

Fig. 1. Experimental configuration for low-temperature electrical tests on nanocomposite samples.

respectively. Reference sample containing no nanofiller was prepared for the purpose of comparison. The mixture was ultrasonically processed at 40 kHz frequency 4 h in a row before drop-casting resulting liquid substance onto glass substrate followed by 15 min centrifugation. Samples were then dried at room temperature for two days. The concentration of nanotubes was higher than typically used to achieve percolation [41, 42], although due to lack of functionalization and advanced deagglomeration procedures, no continuous conducting networks were formed inside the obtained layers. This was partially confirmed by SEM imaging showing the presence of larger separated bundles of carbon nanotubes within the volume of the polymer. This effect is particularly pronounced in the case when multi-walled carbon nanotubes were used as nanofiller [43].

For the electrical measurements, the experimental configuration was supplied with electrodes which were deposited on the film surface with conventional silver based conductive paint. Specific resistance of the paint is $0.01 \Omega\text{-cm}^3$ and it is stable in a wide range of temperatures up until 110°C . To explore temperature dependencies of electrical properties, sample chamber was set up inside custom cryostat equipped with a DE-202A closed cycle cryocooler from Advanced Research Systems (see Fig. 1).

Cooling and heating modes of electrical measurements were realized by exploiting functions of Cryocon 32 temperature controller from Cryogenic Control Systems Inc., *ac* electrical measurements at different frequencies were done with the automated E7-20 RLC-meter from LLC “ZAPADPRIBOR” which allows registering active and reactive resistances in the range from 10^{-5} to $10^9 \Omega$. Standard 1 V sinewave was used as an *ac* excitation signal.

Results and discussion

Figure 2 shows temperature dependencies of the resistances of the pristine PEDOT:PSS layer without any addition of carbon nanotubes measured in *ac* regime at 10 kHz and 100 kHz frequencies.

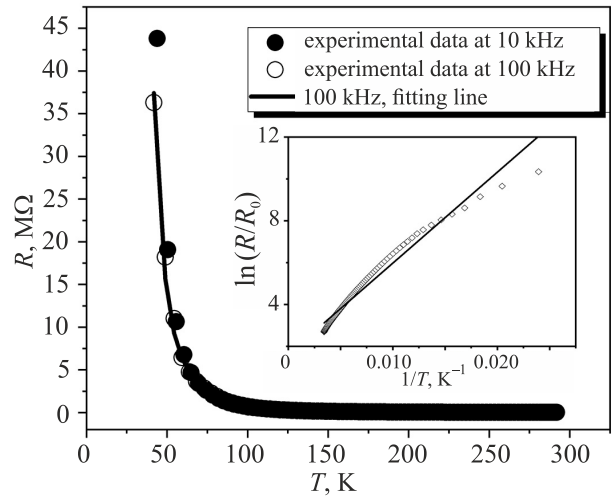


Fig. 2. Resistance vs temperature curves for thin layers of pristine PEDOT:PSS measured at 10 kHz and 100 kHz frequency. Inset demonstrates an attempt of Arrhenius fit of the 100 kHz data.

At higher frequency the resistance drops slightly, though generally the dependencies in Fig. 2 are very similar. They can be described by variable hopping model [44] which is mathematically expressed as

$$R = R_0 \exp \left[\left(\frac{T_0}{T} \right)^{\frac{1}{n+1}} \right], \quad (1)$$

where T_0 denotes characteristic temperature and n is dimensionality parameter.

Fitting results indicate that when $n = 3$, which corresponds to three-dimensional variable hopping, the model produces unrealistically large values of T_0 . Instead, excellent agreement between experimental data and the model is achieved with $n = 2$ (solid line in Fig. 2), being an indication of a few possible mechanisms such as nearest neighbor hopping, tunneling transport or electron-electron Coulomb interactions, the latter being specifically characteristic for low temperature range [45]. For $n = 2$ the model yields T_0 value of 4483 K, which is in line with 4210 K reported for 30 nm thin PEDOT:PSS films [46]. From inset in Fig. 2, it is obvious that conductivity does not follow simple Arrhenius thermal activation process trend, therefore most likely there is a combination of several contributions, which determines R vs T dependence at low temperatures.

Adding multi-walled carbon nanotubes almost does not change the resistance (or conductivity) of PEDOT:PSS layers in the range from 10 to 300 K as can be seen Fig. 3, right graph.

More significant effect was observed in measurement performed at 100 kHz. In this case, the dependence of resistance on temperature for PEDOT:PSS sample reinforced with multi-walled carbon nanotubes deviates substantially from the one described by Eq. 1. Notable non-linearity is observed at the lower end of the temperature range of measurement.

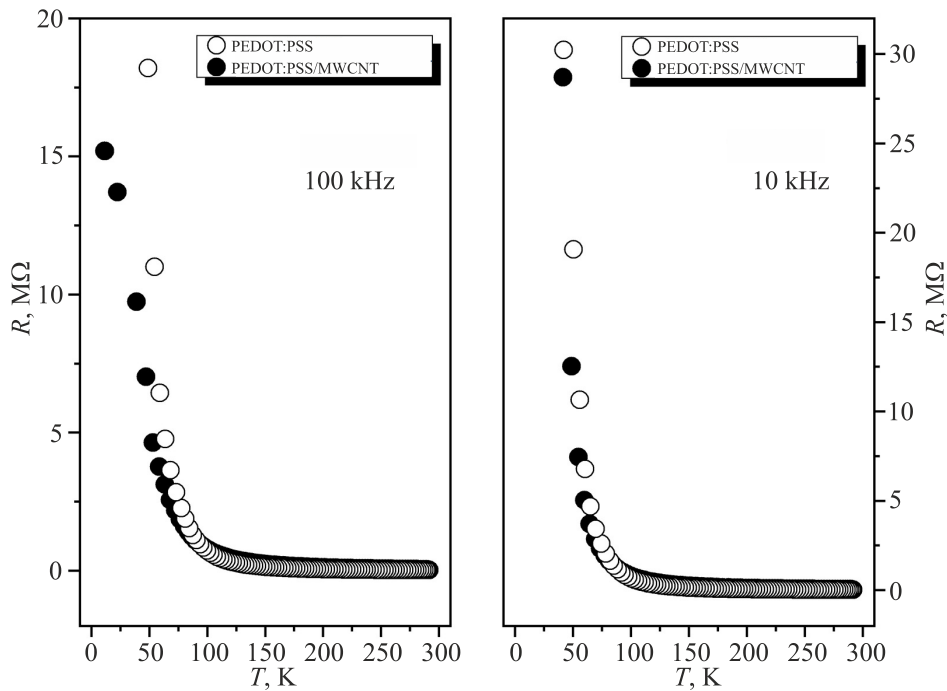


Fig. 3. Temperature variation of resistance for pristine PEDOT:PSS layers and PEDOT:PSS/MWCNT layers.

While one still has to look for an appropriate mechanism to explain such non-linear behavior, the overall decrease in resistance can be attributed to improved coherence of charge transport. Apparently, in the case of PEDOT:PSS with a composite of multiwalled carbon nanotubes, saturation is expected corresponding to a certain maximum resistance value, since the mobility edge is reached at low temperatures.

Another interesting feature observed for carbon nanotubes doped PEDOT:PSS layers in cooling-heating measurement cycles is temperature hysteresis. Measurements in cooling and heating cycles were performed at frequency 50 kHz where non-linear behavior is not pronounced and therefore does not contribute to the effect.

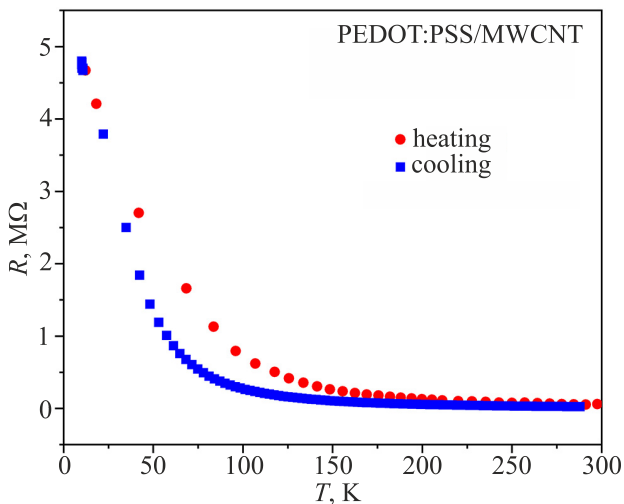


Fig. 4. Temperature dependencies of the resistance of PEDOT:PSS/MWCNT layer measured at 50 kHz in cooling and heating regimes.

Hysteresis which is about 100 K wide may be facilitated by slow nature of the volume expansion/contraction processes in the structure of PEDOT:PSS modified by nanotubes with high aspect ratio.

Thus, the lateral resistance of PEDOT:PSS and PEDOT:PSS/MWCNT composite layers increases non-linearly upon cooling from room temperature down 100 K is followed by rapid increase of resistance as temperature decreases towards 10 K. Layers, containing multi-walled nanotubes usually show lower resistance compared to the original PEDOT:PSS specimens, with the effect being more pronounced at higher frequencies. Generally, the obtained experimental results and their modeling indicate that several conduction mechanisms at low temperatures can be realized simultaneously.

Conclusions

Two types of layers of conductive polymer PEDOT:PSS and polymer PEDOT:PSS with the addition of multilayer carbon nanotubes were prepared, with a thickness in the range of 30–50 μm . The electrical resistance of such layers was investigated depending on the temperature in the range of 10–300 K.

The observed temperature behavior of PEDOT:PSS resistance is consistent line with one-dimensional variable hopping model, which speaks speaking in favor of possible partial contribution of tunneling conduction, as well as thermal activation mechanism and, possibly, Coulomb electron-electron interaction.

The effect of adding nanotubes to the polymer matrix results also leads to the hysteresis of resistance measured

in heating–cooling cycles, which is probably likely to be stimulated by the difference in thermal expansion coefficients of the matrix and the filler and by slow processes determined by these coefficients.

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Вплив температури на електричні властивості полімерних нанокompозитів

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Обговорено результати температурних досліджень нанокompозитів на основі полімерів, які одержані включенням багатостінних вуглецевих нанотрубок у тонкі шари poly(3,4-ethylenedioxythophene):poly(4-styrenesulfonate). Значну увагу приділено особливостям температурної залежності електричних властивостей у широкому інтервалі температур: від температури навколишнього середовища до 10 К.

Ключові слова: полімерні нанокompозити, багатостінні вуглецеві нанотрубки, низькотемпературний гістерезис.