Composites of Polybenzimidazole with SWCNTs – Temperature Dependences of Resistance

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***Abstract* - Electron transport in composites based on dielectric polymer of polybenzimidazole and single-walled carbon nanotubes (SWCNTs) has been studied. The composites were synthesized by flow coating of dispersions (colloidal systems) of SWCNTs in solutions of polybenzimidazole in N-methyl-2-pyrrolidone. Concentration of SWCNTs in the composites was 1, 2, and 3 % (wt.). Electron transport in the film samples of the composites was studied by measuring and analyzing temperature dependences of the electrical resistance of the composites in the range from cryogenic temperature to 300 °C. It was shown that the higher SWCNTs concentration the weaker the dependences were. That is most likely due to a more significant contribution of metallic SWCNTs to the conductivity and weaker dependences correspondingly.**

Keywords - composite; carbon nanotube; SWCNT; polybenzimidazole; PBI; electron transport; resistance; few-layered graphene; graphene

I. Introduction

Electrically conductive polymer composites have been of great interest of late due to mechanical properties of polymer matrixes. New components for electronics applications with outstanding properties different from conventional metallic and semiconducting materials ones can be developed combining various polymer matrixes with electrically conducting fillers.

In order to make different composites, many different polymers have been investigated of late [1,2]. Carbon nanostructured fillers as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene and few-layered graphene (FLG) are the most popular and effective electrically conductive fillers for composites based on dielectric polymer matrixes [3,4].

One of the best polymers in terms of mechanical and thermal properties is polybenzimidazole (PBI) [5]. Previously we investigated composites based on PBI with FLG [6]. The composites were shown to have relative weak temperature dependences of electrical resistance due to semimetallic properties of FLG (FLG – is nanoparticles of graphite). It was shown electron transport occurred generally by tunneling through dielectric gaps between FLG particles.

Composites based on the same PBI representative with SWCNTs as conducting filler were studied in the work. Temperature dependences were measured from cryogenic temperature up to 300 °C and analyzed. The results obtained are discussed with a reference to the early work on composites with FLG.

II. Experimental

A. Synthesis of Composite Films

Commercial SWCNTs (OCSiAl, Russia) were used in experiments. SWCNTs were sonicated in 2% solution of poly[2,2'-(m-phenylen)-5,5'-bisbenzimidazole] (OPBI) in N-methyl-2-pyrrolidone (NMP). The dispersions (colloidal systems) were floated onto glass substrates, dried at 70-80 °C for 24 h. The films were taken off from the substrates and dried in air at 100 °C and 200 °C for 24 h and 2 h respectively. The composites with 1, 2 and 3% (wt.) were obtained.

B. Methods and Apparatures

In order to form samples, the films were cut to strips 1.5 mm in width. Electrical contacts to the samples were made of silver paste. Electrical resistance was measured using four-probe technique with dc power supply of Keysight E36312A and Keithley 2000 multimeter. Temperature dependences of resistance were measured in a homemade heating facility and in a dewar vessel with liquid helium. Scheme of experimental facility for high temperature measurements is shown in Fig. 1, the pressure was as low as 10^{-3} Pa, the rate of temperature change did not exceed 0.4 K/min. Scheme of experimental facility for low temperature measurements is shown in Fig. 2, the rate of cooling was not more than 1 K/min at low temperatures and 2 K/min at higher temperatures, helium gas was used for heat transfer. The lower the rates, the more accurate temperature dependences, but slight increases in the rates do not affect the results obtained.

III. Results and Discussion

The dependences were measured at high temperature first, then at low temperature. The dependences at high (from room temperature up to ~573 K) and low (from ~573 K down to ~7 K) temperatures are shown in Fig. 3

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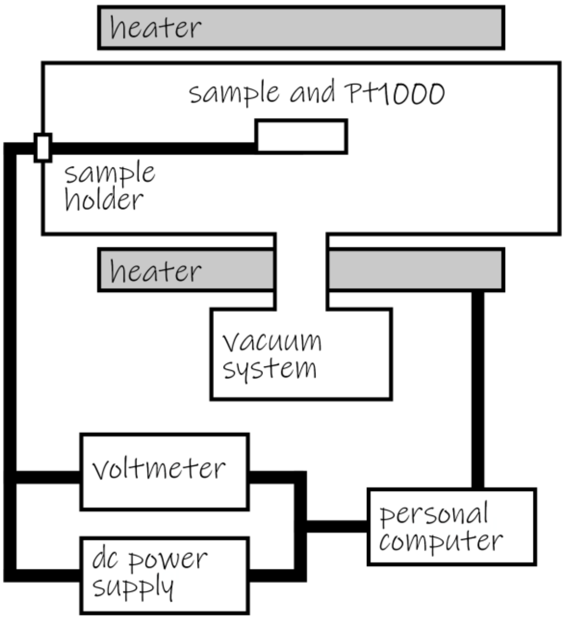

Figure 1. Scheme of experimental facility for high temperature measurements

and Fig. 4 respectively. The inset to Fig. 4 shows high-temperature range of the dependences.

One can see exponential growth of resistance. In the terms of semiconducting and metallic nature of SWCNTs (type depends on structure – chirality) different exponential growth can be explained by lower contribution of metallic nanotubes in electron transport at lower content of SWCNTs in the composite. For a relative thick network consisting of SWCNTs only one should

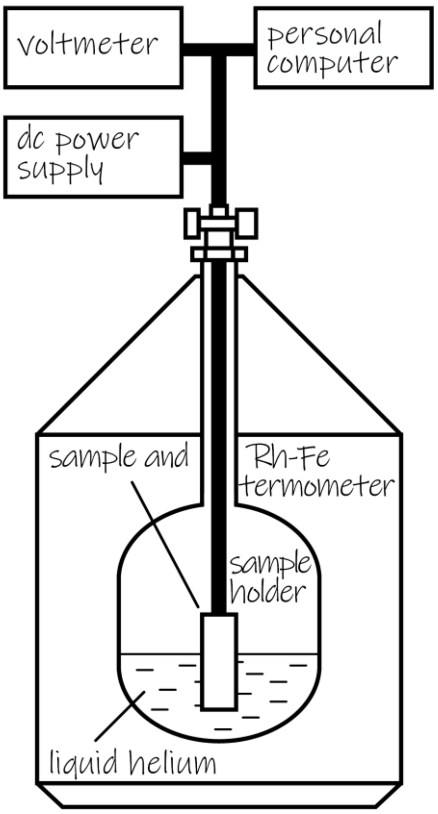

Figure 2. Scheme of experimental facility for low temperature measurements

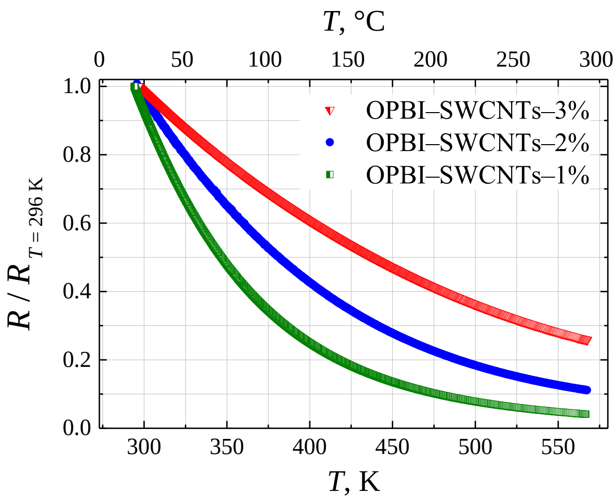

Figure 3. Temperature dependences of electrical resistance normalized to resistance at 296 K at high temperature

expect the dependences to have metallic behavior with weak slope of the experimental curves because of metallic SWCNTs percolation network, like in [7]. But in our case formation of SWCNTs percolation networks is hardly possible, because nanotubes are most likely separated by dielectric polymer gaps. The matter is that the dispersions are very stable, no sedimentation formed for a month at least, what is the obvious result of good wettability of SWCNTs by OPBI solution. And as a result, after the dispersions dried, nanotubes most likely kept surrounded by the polymer, forming gaps for electron transport.

Such a separation we observed for OPBI-FLG composites [6]. For these composites (see Fig. 5) the dependences would have been more similar to the dependence for bulk FLG sample (pressed powder of FLG) if FLG particles contacted to each other without dielectric gaps.

One can see the tendency – the lower SWCNTs content in the composites the stronger the dependences. It should be noted here, that after initial heating cycle resistance increased significantly at first – about 30, 100

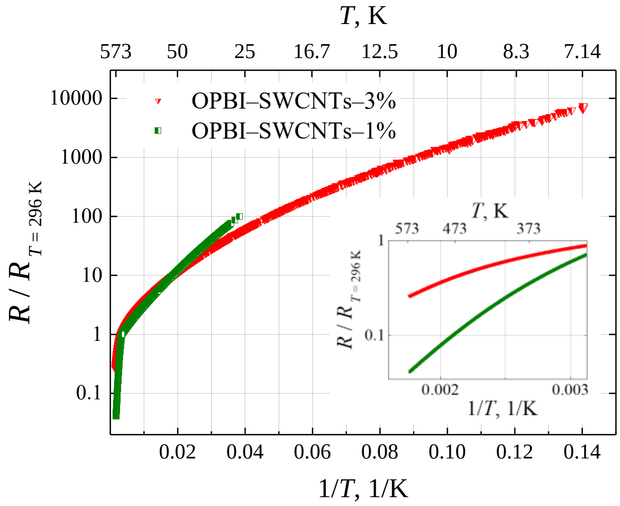

Figure 4. Temperature dependences of electrical resistance normalized to resistance at 296 K at low temperature after high temperature measurements. The inset shows high-temperature range of the dependences

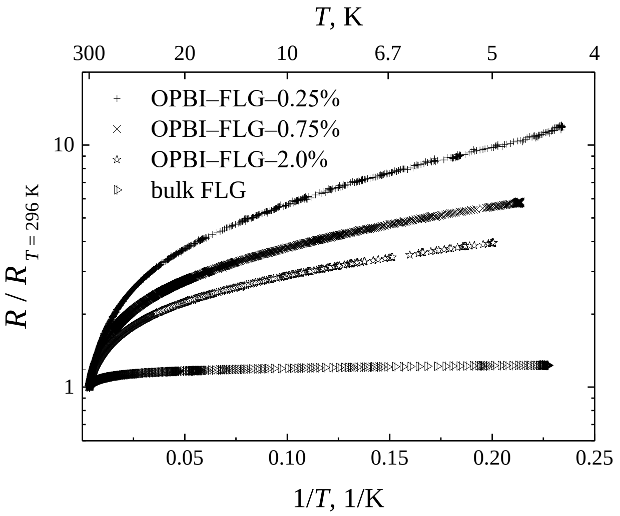

Figure 5. Temperature dependences of electrical resistance of OPBI-FLG composites normalized to resistance at 296 K

and 500 times for 3, 2 and 1% SWCNTs content respectively. Then in the next cycles the dependences repeated. After the samples returned back into air condition the resistance decreased back, but not to exact initial values. This fact can be explained as follows. SWCNTs tend to adsorb oxygen and due to the adsorption resistance changes [8-11], SWCNTs taken at room condition having *p*-type behavior of electron transport. Adsorbed oxygen can be removed at relative high temperature in vacuum. As already mentioned, the pressure was as low as 10^{-3} Pa. Thus, there is no doubt oxygen removed from the SWCNTs surface during heating and as a result their resistance increased due to lower *p*-type doping level (lower amount of oxygen adsorbed). Lower doping level resulted to stronger dependences at low temperatures in contrast to dependences for the samples in initial state (before the heating cycles), that requires further experimental study and discussion in the near future.

Evident step of derivative of the experimental curve for OPBI-SWCNTs-1% around room temperature (see Fig. 4) is due to the fact that the sample kept at room conditions for more significant time period in contrast to OPBI-SWCNTs-3%. If the 1%-sample were kept for fairly short period of time in air before low temperature measurements the derivative would be most likely smooth like it was for 3%-sample.

IV. Conclusion

New perspective composites based on a heat-resistant polymer matrix of polybenzimidazole with single-walled carbon nanotubes of different concentration were synthesized. Experimental study showed resistance-temperature dependences to have semiconducting character with significant change of resistance under vacuum and high temperature conditions during first heating cycle, the value of change dependent on SWCNTs content. More detailed study will be carried out in the near future. But already now we can say that the composites with tunable properties are promising for applications in new electronic components and high temperature electronic devices.

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