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PRESSURE EFFECTS ON THE PERCOLATION BEHAVIOR OF SYSTEMS BASED ON POLYETHYLENE OXIDE AND CARBON NANOTUBES

The percolation behavior of systems based on polyethylene oxide and carbon nanotubes (CNTs) and its dependence on the external pressure in the interval from 0.1 to 150 MPa have been studied,by using the method of impedance spectroscopy. As the external pressure grows, the percolation threshold is found to decrease from 0.3% to 0.14%, with the critical index of conductivity changing from 1.95 to 2.73. The change of critical indices testifies to a structural rearrangement of CNTs in the polymer matrix from their statistical distribution to compact aggregates. The experimental results are described well in the framework of the modified McLachlan model, which considers the dependence of the percolation threshold on the pressure.

Keywords: polymer nanocomposites, carbon nanotubes, conductivity, percolation behavior, external pressure.

1. Introduction

Polymer composites are traditionally used as insulating materials, whereas their application in electronics was rather restricted. When creating composite materials with a high conductivity, a conducting filler is introduced into the polymer composition; for instance, it can be graphene [1], soot [2], fullerenes [3], *etc.* Carbon nanotubes (CNTs) are one of the most studied and promising fillers. They attract a large attention because of their unique properties, such as high rigidity, heat and electric conductivities, and so forth [4, 5]. It is those unique properties of CNTs and a high affinity of the latter to carbon-chain polymers that make CNTs rather an effective reinforcing filler for the creation of polymer nanocomposites [6]. Since there are no chemical bonds between the polymer matrix and CNTs, the adhesion at their interface can be provided only by physical interactions, in particular, van der Waals attraction forces [7].

The conductivity of nanocomposites substantially depends on the nanotube content, morphology of conducting percolation network, and number of contacts between CNTs. Other factors, such as the size, geometrical shape, and hardness of conducting nanofillers, their distribution, the properties of polymer matrix, and the method of nanocomposite preparation also affect the conductivity and the percolation process [8–10]. At a definite content of nanotubes, owing to the formation of a percolation network composed of CNTs, the dielectric polymer matrix becomes conducting. This phenomenon is called percolation, and the critical concentration of a filler is referred to as the percolation threshold. Near the percolation transition, the conductivity considerably depends on the filler content and the structure of a conducting network. In addition, the percolation behavior of polymer systems filled with CNTs depends on other factors such as the temperature, pressure, and magnetic fields, which can affect the formation and structure of conducting paths in the material.

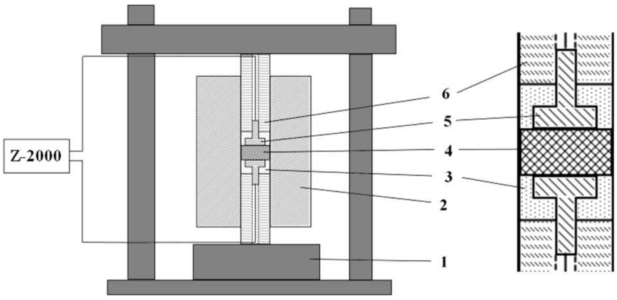

Fig. 1. Schematic diagram of the installation on the basis of a hydraulic press (left) and a cell for the measurements of the conductivity in nanocomposites at high pressures (right): (*1*) press piston; (*2*) external confining cylinder, (*3*) teflon gasket, (*4*) specimen, (*5*) electrode, (*6*) hold-down cylinder

Traditionally, the modification of conductivity induced by the variation of external pressure is called the piezoresistive effect [11]. Piezoresistive substances on the basis of conducting polymer composites are promising to be used as media for strain gauges and sensors of various kinds. Attempts to reveal the mechanisms of change in the conductivity under the pressure variation were made with the help of both the computer simulation and experimental researches. For instance, with the help of simulations using the Monte Carlo method for 2D [12] and 3D [13] systems, the percolation threshold for systems filled with conducting fibers was found to increase from 1.3% to 1.35% if the material was stretched by 30%.

In work [14], the piezoresistive behavior of the system polyepoxy–CNTs was studied experimentally. It was found that the dependence of the conductivity variation on the applied loading can be described by an almost linear law. The mechanism of this phenomenon is described rather well in the framework of the classical theory of charge transfer, when the system transits from the insulating state into the conducting one.

In the literature, a considerable attention is paid to the issue of fabricating the piezoresistive materials containing a minimum quantity of the filler and demonstrating the highest sensitivity [15, 16]. However, there are almost no works devoted to the study of the pressure effect on the percolation behavior of systems consisting of polymer nanocomposites filled with CNTs. This work was aimed at researching the influence of an external pressure on the features in the percolation behavior of nanocomposites fabricated on the basis of polyethylene oxide and carbon nanotubes.

2. Experimental Part

In our researches, we used model nanofilled systems fabricated on the basis of polyethylene oxide and carbon nanotubes. Polyethylene oxide (PEO-10000, HO[–CH$_2$–CH$_2$–O–]$_n$H with $n \approx 225$, the molecular mass $M_w = 10000$, the *Aldrich* company) was chosen as a polymer matrix. At the temperature $T = 298$ K, PEO-10000 is a solid substance, and its density amounts to $\rho = 1070$ kg/m^3. The corresponding melting temperature falls within the interval $T_m = 335 \div 338$ K. Before the application, PEO was dehydrated by heating it in vacuum for 4 h at a temperature of 353–373 K and a residual pressure of 300 Pa.

Multiwalled CNTs (the *Spetsmash* public corporation, Ukraine) were fabricated from ethylene using the chemical vapor deposition (CVD) method, with FeAlMo as a catalyst [17]. The content of mineral impurities did not exceed 0.1%. The specific surface of CNTs was 190 m^2/g, the external diameter $d \approx 20$ nm, the length $L = 5 \div 10$ μm, and the aspect ratio $L/d \approx 250 \pm 170$ [5]. The specific conductance of pressed CNTs (at a pressure of 15 TPa) along the compression axis amounted to 10 S/cm. The CNT density is equal to the density of pure graphite and amounts to $\rho = 2045$ kg/m^3.

The studied nanocomposites were prepared, by using the method of ultrasonic mixing in a melt with the help of an ultrasonic disperser UZN 22/44 at a temperature of 350 K. The dispersion treatment was performed for 3 min at a frequency of 22 kHz and an ultrasound power of 400 W. The CNT content was varied from 0.2 to 1 wt.% (below, %).

The conductivity in polymer nanocomposites on the basis of PEO and CNTs subjected to various external pressures was studied on an installation created on the basis of a hydraulic press. Its schematic diagram is depicted in Fig. 1. The pressure was varied within an interval of 0.1–150 MPa. The scaled-up cell design is also exhibited in Fig. 1. The electrodes were fabricated from steel.

The conductivity was measured on a Z-2000 impedance meter (Russia) using the method of impedance spectroscopy. The specimen was arranged between the cell electrodes, and the real, Z', and imaginary, Z'', parts of its impedance were measured. The dependences of the complex impedance were used to determine the dc conductivity using the technique described in work [18]: $\sigma_{\rm DC} = d/(SR_{\rm DC})$, where S is the specimen area, d the specimen thickness, and $R_{\rm DC}$ the dc system resistance.

3. Results and Their Discussion

In Fig. 2, the percolation curves typical of the examined system PEO–CNTs and measured at various applied external pressures are shown. The step-like change of the conductivity, which is associated with the percolation process, is observed in a concentration interval of 0.1–0.4%. In this concentration region, a percolation cluster composed of nanotubes is formed. In the same concentration interval, the percolation transition is also observed in typical polyether–CNTs systems [19, 20]. At a CNT content of 0.5%, the conductivity is approximately four to five orders of magnitude higher than before the percolation threshold.

The insulator–conductor transition that is observed in Fig. 2 can be described in the framework of the percolation theory, which is usually used for the establishment of a relation between the microstructure of given systems and their physical properties [21, 22]. According to this theory, the relationship between the conductivity above the percolation threshold and the content of a conducting nanofiller is described with the help of the following scaling law [22]:

$$\sigma_{\rm DC} = \sigma_0(\varphi - \varphi_{\rm C})^t, \qquad (1)$$

where δ is the conductivity of the system; φ the mass fraction of a conducting nanofiller; $\varphi_{\rm C}$ the critical mass fraction of a nanofiller at the percolation transition (the percolation threshold); t the conductivity critical index, which mainly depends on the topologic dimension of the system and does not depend on the structure of particles that form clusters, as well as their interaction; and σ_0 is a constant.

In Fig. 3, the percolation curves for the system PEO–CNTs calculated for various pressures with the help of Eq. (1) are exhibited. The parameters of Eq. (1), which were determined from the calculations, are quoted in Table 1. The percolation threshold was determined from the experimental data presented in Fig. 2 as a point where the steepest conductivity growth begins. From Fig. 3, one can see that the scaling equation (1) describes the experimental data rather well in the interval of nanotube concentrations higher than the corresponding percolation threshold.

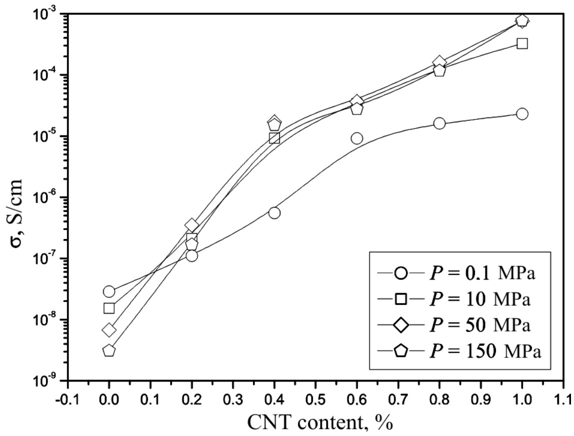

Fig. 2. Experimental dependences of the conductivity on the CNT content for systems on the basis of PEO at various external pressures

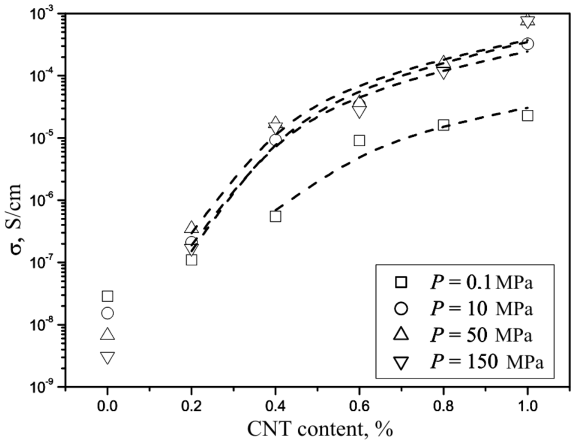

Fig. 3. Experimental dependences of the conductivity on the CNT content for systems on the basis of PEO at various external pressures (symbols) and their approximations by Eq. (1) (dashed curves)

Table 1. **Values of parameters in Eq. (1)**

P, MPa	σ_0, S/cm	$\varphi_{\rm C}$, %	t
0.1	6.2×10^{-5}	0.30	1.95
10	3.7×10^{-4}	0.20	2.52
50	5.6×10^{-4}	0.18	2.53
100	5.4×10^{-4}	0.14	2.73

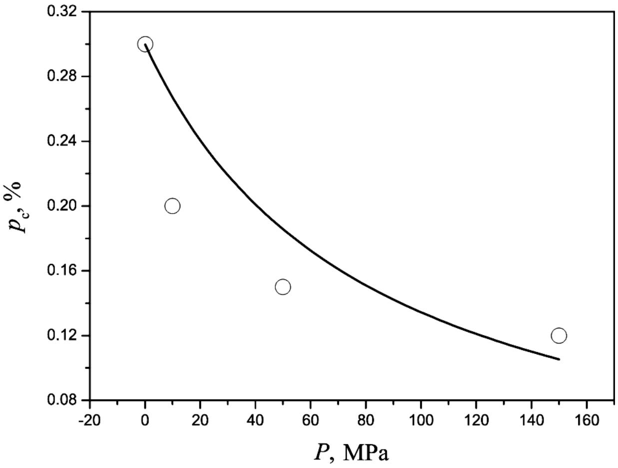

Fig. 4. Dependence of the percolation threshold on the pressure for systems on the basis of PEO and CNTs (symbols) and its approximation by Eq. (5) (solid curve)

From Table 1, one can see that the percolation threshold decreases with the pressure growth. Hence, the percolation threshold is reciprocal to the applied external pressure.

The critical index t, which characterizes the structural organization of a nanofiller in the composite and the structure of clusters, changes from 1.95 to 2.73 as the pressure grows. The critical index t for the system PEO–CNTs not subjected to the external pressure is almost equal to its theoretical value $t = 2$. According to work [21], the value $t \approx 2$ testifies to a statistical distribution of conducting particles in the dielectric medium. In our case, the t-values that exceed the theoretical one do not indicate that the dimension of the system changed. Instead, they can be explained by the processes of CNT aggregate compaction, when an external pressure is applied.

For a more complete correct description of the percolation transition in nanofilled polymer systems, the model proposed by McLachlan [23] is used. It combines the elements of the effective-medium and percolation theories. Therefore, it is more universal and can be used for the description of experimental results on the conductivity in nanocomposites fabricated on the basis of polymer matrices with various types of intrinsic conductivity. The master equation of the McLachlan model looks like

$$\frac{(1-\varphi)(\sigma_m^{1/s} - \sigma_{\mathrm{DC}}^{1/s})}{(\sigma_m^{1/s} + A\sigma_{\mathrm{DC}}^{1/s})} + \frac{\varphi(\sigma_f^{1/t} - \sigma_{\mathrm{DC}}^{1/t})}{(\sigma_f^{1/t} + A\sigma_{\mathrm{DC}}^{1/t})} = 0, \tag{2}$$

where φ is the CNT content; σ_f, σ_m, and σ_{DC} are the conductivity of the filler, polymer matrix, and nanocomposite, respectively; and t and s are the critical indices.

It should be noted that Eq. (2) can include both the complex quantities σ_f, σ_m, and σ_{DC}, and their real parts. The value of the volume fraction φ varies from 0 to 1. The medium is an insulator ($\sigma_{\mathrm{DC}} = \sigma_m$) at $\varphi = 0$, and a conductor ($\sigma_{\mathrm{DC}} = \sigma_f$) at $\varphi = 1$. The critical volume fraction φ_{C}, or the percolation threshold, characterizes the transition from the insulating state into the conducting one and determines the coefficient $A = (1 - \varphi_{\mathrm{C}})/\varphi_{\mathrm{C}}$. Note that, at $t = s = 1$, Eq. (2) is the Bruggeman equation for symmetric media [24].

Equation (2) has two asymptotic solutions:

$$|\sigma_m| \to 0 : \sigma_{\mathrm{DC}} = \sigma_f \left(\frac{\varphi - \varphi_{\mathrm{C}}}{1 - \varphi_{\mathrm{C}}}\right)^t, \ \varphi > \varphi_{\mathrm{C}}, \tag{3}$$

$$|\sigma_f| \to \infty : \sigma_{\mathrm{DC}} = \sigma_m \left(\frac{\varphi_{\mathrm{C}}}{\varphi_{\mathrm{C}} - \varphi}\right)^s, \ \varphi < \varphi_{\mathrm{C}}. \tag{4}$$

These expressions are called the reduced percolation equations.

The dependence of the conductivity on the applied load at the uniaxial squeezing can be described at the semiquantitative level, by using the master equation of the generalized effective-medium theory (Eq. (2)), in which the percolation threshold is a function of the pressure, i.e. $\varphi_{\mathrm{C}} = \varphi_{\mathrm{C}}(P)$. Supposing that the percolation threshold equals $\varphi_{\mathrm{C}}(0)$ in the absence of an external pressure, we may write down the following equation [25]:

$$\varphi_{\mathrm{C}}(P) = \frac{\varphi_{\mathrm{C}}(0)}{1 + mP}, \tag{5}$$

where m is a certain constant, and $\varphi_{\mathrm{C}}(0) = 0.3\%$. Substituting Eq. (5) into Eq. (4), we obtain the dependence $\sigma(P)$:

$$\sigma_{\mathrm{DC}} = \sigma_f \left(\frac{(1 + mP)\varphi - \varphi_{\mathrm{C}}(0)}{(1 + mP) - \varphi_{\mathrm{C}}(0)}\right)^{t^*}. \tag{6}$$

Equation (6) includes three fitting parameters: t^*, σ_f, and m. The parameter t^* in the dependence $\sigma(P)$ describes the conductivity as a function of the pressure and, by value, can differ from the critical index t, which characterizes the conductivity as a function of the CNT concentration.

The value of constant m in Eq. (5) can be determined from the dependence $\varphi_C(P)$ depicted in Fig. 4. Putting $\varphi_C(0) = 0.3\%$ and using Eq. (5) to fit the dependence shown in Fig. 4, we obtain $m = 1.33 \times 10^{-8}$ Pa^{-1}. Provided that the parameters $\varphi_C(0)$ and m are known, Eq. (6) includes only two unknown quantities, which allows them to be determined with a high accuracy.

In Fig. 5, the simulation results obtained with the help of the modified McLachlan equation for the conductivity of systems PEO–CNTs are shown. From this fugue, one can see that the model describes the experimental data rather well in the interval of CNT concentrations exceeding the percolation threshold.

The parameters of Eq. (6) are quoted in Table 2. One can see that the values obtained for φ_C and t^* differ from the corresponding values obtained for the parameters in Eq. (1). However, the character of their variation with the pressure growth is similar. The critical index t^* is larger than the index t obtained by fitting Eq. (1). The dependences of σ_f and t^* on the applied external pressure are exhibited in Fig. 6. From Fig. 6, one can see that the conductivity of the filler increases with the pressure. This fact can be explained by the circumstance that, in the absence of an additional (distinct from atmospheric) external pressure, there are polymer layers between separate nanotubes and their clusters, which considerably reduce the own conductivity of CNTs. As the pressure grows, the distance between the nanotubes diminishes, so that charges can be transferred by means of the tunneling mechanism. As a result, the conductivity of the filler increases considerably. The critical index t^* also increases with the pressure, which testifies to the formation of more compact structures consisting of separate CNTs and their aggregates. The deviation of t^* from its theoretical value testifies to a non-statistical character of the CNT distribution in the polymer matrix.

From Fig. 6, one can see that the plots of $\sigma_f(P)$ and $t^*(P)$ grow drastically in the pressure interval from 5 to 30 MPa. The analysis of the dependences $\sigma(\varphi)$ obtained at various pressures (Fig. 2) shows that, at the same pressure values, the conductivity of the systems PEO–CNTs increases by almost two orders of magnitude. Such a behavior is similar to a typical percolation behavior of nanofilled systems on the basis of polyethers [20, 26]. Unlike the classical percolation transition, in which the properties have a jump at a definite critical filler concentration, in the case concerned, the parameters change at a definite critical pressure.

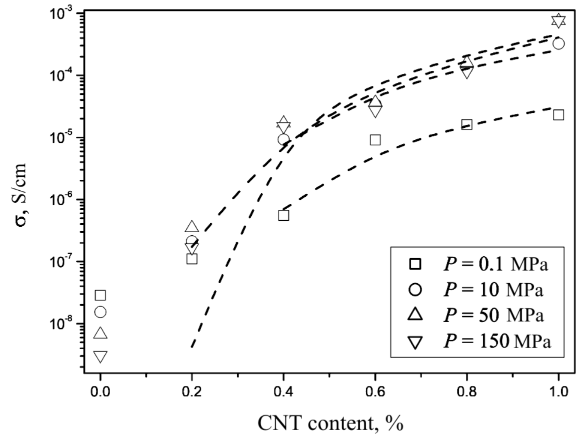

Fig. 5. Dependences of the conductivity on the CNT content for systems on the basis of PEO at various external pressures (symbols) and their approximations by Eq. (6) (dashed curves)

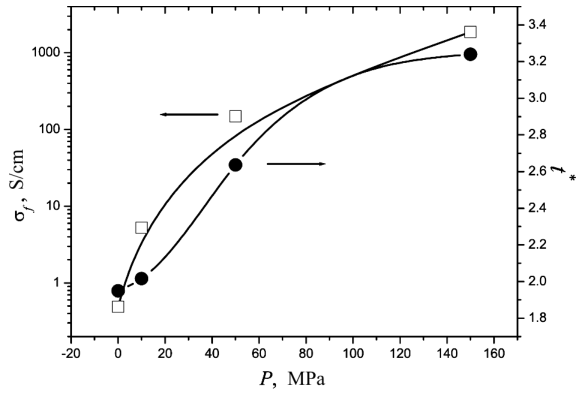

Fig. 6. Dependences of the filler conductivity and the critical index t^* on the applied external pressure for systems on the basis of PEO and CNTs

Table 2. **Values of parameters in Eq. (6)**

P, MPa	σ_f, S/cm	φ_C, %	t^*
0.1	0.5	0.30	1.95
10	5.2	0.27	2.02
50	148.3	0.19	2.643
100	1862.0	0.12	3.24

4. Conclusions

The performed researches allowed us to study the influence of the external pressure varied in the interval from 0.1 to 150 MPa on the conductivity in systems fabricated on the basis of polyethylene oxide and carbon nanotubes. It is found that the systems concerned demonstrate the percolation behavior, which can be described rather well in the framework of the critical percolation theory and the scaling approach. The value of percolation threshold is determined to be reciprocal to the applied pressure; in particular, if the pressure increases, it decreases from 0.3% to 0.14%. The value of critical index t obtained for nanofilled systems without the application of an external pressure testifies to a three-dimensional statistical character of the nanotube distribution in the polymer matrix. As the external pressure grows, the critical index t increases, which evidences the compaction of CNT aggregates. The experimental results are described in the framework of the modified McLachlan model, which makes allowance for the percolation threshold dependence on the pressure. The parameters obtained for this model correlate well with the parameters φ_C and t obtained in the framework of the scaling approach.

To summarize, the application of the external pressure considerably reduces the percolation threshold in systems on the basis of PEO and CNTs. The examined systems demonstrate a substantial jump of their conductivity, when the pressure grows. This fact makes it possible to use nanocomposite materials on the basis of PEO and CNTs for the creation of pressure sensors, strain gauges, and so forth.

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ВПЛИВ ТИСКУ НА ПЕРКОЛЯЦІЙНУ ПОВЕДІНКУ СИСТЕМ НА ОСНОВІ ПОЛІЕТИЛЕНОКСИДУ ТА ВУГЛЕЦЕВИХ НАНОТРУБОК

Резюме

Використовуючи метод імпедансної спектроскопії проведено дослідження особливостей перколяційної поведінки систем на основі поліетиленоксиду та вуглецевих нанотрубок (ВНТ) в залежності від величини зовнішнього тиску. Виявлено, що зі збільшенням зовнішнього тиску поріг перколяції зменшується з 0,3% до 0,14%, а критичний індекс електропровідності змінюється від 1,95 до 2,73. Зміна критичних індексів вказує на зміну структурної організації ВНТ у полімерній матриці зі статистичного розподілу до ущільнених агрегатів із нанотрубок. Експериментальні результати добре описуються у рамках модифікованої моделі МакЛахлана, яка враховує залежність порогу перколяції від тиску.