% до 0,1%, що свідчить про суттєву орієнтацію нанотрубок у полімерній матриці.