

# Thermoelectric Properties of a Composite Based on Polyvinylidene Fluoride and Carbon Nanotubes

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Received November 26, 2020; revised November 26, 2020; accepted December 23, 2020

**Abstract**—The temperature dependences of the Seebeck coefficient and conductance of the nanocomposite composed of polyvinylidene fluoride, multi-walled carbon nanotubes, and carbon nanofibers are measured. It is shown that the thermoelectric properties of the composite are very different from the properties of the initial carbon filler. In particular, the Seebeck coefficient of the nanocomposite at room temperature is almost two times higher than the thermoelectric power of the carbon filler.

DOI: 10.1134/S2635167621030095

## INTRODUCTION

In recent years, thermoelectric (TE) materials for power supplies used in various electronic devices have been actively studied. The high TE figure of merit is by no means always a key requirement for these materials. When creating real energy converters, low cost, environmental friendliness, and mechanical strength of the material are of great importance. Special attention is paid to the creation of flexible TE materials for wearable electronics [1]. These are the properties of composite materials based on polymers and carbon nanotubes (CNTs) [2–4]. CNTs exhibit high electrical conductivity, and their Seebeck coefficient values are comparable in some cases to the thermoelectric power of typical TE materials [5]. However, the high thermal conductivity of CNTs substantially limits their use in TE devices. Polymers have very low thermal conductivity, but their electrical conductivity and thermoelectric power are low. Composites based on these two materials demonstrate the benefits of both components. Therefore, these kinds of composites are currently being actively developed and are of practical interest [2–4, 6–16].

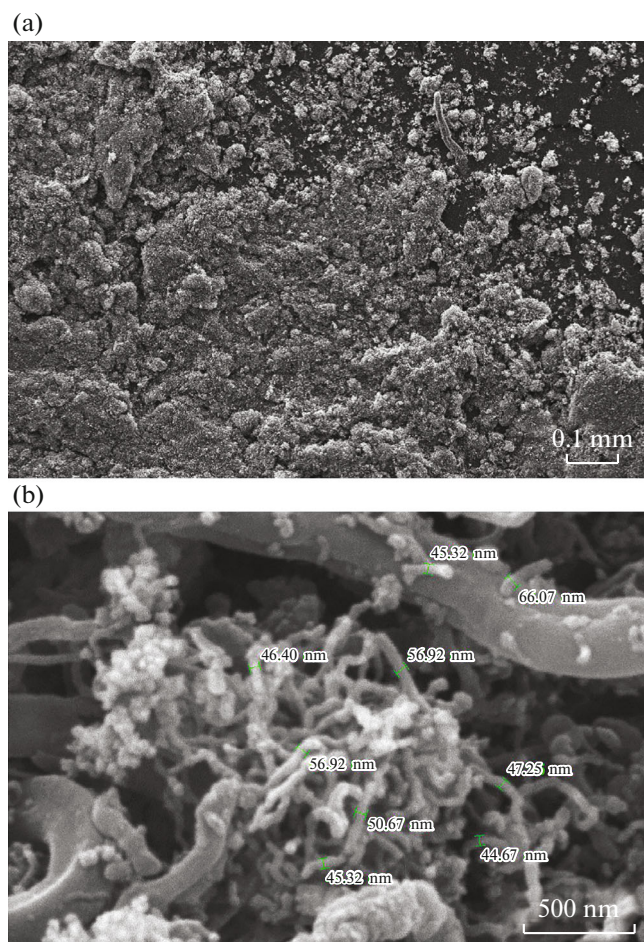
Electron transport in composites based on nanotubes is largely determined by quantum processes, such as the tunneling of charge carriers through potential barriers formed by polymer interlayers. Therefore, the transport properties of such nanocomposites cannot be described in the approximation of the effective medium [17]. In some cases, the thermoelectric power of the composite is higher than the thermoelectric power of the polymer and filler [9]. This feature of the nanocomposite can significantly increase its TE figure of merit as compared to the figures of merit of the starting materials.

In this study, polyvinylidene fluoride and the filler composed of a mixture of multiwalled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs) were used in the preparation of the composite. Polyvinylidene fluoride (PVDF) is an insulator; therefore, the TE figures of merit of materials based on it may be lower than those of the structures based on conducting polymers [4]. However, the effects leading to an increase in the thermoelectric power of the material should be most clearly manifested in the investigated PVDF/MWCNT–CNF nanocomposite. Measurements of the electrical conductance and Seebeck coefficient of the prepared samples confirmed this assumption.

## MATERIALS AND METHODS

Polymer PVDF, solvent *N,N*-dimethylformamide, and carbon filler were used to prepare the nanocomposite films. The carbon filler was a powder uniform in dispersion with a carbon content of at least 98 wt % (Fig. 1a). It comprised of multi-walled carbon nanotubes and nanofibers. Large extended CNFs and individual MWCNTs that are part of the filler can be clearly seen in Fig. 1b. MWCNTs have a diameter of about 50 nm and a length of about 500 nm. The diameter of CNFs varies in the range from 0.25 to 1  $\mu\text{m}$ , and their length reaches several micrometers. The filler used in this study had a bulk density of 0.24 g/cm<sup>3</sup> and a specific surface area of 150 m<sup>2</sup>/g.

The process of making composite films began with dissolving PVDF in *N,N*-dimethylformamide and subsequent ultrasonic treatment of the solution. The polymer solution was then mixed with the carbon filler and sonicated for 30 min. The resulting mixture was



**Fig. 1.** (Color online) SEM images of a carbon filler at magnifications of (a)  $\times 100$  and (b)  $\times 45\,000$ . The sizes of some carbon nanotubes are indicated.

applied to a glass substrate and placed in an oven for solvent evaporation. The compound was dried for at least 2 h at a temperature of  $80^{\circ}\text{C}$ . This time is sufficient to remove the solvent. After drying, the film of the PVDF/MWCNT–CNF composite was removed from the substrate.

With an increase in the concentration of CNTs, the electrical conductivity of the composite increases and the thermoelectric power decreases [12, 18]. In [18], a composite that consisted of MWCNTs in porous PVDF was investigated and it was shown that the TE figure of merit of the material at room temperature reaches a maximum with a nanotube concentration of 15 wt %. As was shown in [12], a composite based on single-walled carbon nanotubes and PVDF has a maximum power factor with a nanotube concentration of 5 wt %. In this study, a nanocomposite with a CNT concentration of 5 wt % was prepared and studied.

The electric conductance and Seebeck coefficient of the initial carbon filler and PVDF/MWCNT–CNF composite films were measured in the temperature

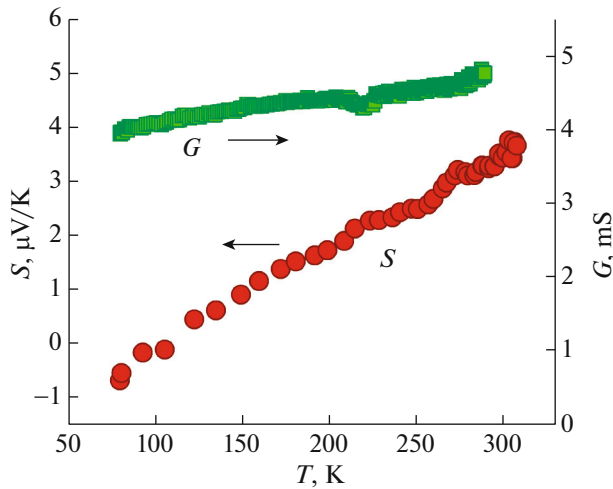
range of 80–400 K on an original device designed to measure the TE properties of ultrathin samples of semiconductor materials.

## RESULTS AND DISCUSSION

The transport properties of CNTs depend on their crystal structure and on the processing and storage conditions. Even doping with atmospheric oxygen can change the sign of the Seebeck coefficient [19, 20]. Therefore, to clarify the effect of the polymer on the electron transport properties of the carbon filler, the thermoelectric power and electrical conductance of both the initial filler and the PVDF/MWCNT–CNF composite prepared on its basis were measured.

The temperature dependences of electrical conductance  $G$  and Seebeck coefficient  $S$  of the carbon filler are shown in Fig. 2. Similar dependences are typical for MWCNTs [20–25]. The finite residual resistance (at  $T \rightarrow 0$ ) and the nearly linear temperature dependence of the thermoelectric power reveal the metallic conductivity. A small increase in conductance with an increase in the temperature is explained by thermally activated hopping and fluctuation-induced tunneling of charge carriers between the outer layers of MWCNTs [21–23]. It is worth noting the change in the sign of the Seebeck coefficient at a temperature of about 100 K. A similar temperature dependence of the thermoelectric power of an ordered MWCNT array is described in [24]. In addition to a change in the sign of the Seebeck coefficient, this dependence is characterized by the presence of a minimum at a temperature of about 40 K. A similar extremum is observed in the temperature dependence of the thermoelectric power of graphite [26, 27]. The authors of [26, 27] explain these features of the Seebeck coefficient of carbon materials by the phonon drag of charge carriers. It should be noted that this interpretation leaves open the question of why the thermoelectric power of phonon drag in CNTs has a sign opposite to the diffusion thermoelectric power at  $T > 100$  K. This effect may be explained by the negative contribution to the Seebeck coefficient of the internal unoxidized MWCNT layers [25].

In the PVDF/MWCNT–CNF composite, nanotubes are separated by potential barriers formed by polymer molecules. Therefore, the tunneling of charge carriers through these barriers should determine the electron transport properties of the material. The temperature dependence of the conductance of the composite is shown in Fig. 3. In the range of 80–230 K, this dependence is well described by the model of fluctuation-induced tunneling of charge carriers [28]. Due to the small size of CNTs, the electrical capacities of the tunnel junctions are very small. Therefore, even small thermal charge fluctuations cause substantial changes in the shape of the barrier and the voltage drop across it. All this leads to an increase in the coefficient of transmission of electrons through the barrier



**Fig. 2.** (Color online) Temperature dependences of the Seebeck coefficient and electrical conductance of the initial carbon filler.

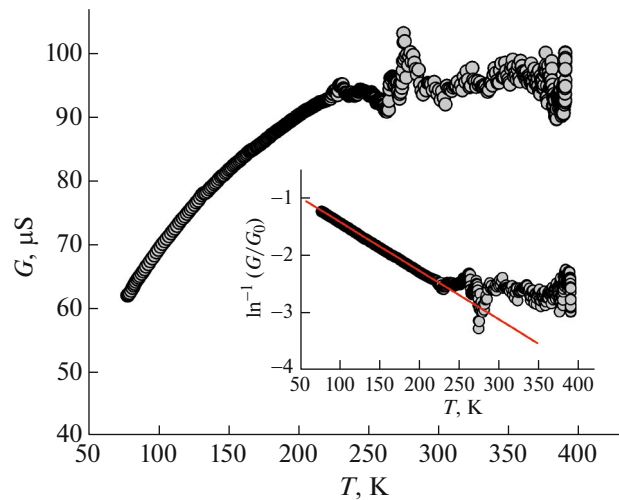
and an increase in the electrical conductivity of the composite. Within the model of fluctuation-induced tunneling of charge carriers, the temperature dependence of the conductance of the nanocomposite is described by the following expression [28]:

$$G(T) = G_0 \exp\left(-\frac{T_1}{T_0 + T}\right), \quad (1)$$

where  $T_0$  is the temperature below which ordinary electron tunneling through the barrier prevails, independent of the temperature;  $T_1$  is the temperature above which thermally activated hopping of carriers is the dominant conduction mechanism. It follows from the above expression that the inverse logarithm of the  $G/G_0$  ratio should be a linear function of the temperature. This dependence is shown in the inset to Fig. 3. As can be seen from the inset, the experimental data in the range of 80–230 K are very well approximated by a linear dependence with parameters of  $T_0 \approx 63$  K and  $T_1 \approx 117$  K.

At temperatures above 230 K, a significant scatter of the experimental points is observed in Fig. 3, which is apparently associated with the percolation nature of the conductivity in the obtained samples. The concentration of MWCNTs and carbon fibers in the studied composite (5 wt %) is close to the percolation threshold [29]. Therefore, the destruction of even one tunnel junction due to thermal deformations can lead to a substantial change in the conductance of the entire sample. An increase in the concentration of CNTs can increase the stability of transport properties of the nanocomposite.

The temperature dependence of the Seebeck coefficient of the PVDF/MWCNT–CNF composite is shown in Fig. 4. It is characterized by an almost two-

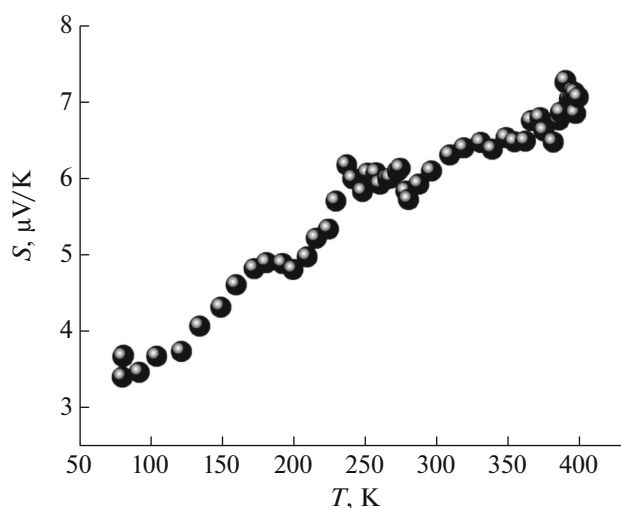


**Fig. 3.** (Color online) Temperature dependence of the electrical conductance of the PVDF/MWCNT–CNF nanocomposite. The inset shows the experimental dependence of  $\ln^{-1}(G/G_0)$  on the temperature ( $G_0 = 140 \mu\text{S}$ ) and approximating function (1) (solid line).

fold increase in thermoelectric power near room temperature in comparison with the value of this parameter in the initial carbon filler (Fig. 2). A similar substantial increase in the thermoelectric power was observed in other composites [9, 30]. This effect cannot be explained within the framework of the classical theory that uses the approximation of the effective medium [17], according to which the Seebeck coefficient of the composite cannot exceed the values of the corresponding coefficients of the components. Because of the low thermal conductivity of the polymer in comparison with the thermal conductivity of CNTs and CNFs, substantial temperature drops occur at the tunnel junctions. Therefore, tunnel junctions between CNTs not only determine the electrical conductivity of the composite but have also a substantial effect on its thermoelectric power. Moreover, potential barriers between CNTs provide energy filtering of charge carriers, which increases the Seebeck coefficient of the composite [14, 31, 32].

It should be noted that the value of the Seebeck coefficient depends on the concentration of charge carriers in MWCNTs, which can change during the synthesis of the nanocomposite. However, a significant change in the carrier concentration is unlikely in this case, since the initial CNTs are not functionalized and the PVDF polymer does not contain functional groups capable of forming covalent bonds with nanotubes [33].

Given the small values of the Seebeck coefficient, the investigated material cannot serve, apparently, as a basis for the creation of TE converters. However, the available published data on the thermoelectric power and TE figure of merit of the PVDF/MWCNT com-



**Fig. 4.** Temperature dependence of the Seebeck coefficient of the PVDF/MWCNT–CNF nanocomposite.

posite are ambiguous. In [18], the synthesis of a porous composite of the indicated composition with anomalously high values of the Seebeck coefficient  $\sim 300$   $\mu\text{V/K}$  is reported, but no one has succeeded in repeating these results up to now, as far as is known. The published values of the thermoelectric power at room temperature [34–36] are comparable with the data obtained in this study. The TE figure of merit and thermoelectric power of the composite can be increased by using conducting polymers and single-walled CNTs [2, 4].

## CONCLUSIONS

The thermoelectric properties of a nanocomposite based on polyvinylidene fluoride and the carbon filler comprised of MWCNTs and CNFs are substantially different from the properties of the initial components. By using a nonconducting polymer, it was shown that tunnel junctions arising between CNTs significantly change the temperature dependences of the electrical conductance and the Seebeck coefficient of the composite in comparison with the temperature dependences of the corresponding parameters of the initial filler. The theory of fluctuation-induced tunneling of charge carriers describes well the temperature dependence of the conductance of the material under study. The thermoelectric power of the nanocomposite near room temperature is almost twice higher than the thermoelectric power of the filler. Such a significant increase in the thermoelectric power is most likely associated with the selective scattering of charge carriers by potential barriers arising between carbon nanotubes and nanofibers.

## ACKNOWLEDGMENTS

The authors thank E.V. Saklakova for preparing nanocomposite films.

## REFERENCES

1. A. Nozariasbmarz, H. Collins, K. Dsouza, et al., *Appl. Energy* **258**, 114069 (2020). <https://doi.org/10.1016/j.apenergy.2019.114069>
2. C. Gao and G. Chen, *Compos. Sci. Technol.* **124**, 52 (2016). <https://doi.org/10.1016/j.compscitech.2016.01.014>
3. G. Chen, W. Xu, and D. Zhu, *J. Mater. Chem. C* **5**, 4350 (2017). <https://doi.org/10.1039/C6TC05488A>
4. J. L. Blackburn, A. J. Ferguson, C. Cho, and J. C. Grunlan, *Adv. Mater.* **30**, 1870072 (2018). <https://doi.org/10.1002/adma.201870072>
5. Y. Nakai, K. Honda, K. Yanagi, et al., *Appl. Phys. Express* **7**, 025103 (2014). <https://doi.org/10.7567/APEX.7.025103>
6. E. Kymakis and G. A. J. Amaratunga, *J. Appl. Phys.* **99**, 084302 (2006). <https://doi.org/10.1063/1.2189931>
7. C. Yu, Y. S. Kim, D. Kim, and J. C. Grunlan, *Nano Lett.* **8**, 4428 (2008). <https://doi.org/10.1021/nl802345s>
8. Q. Yao, L. Chen, W. Zhang, et al., *ACS Nano* **4**, 2445 (2010). <https://doi.org/10.1021/nn1002562>
9. C. Meng, C. Liu, and S. Fan, *Adv. Mater.* **22**, 535 (2010). <https://doi.org/10.1002/adma.200902221>
10. D. Kim, Y. Kim, K. Choi, et al., *ACS Nano* **4**, 513 (2010). <https://doi.org/10.1021/nn9013577>
11. C. Yu, K. Choi, L. Yin, and J. C. Grunlan, *ACS Nano* **5**, 7885 (2011). <https://doi.org/10.1021/nn202868a>
12. C. A. Hewitt, A. B. Kaiser, S. Roth, et al., *Appl. Phys. Lett.* **98**, 183110 (2011). <https://doi.org/10.1063/1.3580761>
13. K. Yusupov, A. Zakhidov, S. You, et al., *J. Alloys Compd.* **741**, 392 (2018). <https://doi.org/10.1016/j.jallcom.2018.01.010>
14. D. Li, C. Luo, Y. Chen, et al., *ACS Appl. Energy Mater.* **2**, 2427 (2019). <https://doi.org/10.1021/acsaem.9b00334>
15. S.-H. Chung, D. H. Kim, H. Kim, et al., *Mater. Today Commun.* **23**, 100867 (2020). <https://doi.org/10.1016/j.mtcomm.2019.100867>
16. M. Bharti, A. Singh, B. P. Singh, et al., *J. Power Sources* **449**, 227493 (2020). <https://doi.org/10.1016/j.jpowsour.2019.227493>
17. D. J. Bergman and O. Levy, *J. Appl. Phys.* **70**, 6821 (1991). <https://doi.org/10.1063/1.349830>
18. F.-P. Du, X. Qiao, Y.-G. Wu, et al., *Polymers* **10**, 797 (2018). <https://doi.org/10.3390/polym10070797>

19. P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, *Science* (Washington, DC, U. S.) **287**, 1801 (2000).  
<https://doi.org/10.1126/science.287.5459.1801>
20. B. Sadanadan, T. Savage, S. Bhattacharya, et al., *J. Nanosci. Nanotech.* **3**, 99 (2003).  
<https://doi.org/10.1166/jnn.2003.186>
21. B. Bourlon, C. Miko, L. Forró, et al., *Phys. Rev. Lett.* **93**, 176806 (2004).  
<https://doi.org/10.1103/PhysRevLett.93.176806>
22. V. Skákalová, A. B. Kaiser, Y.-S. Woo, and S. Roth, *Phys. Rev. B* **74**, 085403 (2006).  
<https://doi.org/10.1103/PhysRevB.74.085403>
23. Z. Li, H. R. Kandel, E. Dervishi, et al., *Appl. Phys. Lett.* **91**, 053115 (2007).  
<https://doi.org/10.1063/1.2767215>
24. K. Yang, J. He, Z. Su, et al., *Carbon* **48**, 756 (2010).  
<https://doi.org/10.1016/j.carbon.2009.10.022>
25. C. A. Hewitt, A. B. Kaiser, M. Craps, et al., *J. Appl. Phys.* **114**, 083701 (2013).  
<https://doi.org/10.1063/1.4819104>
26. T. Takezawa, T. Tsuzuku, A. Ono, and Y. Hishiyama, *Philos. Mag.* **19**, 623 (1969).  
<https://doi.org/10.1080/14786436908216318>
27. K. Sugihara, H. Ohshima, K. Kawamura, and T. Tsuzuku, *J. Phys. Soc. Jpn.* **43**, 1664 (1977).  
<https://doi.org/10.1143/JPSJ.43.1664>
28. P. Sheng, *Phys. Rev. B* **21**, 2180 (1980).  
<https://doi.org/10.1103/PhysRevB.21.2180>
29. A. V. Eletsii, A. A. Knizhnik, B. V. Potapkin, and J. M. Kenny, *Phys. Usp.* **58**, 209 (2015).  
<https://doi.org/10.3367/UFNe.0185.201503a.0225>
30. B. Krause, V. Bezugly, V. Khavrus, et al., *Energies* **13**, 394 (2020).  
<https://doi.org/10.3390/en13020394>
31. S. V. Faleev and F. Léonard, *Phys. Rev. B* **77**, 214304 (2008).  
<https://doi.org/10.1103/PhysRevB.77.214304>
32. M. He, J. Ge, Z. Lin, et al., *Energy Environ. Sci.* **5**, 8351 (2012).  
<https://doi.org/10.1039/C2EE21803H>
33. C.-M. Chang and Y.-L. Liu, *Carbon* **48**, 1289 (2010).  
<https://doi.org/10.1016/j.carbon.2009.12.002>
34. C. A. Hewitt, A. B. Kaiser, S. Roth, et al., *Nano Lett.* **12**, 1307 (2012).  
<https://doi.org/10.1021/nl203806q>
35. Y.-C. Sun, D. Terakita, A. C. Tseng, and H. E. Naguib, *Smart Mater. Struct.* **24**, 085034 (2015).  
<https://doi.org/10.1088/0964-1726/24/8/085034>
36. M. Aghelinejad and S. N. Leung, *Composites, Part B* **145**, 100 (2018).  
<https://doi.org/10.1016/j.compositesb.2018.03.030>

*Translated by O. Kadkin*