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## EFFECT OF DOPING AGENT EVAPORATION ON THERMOELECTRIC PROPERTIES OF CARBON NANOTUBE–POLYANILINE COMPOSITE

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**Abstract.** The paper presents the results of experimental study of the influence of the doping agent (acid) nature on the conductivity, Seebeck coefficient, and thermoelectric power factor of composite material based on multilayer carbon nanotubes coated with polyaniline. Polyaniline was deposited on carbon nanotube surfaces by heterophase synthesis (*in situ* polymerization), by oxidative polymerization of aniline in the presence of nanotubes dispersed in the reaction medium. Hydrochloric, camphorsulfonic and dodecylbenzenesulfonic acids were used as doping agents. The effect of temperature on the conductivity, Seebeck coefficient and thermoelectric power factor of the investigated composite materials has been studied in the range from 300 to 410 K. Comparison of the influence of the acid volatility on the changes in these parameters in the heating-cooling cycle allowed us to conclude that the decrease in conductivity and increase in the Seebeck coefficient when heating composites doped with different acids is caused by the acid removal from the samples.

**Keywords:** thermoelectrics, conducting polymers, carbon nanotubes, conductivity, Seebeck coefficient

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## ВЛИЯНИЕ ИСПАРЕНИЯ ДОПИРУЮЩЕГО АГЕНТА НА ТЕРМОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КОМПОЗИТНОГО МАТЕРИАЛА НА ОСНОВЕ УГЛЕРОДНЫХ НАНОТРУБОК, ПОКРЫТЫХ ПОЛИАНИЛИНОМ

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**Аннотация.** Представлены результаты экспериментального исследования влияния природы легирующего агента (кислоты) на проводимость, коэффициент Зеебека и коэффициент термоэлектрической мощности композиционного материала на основе многослойных углеродных нанотрубок, покрытых слоем полианилина. Полианилин был нанесен на поверхности углеродных нанотрубок методом гетерофазного синтеза (метод полимеризации *in situ*), путем окислительной полимеризации анилина в присутствии нанотрубок, диспергированных в реакционной среде. В качестве легирующих агентов использовались соляная, камфорсульфоновая и додецилбензенсульфоновая кислоты. Влияние температуры на проводимость, коэффициент Зеебека и коэффициент термоэлектрической мощности исследуемых композиционных материалов было изучено в диапазоне от 300 до 410 К. Сопоставление влияния «летучести» кислот на характер изменения этих параметров в цикле нагрев-охлаждение позволило сделать вывод о том, что уменьшение проводимости и увеличение коэффициента Зеебека при нагревании композитов, легированных различными кислотами, связано с "уходом" из образца кислоты, легирующей полианилин.

**Ключевые слова:** термоэлектрики, проводящие полимеры, углеродные нанотрубки, проводимость, коэффициент Зеебека

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## Introduction

Further development of organic (molecular) electronics is impossible to imagine without the use of new organic materials and composites based on them. Organic materials with semiconductor properties, in particular polymers with electronic conductivity, or conducting polymers [1], are currently considered as promising materials for creating thermoelectric generators (TEGs). In addition to the ease of synthesis and low cost, flexible TEGs can be constructed using thermoelectrics based on conductive polymers [2]. Organic-based TEGs demonstrate an acceptable power factor in the temperature range of 200 – 380 K, i.e., they can operate at much lower temperatures than inorganic TEGs. Therefore, such TEGs can be installed in living spaces and can even be incorporated into electronic clothing textiles [3].

Despite the mentioned advantages, organic thermoelectrics are not able to compete with their inorganic semiconductor counterparts due to the fact that they have relatively low conductivity  $\sigma$  and small Seebeck coefficient  $\alpha$  [4]. Significant improvement of thermoelectric properties was achieved through the creation of composite materials based on carbon nanotubes (CNTs) and electrically conductive polymers [4 – 7]. These materials can be produced as nanostructured forms where the nanotubes are encapsulated by a layer of electrically conductive polymer. The properties of such materials depend both on the electrically conductive polymer content in the composite and on its state: the degree of oxidation and doping. In Ref. [8], we have shown that the polymer layer can have a significant effect on the properties of the composite material because it allows us to change  $\alpha$  and  $\sigma$  values of the composite by varying the quantitative content of the doping agent. It can be expected that the introduction of doping agents of different chemical nature into the polymer matrix also provides an opportunity to control the properties of the material.

The ultimate goal is to establish the conditions under which the highest values of thermoelectric power factor (PF) are realized. At a fixed temperature, the latter is defined as

$$PF = \alpha^2 \sigma. \quad (1)$$

Earlier, in Ref. [8], we showed that in multi-walled carbon nanotubes (MWCNTs) coated with polyaniline (PANI) the highest PF value was observed in composites where the level of PANI doped with hydrochloric acid (HCl) being maximal. Moreover, the thermoelectric power factor of such a composite material increased with heating of the samples. The  $\sigma(T)$  cooling curve was found to pass below the one obtained for heating. It was suggested that the loss of water and dopant could be the reason for the conductivity decrease of composite during heating above 370 K. Note that the possibility of realization of such an effect in PANI at elevated temperature was indicated by the authors of Ref. [9].

The aim of the present work was to verify this assumption. For this purpose, we decided to use inorganic and organic acids with different degrees of volatility as dopants and to investigate the features of changes in the conductivity and Seebeck coefficient during heating and cooling of composite material based on MWCNTs coated with PANI doped with these acids.

### Objects and methods of research

MWCNTs obtained by catalytic pyrolysis of hydrocarbons were used as a basis for the composite material. Their diameter was  $17 \pm 5$  nm and the length reached 10  $\mu\text{m}$ . As known, the main charge carriers contributing most to the conductivity of CNTs are electrons, but their thermal conductivity is determined by phonons. The structure of CNTs, usually, is not as perfect as that of single-layer CNTs, but all layers that form the nanotube contribute to the conductivity of CNTs, which increases the value of their conductivity [10].

PANI was deposited on the MWCNT nanotubes surfaces by heterophase synthesis (*in situ* polymerization method [11]), using oxidative polymerization of aniline in the presence of MWCNTs dispersed in the reaction medium. The reaction was carried out in an aqueous-alcohol solution under treatment with ammonium persulfate at 0 °C with vigorous stirring. At the end of the synthesis the product was decanted onto a filter and washed first with acidified aqueous solution and then with acetone. It was dried under normal conditions until the product weight stabilized. The PANI content in the composition of the material was determined by the composite weight gain, which correlated well with the 100 % yield during polymer synthesis. At the end of the synthesis, the mixture was pressed into tablets with a diameter of 16 mm and a thickness of 1 – 3 mm under a pressure of 392 MPa.

The composite morphology was studied using a NANOSEM 450 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Microphotographs of the obtained composite before and after PANI layer deposition on the nanotubes' surface are presented in Fig. 1. It can be seen that the initial MWCNTs (Fig. 1, a) are a homogeneous porous material of chaotically interwoven MWCNTs. After PANI synthesis on the MWCNTs surface (Fig. 1, b), the material structure did not change, but the diameter of the modified tubes increased almost twice, which allows us to estimate the PANI layer thickness at  $\sim 10$  nm.

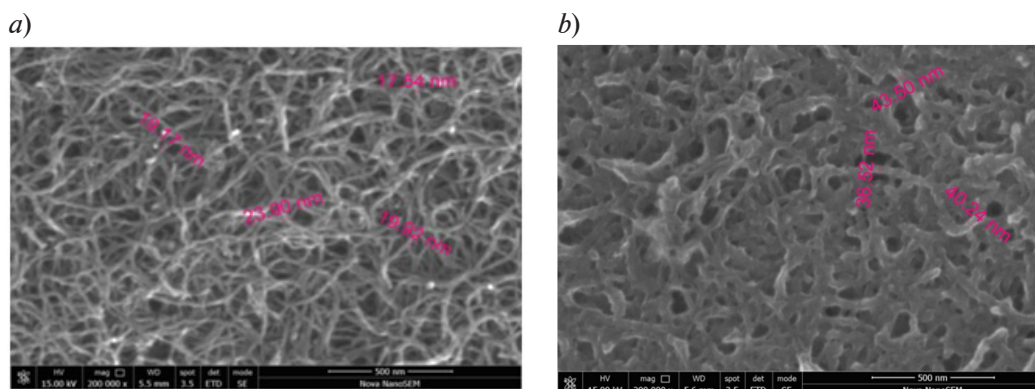


Fig. 1. SEM images of MWCNTs before (a) and after (b) their coating with PANI layer

Various acids were used as dopants: hydrochloric (HCl), camphorsulfonic (CSA), and dodecylbenzenesulfonic (DBSA) ones. Hereinafter, composite material samples doped with these acids are denoted respectively as: MWCNT-PANI-HCl, MWCNT-PANI-CSA and MWCNT-PANI-DBSA.

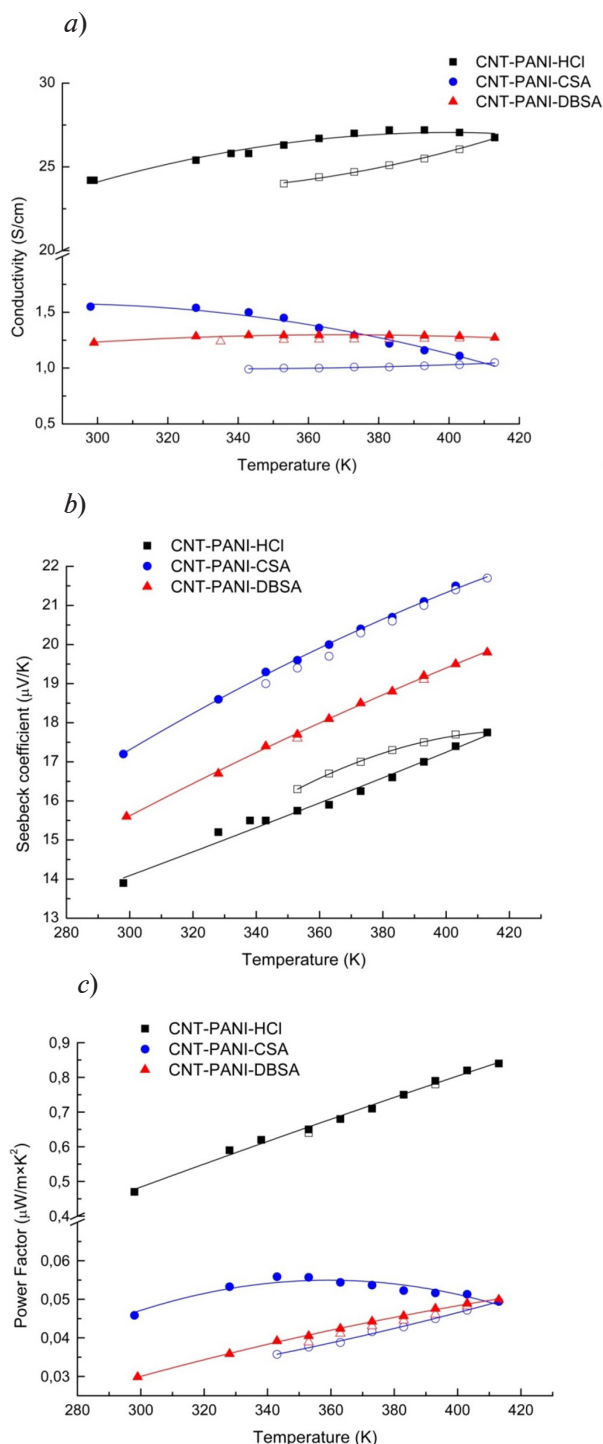


Fig. 2. Temperature dependences of the conductivity (a), Seebeck coefficient (b) and power factor (c) of the samples with different acids used as dopants.

The filled and unfilled symbols correspond to the heating and cooling of the sample, respectively

The specific conductivity and Seebeck coefficient measurements were carried out using a Netzsch SBA 458 Nemesis unit. The four-point method was used to measure the conductivity of the sample. The temperature gradient was created by two microheaters located on the edges of the sample for the Seebeck coefficient measurement. The measuring process of  $\alpha$  and  $\sigma$  values was performed automatically, alternately for each temperature point (with a constant step). The Seebeck coefficient measurement accuracy was 7 % while the accuracy for specific conductivity was 6 – 7 %.

## Results and discussion

To test the assumption of water and dopant loss during heating of the composite which leads to a decrease in its conductivity, the changes in conductivity, Seebeck coefficient and power factor were investigated for doping the MWCNT-PANI composite with hydrochloric acid and organic acids CSA and DBSA. It is important that the molecules of these organic acids are significantly larger than those of HCl and, as a consequence, the organic acids appear to be less volatile. At the same time CSA is more volatile than DBSA.

Fig. 2,a shows the  $\sigma(T)$  dependences of the MWCNT-PANI composite when the previously mentioned acids are used as dopants. Hereinafter, the filled symbols correspond to the heating of the sample, and the unfilled symbols correspond to the cooling. It can be seen that the samples of MWCNT-PANI-HCl are characterized by an increase in the conductivity upon heating. On the contrary, the MWCNT-PANI-CSA sample demonstrates a decrease in the conductivity with increasing temperature, and the  $\sigma(T)$  curve for this composite (as well as for the MWCNT-PANI-HCl composite) shows lower values of the conductivity at cooling than those at heating. The conductivity of the MWCNT-PANI-DBSA sample differs slightly from that of the MWCNT-PANI-CSA sample, but the effect of temperature on the conductivity, both during heating and cooling of the sample, is virtually absent, and the curves  $\sigma(T)$  during its heating and cooling nearly coincide.

The  $\alpha$  value of all studied samples shows a linear growth over the whole temperature range investigated (Fig. 2, b). However, in contrast



to the conductivity temperature dependence, the application of organic acids led to a Seebeck coefficient value increase. It can be seen that its highest value is observed in the sample of MWCNT-PANI-DBSA. When heating this sample from 300 to 410 K, the value of  $\alpha$  increases from 17.3 to 21.5  $\mu\text{V/K}$ . The dependences of  $\alpha(T)$  at heating and cooling of samples of MWCNT-PANI-CSA and MWCNT-PANI-DBSA virtually coincide, but for samples of MWCNT-PANI-HCl type the value of  $\alpha$  at cooling appears to be higher than at its heating.

Based on the results of  $\sigma(T)$  and  $\alpha(T)$  measurements, the power factor temperature dependences of all samples were calculated (see Fig. 2,c). As observed, despite the increase of the Seebeck coefficient for the samples doped with organic acids, the final value of the power factor is much lower than that for the sample doped with HCl. The difference in the power factor value is about an order of magnitude.

An interesting result is that the PF(T) dependences of the MWCNT-PANI-HCl sample almost matched in the heating and cooling cycles. This fact can be explained by the differently directed effect of heating on the conductivity and Seebeck coefficient for the MWCNT-PANI-HCl samples. Indeed, when cooling a MWCNT-PANI-HCl sample immediately after heating, its conductivity at the same temperatures appeared to be less than at heating, and the Seebeck coefficient being larger. Thus, the decrease of one parameter in the Eq. (1) is compensated by an increase of the other.

For the MWCNT-PANI-CSA composite sample, a clear difference in the PF values in the heating-cooling cycle is observed, since it has different  $\sigma(T)$  dependences in the heating-cooling cycle, while the  $\alpha(T)$  dependences coincide. On the contrary, the MWCNT-PANI-DBSA composite shows matching the PF(T) curves in heating and cooling, which is due to the coincidence of the  $\sigma(T)$  and  $\alpha(T)$  dependences in the heating-cooling cycle.

A comparison of the influence of acid volatility on the character of  $\sigma(T)$  and  $\alpha(T)$  changes in the heating-cooling cycle allows us to conclude that the above assumption about the possible loss of dopant in the MWCNT-PANI composite during its heating is valid.

### Conclusion

In this paper, we have studied the nature of the doping agent effect on the electrical and thermoelectric properties of the composite material based on multilayer carbon nanotubes coated with a layer of PANI. It was found that in the temperature range from 300 to 410 K a decrease in conductivity and an increase in the Seebeck coefficient during heating of this composite is associated with the removal (evaporation) of the doping acid from the sample. A differently directed change in  $\sigma$  and  $\alpha$  upon heating of the MWCNT-PANI-HCl composite is responsible for the temperature stability of its thermoelectric power coefficient.

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