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Структура і властивості

Electrical conductivity of polymer/carbon nanotubes nanocomposites at low temperatures

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Electrical properties of two new types of polymer/multi-walled carbon nanotubes (MWCNTs) nanocomposites have been studied at very low temperature: thermoplastic Poly(butylene terephthalate)/MWCNTs, prepared by reactive blending of the mixture of cyclic butylene terephthalates and MWCNTs, and thermosetting Polycyanurate/MWCNT prepared by blending of dicyanate ester of bisphenol E monomer with MWCNT using sonication and subsequent curing. Dimensional characteristics and vibrational properties of MWCNTs were investigated by transmission electron microscopy and Raman spectroscopy. The results of conductivity measurements clearly evidence the presence of a percolation threshold (p_c) at a very small weight fraction of the MWCNTs in the both polymer matrices: $p_c = 0,22$ wt. % and $p_c = 0,38$ wt. % for thermoplastic and thermosetting composites, respectively. The activation energies of conduction in the range 10 – 100 K are very low for all the samples ($<0,001$ eV). It was found, that the temperature dependence of conductivity of the nanocomposites follows the fluctuation induced tunneling model and is weak enough to develop the use of such materials in electronic devices.

Keywords: nanocomposites, carbon nanotubes, electrical properties, poly(butylene terephthalate), polycyanurate networks.

Introduction.

Recently, much attention has been given to the use of CNTs in polymer composite materials to improve their mechanical and electrical properties [1, 2]. Basically, conductive CNTs-polymer composites are generally obtained by dispersion of highly conductive CNTs filler, forming a three-dimensional conductive network in an insulating polymer matrix.

In order to describe the insulator-to-conductor transition in such composites, the percolation theory is used [3, 4]. The electrical conductivity of a composite is strongly dependent on the filler loading. It is due to formation of a continuous, three-dimensional network of the conductive filler in the polymer phase. The higher aspect ratio of nanofiller, the lower the filler content is needed to reach the percolation threshold to get conductive material. Due to their very high shape factor, CNTs are perfect type of filler to achieve the lowest possible percolation threshold in conducting polymer nanocomposite.

There are some critical issues in incorporation of CNTs into polymer matrix. To optimize the advantage of using the CNTs to get effective reinforcement or conductivity

properties for high performance composites, they should not form aggregates and must be well dispersed [5]. So, the first task is to improve the dispersion of CNTs in polymer matrices. There are several techniques such as effective physical blending, in-situ polymerization and chemical functionalization of CNTs to get separated CNTs (or slightly bundled CNTs) [6–8].

Elaboration of conductive nanocomposites starting from monomers (oligomers) with low viscosity mixed with CNTs can provide more effective distribution of the filler particles in the final polymer matrix if compared to work with high viscous melted polymer. In this work, two reactive systems have caught our interest to bring interesting issue for new CPC materials in polymer science and technology

The recently developed macrocyclic polyester oligomers like Cyclic Butylene Terephthalate (CBT) oligomers present important advantages in comparison with conventional monomers and oligomers for processing: low viscosity (water-like), no need to use solvents for polymer synthesis, the capability of rapid polymerization into

high molecular mass Poly(butylene terephthalate) (cPBT) and the ability to be processed using the methods usually applied for thermosetting resins [9–10]. Resulting PBT is a typical engineering plastics among thermoplastic polyester resins that has been extensively used as a raw material of injection- molded devices [11].

Another perspective material used in the present work is Polycyanurate Networks (PCN) originating from Cyanate Ester Resins (CER). They are the most promising group of high-temperature thermosetting polymers. PCN offer an unique combination of excellent thermal and dimensional stability, high glass transition temperatures ($T_g = 220\text{--}270\text{ }^\circ\text{C}$), high purity, inherent flame-retardancy (giving the potential to eliminate brominated flame retardants), and high adhesion to metals at temperatures higher than $250\text{ }^\circ\text{C}$ [12, 13].

The aim of the work is to explore the electrical properties of previously prepared two types of nanocomposites – thermoplastic Poly(butylene terephthalate)/MWCNTs [14], and thermosetting Polycyanurate/MWCNTs [15], to determine the dependence of the electrical conductivity on the MWCNTs content analyzed with the percolation theory. The temperature dependence of conductivity is discussed to establish the mechanism of charge transport in relation to fluctuation induced tunneling model of electrical conductivity.

Experimental.

Materials.

Two batches of CNTs were used in this study: MWCNTs Graphics 4000 supplied from Arkema, France, (used in cPBT/MWCNTs nanocomposites) named MWCNT₁ and MWCNTs by TM “Ukrspetsmash”, Ukraine (used for the preparation of PCN/MWCNTs nanocomposites) named MWCNT₂. Carbon nanotubes provided by the both trademarks were produced by the Chemical Vapor Deposition (CVD) method.

Macrocyclic oligo(1,4-butylene terephthalate) known under the trade name CBT160 was used in the present study. The CBT160 resin on the form of pellets is a mixture of oligomers with the degree of oligomerization from 2 to 7 and containing 0,5 wt. % Fascat 4105 buthyltin dihydroxychloride catalyst and convert under the heat action to high-molecular-weight polybutylene terephthalate. In order to avoid the presence of moisture that inhibits catalyst action [9] CBT160 was degassed for 12 hours at $80\text{ }^\circ\text{C}$ under vacuum before processing. CBT160 and MWCNT₁ were first dry mixed in a flask to distribute the MWCNTs with the pellets then blended in a “DSM 15” twin-screw compounder (DSM Research Netherlands) at $230\text{ }^\circ\text{C}$ during 15 min. All the extruded samples were cooled at room temperature and cut in small grains introduced in square sample mold with a thickness 0,5mm and pressed during 2 min at $240\text{ }^\circ\text{C}$, then cooled with the rate of $9\text{ }^\circ\text{C}/\text{min}$ during 25 min. MWCNT₁ weight content in cPBT was ranged from 0,01 to 2,0 wt.% [14]

Prepolymer of dicyanate ester of bisphenol A (DCBA)

supplied at 75 % of solid in methyl ethyl ketone (BA-230S 75) was used as the initial component for preparation of CNTs-containing Polycyanurates. MWCNT₂ were sonicated in liquid DCBA prepolymer at room temperature at 44 Hz during 45 min on the Ultrasonic Dispresant UZDN-2T. The step by step curing schedule for all the systems consisted of the following stages: 3h at $180\text{ }^\circ\text{C}$, 1h at $210\text{ }^\circ\text{C}$, 1h at $230\text{ }^\circ\text{C}$, 1h at $250\text{ }^\circ\text{C}$ and 30 min at $270\text{ }^\circ\text{C}$. [15]. Concentration of MWCNT₂ was ranged from 0,02 to 1,20 wt.%

Characterizations.

The characterization of the samples was performed by Raman spectroscopy using the Jobin-Yvon Raman Spectrometer T64000 combined with Olympus confocal microscope BX40, with green laser light (514,5 nm) at room temperature. Transmission electron microscopy (TEM) micrographs of MWCNTs were obtained using a Philips CM 120 microscope. The operating voltage was set to 80 kV. MWCNTs were ultrasonically dispersed in acetone and a drop of the obtained dispersion was deposited on a copper microscopy grid covered with a thin polymer film “Formvar”.

Scanning electron microscopy (SEM) of nanocomposites was carried out using SEM HITACHI S800 at the accelerating voltage of 15 kV. The specimens were quenched and fractured in liquid nitrogen and then coated with a thin Au/Pd film (thickness around 10 nm) for investigation.

Measurements of the direct current (dc) electrical conductivity of the samples were performed at room temperature by means of two- or four-point techniques. For this purpose a sample holder was prepared using four narrow strips of flexible graphite foil fixed on an insulating poly(ethylene terephthalate film). The copper wires were attached to these graphite electrodes and junction points were covered by silver paint. The samples were cut into 6 x 12 mm strips and deposited on a sample holder then were pressed against the graphite strips. Two-point technique (using the same holder type but with two electrodes only) was used for determination of electrical conductivity of the samples below the percolation point. Current flowing at fixed value of voltage was recorded until constant value was reached. In the four-point technique used as far as the samples are semi-conductive and conductive, the external wires were connected to current source, and the internal one to the voltmeter. The dc current was applied using regulated power supply (Keithley 6517A Electrometer High Resistance meter). Current flow and voltage were measured with digital multimeter (Keithley 2400 Source meter).

The volume resistivity, c , of all the samples was calculated using the following equation:

$$P = \frac{U}{I} \cdot \frac{\delta \cdot w}{L}, \quad (1)$$

where U is a voltage drop, V; I – current flowing through the sample, A; d – sample thickness, cm; w – width of the sample, cm; L – the distance between internal electrodes connected to the multimeter, cm. Electric conductivity was

determined as $\sigma = 1/\rho$.

In order to describe the mechanism of charge transport in the nanocomposites the temperature dependence of the dc conductivity was measured in a broad temperature range using helium cryostat [16].

Results and discussion.

Morphology of the MWCNTs.

Raman spectroscopy is known as a powerful and useful tool to study the vibrational properties and electronic structure of CNTs [17]. As far as MWCNTs were supplied by different manufacturers it was interesting to perform first their comparative study (in spite of the same method of synthesis). For this purpose structure and morphology of CNTs by Raman spectroscopy and TEM, correspondingly were investigated. The characteristic feature of the graphitic layers in Raman spectrum is so-called G-band. It corresponds to the tangential vibration of the carbon atoms. Other characteristic modes are D-band, indicating the presence of defective graphitic structures, and its second-order related harmonic Gr-band. In addition, there is a fourth mode, radial breathing mode (RBM), which is very sensitive to the diameter of Single-Walled and Double-Walled CNTs but it is not usually observed for MWCNTs since the RBM signal from large diameter tubes is usually too weak [18]. Three features for both types of the investigated MWCNTs are observed (cf. Figure 1): the disorder induced mode, D-band (centered at 1347 cm^{-1}); graphite mode, G-band (centered at 1580 cm^{-1}); and harmonic mode, Gr-band (centered at 2695 cm^{-1}). The D/G and Gr/G area ratios are evaluated according to Lorentzian analysis, giving a measure of the average defectiveness-level and smoothness-degree of graphene sheets, respectively. The corresponding calculations have shown that the ratios of areas under the corresponding

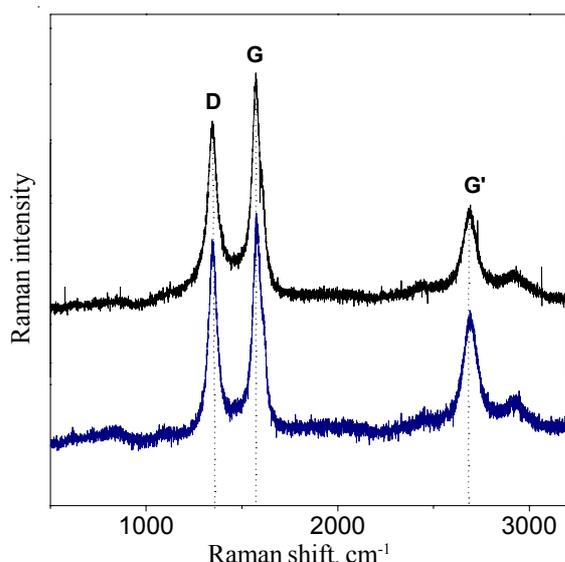


Fig. 1. Raman spectra of the MWCNTs₁ (black line) and MWCNTs₂ (gray line), MWCNTs₁ spectrum was shifted vertically for clarity

peaks (D/G and Gr/G) are very close for the both MWCNTs samples used: D/G = 0,90 and Gr/G = 0,84 for MWCNTs₁; D/G = 0,77 and Gr/G = 1,12 for MWCNTs₂. The D and Gr characteristic bands of the both samples showed the same intensities. These results indicate that the both MWCNTs used have similar graphitic structure and crystallinity.

The MWCNTs samples were investigated also by the transmission electron microscopy (TEM) and the dimensional characteristics of carbon nanotubes were analyzed by *ImageJ* software [http://rsbweb.nih.gov/]. The dimensional characteristics of the both samples are very similar. For example, for the MWCNTs₁ and MWCNTs₂ the values of average outer diameters are the same, $D \approx 10\text{--}15\text{ nm}$ and it is in an agreement with the values reported by the suppliers: for MWCNTs₁ $D \approx 10\text{--}15\text{ nm}$ and for MWCNTs₂ $D \approx 10\text{--}20\text{ nm}$. The values of the measured and reported length (L) of MWCNTs₁ lay in the range of $L \approx 0,1\text{--}10,0\text{ mm}$ that give an aspect ratio $L/D \approx 10\text{--}670$. There is no reference giving the information about the length of MWCNTs₂, so the nanotubes' average length measured with the help of *ImageJ* software is $L \approx 0,2\text{--}12,0\text{ mm}$ resulting to $L/D \approx 40\text{--}600$.

The similar structure observed for both the MWCNTs involved to the present study allows avoiding the supposition that the difference in nanotubes morphology could significantly influence the conductivity behavior of the samples.

Morphology of the nano conductive polymer composites.

Figure 2 shows SEM micrograph of the cryo-fractured surface of cPBT/MWCNTs₁ and PCN/MWCNTs₂

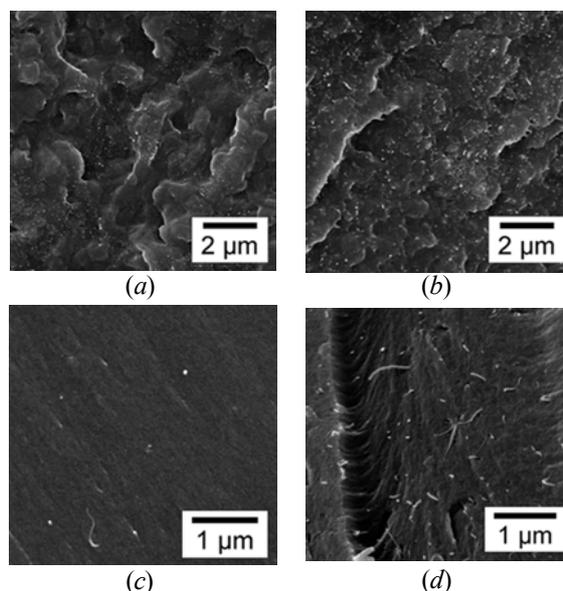


Fig. 2. SEM micrographs for the nanocomposites studied: *a, b* – cPBT/MWCNTs₁ with content of MWCNTs₁ 0,1 and 2,0 wt. %, correspondingly; *c, d* – PCN/MWCNTs₂ with content of MWCNTs₂ 0,08 and 1,2 wt. %, correspondingly

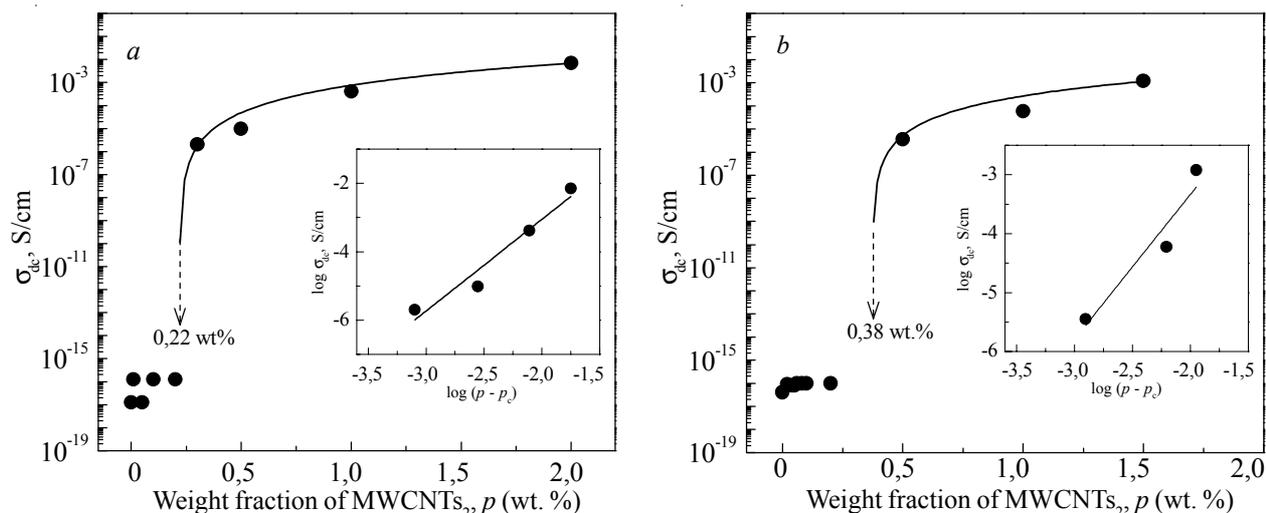


Fig. 3. dc conductivity of nanocomposites studied as a function of MWCNTs₁ contents: *a* – cPBT/MWCNTs₁; *b* – PCN/MWCNTs₂. Insets show the \log – \log plot of dc conductivity with $(p - p_c)$ for $p > p_c$.

nanocomposites indicating a good dispersion of CNTs in polymer matrixes. As it will be discussed in details below, the electrical percolation threshold for cPBT/MWCNTs₁ was fixed at $p_c = 0,22$ wt. % of MWCNTs₁ and that for PCN/MWCNTs₂ nanocomposites is $p_c = 0,38$ wt. %. Two loadings were deliberately chosen for SEM of two types of nanocomposites to reveal the obvious difference before and after percolation threshold (formation of MWCNTs interconnected structures). It is seen from the micrographs that for the samples with low MWCNTs content in both cPBT or PCN matrices (Fig. 2 *a, c*) carbon nanotubes are fully isolated by the polymer while at higher loadings the isolating barrier is rather small and CNTs form interconnected structure (Fig. 2 *b, d*).

Electrical properties.

Percolation theory applied to study the connected pathways in conducting polymer composites CPC made of polymers may provide important information concerning conductivity in such materials. At low filler concentrations the conductivity remains very close to the conductivity of the pure, electrically insulating polymer matrix. When for a critical filler volume fraction the percolation threshold is reached, the conductivity abruptly increases by many orders of magnitude with very little increase in the filler loading.

Such insulator-to conductor transition observed as a function of the volume fraction p of conducting phase in insulating matrix results from a percolation transition [2, 3, 16]. For volume fractions below some critical value p_c , called percolation threshold, there are no connected pathways through the sample whereas for volume fractions above the p_c successively larger numbers of continuous paths are formed. Classical percolation theory predicts that the conductivity should follow an exponential law above p_c [4]:

$$\sigma = \sigma_0(p - p_c)^t, \quad (2)$$

where σ_0 is the scaling factor and p_c is the value of the

percolation threshold, t is the universal exponent, dependent only on dimensionality and topology of the system with calculated values of $t = 1,33$ in two dimensions and $t = 2,0$ in three dimensions [4], while experimental values reported for the CNTs-filled polymer composites varies between $t = 0,7 \div 7,5$ [2].

Experimental results are fitted by plotting $\log \sigma$ versus $\log(p - p_c)$ and incrementally varying p_c until the best linear fit is observed. Note, that as far as the density of carbon nanotubes can only be approximately estimated ($\rho = 1,4 \div 1,9$ g/cm³ [19], $\rho = 2,045$ g/cm³ [20]), mass fraction of MWCNTs is preferred instead of volume fraction.

As it is shown in Figure 3, the electrical conductivity of cPBT/MWCNTs₁ and PCN/MWCNTs₂ agrees well with the percolation behavior given by Eq. (2). One can see that introduction of MWCNTs above p_c increases the conductivity of the composite by up to 10 orders of magnitude in both the cPBT/MWCNTs₁ and PCN/MWCNTs₂ systems.

For cPBT/MWCNTs₁ samples with MWCNTs content between 0,01 and 0,20 wt. % the conductivity is nearly constant being around 10^{-16} S/cm; then in the range of concentrations between 0,2 and 0,3 wt. % of MWCNTs₁ the conductivity drastically increases by 10 orders of magnitude and for the samples with higher concentrations of MWCNTs₁ the conductivity does not rise significantly. In the case of PCN/MWCNTs₂ the composites display a sharp increase by 10 orders of magnitude for the samples with MWCNTs₂ content between 0,2 and 0,5 wt. % and then the conductivity increases moderately at higher concentrations.

The percolation thresholds as well as the critical exponents were calculated for cPBT/MWCNTs₁ and PCN/MWCNTs₂ nanocomposites. Solid lines in Figure 3 are fits to the scaling law of the percolation theory (see Eq. 1). The insets show the percolation scaling law on plots $\log \sigma$ versus $\log(p - p_c)$, where the solid lines correspond

to the best linear fits to experimental data. The values of p_c and t are presented in Table 1. The best fitting to the experimental values resulted in $p_c = 0,0022$ (0,22 wt. %) and $t = 2,68$ for cPBT/MWCNTs. The percolation threshold of $p_c = 0,0038$ (0,38 wt. %) and a critical exponent of $t = 2,46$ were obtained for PCN/MWCNTs₂. The difference in the values of p_c of two nanocomposites can be explained by the difference in method of synthesis of the samples, dispersion technique and the chemical nature of the polymer. A value of p_c of PCN/MWCNTs₂ is almost two times higher than that of cPBT/MWCNTs₁. It is supposed that on the first stages of curing CER/MWCNTs₂ mixture was in liquid state during quite long time (about 5 hours) so the nanotubes could form microaggregates. It is known that CNTs tend to cluster or agglomerate due to physical entanglements of the tubes and van der Waals forces between the carbon surfaces [17]. A huge variety of results concerning studies of electrical properties of CNTs-containing polymer composites have been reported in recent years and in a review paper on electrical percolation in carbon nanotube polymer composites, Bauhofer et al. [2] report that the percolation threshold in polymer/CNTs composites can be influenced by different parameters like CNTs type, its method of synthesis and additional treatment, dimensionality, polymer type as well as dispersion method and can vary from 0,0021 to 50 wt. % and even more. The value of critical exponents received for the both nanocomposites are somewhat higher than theoretically predicted value of $t = 2,00$ (cf. Eq. 2). Such effect relates to system dimensionality [2, 21]. The values of critical exponent t that exceeds a theoretically predicted value ($t = 2,00$) have been derived within a continuum model, the “Swiss cheese model”, where spherical insulating inclusions are introduced in a continuous conductor. However it should be noted that scaling (insets in Fig. 3a and b) is limited to a concentration range that can give mathematical errors. In addition, the results of statistical percolation theory are derived for ideal systems which contain a homogeneous dispersion of identical particles. Due to the dispersion of the CNTs properties, i.e., length, diameter, chirality, entanglement and waviness, the polymer/CNTs composites are far away from being ideal systems [2]. In the literature reported values of t are in the range from 1,30 to 4,00 [2, 8, 22].

Temperature dependence of the CPC electrical properties

Figure 4 (a and b) shows the Arrhenius plots of dc conductivity for the cPBT/MWCNTs₁ and PCN/MWC-

Table 1. The percolation threshold weight fraction p_c and the critical exponent t for cPBT/MWCNTs₁ and PCN/MWCNTs₂

Percolation parameters	cPBT/MWCNTs ₁	PCN/MWCNTs ₂
p_c	0,0022	0,0038
T	2,68	2,46

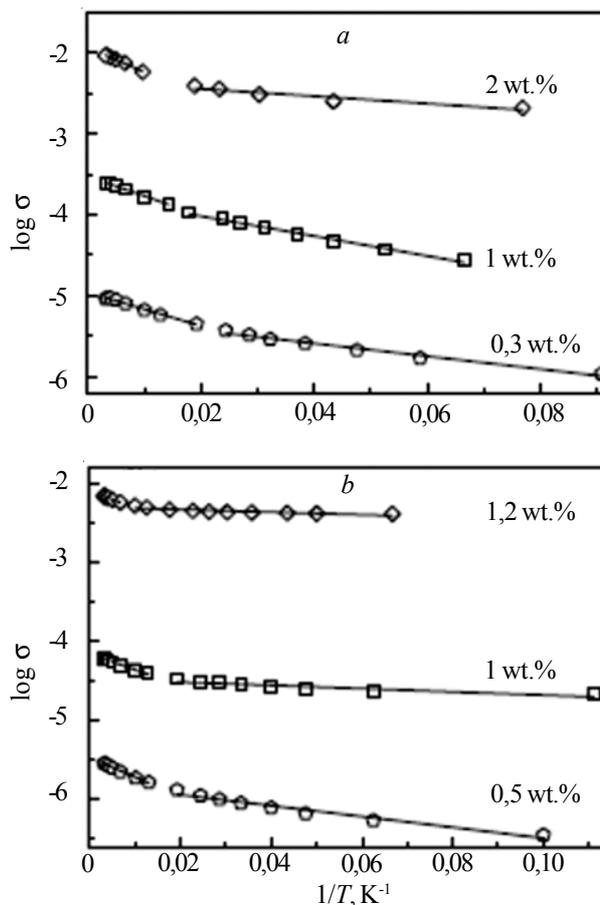


Fig. 4. Arrhenius plots of dc conductivity of the nanocomposites: a – 0,3; 1,0 and 2,0 wt.% of MWCNTs₁ in cPBT/MWCNTs₁ composites (indicated in the plot); b – for 0,5; 1,0 and 1,2 wt.% of MWCNTs₂ in PCN/MWCNTs₂ composites (indicated in the plot). The lines show fittings to Eq.3

NTs₂ nanocomposites in broad temperature range from 10 to 320 K for concentrations above the percolation threshold.

The activation energies (E_a) of electrical conduction were calculated for using the equation:

$$\log\left(\frac{\sigma}{\sigma_0}\right) = \frac{-E_a}{RT} \quad (3)$$

However one can see, that the Arrhenius plots of dc conductivity for the investigated nanocomposites do not yield straight lines and the activation energy (E_a) can be estimated only for limited temperature ranges. With increasing filler loading in the both nanocomposites the E_a values tend to decrease. At low temperatures ($\sim 10 - 100$ K) the E_a values are very low for all the samples (cf. Table 2).

In a review [16], electrical properties in heterogeneous organic polymer systems as well as basic concepts and equations for mechanisms of charge transport controlled by percolation processes are presented and the experimental implications of the theoretical models are

Table 2. Activation energies and fitting parameters T_0 , T_1 for studied composites

MWCNTs content, wt. %	E_a , eV	T_0 , K	T_1 , K
MWCNTs ₁ content in cPBT/MWCNTs ₁ , wt. %			
0,3	0,0007	16	64
1,0	0,0011	14	71
2,0	0,0004	49	119
MWCNTs ₂ content in PCN/MWCNTs ₂ , wt. %			
0,5	0,0006	27	81
1,0	0,0002	30	100
1,2	0,0001	91	129

*Values of activation energy were recalculated from kJ/mol to eV using the following equation: $1\text{eV} = 96,485\text{ kJ/mol}$.

discussed in details. Among the many possible conduction mechanisms, including hopping and tunneling, we have found that the Fluctuation-Induced Tunneling (FIT) model proposed by Sheng [23] is the most suitable for description of charge carrier transport in our materials. The FIT model can be applied to heterogeneous materials in which relatively large conducting islands (or long conducting pathways) are separated by small insulating barriers. The main idea of this model is that thermal noise can induce strong voltage fluctuations over a tunnel junction, which, effectively, narrow and lower the barriers. The analytical expression for the temperature dependence of the FIT conductivity is given by [23]:

$$\sigma = \sigma_0 \exp\left(\frac{-T_1}{T+T_0}\right), \quad (4)$$

where $T_1 = \frac{wA\varepsilon_0^2}{8\pi k_B}$, where σ_0 is a constant, T is the absolute temperature, T_0 is a temperature below which the tunneling is a simple elastic and temperature independent process, and T_1 is the temperature above which the conductivity is thermally activated, k_B is the Boltzmann constant, $\chi = (2mV_0/\hbar^2)^{1/2}$, $\varepsilon_0 = 4V_0/ew$, m is the electron mass, V_0 is the potential barrier height, w is the insulating layer width, and A is the area of capacitance formed at the junction.

The fitting of the experimental results to the FIT model gives a good description of conductivity data within the whole range of temperatures (Fig. 5 *a* and *b*). Both polymer nanocomposites show similar dependence of conductivity on temperature and their conductivity value rises with the increasing weight fraction of MWCNTs. Increase of the filler content results in the enhanced number of intertube connections; consequently numerous conductive paths are available.

The values of T_1 and T_0 , determined from the fitting procedures, for each curve of the both types of the nanocomposites are listed in Table 2. The parameters of T_0 and T_1 have reasonable values and are consistent with the Arrhenius plots, *i.e.* one can correlate the T_1 values with the temperatures above which the experimental points

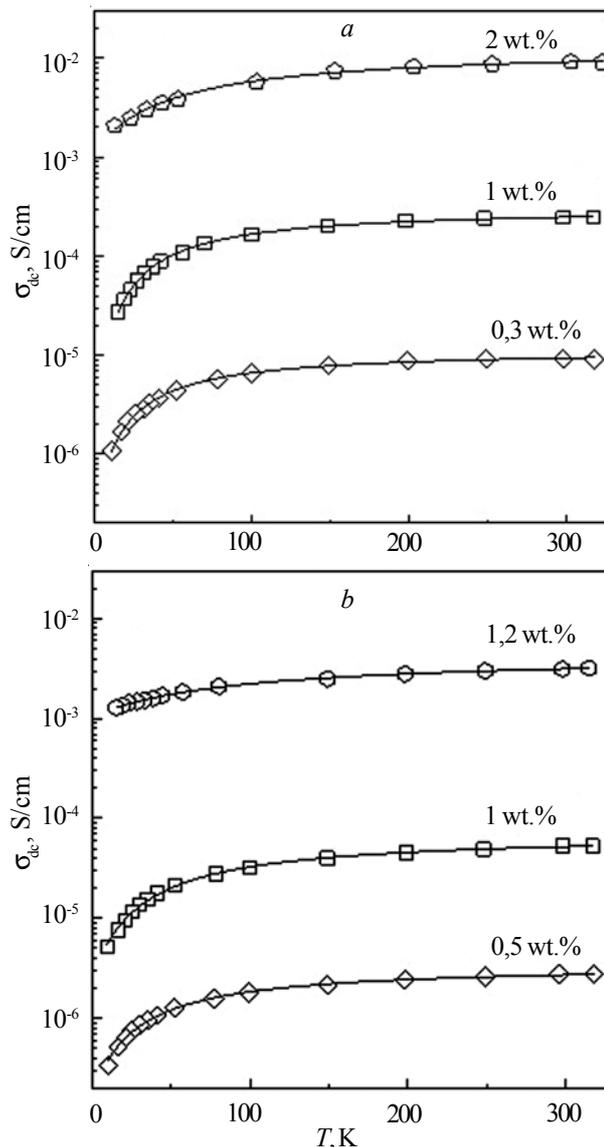


Fig. 5. Temperature dependence of dc conductivity fitted by the FIT model for the nanocomposites: *a* – 0,3; 1,0 and 2,0 wt. % of MWCNTs₁ in cPBT/MWCNTs₁ composites (indicated in the plot); *b* – for 0,5; 1,0 and 1,2 wt.% of MWCNTs₂ in PCN/MWCNTs₂ composites (indicated in the plot). The lines show fittings to FIT theory

yield straight lines in the Arrhenius plots. The values of T_0 and T_1 are much smaller than those reported by Kymakis et al. [24]. This can be due to the fact, that these authors investigated the samples with SWCNTs and with much higher concentrations in the range of 8,0–25,0 wt. %. Our data are in the same range with the values reported by Zhang et al. [26] for the samples with MWCNTs contents from 0,5 to 1,0 wt. %.

Weak temperature dependence of conductivity of studied polymer nanocomposites can find an explanation in nanotubes' chirality, their structural characteristics and polymer nanocomposite morphology. Basically, one can roll up the graphene sheet along one of the symmetry

axis: this gives armchair, chiral or zig-zag nanotube [27]. Chirality of CNTs, affects the conductance of the nanotube [28]. CNTs can be metallic (armchair type) or semi-conducting (three-thirds of CNTs are semi-conducting : chiral and zig-zag). Very weak temperature dependence of conductivity for all the nanocomposites presented in this study indicates metallic conducting behavior of MWCNTs at low temperatures suggesting armchair nanotubes' type. The conductivity of CNTs can be determined by the electron mobility which can be affected by different structural defects formed during the synthesis of nanotubes that promotes the electron dissipation and as a result lower conductivity [29]. Along with such structural defects the presence of adsorbates i.e. different molecules or radicals attached to CNTs surface change their electronic structure. The nature of above mentioned damages of CNTs structure depends on synthesis method of CNTs [29]. Based on these considerations and taking into account very weak temperature dependence of conductivity of the CNTs networks, we can suppose that MWCNTs used in the present study have small amounts of defects. This seems reasonable for non-functionalized CNTs. In polymer/CNTs composites nanotubes are very entangled and form continuous networks within polymer matrix where CNTs are covered by the layer of polymer which acts a barrier in bundle to bundle hopping. That is why some decrease of conductivity at low temperatures is observed. According to FIT theory [23] this polymer layer is rather thin, so electrons could tunnel through the barrier (even without physical bonding between conducting regions).

The electrical behavior of polymer/CNTs nanocomposites under the low temperatures have not yet studied enough. Only a few works on investigation of charge transport in polymer/CNTs composites at low temperatures have been recently published [24–26, 30, 31]. A detailed characterization of the electrical properties of alumina/MWCNTs composites in the temperature range from 5 to 300 K is presented [31]. Taking into account the influence of the structural features on CNTs electrical behavior, the synthesis way of nanocomposites can explain the percolation threshold as well as conductivity behavior under broad ranges of temperatures. In [25] Kim et al. dispersed MWCNTs in toluene with PMMA through stirring and sonication during 24 h and have observed a percolation threshold $p_c = 0,4$ wt. %. The conductivity of studied samples strongly depended on MWCNTs content and varied widely within the temperatures ranging from 0,5 to 300 K. Probably such behavior can be interpreted by the break-down of MWCNTs under the heavy dispersion conditions. It is reported [17, 26] that long nanotubes can be damaged or even broken up into shorter segments at using long time sonication. In our case the temperature dependence of the conductivity is rather weak for both the composites and smooth treatment conditions were applied for nanocomposites preparation so carbon nanotube structure is probably not damaged and that results

in observed conductivity behavior under low temperatures.

Among the recently published papers only Kymakis et al. [24] give some explanation of electrical behavior of polymer/CNTs nanocomposites at the low temperatures. Authors correlate the electrical behavior under the broad range of temperatures of nanocomposites to the CNTs structure. Authors explain weak temperature dependence of conductivity of the samples based on poly(3-octylthiophene) (PO3T) filled by single-walled CNTs (SWCNTs) by the fact that SWCNTs consist of a mixture of semiconducting and metallic nanotubes. At very low temperatures the contribution of semiconducting nanotubes is frozen out. As a result, only the metallic SWCNTs contribute to the conductivity at very low temperatures. Here we should note that PO3T is a semiconducting polymer, which also contributes to the complex conductivity behavior of PO3T/SWCNTs composites. Same conclusion can be withdraw in our work, mentioning that MWCNT present even higher conductivity than SWCNT, due to electrical transport within the multiwalls with large diameters [29,32].

Conclusions.

In conclusion, we have demonstrated that the novel approach of the synthesis of CNTs-based nanocomposites using oligomers with low viscosity allows forming composites with improved electrical properties. The behavior of conductivity as a function of MWCNTs content is characteristic of percolation with a threshold of 0,22 wt. % for cPBT/MWCNTs composite and 0,38 wt. % of MWCNTs for PCN/MWCNTs nanocomposite. Such low values of the percolation thresholds are due to large aspect ratio of MWCNTs and good dispersion of conducting filler in polymer matrix. The conductivity of the materials above the percolation threshold increases by ten orders of magnitude. The Fluctuation-Induced-Tunneling mechanism was efficiently applied to model the nanocomposites' temperature dependent conductivity. The elaborated polymer nanocomposites have very interesting conductivity properties for practical applications (such as antistatic materials of automobile parts, in electronics, as details of aircraft and space constructions): by changing the content of MWCNTs one can get the materials with very different conductivity values but with similar and very weak temperature dependences of the conductivity. The measurements at temperatures > 300 K are planned. It will be interesting to modify the cyanurate based polymer [51,53] and also to look at another aspect of such conductive composites as they must present an high permittivity and a low dielectric loss [52,54], offering other types of applications as in the supercapacity field of interest.

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Електропровідність нанокompозитів полімер / вуглецеві нанотрубки при низьких температурах

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При низьких температурах вивчені електричні властивості двох нових типів нанокompозитів полімер / мультістінні вуглецеві нанотрубки (МСУНТ): термопластичний полі(бутилентерефталат) / МСУНТ, отриманий реактивним формуванням з суміші циклічних олігомерів бутилентерефталата і МСУНТ, і термореактивний поліціанурат / МСУНТ, отриманий з використанням ультразвукового змішування мономера диціанового естеру бісфенолу Е (ДЦБЕ) з МСУНТ і подальшого термотверднення ДЦБЕ. Розмірні характеристики і коливальні властивості МСУНТ були досліджені за допомогою трансмісійної електронної мікроскопії та рамановської спектроскопії. Результати вимірювань електропровідності ясно свідчать про наявність порогу перколяції (p_c) при дуже малій масовій частці МСУНТ в обох полімерних матрицях: $p_c = 0,22$ мас. % і $p_c = 0,38$ мас. % для термопластичних і термореактивних композитів, відповідно. Енергії активації електропровідності в діапазоні 10-100 К виявилися дуже малі для всіх зразків ($<0,001$ eV). Виявлено, що температурна залежність електропровідності нанокompозитів відповідає моделі флуктуаційного індукованого тунелювання, і досить слабка, що свідчить про перспективність використання таких матеріалів в електронних пристроях.

Ключові слова: нанокompозити, вуглецеві нанотрубки, електричні властивості, полібутилентерефталат, поліціануратні сітки.

Электропроводность нанокомпозитов полимер / углеродные нанотрубки при низких температурах

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При низких температурах изучены электрические свойства двух новых типов нанокомпозитов полимер / мультистенные углеродные нанотрубки (МСУНТ): термопластичный поли(бутилентерефталат) / МСУНТ, полученный реактивным формованием из смеси циклических олигомеров бутилентерефталата и МСУНТ, и терморективный полицианурат / МСУНТ, полученный с использованием ультразвукового смешения мономера дицианового эфира бисфенола Е (ДЦБЕ) с МСУНТ и последующего термоотверждения ДЦБЕ. Размерные характеристики и колебательные свойства МСУНТ были исследованы с помощью трансмиссионной электронной микроскопии и рамановской спектроскопии. Результаты измерений электропроводности ясно свидетельствуют о наличии порога перколяции (p_c) при очень малой массовой доле МСУНТ в обеих полимерных матрицах: $p_c = 0,22$ мас. % и $p_c = 0,38$ мас. % для термопластичных и терморективных композитов, соответственно. Энергии активации электропроводности в диапазоне 10-100 К оказались очень малы для всех образцов ($<0,001$ эВ). Обнаружено, что температурная зависимость электропроводности нанокомпозитов следует модели флуктуационного индуцированного туннелирования, и достаточно слаба, что свидетельствует о перспективности использования таких материалов в электронных устройствах.

Ключевые слова: нанокомпозиты, углеродные нанотрубки, электрические свойства, полибутилентерефталат, полициануратные сетки.