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Preparation and Properties of Hybrid Poly(3,4-ethylenedioxythiophene)–Carbon Nanotubes Composites

I.B. Olenych[1,*], O.I. Aksimentyeva[1], I.D. Karbovnyk[1], Yu.I. Olenych[1], L.I. Yarytska[2]

[1] *Ivan Franko National University of Lviv, 50, Dragomanov Str., 79005 Lviv, Ukraine*
[2] *Lviv State University of Life Safety, 35, Kleparivska Str., 79000 Lviv, Ukraine*

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It was investigated the infrared spectra of the hybrid composites poly(3,4-ethylenedioxythiophene)–carbon nanotubes in the 400÷4000 cm^{-1} range. The current-voltage characteristics of the obtained materials have been studied. It is shown that increasing the content of carbon nanotubes in the composite leads to decrease of the resistance of hybrid films. It was investigated the temperature dependence of the electrical conductivity of hybrid nanocomposites in the 80-330 K range. A possible mechanism of charge transfer processes in hybrid composites of poly(3,4-ethylenedioxythiophene)–carbon nanotubes is proposed.

Keywords: Nanocomposite, Conjunction Polymer, Carbon Nanotubes, Conductivity, Infrared Spectroscopy.

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1. INTRODUCTION

The progress in nanoelectronics determines the demand for novel low-dimensional materials, which have specific physical properties due to quantum confinement effect. Recently, hybrid nanosystems on the base of conductive polymers reinforced with carbon nanotubes (CNT) are in the focus of increased attention [1-4]. Various electronic and optical systems as well as sensors developed these days utilize the unique properties of nanotubes [4-7]. As far as hybrid nanostructures are considered one can expect the amplification of already existing effects as well as the appearance of new features. Among the variety of conductive polymers, poly-3,4-ethylenedioxitiophene (PEDOT) is of particular interest due to relatively low resistivity and remarkable optical and electrochemical properties. [8-10].

Carbon nanotubes are considered one of the most prospective materials in the field of nanotechnology and crucial materials for future applications. Although physical and chemical properties of CNT-based composites are widely studied over the globe, transport mechanisms in these structures are not clearly described yet. Hence, the aim of the present work is to synthesize PEDOT – CNT composite systems and investigate the interaction of components in such composites, focusing on electrical properties of hybrid films based on such structures.

2. EXPERIMENTAL PROCEDURE

Hybride composite was prepared based on 3,4-ethylenedioxythiophene in the form of water polymer suspension (1.5 % of main substance stabilized by surface active polystirensulphone acid, PSS). Inset in Fig. 1 shows the chemical formula of PEDOT.

The other component of hybrid composites was the dispersed mixture of multiwall CNTs with diameters ranging from 8 to 15 nm and the average length of до30 microns. The contentration of CNTs was 0,5 miligrams per 1 ml of water. Functionalization of nanotubes was performed by ultrasonic processing of CNTs in the mixture of nitride and sulphide acids taken in 3:1 ratio. CNTs were dispersed due to ultrasonic vibrations. After multiple washing of CNTs with distilled water they were mixed with PEDOT solution and subjected to ultrasonic processing for 8 hours.

Obtained suspension was deposited onto 0.4 mm thick fluoroplastic substrate and then dried at room temperature during 48 hours. Eventually, the monolithic film of hybride PEDOT – CNT nanocomposite was obtained. In experiments, composite films containing ~5,~7 and ~10% of CNTs were investigated. Molecular structure of the PEDOT – CNT composite and the interaction between its components was explored using FTIR spectroscopy. IR transmission spectra were measured with AVATAR spectrometer in 400 – 4000 cm^{-1} range. Literature data were considered in order to identify IR absorption bands [11-13].

In order to study electrical properties of hybride composite films silver contacts were thermally deposited onto the films surface. The thickness of contacts was about 0.5 microns. Current-voltage characteristics were measured according to standard methods. Voltage range was from -4 Volts to 4 Volts with 100 mV. Differential conductivity was measured at zero offset at test frequency of 1 MHz employing *LCR* meter. Temperature dependences of electric conductivity were measured in vacuum (10^{-3} mm Hg) starting from liquid nitrogen temperature. Samples were heated linearly at the rate of 0.1 K/sec.

3. RESULTS AND DISCUSSION

In order to clarify the mechanisms of the interaction between PEDOT-CNT components, IR transmission spectra were investigated. Hibryd films on a silicon substrate were studied. Comparative analysis of IR spectra indicated the decrease in transmission in case of hybrid film due to the additional absorption and scattering of light by nanotubes. (Fig. 1).

Absorption bands at 620 та 1100 cm^{-1} corespond to deformational Si–H mode and Si–O–Si valence vibra-

* iolenych@gmail.com

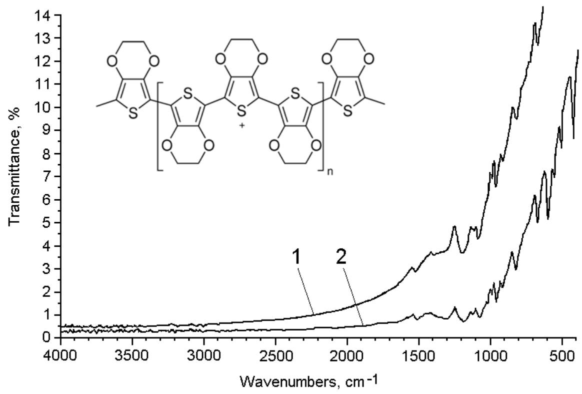

Fig. 1 – IR transmission spectra of PEDOT film (1) and hybrid PEDOT – CNT film on silicon substrate (2)

tions of the silicon substrate, respectively [11]. IR bands between 1080 – 1200 and 1500 – 1550 cm^{-1} are vibrations [12,13]. 700 cm^{-1} absorption can be ascribed to C–S valence vibrations. 850 cм$^{-1}$ band and peaks in 950 – 1000 cm^{-1} range may originate from C–H deformational vibrations [13]. Hybrid PEDOT – CNT films show more intensive absorption bands as comparted to the polymer and a different absorption profile in 620 – 800 cm^{-1} and 1300 – 1420 cm^{-1} ranges. This can be explained by taking into account the interaction between structural parts of the polymer and carbon nanotube atoms. New band at 470 – 520 cm^{-1} may appear due to carbon bonds in CNTs.

Electrical properties of hybrid films depend on gthe composition. Current-voltage curves are symmetric. At low voltages (below 2 V) current scales linearly with voltage. (Fig. 2). Hybrid PEDOT – CNT nanocomposites have significantly lower resistance than polymer films. DC resistance decreases almost 10 times as the concentration of nanotubes increases. (Fig. 3). Since electronic properties of polymers are similar to those of inorganic semiconductors [10], the increase тo of conductivity is probably due to metallic properties of carbon nanotubes.

Temperature dependence of the AC conductivity in the temperature range of 80 – 330 К shows the increase of G with temperature (Fig. 4).

In the low temperature region one observes almost linear increase of the conductivity. For PEDOT – CNT films in the range of 230 – 300 К the dependence of conductivity is more complex. This may be connected with

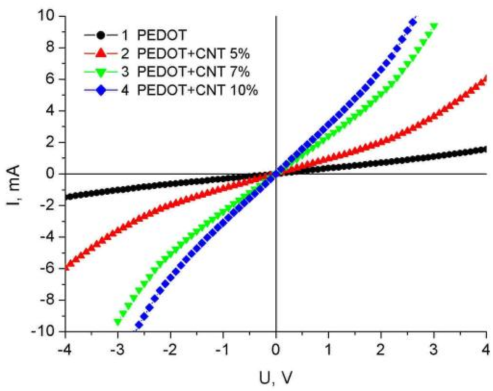

Fig. 2 – Current-voltage characteristic of PEDOT film (1) and hybrid PEDOT – CNT films with 5% (2), 7% (3) and 10% (4) of CNTs

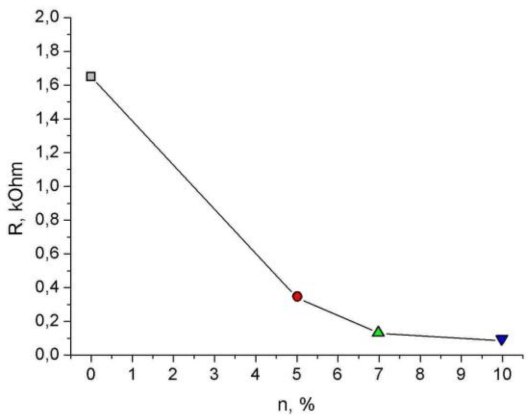

Fig. 3 – Resistance of hybrid PEDOT – CNT films as a function of CNTs concentration

the existence of trapping levels of unequilibrium charge carriers at the CNT – polymer interface. Trapping levels have influence on charge transport in the system of π-electron connections which determines the electrical properties of conductive polymers [10]. In this case the injected as well as thermally stimulated carriers contribute to electrical conductivity processes in PEDOT – CNT hybrid composites.

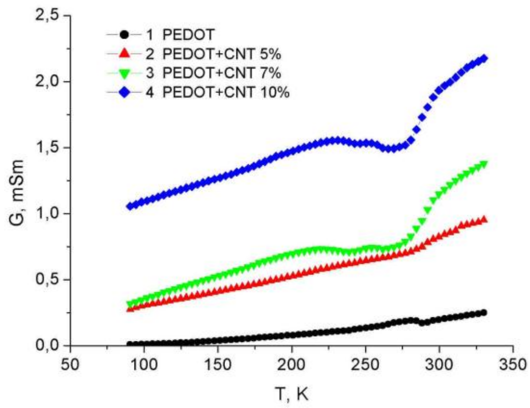

Fig. 4 – Temperature dependence of PEDOT film (1) and PEDOT – CNT hybrid films containing 5% (2), 7% (3) and 10% (4) nanotubes

4. CONCLUSION

Molecular structure and the interaction between components of PEDOT – CNT composites were investigated by means of FTIR spectroscopy. It is established that, principal peaks in IR spectra are related to molecular complexes of the polymer and the interaction between these complexes and CNTs.

It was experimentally proved that the increase of CNTs content in the composite leads to the ten time decrease in the resistivity of hybrid films. The analyses of the temperature dependences of the hybrid composites conductivity in the temperature range of 80-330 К indicates the change of charge transfer character, probably related to the trapping of unequilibrium carriers at the CNT – polymer interface.

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