Thermoelectric properties of carbon nanotube/silicone rubber composites

Zhen-Wu Li
Jiangzhen School of Mechanical Engineering of Heze University, Heze, China

ABSTRACT
In this paper, we have studied the relevant physical quantities to the figure of merit of carbon nanotube (CNT)/polydimethylsiloxane composites at different loadings, and found that with increasing the CNT loadings, the electrical conductivity jumps several orders in magnitude at ‘threshold’, followed by a saturated plateau, and the Seebeck coefficient decreases by a small margin, and the thermal conductivity increases somewhat. According to the formula of the figure of merit, it is found that higher loading composites display a larger figure of merit. We hope the present study provides a new path to high-performance flexible thermoelectric materials.

KEYWORDS
carbon nanotube; composite material; thermoelectric properties; figure of merit

1. Introduction
Thermoelectric materials are a kind of functional materials which are able to convert heat into electricity based on the internal carrier movement, and are mainly used for thermoelectric power generation and refrigeration, etc. [1–3]. The most important parameter to characterise the conversion efficiency of thermoelectric materials is the figure of merit, $ZT = S^2σT/κ$, where $S$, $σ$ and $κ$ are Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. Since carbon nanotube (CNT) was discovered, because of its unique structure, the performance of CNT has been a hot research topic [4–10]. CNT/polymer composites, which combine the advantages of both CNT and polymer, have also attracted much attention [11–14]. Looking for high figure of merit and low-cost manufacturing thermoelectric materials is of practical significance with the increasingly serious energy crisis today. In the thermal power research, as a result of the unique one-dimensional structure, CNTs are expected to enhance carrier mobility and increase the phonon scattering at the wall surfaces, thus can improve the figure of merit as thermoelectric materials. So far, the figure of merit of CNT/silicone rubber composite materials with different CNT loadings has not been reported. In this paper, we prepared a series of CNT/polydimethylsiloxane (PDMS) silicone rubber composites with different CNT loadings by filling different proportions of CNTs into silicone rubber, and measured their electrical...
conductivity, Seebeck coefficient and thermal conductivity, and, finally, calculated their figure of merit. This work may provide a new path to high-performance flexible thermoelectric materials.

2. Experiment

2.1. Experimental reagents and instruments

Reagents are: multi-wall CNTs (diameter of 10–30 nm, length of 5–20 μm); dimethylsiloxane; ethyl acetate; tetraethyl orthosilicate; ethanol (AR) and 0.1 mol/L hydrochloric acid.

The main instruments are scanning electron microscope (The Netherlands FEI Sirion 200); ultrasonic cell disrupter (800–1200 W); nanovoltmeter (Keithley 2182); infrared thermometer (Germany Oupu OPTRIS LS).

2.2. Preparation and characterization of samples

2.2.1. Preparation of CNT–PDMS composites

As used herein, the chemical vapour deposition grown multi-walled CNTs must be cleaned before the preparation of composites to remove the residual catalysts. The cleaning process is as follows: first, the CNTs were ultrasonicated for 5 min in 0.1 mol/L hydrochloric acid, followed by rinsing with deionized water to pH = 7, and then placed in an oven for drying the CNTs.

Procedures for preparing CNT–PDMS composite materials are as follows: first, dimethylsiloxane was dissolved in ethyl acetate, and stirred to obtain a clear non-viscous liquid. Then a determined ratio of CNTs was added to the liquid, followed by a strong ultrasonication for 20 min using an ultrasonic cell disrupter. Then ethyl acetate was evaporated with a plate heater, and tetraethyl orthosilicate cross-linking agent was added with a ratio to dimethylsiloxane 6:100. Finally, the mixture was dropped on a hard plastic plate, forming an evenly distributed film. Then the film was placed in vacuum for 5 min to eliminate the remnant bubbles and left at room temperature for 24 h for curing.

Using these methods, we prepared a series of CNT–PDMS composites of 0.1%, 0.2%, 0.35%, 0.5%, 1%, 2%, 5% (mass fractions).

2.2.2. Morphological characterization

Since PDMS is an excellent flexible polymer material, CNT–PDMS composite materials also have good flexibility. Pure PDMS is a transparent elastomer, and CNT–PDMS composite materials appear black due to the incorporation of the CNTs. Scanning electron microscopy (SEM) characterization of the 5% loading composite material was shown in Figure 1. As is seen, although there are still a small amount of CNT agglomerations, the distributions are basically uniform (the bright filament-like substances in SEM image are CNTs).
3. Results and discussion

3.1. Conductivity of CNT–PDMS composites

The conductivities of the samples were tested with a four-point method, in which the current data were collected with the outer two ends and the voltage data were collected with the inner two ends. The copper electrodes were fabricated by curing with the composites. The current and voltage data were detected by Keithley2182 nanovoltmeter. The $I-V$ curve of 0.35 wt% CNT–PDMS composite is shown in Figure 2. It can be seen that the IV curve shows a good linearity. Through the figure, the resistance $R$ can be calculated. Then using the formula $R = l/\sigma S$, the conductivity $\sigma$ can be determined, where $R$ is the resistance between the inner two ends, $l$ is the length between the inner two ends and $S$ is the cross-sectional area.

The conductivities versus the mass fraction of the composites are shown in Figure 3. As can be seen from Figure 3, when the content of CNT is small, the conductivity of the
composite material is very low, on the level of an insulator; when CNT content reaches 0.2%, the conductivity of the composite increases sharply, which implies the formation of conductive networks; with further increase of the CNT content larger than 2%, the conductivities of the composites tend to be ‘saturated’.

Three-dimensional conductive networks are formed in CNT–PDMS composites, and the conductivity can be explained using the ‘percolation’ theory [15]. The conductivity of the composite is determined by the equation \( \sigma \sim (p - p_{th})^t \), where \( p \) is the volume fraction of electrically conductive reinforcing material, \( p_{th} \) is the percolation threshold, which is the desired content of the reinforcing material to form an electrically conductive network, \( t \) is a parameter value that reflects the dimension of the conductive network. Forming a two-dimensional conductive network, the value of \( t \) is 1.3; forming a three-dimensional conductive network, \( t \) is 2.0. We used this formula to fit the electrical conductivity of CNT–PDMS composite materials and obtained \( \sigma \sim (p - 0.18\%)^{1.8} \), namely the conduction mode agrees well with the three-dimensional conductive percolation theory, and the percolation threshold is 0.18%. The parameter \( p \) in the formula should be the volume fraction, but the density of the CNT is close to that of silicone rubber matrix, so we can use the mass fraction instead of the volume fraction for an approximation. From Figure 3, we have also seen that the conductivity of the composite increases rapidly with increasing the content of the CNT. When the CNT content reaches greater than 1%, the composite conductivity then changes slowly with the CNT loading. The main explanations to the trends of the electrical properties of the CNT materials are as follows. CNTs have a large aspect ratio and therefore only a small amount of CNT can form an effective conductive path. After forming the conductive path, the increase of the CNT loading will contribute to the conductivity less significantly.

Typical conductivity of the insulator is less than \( 10^{-8} \) S/m, and the conductivity of the conductor is typically about \( 10^5 \) S/m. Therefore, from the conductivity point of view, moderately CNT-loaded silicone rubber composites can be used as a semiconductor material.

Figure 3. CNT–PDMS composite conductivity with different CNT loadings.
3.2. Seebeck coefficient of CNT–PDMS composite

The CNT–PDMS composite films are made into strips. One end is heated by contacting with hot objects, and the other end is without heating. The temperature data were collected with an infrared thermometer at both ends and with the electrical potential differences are measured by nanovoltmeter 2182. The temperature differences between the high and low ends are basically around 10 K. The Seebeck coefficient test schematic is shown in Figure 4(a). The Seebeck coefficient dependence on the CNT content is plotted in Figure 4(b), where the sample of 100% refers to a pure CNT plate. Seebeck coefficient can be derived from the formula \( S = \Delta V/\Delta T \), where \( \Delta T \) is the temperature difference between the high- and low-temperature ends and \( \Delta V \) the corresponding voltage output. As can be seen from Figure 4(b), the Seebeck coefficients of the composite materials

![Seebeck coefficient test schematic of CNT-PDMS composites](image)

**Figure 4.** (a) Seebeck coefficient test schematic of CNT–PDMS composites; (b) Seebeck coefficient dependence on the content of CNTs; (c) Seebeck coefficient dependence on electrical conductivity.
decrease with increasing the amount of CNTs. As the conductivity has been previously tested for each sample, the Seebeck coefficient dependence on the conductivity is plotted in Figure 4(c). From Figure 4(c), the relationship $S \sim \ln \sigma$ can be obtained. This relationship between Seebeck coefficient and electric conductivity has also been reported in polyacetylene, polypyrrole and other organic semiconductors [16].

CNT–PDMS composite materials can be considered as semiconductors, and the Seebeck coefficient of doped semiconductor is given by the following formula [17]:

$$s = \frac{s \pi^2 k_B^2}{3e h^2} m^* (\frac{\pi}{3n})^{2/3},$$

where $n$ is the carrier concentration, $m^*$ is the effective mass, $k_B$ is the Boltzmann constant, $e$ is the electron charge and $h$ is Planck’s constant. From this equation, as the carrier concentration increases, Seebeck coefficient will decrease. The relationship between the Seebeck coefficient and CNT content of the composite materials in Figure 4(c) is qualitatively consistent with the formula, as higher loading CNT composites imply higher carrier concentrations.

### 3.3. Thermal conductivity of CNT–PDMS composites

The test schematic for the thermal conductivities of CNT–PDMS composites with different CNT loadings is shown in Figure 5. The CNT–PDMS composite is sandwiched between two copper blocks, of which one is heated by electric heating an array of rods embedded therein and the other is not heated. The overall system is encapsulated by polymer materials with good thermal insulations. Two copper blocks can be considered as heat sinks with constant high and low temperatures. Then the thermal conductivity is calculated by $\kappa = \frac{Qd}{(T_1 - T_2)A}$, wherein, $d$ is the thickness of the composite material, $T_1$, $T_2$ are high and low temperatures at two ends, $A$ is the cross-sectional area of the composite material transferring heat and $Q$ is the heat transfer per unit time. When the system is thermal equilibrated, the system does not exchange heat with the outside environment, so that the heat transfer $Q$ equals to total electric power $VI$. The relationship between the

![Figure 5](image.png)

*Figure 5. Thermal conductivity dependence on the content of CNTs (inset: test schematic for thermal conductivity).*
thermal conductivities of CNT–PDMS composites and the corresponding mass fractions is shown in Figure 5. The thermal conductivity of the composite increases with increasing the content of CNTs, and the curve is approximately linear. The magnitudes of the changes are small. This result is consistent with that from Jarmila et al. [18].

Simplex CNTs have a high thermal conductivity, on the order of $10^3 \text{ W/m-K}$, while the thermal conductivity of polymers is generally low, on the order of $0.1 \text{ W/m-K}$. Unlike the electrical conductivity of the composite jumps, several orders of magnitude when incorporating a small amount of CNTs, the improvement of the thermal conductivity of CNT–PDMS composite is quite limited, basically several times at the most. For example, Biercuk et al. [19] reported that 1% single-walled CNT loading in epoxy results in 125% improvement of the thermal conductivity. Choi et al. [20] reported an increment of more than 300% in thermal conductivity of 3% SWNT–epoxy composite compared to pure epoxy. The main reason is that the electrical conductivity is attributed to electron transport between the carbon tubes, while the thermal conductivity is attributed to phonon transport between the CNTs and the polymer. The phonons of the nanotubes do not match with the phonons of the polymers, which resulted in a large interfacial thermal resistance, thereby constraining the thermal conductivity properties of the composites. Since the samples were fabricated in a film shape, the CNTs show different distributions in parallel and perpendicular to the thickness direction, i.e. they tend to distribute in the in-plane alignment of the films. Previous studies show that the thermal conductivity across the alignment direction is smaller than that along the alignment direction [21,22]. Therefore, herein, CNT alignments may also contribute to the limited increase in the thermal conductivities of the composites.

3.4. The figure of merit of CNT–PDMS composites

The figure of merit $ZT$ is calculated by the formula $ZT = S^2 \sigma T / \kappa$. Figure 6 gives the dependence of the figure of merit of CNT–PDMS composites on the mass fraction of CNT. The figure of merit of the composite first increases with a rapid growth, and then gradually levels off when CNT content further increases.

![Figure 6](image.png)

**Figure 6.** Dependence of the figure of merit of CNT–PDMS composite on the mass fraction of CNT.
Despite low CNT loading composites display a higher Seebeck coefficient, the conductivity is very low, resulting in a small figure of merit. Therefore, low-loading CNT–PDMS composites are not suitable for thermoelectric materials. With increasing CNT loadings, the conductivity increases by orders of magnitude, and the Seebeck coefficient decreases with quite a limited range, and therefore, the high CNT loading composite materials have a large figure of merit. Yu et al. [23] studied the thermoelectric properties of the CNT–polyvinyl acetate composite materials and found that with increasing the amount of CNTs, the conductivity increases and both Seebeck coefficient and thermal conductivity maintain substantially constant, which leads to a rapid improvement of figure of merit. When the amount of carbon tube is 20 wt% in the polyvinyl acetate composite, the figure of merit at room temperature reaches 0.006. Here, for 5% CNT loading silicone rubber composite at 300 K, the conductivity is 43.65 S/m, the Seebeck coefficient is 44.15 μV/K and the thermal conductivity is 0.214 W/m-K, hence the calculated figure of merit is $1.19 \times 10^{-4}$. Despite there is still a large distance from the commercial application, there may be still ways to improve the figure of merit, e.g. by further doping.

As expected, CNT–PDMS composites are stretchable materials, as pure PDMS. Previous studies have shown that deformation from the original shape will result in a significant decrease in the electrical conductivity, and a little decrease in the Seebeck coefficient in CNT–elastomer composites [24,25]. Since the phonon transportation mechanism in the thermal conductivity, the influence of deformation on the thermal conductivity is expected to be quite limited. Therefore, the figure of merit of CNT–PDMS composites will be greatly reduced by deformations. But Lü et al. [25] also reported that when the deformation is recovered, the resistance will also recover to its original value. Hence, the figure of merit of CNT–PDMS composites will also probably recover when external force is removed, i.e. the thermoelectric material could probably work under deformations.

4. Conclusion

CNTs/silicone rubber composite material is of high stability, high flexibility and can be cost-effective for preparing large-area materials. In this paper, we prepared various loading CNT–PDMS composite materials, and analysed the figure of merit and the related physical quantities, and found that the conductivity of the composites jumps several orders of magnitude with increasing the amounts of CNT at the ‘threshold’, and then gradually becomes saturated. The Seebeck coefficient decreases somewhat with increasing the amount of CNT; the thermal conductivity slightly increases with increasing the amount of CNT. According to the formula of the figure of merit, it is found that higher loading composites display a larger figure of merit.

Disclosure statement

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References

[1] Sun Y, Wang CL, Wang HC, et al. Influence of sintering temperature on thermoelectric properties of La0.1Sr0.9TiO3 ceramics. Acta Phys Sin. 2012;61:167201. Chinese.

[2] Wang HC, Wang CL, Su WB, et al. Influence of sintering temperature on thermoelectric properties of La0.9Sr0.1FeO3 ceramics. Acta Phys Sin. 2010;59:3455. Chinese.

[3] Ma YH, Tong XL, Zhu B, et al. Theoretical and experimental investigation on thermophysical properties of metal rubber. Acta Phys Sin. 2013;62:048101. Chinese.

[4] Chen H, Zeng S, Chen M, et al. Fabrication and functionalization of carbon nanotube films for high-performance flexible supercapacitors. Carbon. 2015;92:271.

[5] Zaumseil J. Single-walled carbon nanotube networks for flexible and printed electronics. Semicond Sci Technol. 2015;30:074001.

[6] Zhao MQ, Ren CE, Ling Z, et al. Flexible MXene/carbon nanotube composite paper with high volumetric capacitance. Adv Mater. 2015;27:339–345.

[7] Li ZW. Opto-electronic properties of CdS nano particle/carbon nanotube composites. Acta Phys Sin. 2012;61:016103. Chinese.

[8] Li ZW. Kondo effect on the electrical transport properties of carbon nanotubes. Acta Phys Sin. 2013;62:096101. Chinese.

[9] Li ZW. Opto-electronic properties of the single-walled carbon nanotube film and melamine formaldehyde resin composite. Acta Phys Sin. 2014;63:106101. Chinese.

[10] Cao MS, Yang J, Song WL, et al. Ferroferric oxide/multiwalled carbon nanotube vs polyaniline/ferroferric oxide/multiwalled carbon nanotube multiheterostructures for highly effective microwave absorption. ACS Appl Mater. Interfaces 2012;4:6949.

[11] Feng DL, Feng YH, Chen Y, et al. Effects of doping, Stone–Wales and vacancy defects on thermal conductivity of single-wall carbon nanotubes. Chin Phys B. 2013;22:016501.

[12] Qu JR, Zheng JB, Wang CF, et al. Effect of carbon nanotubes on the properties of polymer MOPPV–PbSe quantum dot composites. Acta Phys Sin. 2013;62:128801. Chinese.

[13] Zhang XR, Lin YH, Zhang JF, et al. Photoinduced charge carrier properties and photocatalytic activity of N-doped TiO2 nanocatalysts. Acta Phys Chim Sin. 2010;26:2733. Chinese.

[14] Dai SY, Kong FT, Hu LH, et al. Investigation on the dye-sensitized solar cell. Acta Phys Sin. 2005;54:1919. Chinese.

[15] Kirkpatrick S. Percolation and conduction. Rev Mod Phys. 1973;45:574.

[16] Mateeva N, Niculescu H, Schlenoff J, et al. Correlation of Seebeck coefficient and electric conductivity in polyaniline and polypyrrole. J Appl Phys. 1998;83:3111.

[17] Snyder G, Toberer E. Nat Mater. 2008;7:105.

[18] Jarmila V, Robert M, Petr S, et al. Effect of surfactants and manufacturing methods on the electrical and thermal conductivity of carbon nanotube/silicone composites. Molecules. 2012;17:13157–13174.

[19] Biercuk M, Llaguno M, Radosavljevic M, et al. Carbon nanotube composites for thermal management. Appl Phys Lett. 2002;80:2767.

[20] Choi ES, Brooks JS, Eaton DL, et al. Enhancement of thermal and electrical properties of carbon nanotube polymer composites by magnetic field processing. J Appl Phys. 2003;94:6034.

[21] Borca-Tasciuc T, Mazumder M, Son Y, et al. Anisotropic thermal diffusivity characterization of aligned carbon nanotube-polymer composites. J Nanosci Nanotechnol. 2007;7:1581–1588.

[22] Zhou B, Luo W, Yang, JQ, et al. Thermal conductivity of aligned CNT/polymer composites using mesoscale simulation. Compos Part A. 2016;90:410–416.

[23] Yu C, Kim Y, Kim D, et al. Thermoelectric behavior of segregated-network polymer nanocomposites. Nano Lett. 2008;8:4428–4432.

[24] Jiang MJ, Dang ZM, Xue HP, et al. Significant temperature and pressure sensitivities of electrical properties in chemically modified multiwall carbon nanotube/methylvinyl silicone rubber nanocomposites. Appl Phys Lett. 2006;89:182902.

[25] Hu CH, Liu CH, Chen LZ, et al. Resistance-pressure sensitivity and a mechanism study of multiwall carbon nanotube networks/poly (dimethylsiloxane) composites. Appl Phys Lett. 2008;93:033108.