Excluded volume effect on the power factor of Carbon Nanotube based polymer composite

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Abstract:
Investigations into polymeric materials as flexible thermoelectric (TE) materials have encountered issues, such as conflicting thermoelectric property behaviors that result in a low power factor. To tackle these issues, we propose the use of two unique sorts of fillers- carbon nanotubes (CNT) and silica particles, embedded in polymer matrix for enhanced TE properties. Embedding micro-scale segregated structures as the secondary fillers creates an excluded volume within CNT networks, which leads to the simultaneous increase in the electrical conductivity and Seebeck coefficient of the composite. Polydimethylsiloxane (PDMS) is used as a suitable matrix because of its merits such as solution processability, light weight, low thermal conductivity and an internet of things. As silica content increased up to 40 wt%, electrical conductivity and Seebeck coefficient increases in the segregated composite framework, resulting in maximum power factor of approximately 25.96 μW/mK² and 42.89 μW/mK² for 1 μm size and 3 μm size silica particles, respectively. Moreover, using much lower CNT content, such as 10 wt% CNT stacking, results at a desired level of electrical conductivity and Seebeck coefficient. This study ultimately develops the hypothesis that the network topology of CNT-based polymer composites depends on the size and characteristics of the secondary fillers.

KEYWORDS: silica, carbon nanotube, flexible thermoelectric material, elastomer composites
1. Introduction

Sustainable efficient power energy has acquired developing consideration due to the nonrenewable conventional petroleum products. Moreover, their broad use is causing an ever-increasing number of environmental challenges.\(^1\)\(^-\)\(^5\) Thermoelectric (TE) power is seen as a substantial improvement over nonrenewable, efficient power sources such as nuclear, solar and wind energies, among others.\(^3\)\(^,\)\(^6\) This technology presents a possible way for transforming heat directly into electricity without emitting any pollutants.\(^7\)\(^,\)\(^8\) The Seebeck coefficient (µV/K), electrical conductivity (S/cm), thermal conductivity (W/m.K), and absolute temperature (K), are all represented by a dimensionless figure of merit which is given by \(ZT = S^2\sigma T/\kappa\). A high ZT is vital for proper thermal to electrical energy conversion.\(^9\)\(^-\)\(^12\) As a result, high \(S\), high \(\sigma\) and low \(\kappa\) is needed. It is worth mentioning that there are certain difficult conflicts between electrical conductivity and the Seebeck coefficient and/or thermal conductivity which has over the years limited the ZT values of organic based TE composite materials.\(^5\)\(^,\)\(^13\)\(^,\)\(^14\) For researchers, the goal aligns in investigating cost-effective materials that have good TE performance which can be determined by ZT. To this end, decoupling the parameters of ZT is imperative to achieve this goal. The power factor (PF) term is simply a portion of the numerator of ZT which is given by \(S^2\sigma\), it establishes the power output at a specified temperature difference. While TE energy conversion gadgets address a possibly encouraging methodology for recuperating energy from squandered heat sources across an expansive scope of temperatures, a considerable lot of the semiconductors that presently convey the best TE efficiencies are generally expensive to produce and depend on components that are somewhat scant as well as potentially dangerous. Inorganic semiconductors and their alloys, such as Bi\(_2\)Te\(_3\), PbTe, and Sb\(_2\)Te\(_3\), are among the most extensively used thermoelectric materials.\(^15\)\(^-\)\(^18\) As a result, the value per watt of supplied power is restrictively expensive, and TE energy transformation systems have yet to find a significant market\(^19\). Additionally, inorganic TE materials frequently lack sufficient mechanical flexibility, are hazardous, heavy, and expensive to produce, all of which limit their ability to be applied to recently innovative technologies notably flexible sensors and biosensing.\(^20\)\(^-\)\(^22\) In contrast, organic TE materials have proven their distinct advantages, including affordability, excellent biocompatibility, light in weight, minimal thermal conductivity, ease of manufacture, and superior mechanical flexibility.\(^23\)\(^,\)\(^24\) These advantages have recently attracted a
lot of interest for manufacturing flexible TE devices. Due to their inherent flexibility and conductivity, conductive polymers, such as poly(3-butylthiophene) (P3BT), poly(3-hexylthiophene-2,5-diyl) (P3HT), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PA), polythiophenes (PTs), and polypyrrole (PPy), have been utilized in terms of material development.\textsuperscript{10,24–31} Nevertheless, when compared to their equivalents – inorganic TE materials, organic TE materials exhibit lower electrical and Seebeck coefficient.\textsuperscript{4,32,33}

The filler particles within the polymer matrix leads to the formation of conductive channels, thus, increasing the electrical conductivity. Several important factors such as geometry, inherent conductivity, and condition of dispersion of the appropriate fillers all influence the creation of these conductive channels, and hence, the percolation threshold\textsuperscript{34,35}. The percolation threshold simply describes the lowest filler content at which a filler network is formed, and electrical conductivity dramatically increases, technically conveying the idea of a probability that any given region of the medium is sufficiently connected to the rest for conduction to take place\textsuperscript{36}. Carbon nanotubes (CNTs) has drawn a lot of interest due to its high aspect ratio, high flexibility, low density, and great mechanical and functional capabilities.\textsuperscript{20,23,37–41} It serves as a potential conductive filler because of its sp\textsuperscript{2}-hybridized structure, which gives them excellent electrical conductivity.\textsuperscript{42,43} CNTs are made up of rolled graphene sheets, which prompts a high aspect ratio and allows for the formation of a conductive filler network even with a low filler content. This is advantageous when considering applications for electrically conductive polymer-based composites that demand great flexibility, softness and low weight.\textsuperscript{44,45} Also, with just 10 wt\% CNT stacking, our proposed segregated CNT composite could alleviate the cost issue related to CNTs when compared to other hybrid CNT composite systems made up of just CNT as the filler material. The effect of the secondary filler – silica, has not been extensively studied up to date. Silica particles are of great interest due to its unique properties such as high specific surface area, significant toughening, strengthening, and large pore volume.\textsuperscript{46} Furthermore, it has the potential to increase the electrical conductivity of polymer composites by forming an excluded volume resulting in a segregated CNT network.\textsuperscript{21,47–49} Due to the inclusion of secondary fillers, which has the tendencies to impede the interconnection of the CNTs, previous investigations have seen conflicting trends in electrical conductivity of the hybrid composite system.\textsuperscript{50,51} In this work, we focus on using nonconducting polymer such as polydimethylsiloxane (PDMS) as the effective matrix alongside two unique secondary fillers – silica and CNT. We have investigated the
morphology, mechanical and TE properties of the CNT-based polymer composites. With improved synthesis process – effective sonication, dispersion, mechanical stirring and annealing of the composite’s constituents, both electrical conductivity and Seebeck coefficient increase gradually up to 40 wt% Si resulting in high power factor values. In addition, the electron transport physics within the composite is also examined.

2. Materials and Methods

2.1. Materials

Single walled carbon nanotubes (SWCNT), silica micro-particles, PDMS, and chloroform are the raw ingredients for the CNT based polymer composite material development. Dow Corning supplied commercially available PDMS (PDMS: Sylgard 184 SILICONE ELASTOMER BASE) for the synthesis of the CNT-based polymer composite. Single walled carbon nanotubes (SWCNTs) with an average diameter of 1.6 nm and a length of > 5 µm was utilized. The SWCNTs used is a hybrid of both semiconducting and metallic carbon nanotubes. Silica powders of 1 µm, and 3 µm particle size were bought from Sigma Aldrich. The aforementioned raw materials were all used as received.

2.2. Synthesis and characterization of polymer composite

It’s imperative that the two fillers (SWCNT and silica) disperse evenly in the polymer matrix. Despite their comparable structure and materials, poor distribution conditions of the two fillers in the polymer matrix can generate opposing or irregular trends in electrical conductivity. Ultrasonication was employed to guarantee good mixing and dispersion of entangled CNTs and silica particles inside the polymer matrix. They were disseminated in chloroform using ultrasonic agitation at a frequency of 20KHz initially. The ultrasonic dispersion was done with a probe sonicator (12 mm probe, 500W maximum, pulse mode operation was also permitted). The probe sonicator was manufactured by Qsonica. Pulse mode operation was employed to avoid overheating and breaking the CNTs during the dispersion cycle. These processes resulted in the dispersion conditions of the fillers in the polymer matrix, which can be observed from the scanning electron microscopy (SEM) images illustrated in Figure 1. Apreo SEM was used to examine the morphological and structural characteristics of the CNT-based polymer composites. To improve
imaging contrast, the surfaces were coated with gold. A gold coating on the examination sample surface is required for conducting SEM. A conducting surface is required to interact with the blasted electron beam; otherwise, the electron beam’s contact with the sample surface electron would be weak (depending on how much the sample is conducting). To that end, gold was sputtered on at the thickness of approximately 50 nm on the CNT based polymer composite samples. The samples were also examined using Raman spectroscopy (Renishaw inVia, stimulated by a 514 nm Ar–ion laser with a laser spot size of approximately 1 \( \mu \text{m}^2 \)), which demonstrated that the composites have some physical characteristics representing those of CNTs, including its D band peak (near 1350 cm\(^{-1}\)) and a noticeable G band peak (at 1580 cm\(^{-1}\)).

3. Results and Discussion

3.1. Polymer composite morphological examination

Due to the limitation of the mixing process regarding viscosity and brittleness issues, the maximum loading contents of silica are limited to 40 wt% Si, while 10 wt% CNT loading was applied. Also, Fig 1a-1f display the cross-section SEM images for the CNT-based polymer composites revealing the morphologies of CNT-PDMS composites after incorporating with different silica content. Compared with sample without silica, all other samples showed hair-like morphology of CNT uniformly distributed among the silica particle surfaces. The latter proves the creation of excluded volume due to the silica particles. Moreover, it can be observed that as the silica content increased, the excluded volume becomes more apparent and also the interconnectivity between the CNTs become more evident, thus contributing to the effective increase in electrical conductivity.
Fig. 1: SEM images for carbon-based polymer composites, silica size=3 μm of: a) wt% silica=0, b) wt% silica=10, c) wt% silica=20, d) wt% silica=30, e) wt% silica=40, f) wt% silica=50

3.2. Raman Spectroscopy analysis
All the PDMS- CNT- Silica composites along with SWCNT, CNT -PDMS and compressed CNT were analyzed using Raman spectroscopy. A 514nm laser with spot size of 1 μm² was used where Raman peak analysis was done using VOIGT (convolution of Gaussian and Lorentzian) peak fitting using Origin 9 Pro. The position of G + peak was tracked to understand the effect of compression on CNT’s in the composites. Raman spectra of the composites containing 1 um silica particles at different weight ratios were shown in Fig 2 which showed a spectrum similar to SWCNT raman spectra shown in Fig 3.
CNT spectra dominated the raman spectra of the composites where no silica and PDMS peaks were observed in all the spectra. The improved electrical conductivity and seebeck coefficient due to the excluded volume may also bring some physical change to the components of the composite.
Tracking the position of G+ peak can help understand the type of stress that the CNT’s in the composite underwent. Fig 4 shows irrespective of the presence of PDMS or by compressing freely staked CNT powder, G+ peak didn’t change higher than 1 cm$^{-1}$ thus clarifying that the stress was not high or the addition of PDMS will induce an obvious strain.

![Fig 4: G+ position of various materials](image)

But this trend seemed to change when silica (3 um) was added to the composite where the pristine composites spectra with G+ peak position like CNT G+ Peak position where the compressed composites exhibited spectra with a clearly shifted G + peak to lower raman shift values as shown in Fig. 5. Further, when the silica size was decreased to 1um, no clear change in the G+ peak position was observed when compared to compressed composites with 3um silica powder, shown in Fig 6.

![Fig 5: G+ position of various composites](image)
The plots presented above clarify that the stress induced in the CNT’s is not solely due to compression rather due to compression of CNT’s by the silica particles considering their rigid behavior in contrast to the flexible and easily deformable behavior as seen in PDMS.

3.3. Electrical conductivity as a result of secondary filler

The CNT content is set at 10 wt% to explore the size influence of secondary particle fillers on the electrical conductivity of the composites. With different silica contents, the electrical conductivity is measured and analyzed. It can be observed from the SEM images, the inclusion of the micro-size silica filler activates the effect of the excluded volume and the agglomeration of more CNT networks, ultimately boosting the composite’s electrical conductivity\textsuperscript{52,54–56}. The increase in the total number of interconnecting junctions in the percolating network is explicit evidence of the conductivity increment of the network, due to an increased current path\textsuperscript{57}. It can be seen in Figure 4 that the electrical conductivity of the CNT-based polymer composites with silica wt% for both 1 and 3 μm particle size shows a significant increase in electrical conductivity starting from 20 wt% Si through 40 wt% Si. This is because as silica content increases, more excluded volume is created which leads to more interconnection of the CNTs, resulting in a denser electron transport path. The effect of compression is also examined in the CNT-based polymer composite. Before compression, it is observed that for both 1 and 3 μm silica particle size, as the silica content increases, more CNT alignments take place within the composite which is attributed to the effect of the excluded volume generated. To further propagate CNT alignments within the CNT-based
polymer composite which in some cases as observed in the SEM images transcends to CNT bundles, the samples were compressed from the range (0.8mm – 2mm) to the range (0.4 mm – 0.9mm). The compression effect in conjunction with the creation of excluded volume led to a drastic increase, approximately 50% increase in the electrical conductivity of the CNT-based polymer composite specifically for high content of silica particles (30 and 40 wt% Si).

![Graph showing electrical conductivity as a function of silica wt% for both 1 μm and 3 μm particle size, pore size – 2 nm (before and after compression), 10 %wt CNT](image)

Figure 7: Electrical conductivity as a function of silica wt% for both 1 μm and 3 μm particle size, pore size – 2 nm (before and after compression), 10 %wt CNT

Examination of individual samples and their response to the effect of compression specifically for 3 μm, we found out that for some of the samples, when the thickness decreased, the conductivity increased in a similar ratio (as seen in Fig. 8a, b, c and e) while some samples (Fig. 8d), it didn’t show that exact correlation. For the samples that do not follow the exact correlation, this can be attributed to inhomogeneity of the entire CNT-based polymer composite, whereby the PDMS wrapped all the CNT and after compression, the CNT structure remains and no damage is done to the flow of the current path while for some samples, there is a possibility that the CNT were not properly wrapped by PDMS and thus after compression, damage is done to the overall CNT network and doesn’t fully attain the ratio comparison between compression rate and electrical conductivity increase.
Fig. 8: Effect of compression on Electrical Conductivity property of the carbon-based polymer composites, silica size=3µm of: a) wt% silica=10, b) wt% silica=20, c) wt% silica=30, d) wt% silica=30, e) wt% silica=40

3.4. Seebeck coefficient as a result of secondary fillers

Figure 5 shows the behavior of the CNT based polymer composite before and after compression.

As can be seen from Fig. 5, the values obtained are all positive which is a clear indication that the majority carriers are holes, this is solely because the oxidation of CNTs generally makes them p-type unless they are treated with chemicals. For the Seebeck coefficient, the effect of compression on the CNT based polymer composite is not as glaring when compared to the case of...
electrical conductivity but also increases for high content of silica particles (30 and 40 wt% Si), particularly for 3 µm silica particle size. The general increase in the Seebeck coefficient as the silica content increases can be attributed to a decrease in CNT junction distances within the CNT based polymer composite. Beyond 40 wt% Si, a decrease in Seebeck coefficient is observed which can be attributed to difficulty in the processing, inhomogeneity and disruptive CNT networks.

3.5. Power factor of CNT based polymer composites

According to Figure 6, the addition of silica content to the polymer matrix can exponentially enhance the power factor for both 1 and 3 µm particle size. Beyond 40 wt% Si, both electrical conductivity and Seebeck coefficient decreases, resulting in the decrease of power factor. Our hypothesis for the decline includes a few factors such as more disruptive CNT interconnection within the CNT based polymer composite, interfacial adhesion between the filler-polymer matrix and lastly, the difficulty in the alignment of the nanotubes due to a higher percentage of the silica content.

Shown below is a plot for the power factor of 1 µm and 3 µm.
Figure 10: Power factor ($S^2\sigma$) as a function of silica wt% for both 1 μm and 3 μm particle size, pore size – 2 nm (before and after compression), 10 %wt CNT

3.6. Bending and Tensile performance of CNT based polymer composites

The high stability of the obtained CNT-based polymer composite films was characterized by radius-dependence conductivity measurement with silica content=0, 10% and 40%. As shown in Fig. 7, the electrical conductivity of composite film was measured with different bending radius. For bending up to 30mm to 30mm, a small reduction (~2%) in electrical conductivity was observed. The maximum decrease was found at a bending radius of 10 mm with 4% loss compared with electrical conductivity measured for flat sample without bending. These results suggest that the CNT-based polymer composite films exhibit excellent mechanical stability and reproducible TE performance despite bending, thus making it a promising candidate for wearable TE device fabrication.
Fig.11: Bending radius-dependent electrical conductivity for CNT-based polymer composites after compression for silica size=3µm with wt% silica=0, 10 and 40 respectively

4. Conclusion

It is demonstrated in our work that the addition of fillers, the size of the fillers, the amount of the filler and the effect of compression all play a significant role in the enhancement of both electrical conductivity and Seebeck coefficient leading to significant high power factor values obtained for 30 and 40 wt% silica, with a minimal loading of just 10 wt% CNT. Further improvements on the material composition and ability to ensure very stable homogeneity rates from sample to sample is a plausible direction for enhancing the TE properties of CNT-based polymer composites.
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Excluded volume effect on the power factor of Carbon Nanotube based polymer composite

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Synthesis of polymer composites

Dow Corning supplied commercially available polydimethylsiloxane (PDMS: Sylgard 184 SILICONE ELASTOMER BASE) for the synthesis of the CNT-based polymer composite. Single walled carbon nanotubes (SWCNTs) with an average diameter of 1.6 nm and a length of > 5 µm was utilized. The SWCNTs used is a hybrid of both semiconducting and metallic carbon nanotubes. Silica powders of 200 nm, 1 µm, and 3 µm particle size were bought from Sigma Aldrich. Ultrasonication was employed to guarantee good mixing and dispersion of entangled CNTs and silica particles inside the polymer matrix. They were disseminated in chloroform using ultrasonic agitation at a frequency of 20KHz initially. The ultrasonic dispersion was done with a probe sonicator (12 mm probe, 500W maximum, pulse mode operation was also permitted). The probe sonicator was manufactured by Qsonica. The CNT dispersion was done utilizing the probe sonicator for a duration of 15 minutes at 30% amplitude, pulse mode – 40 seconds ON and 20 seconds OFF. Given the ON time, this meant that the overall time for dispersion was 10 minutes. Pulse mode operation was employed to avoid overheating and breaking the CNTs during the dispersion cycle.
Similarly, the PDMS prepolymer was sonicated for 3 minutes in chloroform enabling uniform dispersion. The resulting dispersed solution was then mixed with the solution containing the dispersed CNT and further sonicated for an extra 15 mins keeping the same conditions for sonication (30 percent amplitude, pulse mode - 40 seconds ON and 20 seconds OFF). Afterwards, silica particles were added to the solution and was also sonicated.

To allow extra chloroform to evaporate, the mixture was shear mixed (at 200rpm) at 100°C. The curing agent (10% of the PDMS pre-polymer) was added and combined with the CNT-Silica-PDMS prepolymer paste after most of the chloroform had dissipated. Varied proportions of silica and PDMS base elastomer were mixed to make the paste. To make the CNT/silica paste, the elastomer base and curing agent were mixed in a 10:1 (w/w) ratio, then mixed with CNT/silica. Because a significant quantity of heat is created during ultrasonication as well as while heating for solvent evaporation, the curing agent ought not be introduced at the start of the process. The curing agent is energized by heat, and it begins polymerizing the monomer, resulting in ineffective dispersion and non-uniform samples. Hence, to achieve homogeneous polymerization, it is introduced as a final step before annealing in the mold.

**Figure S1.** Step by step explanation of processing steps involved in sample preparation.
After that, the slurry was poured into a metal mold (with cut-in sample dimensions of 20 mm x 10 mm x 1 mm). In order for annealing to take place, the metal mold was placed on a hot plate and the temperature was set to 100 °C for approximately 35 minutes to produce elastomer films with thickness ranging from 0.8 mm to 1 mm or higher, electrical conductivity and Seebeck measurements were taken as shown in preceding sections and termed as “before compression.

The CNT based polymer composites were further subjected to compression rolling to achieve composite thickness of 1.0 ± 1.05 mm and 0.5 ± 0.05 mm, and was termed as “1 mm compression and 0.5 mm compression” respectively. These were used for all the final measurements reported in this study.

Table 1 shows the weight percent of CNT and different weight percentages of Silica and PDMS utilized in the elastomers.

Table 1: The percentages and weights of constituent CNT, Silica and PDMS (prepolymer and curing agent)

| CNT wt% | Silica wt% | PDMS [A+B Prepolymer mg | Curing Agent mg |
|---------|------------|-------------------------|-----------------|
| 10%     | 0%         | 405                     | 45              |
| 10%     | 10%        | 360                     | 40              |
| 10%     | 20%        | 315                     | 35              |
| 10%     | 30%        | 270                     | 30              |
| 10%     | 40%        | 225                     | 25              |

These weight percentages are based on a 500 mg total elastomer weight. It is worthy to note that for the CNT dispersion, up to 40 mL chloroform was utilized, and for PDMS prepolymer dispersion, up to 20 mL was utilized.

Also, as predicted, CNT percent samples with larger percentage of PDMS matrix were proven to be more flexible.
Figure 2 depicts a flexible elastomer made up of 10% carbon nanotubes, 20% silica, and 70% PDMS. Above 30% Silica content the elastomers become less flexible with 40% Silica content observed as the most brittle.

**Figure S2.** (a) The synthesized CNT based polymer composites showing flexibility (b) CNT based polymer composite sample of dimensions 20 mm x 10 mm x 1 mm

**Components and solvents utilized to make the CNT based polymer composites**

Table 2. Details of the materials used in the CNT-PDMS elastomer synthesis

| Materials            | Description                                                                 | Aim                                      |
|----------------------|-----------------------------------------------------------------------------|------------------------------------------|
| SWCNT                | Average diameter ~1.6 nm, Length >5 μm, (~80% SWCNTs, ~12 Metallic impurities) from Sigma Aldrich | CNT networks, primary filler - creates a conduit for electrical conduction |
| Silica               | • Mesoporous, 1 μm particle size, pore size – 2 nm<br>• Mesoporous, 3 μm particle size, pore size – 2 nm<br>Both from Sigma Aldrich | Secondary filler - creates excluded volume |
| PDMS - Poly(dimethylsiloxane) | Sylgard 184 PDMS prepolymer (elastomer base) and curing agent from Dow | Matrix - electrically insulating and low thermal conductivity |
Raman Spectroscopy

Given that the same CNTs were utilized for the composites, it is not surprising that the D/G ratio does not change for both 1 and 3 \( \mu \text{m} \) silica particles. Other noteworthy peaks (at around 2800 cm\(^{-1}\)) are associated with PDMS, although less intense.

Table 3. Comparison between the D/G ratio and G- peak for CNT-based polymer composites

| Materials | 10% D/G ratio | 20% D/G ratio | 30% D/G ratio | 40% D/G ratio |
|-----------|---------------|---------------|---------------|---------------|
| 3 \( \mu \text{m} \) Silica Particle size | 1573.35 cm\(^{-1}\) | 1573.35 cm\(^{-1}\) | 1573.35 cm\(^{-1}\) | 1573.35 cm\(^{-1}\) |
SEM images of CNT-based polymer composites

Figure S3. SEM images for carbon-based polymer composites before compression, silica size=1µm of: a) wt% silica=10, b) wt% silica=20, c) wt% silica=30, d) wt% silica=40
Figure S4. SEM images for carbon-based polymer composites after compression, silica size=1µm of: a) wt% silica=10, b) wt% silica=20, c) wt% silica=30, d) wt% silica=40
Figure S5. SEM images for carbon-based polymer composites after compression, silica size=3μm of:
a) wt% silica=10, b) wt% silica=20, c) wt% silica=30, d) wt% silica=40