

<https://doi.org/10.15407/ujpe67.2.140>

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INFLUENCE OF CARBON NANOTUBES ON THE ELECTRICAL CONDUCTIVITY OF PVDF/PANI/MWCNT NANOCOMPOSITES AT LOW TEMPERATURES

The electrical properties of films of a new ternary nanocomposite – the dielectric polymer polyvinylidene fluoride (PVDF), the conducting polymer polyaniline doped with dodecylbenzenesulfonic acid (PANI), and multi-walled carbon nanotubes (MWCNTs, 0–15 wt.%) – have been studied. Based on the results of electrical resistance, R , experiments in a wide temperature, T , interval of 4.2–300 K, it is shown that, at low temperatures, the charge transfer in the nanocomposites with the indicated MWCNT contents takes place via the tunneling of charge carriers between localized states and following the mechanism of variable-range hopping conductivity, $R \sim \exp[(T_0/T)^{1/2}]$. It is found that the characteristic temperature T_0 and the temperature interval of the hopping conductivity depend on the MWCNT content. In particular, the increase of the MWCNT content in the nanocomposite films lowers the characteristic temperature T_0 by two orders of magnitude and narrows the temperature interval, where the hopping conductivity is observed, with the most pronounced changes occurring within an MWCNT content interval of 5–7.5 wt.%.

Key words: nanocomposites, conducting polymers, polyaniline, carbon nanotubes, electrical properties.

1. Introduction

Carbon nanotubes (CNTs) and conducting polymers – in particular, polyaniline (PANI) – attract considerable interest because of their unique physical and chemical properties that are not inherent to conventional semiconductors. The combination of carbon nanotubes and conducting polymers makes it possible to create multifunctional conducting composites,

which, in turn, acquire synergetic and, in some cases, even unique properties that are suitable for creating new electronic devices [1–4]. Such nanocomposite materials can be used in electronic and thermoelectronic devices, batteries, supercapacitors, sensors, antennas, and so forth [5–9]. The application scope of composite materials based on CNTs and conducting polymers can be extended and their characteristics can be improved by doping them with a third component, a non-conducting polymer, which will perform the function of a mechanically and chemically stable carrier matrix. Ternary nanocomposites can be used

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to create antistatic protection, as a material capable of screening electromagnetic radiation, as anti-corrosion coating and membranes [10–15].

Despite the fact that there are a large number of works where the properties of binary systems containing PANI or CNTs have been researched in detail (see, e.g., works [1, 3, 6, 7, 10, 11, 14, 16, 17]), the specific features of electric transport in ternary hybrid nanocomposites have not been studied enough. Unlike single-component materials, the mechanisms of charge transfer in multicomponent materials including both CNTs and conducting polymers are more complicated [18–23]. One should also bear in mind that the resulting properties of ternary nanocomposites can be affected by the specific interaction between the conducting and non-conducting components, as well as by the distribution of conducting fillers over the dielectric matrix. Depending on the synthesis method, the formation of conducting networks with different structures or even demonstrating double percolation is possible [7, 11, 14, 16, 17]. As a result, the properties of a ternary nanocomposite material may differ substantially from the properties of its components.

Earlier [24], we have analyzed the specific interaction of components in the ternary nanocomposite polyvinylidene fluoride (PVDF)/PANI/multi-walled carbon nanotubes (MWCNTs). It was created on the basis of PANI doped with dodecylbenzenesulfonic acid (DBSA) and MWCNTs distributed over the PVDF dielectric matrix. The PVDF/PANI/MWCNT films were obtained by pressing MWCNTs and the pre-synthesized binary powder with the core-shell morphology, in which a submicronic PVDF particle played the role of the core, and a thin PANI layer was the shell. It was found that, as a result of interaction between the conducting PANI and MWCNT fillers, the nanocomposite, in whole, demonstrates synergetic properties that are not inherent to its components taken separately. Furthermore, changes in the morphology and electronic structure of the PANI component of these nanocomposites were accompanied by substantial modifications in their electrical properties with the growth of the MWCNT content.

As a result, the production of PVDF/PANI/MWCNT nanocomposites with prescribed properties requires the study and understanding of the mechanisms of their electrical conductivity in a wide temperature interval. Therefore, in this work, we studied

and analyzed the influence of MWCNTs presenting in a wide concentration interval (0.1, 0.5, 1, 3, 5, 7.5, 10, and 15 wt.%) on the electrical conductivity of the ternary PVDF/PANI/MWCNT nanocomposite in the low-temperature interval above the liquid helium temperature. The analysis of the temperature dependences of the electrical resistance allowed us to establish that, at low temperatures, the charge transfer in the examined specimens takes place according to the mechanism of variable-range hopping conductivity. At the same time, the variation of electrical properties with the growth of the MWCNT content testifies to considerable qualitative and quantitative changes in the conductive percolation network in the PVDF/PANI/MWCNT films as compared with the PVDF/PANI or MWCNT ones.

2. Experimental Part

A detailed description of producing ternary PVDF/PANI/MWCNT nanocomposites can be found in our previous work [24]. In brief, the fabrication procedure can be divided into two stages. At first, the binary PVDF/PANI nanocomposite with the “core-shell” structure was synthesized, where PVDF was the core, and the role of shell was played by PANI doped with DBSA. The content of the conducting filler (PANI) in the studied composites was 4.8 wt.%. After the completion of polymerization process, the dispersed phase of the binary PVDF/PANI nanocomposite was washed out and then dried in the dynamic vacuum at a temperature of 333–343 K for 3 h.

The so-prepared powder of PVDF/PANI nanocomposite was used for producing both PVDF/PANI nanocomposite films (without adding CNTs) and films with MWCNT (Arkema, France) contents of 0.1, 0.5, 1, 3, 5, 7.5, 10, and 15 wt.%. The films were obtained by means of high-temperature (at 473 K) compression of the mixtures of initial PVDF/PANI and MWCNT powders on a *Specac* press under a load of 3 tons on the specimen for 1 min. The thickness of examined films was 0.17 mm. Below, the ternary nanocomposites are denoted as PVDF/PANI/MWCNT $_{xx}$, where xx is the MWCNT content in wt.%.

Electrical measurements were performed in a helium cryostat in a wide temperature interval of 4.2–300 K. The temperature was stabilized with the help of a temperature regulator UTRECS K43, which allowed the temperature in the cryostat to be controlled with an accuracy of 0.01 K. High-quality electrical

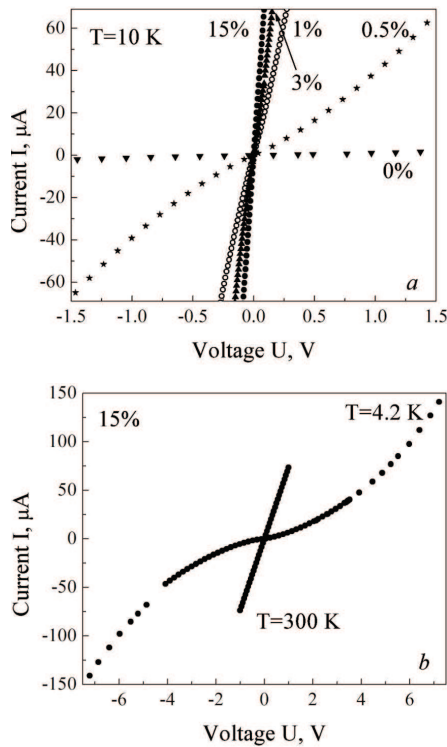


Fig. 1. Current-voltage characteristics of the ternary nanocomposites: PVDF/PANI/MWCNT nanocomposites with MWCNT contents of 0–15 wt.% at 10 K (a), PVDF/PANI/MWCNT15 nanocomposite at 4.2 and 300 K (b)

contacts were provided by applying silver paste. The choice of silver paste was associated with the fact that the electron work function of silver is approximately equal to the electron work functions of the electrically conducting polymer polyaniline and carbon nanotubes. No differences between the obtained resistance values were observed when the measurements were carried out using the two- and four-contact methods. The resistivity values were obtained from the measurements in the van der Pau configuration and calculated by averaging over four contact pairs and two current directions. The current-voltage characteristic (CVCs) were registered using the two-contact method. They were found to be symmetrical, being linear at room temperature. At low temperatures, the CVCs demonstrated non-ohmic behavior but remained symmetrical.

3. Results and Their Discussion

In Fig. 1, the CVCs of the fabricated films of PVDF/PANI/MWCNT nanocomposites are exhib-

ited. For all examined PVDF/PANI/MWCNT specimens (with MWCNT contents of 0–15 wt.%), the CVCs are symmetrical and do not depend on the electric current direction. The curve corresponding to an MWCNT content of 0.5 wt.% (Fig. 1, a) shows a pronounced nonlinear character at a temperature of 10 K. Such a behavior manifests itself at voltages higher than 0.5 V. A similar character is inherent to the curve measured at a temperature of 4.2 K for the specimen with an MWCNT content of 15 wt.% (Fig. 1, b). The nonlinearity of CVCs may testify that, at temperatures close to helium ones, the charge transfer in the PVDF/PANI/MWCNT nanocomposites is governed by the electric field, and there is the Coulomb interaction between the charge carriers.

The resistivity of the researched binary nanocomposite PVDF/PANI made of pre-synthesized core-shell particles was $5 \times 10^{-2} \Omega \cdot m$ at 300 K. This value is lower than the corresponding values for analogous films produced using other methods [24–27], but it agrees with the results of known studies of the electrical properties of similar PVDF/PANI-DBSA nanocomposites with a percolation threshold of about 3.5 wt.% [28]. This fact points to the availability of a high-quality electrically conductive percolation network of doped PANI in the examined nanocomposite.

It was found that if CNTs are added to the binary PVDF/PANI nanocomposite, the electrical resistivity of the obtained ternary PVDF/PANI/MWCNT $_{xx}$ nanocomposites weakly depends on the MWCNT content at room temperature, being only a few times lower (for the PVDF/PANI/MWCNT15 nanocomposite, the corresponding value equals $1.1 \times 10^{-2} \Omega \cdot m$, see Fig. 2). However, at low temperatures (4.2 K), the resistivity of the initial binary PVDF/PANI nanocomposite is about eight orders of magnitude higher than that at room temperature. Accordingly, the effect of doping with MWCNTs is much stronger and is accompanied by a nonlinear reduction of the electrical resistivity of ternary nanocomposites to lower values. The latter, however, are slightly higher than the room-temperature values (Fig. 2). For instance, adding only about 0.1 wt.% of CNTs reduces the resistivity by about two orders of magnitude at a temperature of 4.2 K (for the PVDF/PANI/MWCNT0.1 nanocomposite). A further growth of the MWCNT content in an interval of 0.1–3 wt.% brings about some stabilization of the na-

nocomposite state with an insignificant reduction of their resistivity. However, if the MWCNT content increases to 5–7.5 wt.%, a substantial decrease of resistivity (by about four orders of magnitude) is observed again in the ternary PVDF/PANI/MWCNT xx nanocomposites, which is followed by the attainment of an asymptote typical of percolation systems [28]. Such a specific behavior of the studied nanocomposites not only testifies to the formation of a percolation network of CNTs but also allows us to suppose the existence of its qualitatively different states at MWCNT concentrations of 3 and 7.5 wt.%. Although further studies of analyzed nanocomposites are required in order to better understand this difference, now we may assume that the factors responsible for the existence of such states include specific physicochemical interactions of both conducting components, PANI and MWCNTs [24].

In Fig. 3, the temperature dependences of the resistivity normalized to its value at a temperature of 300 K measured for the PVDF/PANI/MWCNT nanocomposite materials with various compositions are depicted. For all specimens, the temperature dependences have a semiconductor character ($\partial R/\partial T < 0$). However, as the MWCNT content increases, the dependences gradually change. In particular, the binary PVDF/PANI nanocomposite demonstrates a resistance growth by more than six orders of magnitude as the temperature decreases to helium ones (Fig. 3, curve 1). But if MWCNTs are added, the ratio between the resistances registered at the minimum and maximum measurement temperatures decreases. For example, for the specimen with the maximum MWCNT content (15 wt.%, PVDF/PANI/MWCNT15), its resistance at $T = 4.2$ K is eight times higher than that at $T = 300$ K (Fig. 3, curve 4). As was shown earlier [24], such changes in the ternary nanocomposite may occur owing to two factors, namely, a high MWCNT content and a specific physicochemical interaction between the MWCNT and PANI components. For comparison, Fig. 3 demonstrates the temperature dependence of the electrical resistance for the specimen composed of pressed MWCNTs (curve 5). As one can see, the temperature dependence for the PVDF/PANI/MWCNT15 nanocomposite differs substantially from the curve measured for pressed MWCNTs. In particular, the resistivity of the latter increases only by a factor of five at helium temperatures. Such differences can probably

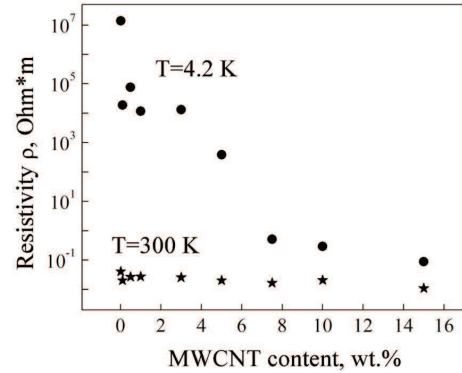


Fig. 2. Dependences of the resistivity of the PVDF/PANI/MWCNT nanocomposites on the MWCNT content at 4.2 (circles) and 300 K (asterisks)

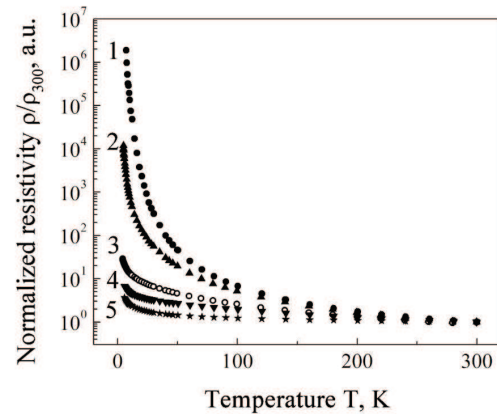


Fig. 3. Temperature dependences of the resistivity normalized to its value at a temperature of 300 K for nanocomposite materials: PVDF/PANI (1), PVDF/PANI/MWCNT5 (2), PVDF/PANI/MWCNT7.5 (3), PVDF/PANI/MWCNT15 (4), and pressed MWCNTs (5)

point to different quality of percolation networks in those specimens.

Earlier [24], we showed that in the region of low temperatures the electrical conductivity of the ternary PVDF/PANI/MWCNT1 and PVDF/PANI/MWCNT10 nanocomposites corresponds to the mechanism of hopping conductivity,

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^p, \quad (1)$$

where ρ_0 is the prefactor, T_0 the characteristic temperature, and p the power exponent, the magnitude of which is determined by the conductivity mechanism. According to Eq. (1), the value of p , as well as the limits of the temperature interval where the

Parameters of ternary PVDF/PANI/MWCNT composites

Specimen	Content, wt.%			T-interval for Eq. (1), K	Power exponent <i>p</i>	<i>T</i> ₀ , K
	PVDF	PANI	MWCNTs			
PVDF/PANI	95.2	4.8	0	4.2–300	0.52	2153
PVDF/PANI/MWCNT0.1	95.1	4.8	0.1	4.2–260	0.47	1005
PVDF/PANI/MWCNT0.5	94.7	4.8	0.5	4.2–220	0.48	1234
PVDF/PANI/MWCNT1	94.2	4.8	1	4.2–240	0.48	930
PVDF/PANI/MWCNT3	92.2	4.8	3	4.2–16	0.50	600
PVDF/PANI/MWCNT5	90.2	4.8	5	4.2–20	0.48	376
PVDF/PANI/MWCNT7.5	87.7	4.8	7.5	4.2–20	0.50	21
PVDF/PANI/MWCNT10	85.2	4.8	10	4.2–20	0.50	10
PVDF/PANI/MWCNT15	80.2	4.8	15	4.2–20	0.47	8.5

hopping conductivity is realized is convenient to determine using the logarithmic derivative [22, 29]

$$W = -\frac{\partial \ln \rho(T)}{\partial \ln T} = p \left(\frac{T_0}{T}\right)^p \quad (2)$$

An analysis shows that the temperature behavior of the resistance of the ternary PVDF/PANI/MWCNT nanocomposites with MWCNT contents of 0–15 wt.% in the low-temperature interval corresponds to dependence (1) with $p = \frac{1}{2}$ (see Table). This value is inherent to two mechanisms of variable-range hopping conductivity, namely, conductivity according to the Mott and Efros–Shklovsky models, which describe the charge transfer as the tunneling of charge carriers between localized states [22, 30]. Unlike the Mott model where the density of states near the Fermi level is considered to be constant, the Efros–Shklovsky model assumes that the density of states is reduced here due to the Coulomb interaction between the charge carriers. The nonlinear behavior of CVCs (Fig. 1, *b*) and large changes of the resistivity as the temperature decreases from 300 to 4.2 K ($\rho_{5\text{ K}}/\rho_{300\text{ K}} > 1000$) testify that the charge transfer in the examined specimens occurs according to the mechanism of variable-range hopping conductivity described by the Efros–Shklovsky model [29, 30].

The values of the characteristic temperature T_0 and the upper limit of the temperature interval where the hopping conductivity takes place depend on the MWCNT content in the specimen. In particular, the hopping conductivity in the PVDF/PANI film is observed in almost the whole analyzed temperature interval, 4.2–300 K (Figs. 4, *a* and *b*). With the growth

of the MWCNT content to 3 wt.%, the upper temperature at which the hopping conductivity is observed decreases. A further growth of the MWCNT content to 15 wt.% does not narrow this temperature interval, and the electrical conductivity at temperatures of 4.2–20 K is described by Eq. (1) (Figs. 4, *c* and *d*).

If the MWCNT content increases from 0.1 to 15 wt.%, the characteristic temperature diminishes by two orders of magnitude (Fig. 5). It should be noted that an insignificant variation of the MWCNT concentration in the ternary composite from 5 to 7.5 wt.% results in the most pronounced changes of the characteristic temperature T_0 : this parameter becomes almost 18 times lower. This fact, as well as the absence of changes in the width of the temperature interval where the hopping conductivity takes place (4.2–20 K) for specimens with MWCNT contents higher than 5 wt.% (see Table), testifies to strong qualitative changes in the conductive network. The obtained results are in good agreement with the high content of MWCNTs and/or with the specific physicochemical interaction of the components in the ternary PVDF/PANI/MWCNT nanocomposite, which was found by us earlier [24]. They point to a probable strong transformation of the electronic structure in the researched specimens at an MWCNT content of about 5 wt.%.

Attention should also be paid to the fact that the characteristic temperature in the PVDF/PANI/MWCNT nanocomposites can be even lower than that in the specimen consisting of only carbon nanotubes (Figs. 4, *d* and *f*). For instance, the character-

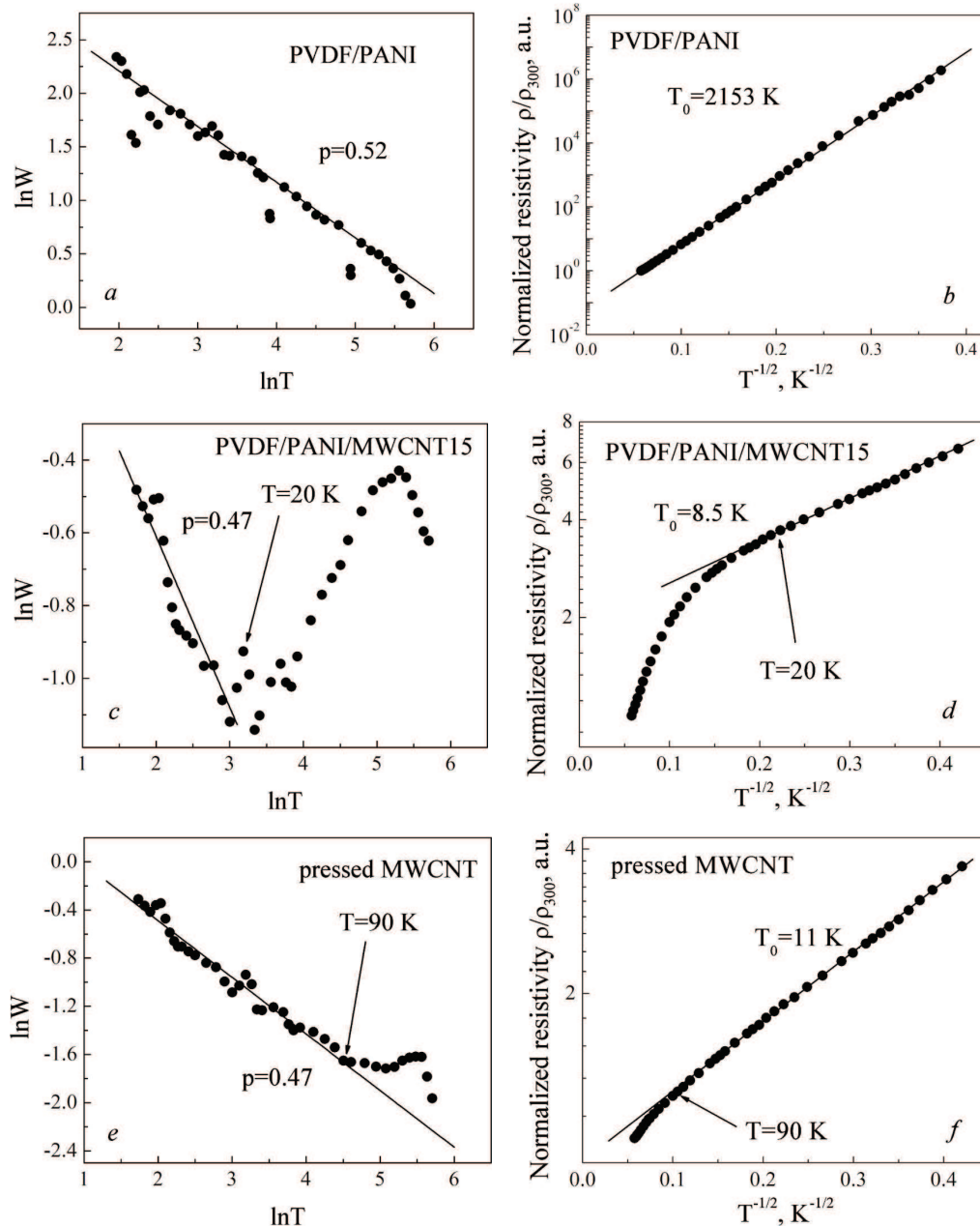


Fig. 4. Determination the power exponent p in Eq. (1) as the slope of the $\rho(T)$ -dependence in the $\ln \rho$ versus $\ln T$ coordinates (a, c, e). Determination of the characteristic temperature T_0 as the slope of the $\rho(T)$ -dependence in the $\rho/\rho_{300\text{ K}}$ versus $T^{-1/2}$ coordinates (b, d, f). PVDF/PANI (a, b), PVDF/PANI/MWCNT15 (c, d), pressed MWCNTs (e, f)

istic temperature for the PVDF/PANI/MWCNT15 film equals $T_0 = 8.5$ K, which is lower than $T_0 = 11$ K for the specimen fabricated from pressed MWCNTs. A lower value of the characteristic tem-

perature testifies to better conditions for the electric current to run. In addition, the temperature interval of hopping conductivity in the nanocomposite with an MWCNT content of 15 wt.% equals

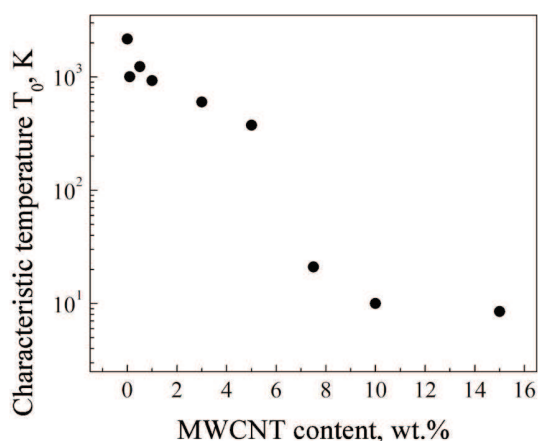


Fig. 5. Dependences of the characteristic temperature T_0 on the MWCNT content in the PVDF/PANI/MWCNT nanocomposites

4.2–20 K, which is much narrower than the corresponding interval of 4.2–90 K for the specimen with pressed MWCNTs. According to the results of our previous studies [24], the temperature interval where the indicated mechanism of hopping conductivity is observed in the PVDF/PANI/MWCNT nanocomposites becomes narrower as the MWCNT content increases because of the delocalization of charge carriers. The delocalization of charge carriers at lower temperatures also points to a high quality of the PVDF/PANI/MWCNT conductive network. Thus, a comparison of the electrical properties of the PVDF/PANI/MWCNT15 and MWCNT specimens shows that the physicochemical interaction between the conducting PANI and MWCNT components brings about the formation of a percolation network that can demonstrate characteristics surpassing the properties of single-component MWCNT specimens.

4. Conclusions

It has been shown that the transfer of charge carriers in the ternary PVDF/PANI/MWCNT nanocomposites at low temperatures occurs in accordance with the mechanism of variable-range hopping conductivity and is described by the dependence $R \sim \exp[(T_0/T)^{1/2}]$. The increase of the MWCNT content reduces the characteristic temperature T_0 and narrows the temperature interval where the hopping conductivity is observed to 4.2–20 K. The most pro-

nounced changes of the characteristic temperature start from the MWCNT contents of 5–7.5 wt.%. This fact means that, at such MWCNT contents, strong transformations take place in the electronic structure of the specimens, either because of the high MWCNT content and/or owing to the specific physicochemical interaction between MWCNTs and the conducting polymer PANI.

The narrowing of the temperature interval where the hopping conductivity is observed and the lower value of the characteristic temperature T_0 for the researched ternary nanocomposites with high MWCNT contents in comparison with those for the specimen fabricated from pressed MWCNTs testify to the formation of a percolation MWCNT network in the formed ternary nanocomposites. This network demonstrates better conditions for the passage of electric current and a possibility of charge delocalization at lower temperatures in comparison with single-component MWCNT specimens.

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Received 30.08.21.

Translated from Ukrainian by O.I. Voitenko

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ВИВЧЕННЯ ВПЛИВУ
ВУГЛЕЦЕВИХ НАНОТРУБОК НА ЕЛЕКТРИЧНУ
ПРОВІДНІСТЬ ТЕРНАРНОГО
НАНОКОМПОЗИТА ПВДФ/ПАНІ/МСВНТ
ПРИ НИЗЬКИХ ТЕМПЕРАТУРАХ

У даній роботі представлено результати дослідження електричних властивостей плівок нових тернарних наноконкомпозитів діелектричного полімеру полівініліденфториду

(ПВДФ), провідного полімеру поліаніліну, допованого додецилбензолсульфоною кислотою (ПАНІ), з різним вмістом мультистінних вуглецевих нанотрубок (МСВНТ). На основі результатів досліджень електричного опору нанокompозитів у широкому інтервалі температур 4,2–300 К показано, що при низьких температурах для нанокompозитів із вмістом МСВНТ 0–15 мас.% перенесення електричних зарядів відбувається за рахунок тунелювання носіїв заряду між локалізованими станами відповідно до механізму стрибкової провідності зі змінною довжиною стрибка $R \sim \exp[(T_0/T)^{1/2}]$. Встановлено, що величина характери-

стичної температури T_0 і температурний інтервал стрибкової провідності залежать від вмісту МСВНТ. Збільшення вмісту МСВНТ у плівках нанокompозитів від 0–15 мас.% приводить до зменшення характеристичної температури T_0 на два порядки і звуження температурного інтервалу, в якому спостерігається стрибкова провідність, причому найбільш виражені зміни відбуваються в інтервалі вмісту МСВНТ 5–7,5 мас.%.

Ключові слова: нанокompозити, провідні полімери, поліанілін, вуглецеві нанотрубки, електричні властивості.