Temperature Dependence of Conductivity in Conjugated Polymers Doped by Carbon Nanotubes

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The structure and temperature dependence of conductivity in conjugated polymers - polyaniline and poly-3,4-ethylenedioxythiophene doped by multiwall carbon nanotubes (MWCNT) with their content near percolation threshold were studied. It was found that temperature dependence of specific volume resistance follows by activation low and is linear in $\ln\rho$-$1/T$ coordinates in the temperature interval of 273-403 K. Introduction of carbon nanotubes in concentration near percolation threshold (0.13-0.64%) leads to increase of conductivity in polymer nanocomposites in 4.4-9.5 times. Simultaneously the activation energy of charge transport increasing for conjugated polymers-MWCNT nanocomposites comparatively with initial polymers.

According to X-ray powder diffraction a process of polymer doping by MWCNT leads to increasing polymer crystalline level in result of formation the ordered "domains" in the amorphous polymer matrix. This structural streamlining leads to an increase of the energy required overcoming areas of amorphous phase and charge carriers are localized in the areas of crystallinity.

Keywords: Conducting polymers, Doping, Charge transport, Carbon nanotube, Structure, Activation energy.

1. INTRODUCTION

The Nobel Prize in Chemistry (2000) demonstrated the importance of polymers with conjugated backbone and controlled electron characteristics [1-3]. On the basis of such polymers, new organic materials are being developed for molecular electronics and sensors [4, 5]. Conducting polymer systems present electron delocalization, arising from conjugated double bonds in the polymer backbone. They show electrical conductivity in doped states (p-doping or n-doping) and are insulators when they are undoped (neutral state). As a result of doping-dedoping processes the electronic properties (e.g. band gap) of the conjugated polymers can be essentially varied. However the conductivity of most polymers can vary substantially depending on molecular weight distribution, purity, conformation, and defect concentration.

Among the family of conducting polymers the polyaniline (PAN) and poly-3,4-ethylenedioxythiophene (PEDOT) have the advantages due to thermal and oxidative stability, good workability and high electrical conductivity. The synthesis of these polymers is relatively simple and regulated, which means a bright future in application [3, 4].

Nanosystems based on conducting polymers doped by carbon nanoclusters (graphene, fullerene, carbon nanotubes) are promising materials for memory devices, plastic solar cells, and sensors [6-13]. The carbon nanotubes (CNTs) are considered as 1D nanomaterials for the field of nanotechnology and sensor-related applications [7, 12] due to excellent mechanical and electronic properties, ability to increase a conductivity of polymers and their sensitivity to different gases and vapors of organic solvents [13]. Over the last years, "in situ" polymerization in the presence of carbon nanotubes has been intensively explored for the preparation of polymer-grafted nanotubes and processing of the corresponding polymer-composite materials. The main advantage of this method is that it enables a better nanotube dispersion and formation of a strong interface between the nanotube and the polymer matrix [7, 11].

The electrical transport properties of the hybrid nanosystems formed by the conjugated polymers and CNTs demonstrated behavior follow to semiconductor at room temperature [7]. In the composite film the changes in the electrical resistance can be explained in terms of interaction of polymer with the nanotubes [7, 12].

For CNT low concentrations, the conductivity of doped polymers remains at the same level than the polymer matrix. At a certain critical CNT concentration (percolation threshold), the conductivity starts a sudden increase. Polymer composite formation from low to high nanotube concentration increases the conductivity dramatically by ten orders of magnitude, indicative of percolate behavior [8, 11].

The percolation threshold for conjugated polymer-nanotube composites is ranging between 0.02 wt.% and 0.05 wt.% [11], or 5 and 8.4 wt.% [8], or 0.13-0.64 wt.% in our study [14].

Most research in this area is concerning the charge transport in composites at CNT contents above the percolation threshold, where conductivity is provided by high-conductive nanotubes [9]. However, effect of carbon nanotubes on the parameters of charge transport at low level of polymer doping is insufficiently studied.

In order to estimate the effect of doping on the parameters of charge transport in the polymer nanocomposites in conditions near the percolation threshold, we studied the structure and temperature dependences of conductivity of conjugated polymers - polyaniline (PAN) and poly-3,4-ethylenedioxythiophene (PEDOT) doped

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by multiwall carbon nanotubes (MWCNT) in the temperature interval of 273-403 K.

2. EXPERIMENTAL

The samples of PAN powder were prepared by known method of oxidative polymerization of aniline in the presence of equimolar amount of ammonium persulphate as oxidant in 0.5 M sulfuric acid [3, 4]. For synthesis of PEDOT the oxidative polymerization of 3,4-ethylenedioxythiophe (EDOT) in the presence of ammonium persulphate was carried out in the mixture solution 0,5 M $H_2SO_4:C_2H_5OH = 1:1$. The molecular structure of polymers is presented in the Fig. 1.
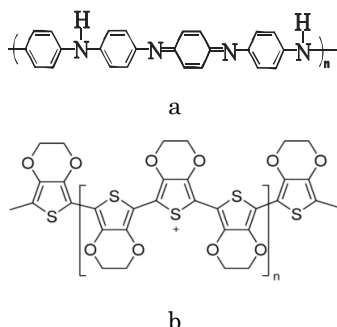

a

b

Fig. 1 – Chemical structure of elementary link of polyaniline (a) and poly-3,4- ethylenedioxythiophene (b)

The synthesis of nanocomposites was realized by the procedure described above by "in situ" polymerization of aniline or EDOT at the presence in reaction mixture the nanosize filler – multiwalled carbon nanotubes (MWCNT). Nanotubes were purchased from Aldrich, with the degree of purification > 95 %, diameter of nanotube is 8-15 nm, length – 25-30 µm and content of hydroxyl groups (– OH) near 5 %. The content of MWCNT in composition was 0.13 wt.% and 0.64 wt.% [14]. Process of functionalization of nanotubes was performed by the ultra sound treatment of MWCNT in the mixture of strong inorganic acids – nitric and sulfuric in their volume ratio of 3:1 [15].

The data of X-ray powder diffraction (XRD) were collected on an automatic diffractometer STOE STADI P with a linear PSD detector (transmission mode; Cu $K_{\alpha 1}$ radiation, a curved germanium (111) monochromator); 2θ-range: $4 \le 2\theta \le 110$. X-ray phase analysis was performed using the Powder Cell [16] and LATCON [17] programs. Determination of the average apparent size was performed by simplified integral breadth methods, using the profile fitting procedure.

Measurements of the specific volume conductivity and temperature dependence of resistance were carried out at dynamic temperature change (5 K/min) by two-probe method in the air. Powder sample was placed in quartz cylinder ($d = 3.6$ mm, $h = 2$ mm) between two nickel disc contacts with built-in thermo-couple and under pressure of 10 N/cm² as described in [3].

3. RESULTS AND DISCUSSION

Conductive polymers investigated in the work are characterized by the values of specific volume resistivity (ρ) referred to organic semiconductors [1-4]. Synthesized by oxidative polymerization powders of conduct-

ing polymers are self-doped by sulfuric acid with $\rho_{293} = 1.97$ Ohms·m (PAN) and 1.15 Ohms·m (PEDOT). The data of the temperature dependence of resistance in the range of $T > 293$ К were elaborated within the band model [3, 19] using an exponential equation

$$\rho = \rho_0 \cdot \exp(E_a/2kT),$$

where E_a - activation energy of charge transport, ρ_0 – constant.

The dependence of polymer's specific volume resistance, normalized to resistance defined at room temperature (ρ/ρ_{293}) from $1/T$ is linear for PAN in the temperature interval 303-393 К and for PEDOT in the range of 303-363 К. The linear dependence of $\ln(\rho/\rho_{293}) - 1/T$ gives a possibility to determine activation energy of charge transport (E_a) for this temperature range. It found the E_a values for sample of polyaniline is 0.072 eV and $E_a = 0.196$ eV for PEDOT (Table 1).

Introducing the MWCNTs in polymers at low amount 0.13 wt.% almost does not affect the values of the resistivity, but leads to a certain increase in the activation energy of conductivity (Table 1). The decrease of ρ value becomes noticeable at MWCNTs content near 0.64 wt.% leading to increase of conductivity in the polymer nanocomposites in 4.4-9.5 times. Temperature dependence of specific volume resistance for PAN and PEDOT, doped by multiwall carbon nanotubes (Fig. 2 and 3) also follows by activation law and is linear in the temperature interval 303-393 K.
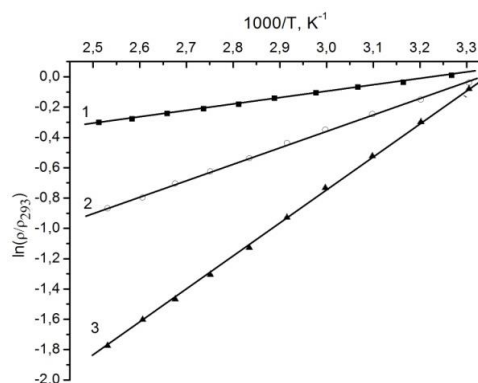

Fig. 2 – The temperature dependence of resistance for polyaniline doped with carbon nanotubes at their content: $1 - 0$; $2 - 0.13$ % MWCNT; $3 - 0.64$ % MWCNT

It noted that decrease in specific resistance of doped polymers associated with rising of the activation energy of charge transport (Table 1). Numerical values of the activation energy and parameter ρ_0 are listed in the Table 1.

To understand the nature of the influence of doping on the activation parameters of conductivity the structural studies of PAN and PEDOT doped with MWCNTs were carried out. Fig. 4 presented the X-ray diffraction pattern for doped by nanotubes and undoped PAN. Basic diffraction pattern of acid doped PAN without MWCNT contains several strongly widening diffraction peaks (amorphous halo) and indicates the formation of almost amorphous phase PAN.

The exact definition of microstructural parameters carried out. Fig. 4 presented the X-ray diffraction the

Table 1 – The parameters of charge transport for conducting polymers and their composites with carbon nanotubes

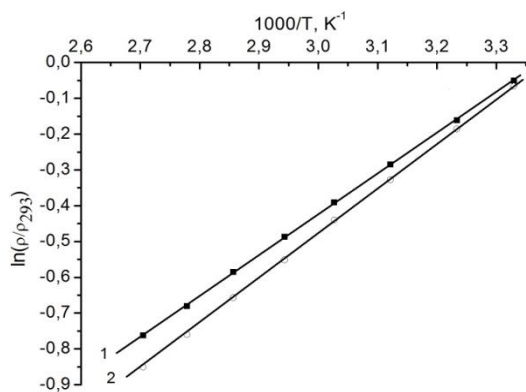| Polymer	ρ_{293}, Ohms·m	ρ_0, Ohms·m	E_a, eV
PAN	1.97	$9.24\ 10^{-2}$	0.072 ± 0.001
PAN – 0.13 % MWCNT	1.98	$6.9\ 10^{-2}$	0.186 ± 0.003
PAN – 0.64 % MWCNT	0.45	$2.8\ 10^{-2}$	0.348 ± 0.003
PEDOT	1.15	2.15	0.196 ± 0.001
PEDOT – 0.64 % MWCNT	0.12	1.13	0.216 ± 0.001

Fig. 3 – The temperature dependence of resistance for PEDOT doped with carbon nanotubes at their content: 1 – 0; 2 – 0.64 % MWCNT
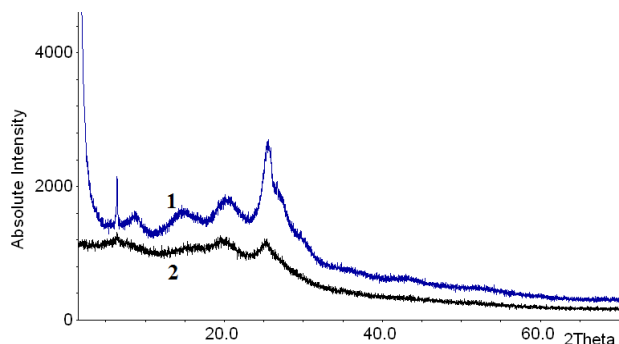

Fig. 4 – X-ray patterns of PAN-MWCNT(1) and PAN (2)

activation parameters of conductivity the structural studies of PAN and PEDOT doped with MWCNTs were pattern for doped by nanotubes and undoped PAN.

Basic diffraction pattern of acid doped PAN without MWCNT contains several strongly widening diffraction peaks (amorphous halo) and indicates the formation of almost amorphous phase PAN. The exact definition of microstructural parameters (size of coherent scattering domains, approximation – the linear average of particle size of crystallites) is difficult because of the strong widened reflections and the background, but it can be assumed that the estimated size of domains coherent scattering is ~ 20-30 Å [3]. In the presence of MWCNT in composite even in such small quantities as 0.64 %, a shape of diffraction picture significantly changed (Fig. 4, curve 1)

The series of crystalline maximums with higher intensity are appeared. Diffraction pattern of PAN-MWCNT is amorphous-fractal, as evidenced by a sharp increase in intensity at low angles and extended highs of diffraction maxima. However, the observed diffraction pattern includes a narrow, well-formed diffraction peak at $2\theta = 6.417°$ (interplanar distance $d = 13.763$ Å). You can note that this reflection diffraction peak corresponding to the first one for sample acid doped PAN (Table 2). Obviously, the basic structure of nanocomposites in the formation of carbon nanotubes changes, and it produced enough area with a high degree of crystallinity. Thus, the average linear size of crystallites calculated from this diffraction peak are ~ 514 Å.

Compared with polyaniline, the PEDOT characterized by a more pronounced amorphous halo with broad peaks of crystallinity in X-ray diffractograms. Doping of PEDOT by MWCNT causes the increasing of crystallinity level, as well for PAN, while not creating additional peaks (Fig. 5).

Table 2 – The parameters of charge transport for conducting polymers and their composites with carbon nanotubes

Sample	Reflection maxima, 2θ, degrees	Interplanar distance, d, Å	Crystallite size, L, Å	Degree of crystallinity, I, %
PAN	25.267 20.101 15.933 6.396	3.522 4.414 5.558 13.808	30 ± 2	15 ± 3
PAN-MWCNT (0.64 %)	28,68 22.15 15.93 6.417	3.112 4.063 5.558 13.763	514 ± 2	29 ± 3
PEDOT	7.2 19.8 22.5	12.28 4.48 3.95	59.4 ± 0.6	9.6 ± 0.8
PEDOT-MWCNT (0.64 %)	6.8 11.9 19.9 26.1	12.99 7.44 4.46 3.41	90.8 ± 0.9	15.4 ± 0.8

According to X-ray powder diffraction a process of polymer doping leads to increasing polymer crystalline level in result of formation the crystalline "domains" in the amorphous polymer matrix.
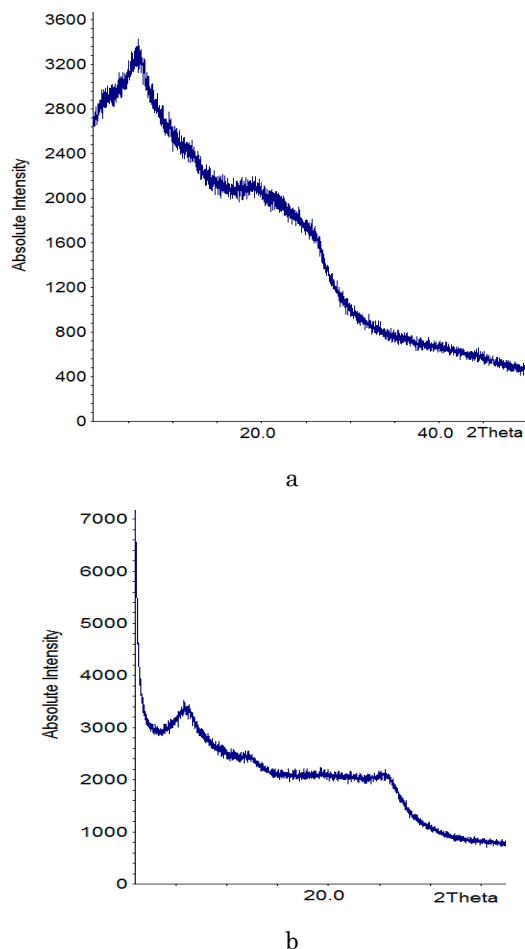

Fig. 5 – X-ray diffraction patterns of PEDOT (a) and PEDOT-MWCNT (b)

Charge transport in low-dimensional polymer nanosystems may be considered in the frame of "domain" or "granular" model of conductivity. According to these representation in polymer there are existed the ordered areas (domain or crystallites) with high conductivity. Charge transport between these domains occurs by

hopping mechanism across the low-conductive amorphous shells, which create the energetic barrier to conductivity [18, 19]. It may be expected that inside crystallinity domains the significant interchain overlapping of wave function by all domain volume take a place [19].

Structural features suggest that the increase in temperature allows the charge transfer between the regions of crystallinity across the disordered polymer phase. In result of doping the area of conductive domains (crystallites) is increased, for example, for PEDOT from 60 to 92 Å, degree of crystalline is twice higher (see Table 2). According to X-ray powder diffraction a process of polymer doping leads to increasing polymer the degree of crystallinity in result of formation the crystalline "domains" in the amorphous polymer matrix. But at MWCNT contents lower than percolation threshold the main processes of charge transport occur in polymer matrix. This structural streamlining leads to an increase of energy required overcoming areas of amorphous phase and charge carriers are localized in the areas of crystallinity.

4. CONCLUSION

Incorporation of carbon nanotubes in conducting polymers causes an improving the charge transport parameters due to structural ordering of polymer chains under influence of MWCNT acting as conductive admixture. Introduction of carbon nanotubes in concentration near percolation threshold leads to increase of conductivity in polymer nanocomposites in 4.4-9.5 times. Simultaneously the activation energy of charge transport increasing for conjugated polymers-MWCNT nanocomposites comparatively with initial polymers.

According to X-ray powder diffraction a process of polymer doping by MWCNT leads to increasing polymer degree of crystallinity in result of formation the crystalline "domains" in the amorphous polymer matrix. This structural streamlining leads to an increase of the energy required overcoming areas of amorphous phase and charge carriers are localized in the areas of crystallinity.

Температурна залежність провідності спряжених полімерів, легованих карбоновими нанотрубками

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Досліджено структуру і температурну залежність провідності спряжених полімерів – поліаніліну і полі-3,4-етилендіокситіофену, легованих багатостінними карбоновими нанотрубками (БСКНТ) з їхнім вмістом близьким до порогу перколяції. Встановлено, що температурна залежність питомого опору підпорядковується активаційному закону і спрямляється в координатах $\ln\rho$ - $1/T$ в інтервалі темпера-

тур 273-403 К. Додавання карбонових нанотрубок концентрацією в області порогу перколяції (0.13-0.64%) спричиняє зростання провідності полімерного нанокомпозиту в 4.4-9.5 рази. Разом з тим енергія активації переносу заряду в нанокомпозитах спряжений полімер – БСКНТ є більшою порівняно з вихідним полімером.

Згідно даних Х-променевої порошкової дифрактометрії процес легування полімерів БСКНТ спричиняє збільшення рівня кристалічності в результаті формування упорядкованих «доменів» в аморфній полімерній матриці. Таке структурне впорядкування приводить до збільшення енергії, необхідної для подолання ділянок аморфної фази і локалізації носіїв заряду в областях кристалічності.

Ключові слова: Електропровідні полімери, Легування, Перенесення заряду, Карбонові нанотрубки, Структура, Енергія активації.

Температурная зависимость проводимости сопряженных полимеров, легированых карбоновыми нанотрубками

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Исследованы структура и температурная зависимость проводимости сопряженных полимеров – полианилина и поли-3,4-этилендиокситиофена, легированованых многослойными карбоновыми нанотрубками (МСКНТ) с содержанием, близким к порогу перколяции. Установлено, что температурная зависимость удельного сопротивления подлежит активационному закону и спрямляется в координатах $\ln\rho$ - $1/T$ в интервале температур 273-403 К. Введение карбоновых нанотрубок при концентрации, близкой к порогу перколяции (0.13-0.64%) приводит к росту проводимости полимерного нанокомпозита в 4.4-9.5 раз. Вместе с тем энергия активации переноса заряда в нанокомпозитах сопряженный полимер - МСКНТ имеет большее значение по сравнению с исходным полимером.

Согласно данным рентгеновской порошковой дифракции процесс легирования полимера МСКНТ приводит к увеличению уровня кристалличности в результате формирования упорядоченных «доменов» в аморфной полимерной матрице. Такое структурное упорядочение приводит к увеличению энергии, необходимой для преодоления участков аморфной фазы и локализации носителей заряда в областях кристалличности.

Ключевые слова: Электропроводящие полимеры, Легирование, Перенос заряда, Карбоновые нанотрубки, Структура, Энергия активации**.**

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