

Influence of CNT Concentrations to Polyurethane / Multi-walled Carbon Nanotube Composites on the Thermoelectric Performance

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ABSTRACT

In this work, we investigated the possibility of applying polyurethane in thermoelectric application, and the influence of MWNT concentrations to polyurethane / multi-walled carbon nanotube composites on the thermoelectric performance. The composites were prepared by solution blending method. Different MWNT concentrations from 5% to 60% were added into the polyurethane matrix. The electrical conductivity, Seebeck coefficient and thermal conductivity of the prepared composites were measured. The electrical conductivity was increased with the addition of more MWNTs. The Seebeck coefficient decreased slightly with the increase of the MWNT loading. The thermal conductivities increased with the addition of more MWNTs. A reasonable Seebeck coefficient of $\sim 33\mu\text{V/K}$ suggested that polyurethane can be used in thermoelectric application. These flexible and stretchable composite films could be used for some special applications where flexibility and stretchability are needed.

Keywords: polyurethane, carbon nanotube, nanocomposites, thermoelectric.

1 INTRODUCTION

Thermoelectric technology, which can directly convert thermal energy into electricity and no pollution exist during the process, would be one of the most promising energy harvesting technology in the future.[1] Even the low quality waste heat such as body heat can also be utilized in thermoelectric conversion system.

Thermoelectric materials are the indispensable components in a thermoelectric generator, which are used to convert temperature difference into electrical voltage. The efficiency of a thermoelectric material are evaluated by thermoelectric figure of merit, which can be defined as

$$ZT = \frac{S^2\sigma}{\kappa}T \quad (1)$$

In the equation, S is Seebeck coefficient (thermopower), σ is electrical conductivity, κ is thermal conductivity, T is the absolute temperature. A higher ZT vaule means the better thermoelectric performance of a material, and there is no upper limit on the value of ZT.[2] Sometimes, without the precise data of the thermal conductivity, the thermoelectric performance of materials with similar

thermal conductivity can also be compared by the value of $S^2\sigma$ (power factor).

In the past few decades, many types of materials have been investigated to explore their application as effective thermoelectric materials. The most widely researched materials are inorganic semiconductors, such as bismuth telluride, which often have relatively higher ZT value than organic polymers. For example, Bi₂Te₃, as a successful commercially available thermoelectric material, has a ZT value of 1.2 at room temperature;[3] one recent research showed that the highest ZT value of a PbTe material is 2.2.[4] However, most of these inorganic thermoelectric materials are rare and toxic materials, which is difficult to use in daily life and uneconomical to produce on a large scale.[5]

Polymer based organic thermoelectric materials just arose attention in recent years with the rapid development of organic electronics. The efficiency per unit of most polymer based thermoelectric materials is much lower than the inorganic ones, but it can be compensated by applying into large areas due to the cheap and easy-to-process properties of polymers. Polyurethane is one of the most commonly used thermal insulation materials with very low thermal conductivity, superior flexibility, which made it a great choice for thermoelectric polymer matrix. In this paper, we investigated the possibility of applying polyurethane in thermoelectric application, and evaluated the influence of MWNT concentrations to polyurethane / MWNT composites on their thermoelectric performance.

2 EXPERIMENT

2.1 Materials and Preparation

The desired contents of MWNTs (Multi walled carbon nanotubes synthesized by the CVD method were purchased from Timesnano, Co. Purity:>95wt% ID: 2-5nm OD: <8nm Length: 10-30 μm) were dispersed in the dimethylacetamide (DMAc) solution (purchased from Sigma Aldrich) and sonicated for 15 min in a sonic bath. Then, the polyurethane (HT-751, Mw is $\sim 900'000$, Mn is $\sim 300'000$, purchased from Hong Kong Hi-Tec Enterprises Limited.) was added into the dispersion and stirred at 80 °C for 2 hours. The mixtures contain 7.9wt% total solids. After that, the mixtures were subject to another 20 min sonication in a sonic bath. Finally, the resulting mixture solutions were

placed in a 49 cm² teflon mold and evaporate the solvent in an oven at 50°C, followed by 12 hours annealing process at 100°C. The MWNT concentrations of 5, 10, 15, 20, 30, 40, and 50wt% in the polyurethane/MWNT composites were investigated. (These concentrations are the total dry weight of the composite.)

2.2 Characterization

The morphology of the composites was observed by a field emission scanning electron microscope (FE-SEM). The composites were soaked in liquid nitrogen and freeze-fractured first, and the surfaces of the cross-section were sputter-coated with platinum. Then, the morphology of the cross-section can be observed.

To measure the electrical conductivity and thermopower, samples were cut into a rectangular shape with a size of 30mm×10mm. To avoid deviation of sample evenness, the measurement of electrical conductivity and thermopower are using the same sample. Both electrical conductivity and thermopower were measured along the in-plane direction.

The electrical conductivity was measured by a four-probe method at room temperature. Four electrically conductive metal lines were pressure placed at both ends of the sample patterned with silver paint as electrode. The outer sides of two metal lines connected with a GW-3635 power source (Good will Instrument Co., LTD) were used for imputing electrical current. The inner sides of the two metal lines connected with a Keithley 2000 multimeter (Cleveland, OH) were used to measure the electrical voltage. By sweeping measurement of the current-voltage (I-V) across the sample, the electrical resistance can be obtained from the slope of the I-V curve. The resistivity can be then calculated by multiplying the resistance with the thickness of the sample and divided by the distance between the two inner probes. The electrical conductivity can be converted by taking the inverse of the resistivity value.

In the thermopower (Seebeck coefficient) measurement, a heater was equipped on one side of the sample to create temperature difference, and the other side of the sample was exposed to air. Two K-type thermocouples were used to measure the temperature of the two ends of the sample. As the temperature of the hot side increased, thermoelectric voltage between two ends of the sample can be measured by the Keithley 2000 multimeter. The slope of the V-ΔT curve is the thermopower (Seebeck coefficient). The schematic arrangement of the device was described in Figure 1.

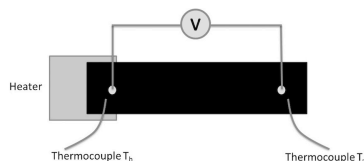


Figure 1: The schematic arrangement of Seebeck coefficient measurement device

The thermal conductivity in the out of plane direction can be measured according to ASTM D5460 standard. The measurement device is KE5F7, Thermo Lab 2 system, KATO TECH Co. LTD.

3 RESULTS AND DISCUSSION

The thickness of the prepared polyurethane/MWNT composites was in the range from 0.16mm to 0.21mm. The prepared composites are freestanding and flexible films. However, sample with MWNT concentrations of 60% will lose its flexibility and cannot form a complete film to do the following test.

Figure 2a, 2b shows the prepared freestanding polyurethane/MWNT composite film with 20wt% MWNTs. The film can be easily bent and stretched, which means the composite can still keep the flexibility and elasticity of polyurethane. The cross-section SEM image of the composite are presented in Figure 2c. The dispersion of MWNTs in polyurethane is not quite even. Many MWNTs are aggregated into bundles and separated by polyurethane. Only a few MWNTs are connected across the polyurethane. This may create a weak connected conductive network throughout the film, which may result in a low electrical conductivity but a higher thermopower in the composite, owing to the coupling effect of these two parameters. This morphology may because of the low drying temperature and the lack of stabilizer during the preparation of the film.

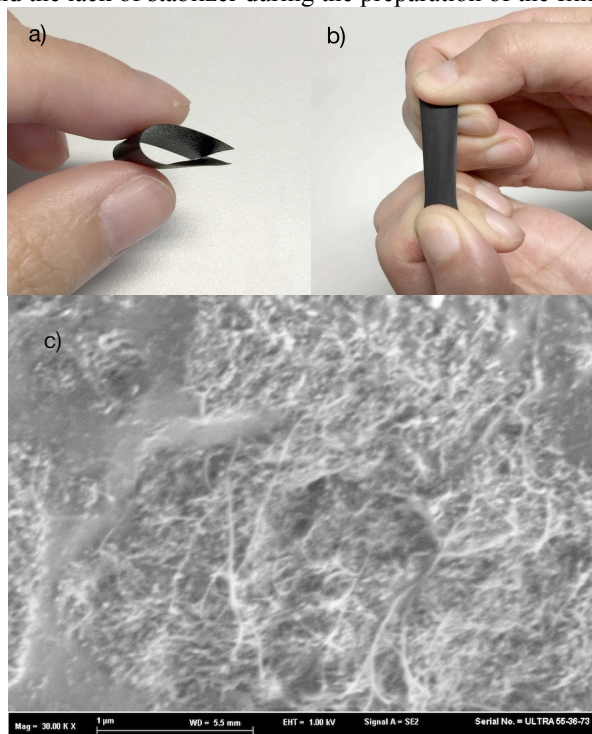


Figure 2: a) The composite with 20wt%MWNT was bent; b) The composite with 20wt%MWNT was stretched; c) The SEM image of the cross-section of the composite with 20wt% MWNT.

The electrical conductivities of the composites with different MWNT concentrations are showed in Figure 3. It can be observed that the electrical conductivity of the composite enhanced with the increase of CNT contents. However, the overall conductivity of the prepared composites are still in a low level. Especially samples whose MWNT contents lower than 20wt% can not even be tested. This may due to the weak connected conductive network of MWNTs and the quality of MWNT.

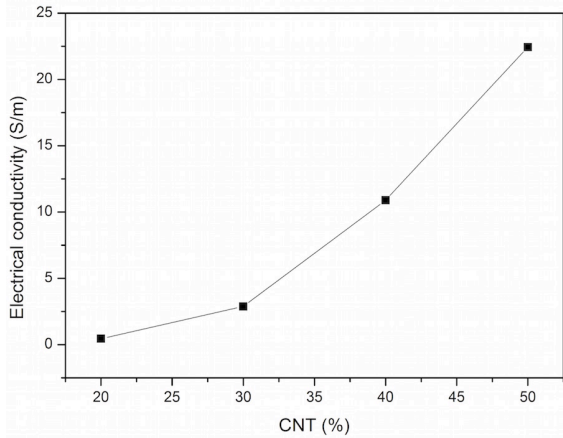


Figure 3: The electrical conductivities of 20, 30, 40, and 50 wt% CNT composites

The Seebeck coefficient of the composites are showed in Figure 4. Although the electrical conductivities of the composites is low, the resulted thermopower are relatively high and could achieve $\sim 33\mu\text{V/K}$ when the MWNT contents at 40wt%. As for samples with low electrical conductivity, the thermopower also can not be measured. Despite the increase of electrical conductivity, the thermopower changed slightly with the increased MWNT loading. To some extent, the thermopower increased a little until the MWNT concentrations reach to 40wt%. The Seebeck coefficient seems independent at low conductive composites.

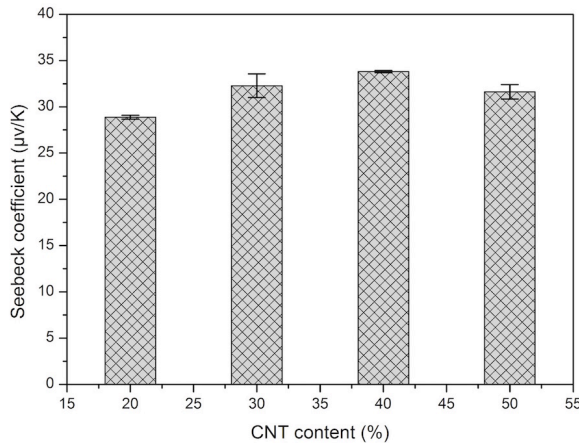


Figure 4: The Seebeck coefficients of 20, 30, 40, and 50 wt% CNT composites

The calculated power factors ($S^2\sigma$) are showed in Figure 5. The resulted power factors of the composites are also increased with the addition of more MWNTs. However, the overall power factors are still in a low level. Since the Seebeck coefficient of the prepared composites is relatively constant, this low power factor is strongly attributed to the low electrical conductivity. Improve the MWNT quality and the manufacturing process may increase the electrical conductivity.

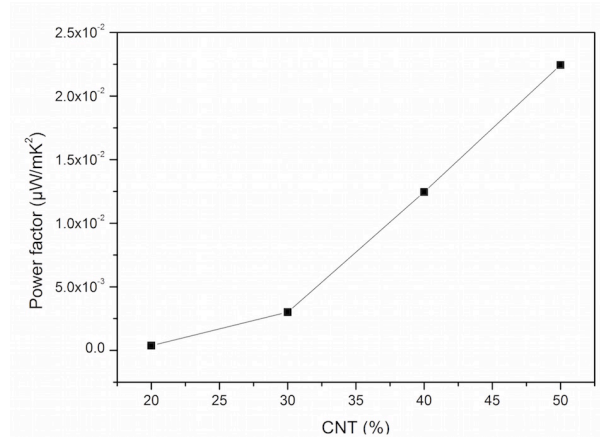


Figure 5: The power factors of 20, 30, 40, and 50 wt% CNT composites

The thermal conductivities of the composites are showed in the Figure 6. The thermal conductivities increased with the increase of CNTs contents. However, the growth rate is slowed when CNT loadings increased from 40wt% to 50wt%. It seems that the thermal conductivity of CNTs is limited by the polymer-CNT interface. It is known that the thermal conductivity of single CNT could be extremely high, but the thermal conductivities of the prepared polyurethane/MWNT composites only increased slightly after the addition of CNTs. This may due to the weak connection between CNT junctions, which not only weakened the electrical conductivity but also suppresses the phonon transmission between the CNTs.

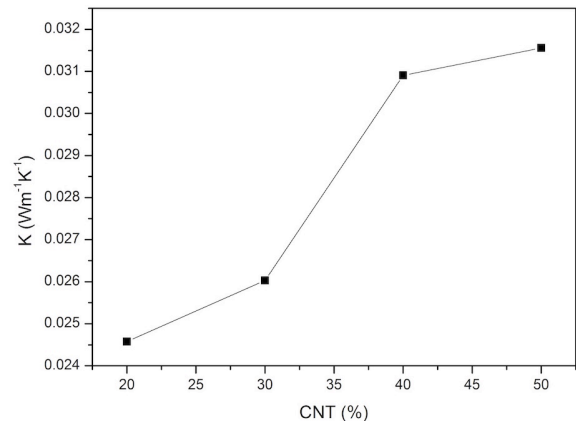


Figure 6: The thermal conductivities of 20, 30, 40, and 50 wt% CNT composites

4 CONCLUSIONS

Composite films with different MWNT concentrations in polyurethane matrix were prepared. The cross-section morphology of sample with 20wt% MWNTs contents was observed by FE-SEM. The electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity, which can represent the thermoelectric performance of those composites, were investigated at ambient temperature. Our results showed that the electrical conductivity of polyurethane/MWNT can be improved by the increase of CNT concentrations, while the Seebeck coefficient can keep relatively constant and could achieve $\sim 33 \mu\text{V/K}$ at 40wt% CNT loadings. The incorporation of MWNT in the polyurethane matrix resulted in slightly increase of thermal conductivity, but this improvement seems to be limited by the polymer/CNT interface.

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