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SEM and Electrical Studies of Carbon Nanotube Reinforced PEDOT:PSS Layers

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***Abstract*—Nanocomposite layers of PEDOT:PSS polymer which incorporate randomly dispersed carbon nanotubes were thoroughly examined by means of high-resolution scanning electron microscopy and subjected to electrical studies at different frequencies in a wide range of temperatures. Comparison between the performance of pure PEDOT:PSS layers, layers reinforced with single-walled nanotubes and those reinforced with multi-walled nanotubes is made.**

Keywords—nanocomposite, polymer, scanning electron microscopy, conductivity

I. INTRODUCTION

Carbon nanotubes are cylindrical objects that are formed as the result of envelopment of the graphene layer. In the case of one graphene layer, the resulting structures are called single-walled carbon nanotubes. Since its inception in [1,2], tremendous efforts have been put into the study of the properties of carbon nanotubes, which in many respects are unique. Composites based on nanotubes and having good homogeneity are of considerable interest for a wide range of applications, from simple protection from electromagnetic interference to complex optical devices [3,4].

Nanocomposites formed by the addition of nanosized filling elements into dielectric (often polymer) matrix are known to have extraordinary mechanical, thermal and electrical properties [1-4]. Among such nanocomposites of significant interest are PEDOT:PSS polymer matrices reinforced with carbon nanotubes which show great potential for sensor and other applications [5-7]. This particular polymer is one of the most studied and a lot of works have contributed to better understanding of PEDOT/PSS tailorable properties [8,9].

To provide a few examples, embedding of single-walled carbon nanotubes with PEDOT/PSS in dimethyl sulfoxide was shown to be promising for the production of transparent conducting films [10,11] and recently highly flexible conducting PEDOT:PSS/multi-walled carbon nanotubes composite thin films were synthesized by simple, cost effective technique [17-20].

Many works focus on the interaction of external fields with PEDOT structures [5-8], as well as the recently widely studied behavior of electrical properties of nanocomposites as a function of frequency. However, not very much is known about the change in the conductivity or dielectric properties of such composites in the region of low temperatures. That said, information about nanofiller's influence on composite parameters such as loss tangent or dielectric permeability is crucial as far as functional applications are considered [15].

Nanotubes chaotically dispersed in a dielectric medium can form conductive networks that determine the electrical properties of a composite system as a whole [15,16]. Typically, a low concentration of carbon nanotubes already considerably alters system behavior, since the tubes have an elongated shape with a large ratio of length to diameter [17,18].

A bunch of other parameters, such as chirality and or junction resistance between individual tubes influences strongly the ultimate properties of nanocomposite layers. The overall performance of such layers can be even more improved if one precisely controls the dispersion and alignment of the incorporated nanotubes [19,20]. Unlike our previous work concerning computer simulations of nanotube networks [21,22] in this of work we experimentally analyze structural features and electrical behavior of PEDOT:PSS polymer layers with inclusions of high-purity single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) – two types of nanotubes that are characterized by high structural perfection.

II. EXPERIMENTAL

Composite layers with the "polymer – carbon nanotubes" structure were obtained from aqueous suspension (1%) of poly-3,4, ethyldioxythiophene (PEDOT), stabilized with a surface-active anionic substance. Single-walled carbon nanotubes (SWCNTs) with a mean diameter of several nanometers and multi-walled carbon nanotubes (MWCNTs) with an average external diameter of 65 nm and an average internal diameter of about ten nanometers were used as nanofillers [13,14]. Commercially available carbon nanotubes in a form of powder were purchased from US Research Nanomaterials, Inc.

The suspension described above was mixed with the polymer solution and held in an ultrasonic mixer for 4 hours. After such treatment, the mixture was deposited onto glass substrates by centrifugation for 15 minutes. Ultimately, formation of composite layers of PEDOT:PSS reinforced by carbon nanotubes was completed by drying at room temperature for 48 hours. The thickness of the obtained layers was about 20 microns. By adjusting the concentration ratio between the solution and the mass fraction of nanotubes, samples with nanofiller loading of 12 wt. % were obtained.

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Electrical contacts were applied to the upper surface of the fabricated layers by depositing of a conductive paint on the opposite sides of the sample and attaching copper wires to the painted point. The distance between the contact points was 3 mm.

High-resolution imaging of the prepared samples was done using ZEISS Ultra Plus scanning electron microscope equipped with two secondary electrons detecting systems.

Electrical studies were performed using E7-20 RLC measuring instrument. This instrument is designed to measure the parameters of samples represented by a parallel or serial two-element equivalent circuit. Harmonic voltage (1 V) in the frequency range from 1000 Hz up to 1 MHz was used as an excitation signal. The instrument ensures the 3% accuracy of impedance absolute value measurements.

For the purpose of measurement at different temperatures we exploited custom-designed cryostat. DE-202A closed cycle cryocooler from Advanced Research Systems was used as additional equipment. Temperature regulation capabilities were provided by Cryocon 32 controller from Cryogenic Control Systems Inc. Measurements in cooling and heating regimes were carried out, though in the present report mainly data, obtained in cooling regime are analyzed.

III. RESULTS AND DISCUSSION

Obtained composite film nanostructures were first thoroughly examined by high-resolution scanning electron microscopy. Recorded SEM images at different magnifications allow to identify clear enough contours of individual nanotubes. One typical image of bended single-walled tube is presented in Fig. 1.

Fig. 2 shown several interconnected single-walled nanotubes, *i.e.* a small building block of a conducting network, which at certain conditions can be formed inside the matrix.

SEM studies also indicated that aggregation of nanotubes is more likely to occur in MWCNTs composites. To give an example, a typical bundle of multi-walled nanotubes inside polymer is shown in Fig. 3.

To see the difference in the electrical performance of obtained samples, impedance tests were carried out. Based on the readings from E7-20 instrument, which initially measures absolute value of the impedance of the sample and phase angle between applied voltage and current through the sample, we have recalculated real and imaginary parts of the impedance.

First, measurements were made at room temperature and then samples were cooled in helium cryostat down to temperatures as low as 40 K. Real part of the lateral impedance Re(Z) as a function of frequency in the range 1 kHz – 1 MHz is shown in Fig. 4, Fig. 5 and Fig. 6 for the polymer samples without any nanofiller as well as for those with 12 wt.% loadings SWCNTs and MWCNTs, respectively. Results obtained for various temperatures are presented.

As expected, the lowest impedance of PEDOT:PSS based composites is registered at room temperature. Changes of Re (Z) with temperature and frequency indicate that dispersion of nanotubes is not good enough to form percolating network and conductivity is realized due to polymer features. This assumption is in line with scanning electron microscopy observations, that revealed unevenly distributed bundles of nanotubes.

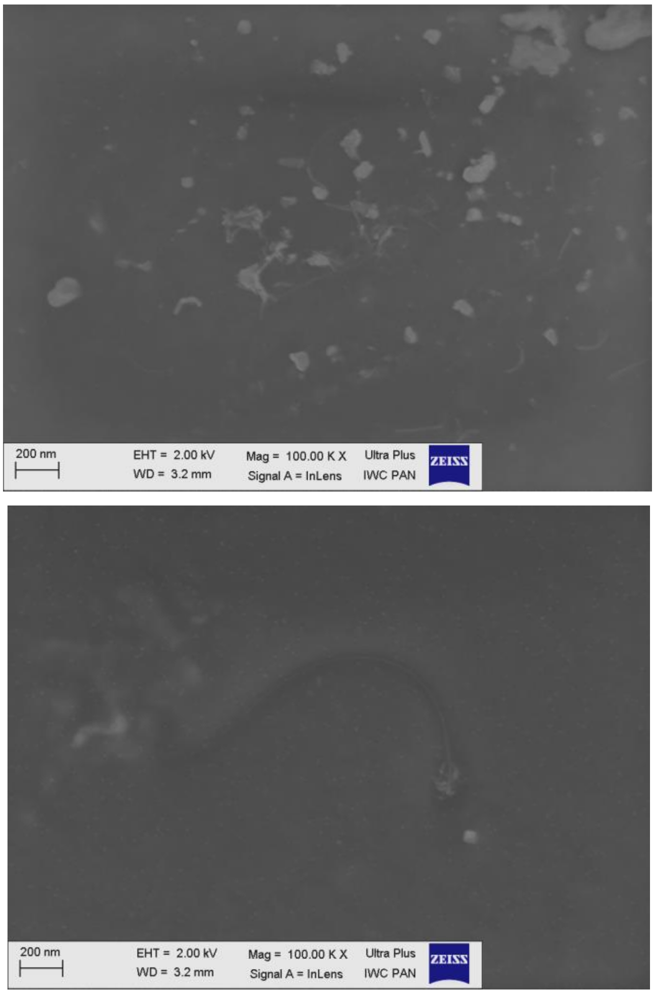

Fig. 1. SEM image of an individual single-walled nanotube inside PEDOT:PSS/12 wt. % SWCNTs composite.

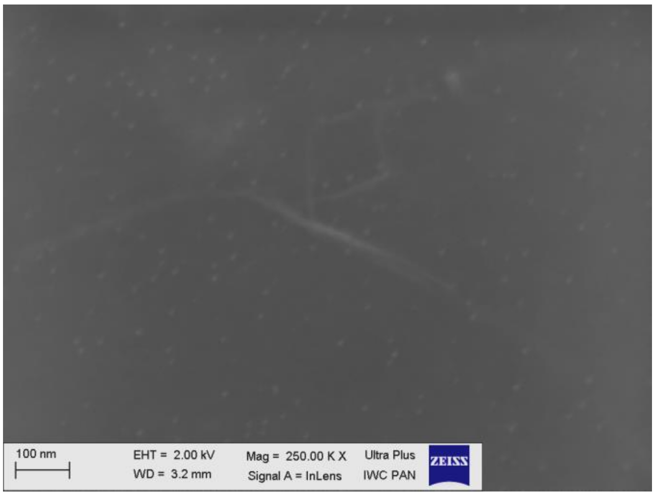

Fig. 2. SEM image of a conductive path formed by several individual single-walled nanotubes inside PEDOT:PSS/12 wt. % SWCNTs composite.

All investigated samples show lowest impedance (highest conductivity) at room temperature and electrical conductivity decrease upon cooling. General trend is that Re(Z) slightly increases with frequency from 1 kHz to up to some threshold frequency and then drops rapidly. This threshold frequency for pure PEDOT:PSS and PEDOT:PSS/SWCNTs samples is about 100 kHz and is somewhat lower for composite layers with MWCNTs.

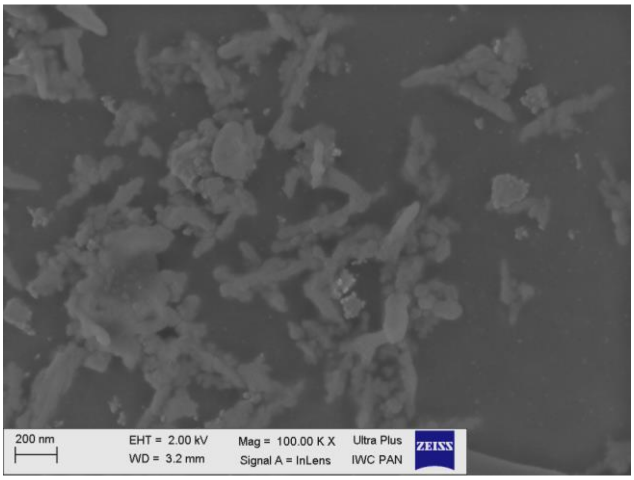

Fig. 3. SEM image of bundles of MWCNTs inside (PEDOT:PSS/12 wt. % MWCNTs composite).

Most notable temperature effect on the real part of the impedance of fabricated polymer/CNTs composite layers is that Re (Z) increases drastically starting from certain temperature, which is different for samples with different composition. For pure polymer this occurs already at 80…90 K and below 60 K Re (Z) is almost out of the measurable range.

For layers reinforced with SWCNTs, increase of impedance is more gradual and even more so for MWCNTs-reinforced composites. In the latter case, reliable measurements can be performed even at temperatures as low as 40K.

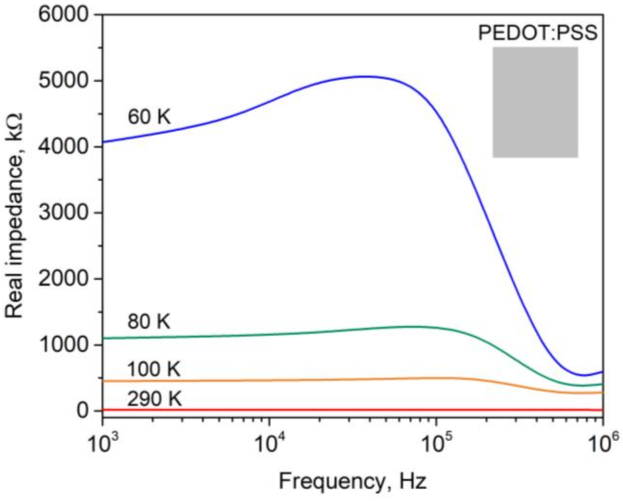

Fig. 4. Real part of the pure PEDOT:PSS layer impedance as a function of frequency at different temperatures.

Such specific temperature behaviour of electrical properties may be a consequence of the change in water contamination [22-24]. In samples with incorporated CNTs the conditions for residual water storage are potentially different due to structural changes introduced by specific nanofiller, so that time needed for complete water removal is different and the process is eventually finished at different temperature. This assumption is further supported by the fact that samples with MWCNTs show slower growth of real impedance with decreasing temperature and generally have higher conductivity at lowest measured temperatures.

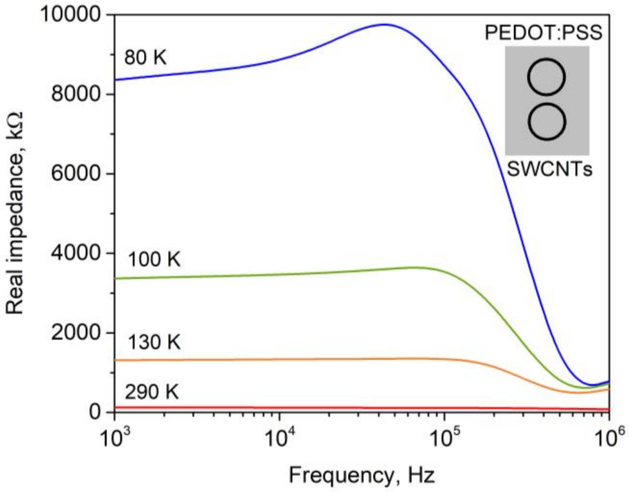

Fig. 5. Real part of the PEDOT:PSS – SWCNTs composite layer impedance as a function of frequency at different temperatures.

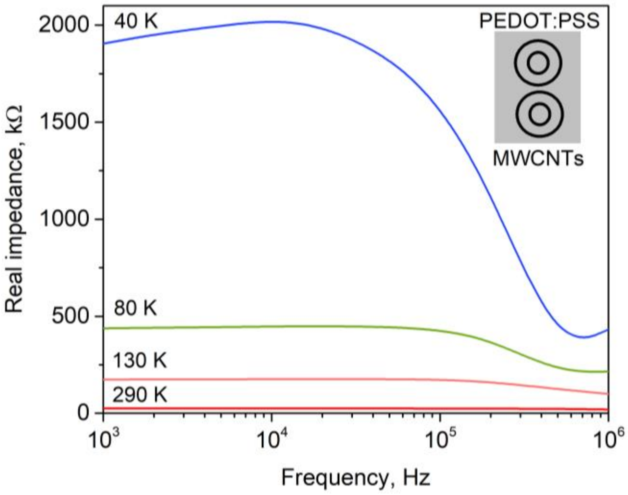

Fig. 6. Real part of the PEDOT:PSS – MWCNTs composite layer impedance as a function of frequency at different temperatures.

To support this discussion, plots of real impedance vs. temperature in cooling regime are presented in Fig. 7 for different composite layers.

As can be seen from Fig. 7, one can confirm that characteristic exponential change of impedance with temperature takes place in case of all samples. It was also found that impedance dependence on temperature follows different trends during cooling and heating sequences in the measurement procedure. This effect as well as additional conductivity vs. temperature data will be discussed in details in a separate report.

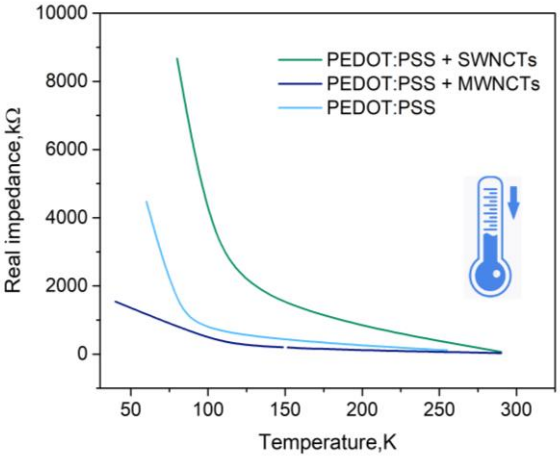

Fig. 7. Real impedance of obtained layers vs temperature at 100 kHz frequency (cooling regime). Solid curves are the result of measured temperature points interpolation.

IV. CONCLUSION

Composite layers of PEDOT:PSS polymer reinforced with single-walled and multi-walled carbon nanotubes were obtained. Scanning electron spectroscopy confirmed strong tendency of nanotube bundles formation, especially in the case of multi-walled nanotubes. Local fragments of conductive network formed by nanotubes were found. Systematic electrical studies of the obtained layers were performed in a wide range of frequencies and temperatures. It is shown that SWCTNs and MWCNTs change temperature dependence of the lateral impedance of polymer layers, probably due to structural changes that affect the process of water removal like in case of other materials [35,26].

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