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Thermoelectric Performance Enhancement of Naturally Occurring Bi and Chitosan Composite Films Using Energy Efficient Method

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Abstract

The main aim of this work is to report an alternative energy efficient technique of fabricating flexible thermoelectric generators (TEGs) using printable ink. In this process, we have fabricated thermoelectric (TE) composite thick film and we are experimenting several ways to overcome the challenges of conventional and additive manufacturing methods. Two different mesh sizes of n-type bismuth particle, various binder to thermoelectric (TE) material weight ratio, and two different pressure (200 MPa and 300 MPa) were employed for optimizing the thermoelectric properties of TE composite films. We are also exploring naturally occurring chitosan as a binder. Dimethyl sulfoxide (DMSO) dissolved chitosan was used for the binder and less than 0.2 wt% of chitosan was sufficient for the fabrication of TE inks and composite films. Low energy intensive curing process was employed to evaporate the solvent from the drop casted inks. External uniaxial pressure not only eliminated high energy intensive curing processes but also increased the packing density of the film by removing pores and voids in the chitosan-bismuth composite film. The microstructure analysis reveals that bulk-like structure, which rarely has voids, pores and grain boundaries, was observed in the composite films pressed at sufficiently high pressures. The highest performing composite film was obtained with the conditions of 1:2000 binder to bismuth weight ratio, 100 mesh of particle size, and 300 MPa of pressure. The best performing bismuth chitosan composite film pressed at 300 MPa had the power factor as 4009 ± 391 μW/m·K^2 with high electrical conductivity value of 7337 ± 522 S/cm. The measured thermal conductivity of the best performing chitosan-bismuth composite film was 4.4 ± 0.7 W/m·K and the figure of merit calculated from the thermal conductivity was 0.27 at room temperature.

Introduction

As the rapid growth of the energy consumption market, the energy conversion processes are facing great challenge to meet the demand. Considering that most of the energy has been wasted in the form of heat during device and machine operations (e.g. automobile engines, power transistors, light bulbs, industrial processes, etc.), energy harvesting device, Thermoelectric Generator (TEG), can utilize the waste heat energy and convert it into electricity [1]. TEG has a long lifespan to provide electrical energy and fewer replacement requirements than other devices, such as solar cells. Thus, TEGs have been applied in a vast number of areas, including wireless sensor network, medical field, wearable devices, industrial, military, remote monitoring system, etc. [2,3]. The conventional way of manufacturing TEGs is to dice an ingot bulk material and assemble and integrate the diced piece. The conventional pick-and-place methods for thermoelectric device manufacturing are limited to low aspect-ratio elements. And micro-fabrication technology has a limited cost-effective scalability. Due to the disadvantages of this method, additive methods [4,5] (such as dispenser printing, screen printing, stencil printing and inkjet printing, etc.) have been introduced to overcome the conventional methods' limitations.

Various research groups have proven that these additive methods promise a simple, cost-effective and scalable way to manufacture TEGs [6,7].

The theoretical maximum efficiency [8]of the energy conversion process of a thermoelectric material is determined by the figure of merit (ZT), given by

$$ZT = \frac{\sigma\alpha^2 T}{\kappa} - (1)$$

Where σ is the electrical conductivity, α is the Seebeck coefficient, T is the temperature and κ is the thermal conductivity. A thermoelectric material, which has a high electrical conductivity and seebeck coefficient, and a low thermal conductivity can achieve high figure of merit. However, achievement of high ZT is challenge because the factors in ZT, electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (κ) are determined by the natural properties of the material itself property. Electrical conductivity and seebeck coefficient for TE materials have an inverse relation [9]. In addition, materials with high electrical conductivity generally have high thermal conductivity. Thus, there are numerous efforts to improve ZT of thermoelectric materials by doping, hybrid, and structural(nano material) methods [3,8,10–12].

Thermoelectric inks made from the combination of thermoelectric materials and binders are indispensable for the additive process. A binder enables the solution process before the curing process and retains the thermoelectric particles in the form of thermoelectric films with its own adhesive strength. Various types of materials have been applied as binders for the thermoelectric films, such as removable binders [9,10], thermoset polymers [11,12], and biomaterials [17]. Large amounts of binder residues of epoxy resins in TE composite films reduce electrical conductivity, and epoxy resins require high temperatures and long times to cure [18]. In order to improve the electrical conductivity of TE-epoxy composite films, Madan et al. used various sintering methods and added different additives and the maximum ZT of 0.41 was achieved for p-type epoxy binding TE composite films [11,15]. Other research groups used removable binder and they achieved higher ZT on p- and n-type TE films, but they could not eliminate the curing process that required high temperature and long duration [16-18]. A new biomaterial nano-fibrous cellulose (NFC) was introduced as a binder in the thermoelectric area by Jang et al. and proved that the nano-fibrous cellulose (NFC) material was quite successful binder for thermoelectric composite films [17]. The small amount of NFC binder had high enough adhesive strength to hold the TE particles and thus reduce the insulating binder content in TE composite films, which lead to high electrical conductivity at room temperature.

Pressing method during the curing process has been considered to increase the density of the composite films. Cao et al. and Choi et al. proved that better alignment, closer particle distance and more contact between active particles have been observed through SEM after pressing, which in theory, would demonstrate better electrical conductivity [19,20]. However, they used the pressing method during and after a long duration of high temperature curing. Jang et al. also introduced pressing as the post annealing method to densify their composite films. In this study, the pressing method not only increased the density of the film but also eliminated pores, voids and the high energy intensive curing process. The pressed denser films had higher electrical conductivity without using energy intensive steps [17].

The effect of grain size has been studied on bulk TE materials by various research groups. If the particle size is small enough, electrical conductivity has been shown to significantly decrease due to potential barrier scattering at the grain boundary [25]. Small particle sizes form a potential barrier, which reported that a charge carrier without sufficient energy could not jump over the potential barrier. This phenomenon lowers the electrical conductivity [26]. Takashiri et al. reported that as the grain size decreased, the number of defects at the grain boundary increased and this result in lower electrical conductivity and a sharp decrease in the figure of merit ZT [27]. However, to the best of our knowledge, no one has reported research on particle size effects on TE properties of printed TE composite films.

This study reports an experimental study to understand the effect of TE particle size on the electrical conductivity of composite TE films. In this work, we employed two different mesh sizes of bismuth particle (100 mesh and 200 mesh) and mixed the naturally occuring chitosan binder to prepare the TE inks. Water free property of DMSO-chitosan makes the composite films more stable due to less oxidation issues. Besides, high adhesive strength of chitosan holds the TE particles well. The external applied pressure helped to densify the films and eliminate the pores and voids. Characterization of thermoelectric properties with respect to various conditions of fabricating TE films, such as mesh sizes (100 mesh and 200 mesh), pressures (200 MPa and 300 MPa), and binder to TE material weight ratio (1:500, 1:1000, 1:2000, and 1:5000) was demonstrated. We successfully made high performing chitosan-bismuth composite TE films and their electrical conductivity and seebeck coefficient were comparable to the values of bulk bismuth [1,24]. SEM images and density value confirmed that the chitosan-bismuth composite films had bulk-like structure. The achievement of bulk like structure in n-type TE composite films improved the electrical conductivity of chitosan-bismuth composite TE film drastically and resulted in high power factor.

Method

Purchased 100 mesh bismuth particle (Santech Inc., China) and 200 mesh bismuth particles (Fisher scientific) were used as TE material without further purification and grinding. Chitosan (MP Biomedicals, LLC) and dimethyl sulfoxide (DMSO, 99.7+%, extra dry, ACROS Organics) were purchased and used as received. The method for synthesizing the chitosan binder was as follows. 98.4 mg of salicylic acid particle was added to 15 ml of DMSO and mixed with a vortex mixer until the salicylic acid particles were completely dissolved. For the thicker chitosan binder, 150mg of chitosan powder was added to the DMSO blend, and for the light chitosan binder, 50mg of chitosan powder was added to the DMSO blend. Using vortex mixer, agglomerated chitosan was dispersed, and for complete dissolution, the binder solution was placed on a hot plate with magnetic stirring at 75°C and 300 rpm overnight. Four different weight ratios 1:500, 1:1000, 1:2000 and 1:5000 between binder and thermoelectric (TE) particle of inks were synthesized, and for 1:5000 ratio of ink, an additional amount of DMSO was added to attain proper viscosity. For homogeneity of the inks, mixing using a vortex mixer for 1 minute and then sonicating in an ultrasonic bath for 30 minutes were conducted.

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Chitosan coated Kevlar (Fibre Glast Development Corp., KEVLAR® Plain Weave Fabric) was chosen as the substrate. Chitosan coating made the Kevlar attain more uniform surface. 0.1M of acetic acid and 150 mg of chitosan were added to 15ml of deionized (DI) water and magnetically stirred on a hot plate as before to obtain diluted chitosan. The diluted chitosan was applied on kevlar substrates and the coated substrates were dried for overnight. TE films were made by drop casting the homogeneous inks on a chitosan coated kevlar substrate and the diameter of deposited TE inks were approximately 5mm. The deposited inks were cured at 120°C for 10 minutes in an oven until solvent evaporation was complete. After drying of the inks, external pressures (200 and 300 MPa) were applied to the cured films. A hydraulic press (MTI corp., YLJ-CSP-30) applied pressure to the films for 5 minutes with, and the pressure was determined by previous work of our research group [17]. A polyethylene film covered the TE films to protect the TE films during the pressing.

In order to measure the electrical conductivity and charge carrier concentration, the Hall Effect measurement system (ECOPIA, HMS-5500) was employed. To reduce the error, multiple TE films were fabricated from each TE ink and measured TE properties. The average of the measuring results was used and all measurements were performed in ambient air. Prior to electrical conductivity measuring, a vernier caliper (Mityutoyo, 293-340-30) was used to measure the thickness of the sample. The TE films thickness (200~300 µm) was obtained by calculating the difference between substrate thickness (250 µm) and whole thickness (450~550 µm). A custom-built seebeck measurement setup was used to measure the seebeck coefficient. Two peltiers were used to generate temperature differences (0K, 2K, 4K, and 6K) across the sample by enforcing various voltages (0V, 0.7V, 1.4V, and 2.1 V) to the peltiers. 65 seconds were given to each stage to stabilize the temperature of the peltiers and the TE films. A gold tip probe and a thermocouple were used on each of the ends of the sample to measure the voltage differences (ΔV) and the temperature differences (ΔT) respectively across the sample. Multiple measurements (50 times at each different temperature stage) of both voltages and temperatures were recorded to minimize the error. The seebeck coefficient was then calculated as the slope of the ΔT (x-axis) and ΔV (y-axis) straight line.

Thermal conductivity measurement was conducted using the TCi thermal conductivity analyzer (C-Therm Technologies Ltd.). The blotter method with a silicon pad was employed for thick film thermal conductivity measurement. To make a sufficiently large TE sample, the TE ink was dried in the oven (120-130°C for 30 minutes) and transferred to a metal rod wrapped side with a PE film. The transferred composite particle was covered with a pressing metal rod and pressed with 200 MPa. Thermal grease was used for contacting the TE films with the MTPS sensor well. Collectively the order, from bottom to the top was as follows: the MTPS sensor, the thermal grease, the sample, the silicon pad, and a weight for good contact. After four times of measurements with and the other four times without the silicon pad, the voltage charts were checked whether the measurements with and without blotter were properly done. Density of the TE films were calculated with the measured films' weight and the measured films' volume. TE film's weight was measured with weighing balance (SARTORIUS, TE214S Analytical Balance) and the volume was measured with the 3D laser scanning microscope (KEYENCE, VX-X1000). Density of the films were calculated by dividing the measured weight with the measured volume.

Result and Discussion

Two different particle sizes of n-type bismuth particle (100 mesh and 200 mesh) were used for fabrication of chitosan-bismuth composite films. SEM were performed on the purchased Bi particles. Figure 1 shows the SEM images of different size particle distribution of bismuth particles for 100 mesh

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and 200 mesh size. It is obvious that the 100-mesh bismuth particle is composed of larger range of particle size (submicron to 150 µm) from the figure 1-(a). Figure 1-(b) shows the narrower range (submicron to 80 µm) of Bi particles than 100 mesh Bi particles. We also used image J to count the number of particles for 100 mesh and 200 mesh Bi particles as shown in figure2. Figure 2 shows that 100 mesh bismuth particles have combination of coarse particles (150 µm) fine particles (20 µm) . 200 mesh bismuth particles have more uniform fine particle size distribution.

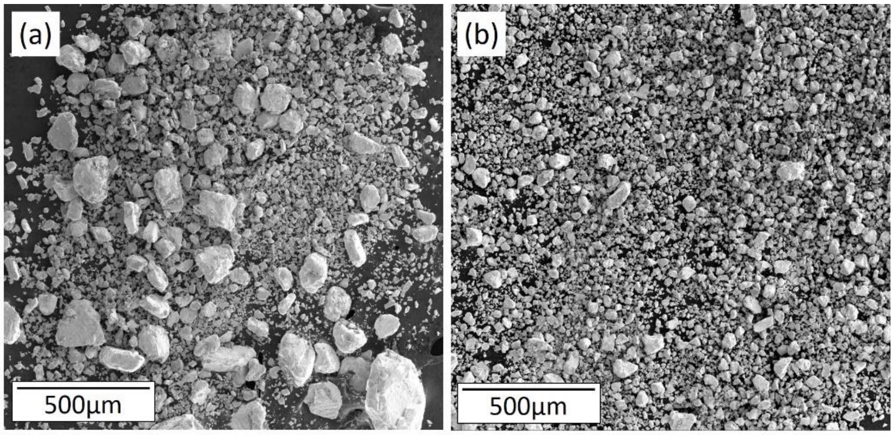

Figure 1. SEM images of (a) 100 mesh bismuth particles and (b) 200 mesh bismuth particles

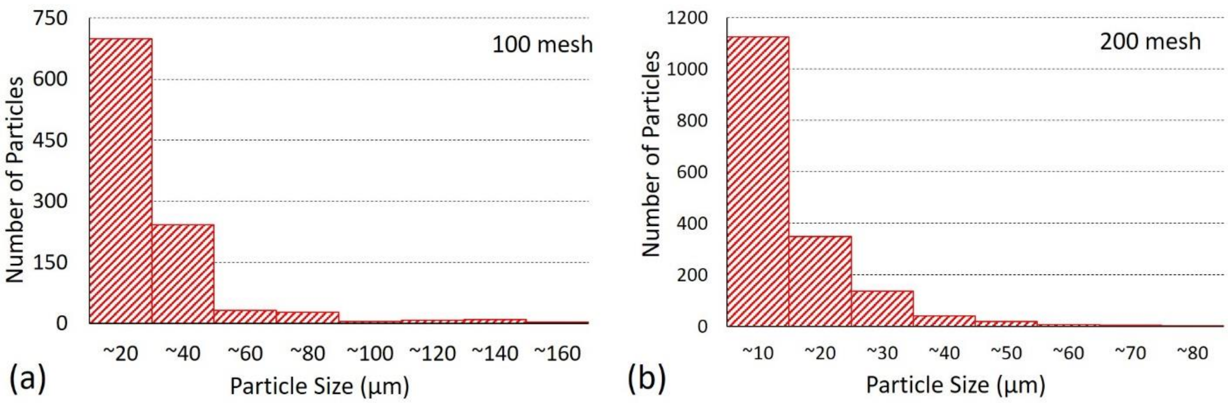

Figure 2. Particle size distribution of (a) 100 mesh and (b) 200 mesh

Figure 3 shows the thermoelectric properties of externally pressed chitosan-bismuth composite TE films. chitosan- 100 mesh bismuth composite films pressed at 200 MPa (red square) and 300 MPa (blue circle), and chitosan- 200 mesh bismuth composite films pressed at 300 MPa (black diamond) were shown on the graphs. The measured electrical conductivity, absolute value of seebeck coefficient, absolute value of carrier concentration, and calculated power factor were plotted on the graph with four different weight ratios between binder and bismuth on x-axis such as 1:500, 1:1000, 1:2000, and 1:5000.

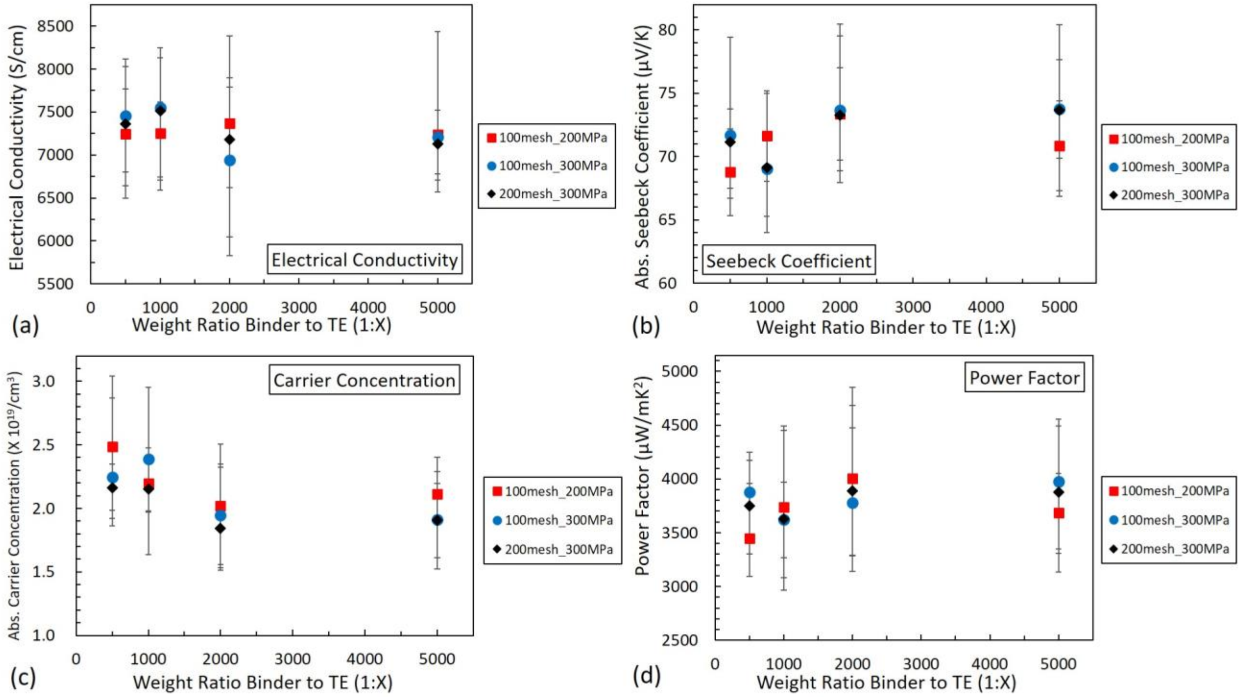

Figure 3. (a) Electrical conductivity, (b) Absolute value of seebeck coefficient, (c) Absolute value of charge carrier concentration, and (d) Power factor of various chitosan-bismuth TE composite films

In figure 3-(a), the highest electrical conductivity value (7548 ± 518 S/cm) was obtained from the 1:1000 binder to 100 mesh bismuth weight ratio TE composite films pressed at 300 MPa. The lowest electrical conductivity value (6938 ± 544 S/cm) was obtained from the 1:2000 binder to 100 mesh bismuth weight ratio TE composite films pressed at 300 MPa. Those values are comparable to each other. For experimental purpose we also pressed 100 mesh 1:500 wt ratio of binder to active particles at 5 MPa and 50 MPa and the electrical conductivity was (870.8 ± 224 S/cm) and (4772 ± 673 S/cm) respectively. The electrical conductivity of the TE films pressed with higher pressure (≥ 100 MPa) was higher discussed above in this paragraph and shown in figure 3-(a). Therefore, for this work we use external pressure 200 MPa and 300 MPa respectively and achieved high electrical conductivity.

The Electrical conductivity values were observed to be similar through all the various weight ratios of binder to bismuth (1:500, 1:1000, 1:2000, and 1:5000) for different mesh size films and at different pressure. This phenomena can be explained on the basis of the percolation theory of composite materials. Once the fraction of conductive material hits the percolation threshold, the conductive path forms in the composite material and electrical conductivity increases drastically [27,28]. In our previous work we have shown that 1:100 weight ration of binder to TE material the electrical conductivity was much lower than other two higher weight ratio 1:1000 and 1:10,000 respectively [17]. This can be evident that the percolation threshold lies between 1:100 and 1:500 weight ratio of binder to active material. Therefore, in this work we have chosen four different weight ratios (1:500, 1:1000, 1:2000, and 1:5000) and it seems all the weight ratios are above percolation threshold.

The electrical conductivity values did not change much by increasing the pressure from 200 MPa to 300 MPa, it means 200 MPa pressure was sufficient to densify the films and eliminate the pores and voids.

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Moreover, 100 mesh and 200 mesh Bi particles did not play much role in changing the electrical conductivity of TE composite films. To sum up we have gained electrical conductivity in all different TE composite films very similar to bulk Bi electrical conductivity 8333 – 8900 S/cm [25,26]. The enhancement in electrical conductivity is due to different grains (100 mesh or 200 mesh) Bi particles. Moreover, the external applied pressure also played important role to densify the wide range distribution of particles. To confirm this phenomenon, we have performed SEM on TE composite films and images are shown in figure 4.

From the SEM images, it was observed that bismuth particles were well coalesced due to the sufficient pressure. Since Bi is a ductile metal when we applied external pressure Bi particles easily coalesced with each other and formed bulk like structure. Therefore, 100 mesh and 200-mesh particles size did not play much role in these TE films. Therefore, the electrical conductivity was high and same as Bi bulk material. Moreover, the electrical conductivity was similar for 100 mesh and 200 mesh TE composite films. External applied pressure (200 MPa and 300 MPa) helped to densify the films and removes the pores and voids. Therefore, the electrical conductivity for different mesh and different weight ratio TE composite films have high electrical conductivity. For comparison purposes we have performed SEM on 1:500 wt. ratio of binder to particles and applied very low pressure 5MPa as shown in figure 4(a) and 4(c). It is clear from these images that we can see many grains and grain boundaries which resulted in lower electrical conductivity for these films.

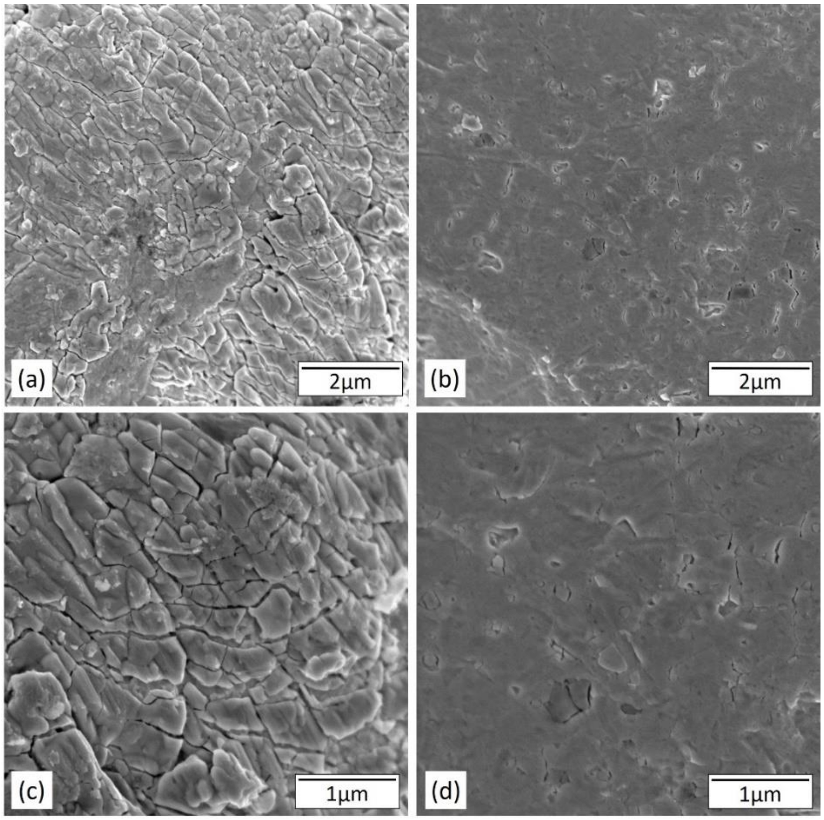

Figure 4. SEM images of various Chitosan-bismuth composite films. (a) 1:500 (weight ratio binder to 200 mesh Bi) pressed with 5 MPa, (b) 1:2000 (weight ratio binder to 200 mesh Bi) at 300 MPa, (c) 1:500 with

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5 MPa (weight ratio binder to 200 mesh Bi), and (d) 1:2000 (weight ratio binder to 200 mesh Bi) at 300 MPa

We also performed density measurement of 1:1000 (weight ratio binder to 200 mesh Bi) at 200 MPa .The measured density of this TE composite film was 9.5 g/cm^2 and the reported density of bulk bismuth is 9.78 g/cm^2 [31]. Our composite film values are comparable to bulk Bi values again confirming that particles packed very well and resulted in bulk like structure and leaded to high electrical conductivity [32].

Figure 3-(b) shows the measured absolute value of Seebeck coefficients of various TE composite films. The highest absolute seebeck coefficient value (73.7 ± 4.6 μV/K) was obtained from the 1:5000 binder to 100 mesh bismuth weight ratio TE composite films pressed at 300 MPa. Since Bi is n-type material the measured seebeck coefficient of composite films were negative. Actually, the Seebeck coefficient values are very similar to each other for different mesh size and different weight ratio TE composite films. We did not find any trend in TE composite films by varying the grain size or weight ratio or external pressure. The overall seebeck coefficient was obtained from this study was -68 μV/K to -74 μV/K and this value is almost same to that of bulk bismuth (-72 μV/K) [32]. However, Madan et al. fabricated epoxy-bismuth composite films and their seebeck values were 10 μV/K higher than ours [19]. This can be explained because the epoxy-bismuth composite film contained high amount of insulating binder and the electrical conductivity of their composite films were much lowers than ours and their Seebeck coefficient values were slightly higher.

The measured absolute values of charge carrier concentration were shown in the figure 3-(c). Power factor of each TE film was calculated with the equation, $\mathrm{Pf} = \alpha^2 \times \sigma$ and the averages of the power factor of various combinations were plotted in the figure 3-(d). The overall power factor values were relatively similar. The highest power factor value (4006 ± 391 μW/mK^2) was obtained from the 1:2000 binder to 100 mesh bismuth weight ratio TE composite film pressed at 200 MPa. However, no significant difference was observed in terms of power factor by changing the weight ratio, grain size or external applied pressure. The overall power factor of chitosan-bismuth TE composite films was in the range of 3500 - 4000 μW/mK^2. This value is two order of magnitude higher than epoxy-bismuth composite films [19]. In this work we are using energy efficient method to achieve high electrical conductivity in contrast to other reported work for composite films and achieved electrical conductivity similar to bulk values. Based on the electrical conductivity and seebeck values of bulk bismuth [31], [32], the power factor of chitosan-bismuth composite films in this work should be similar to that of bulk bismuth.

The thermal conductivity of chitosan-bismuth TE composite films was measured by P. Hopkins research group in university of Virginia by using steady-state thermo reflectance method. The steady-state thermoreflectance method employs pump laser to give periodic heat to the sample and measures the reflection change by the temperature increase. By applying Fourier's law, we can determine the thermal conductivity of a sample using a linear relationship between temperature and heat flux, and a proportional relationship between the magnitude of the reflected signal and the temperature rise [33]. They measured four chitosan-bismuth composite samples and the average value of the measured thermal conductivity was 4.4 ± 0.7 W/m·K. This thermal conductivity values are much lower than bulk thermal conductivity and it was caused by the presence of binder, voids and interfaces of the composite

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film [34]. Based on the figure of merit equation (1), the calculated ZT value of 100 mesh chitosan-bismuth composite film was 0.273 at room temperature. The ZT value of Bi composite film is slightly higher than that of bulk bismuth (0.16) by the attribution of lower thermal conductivity. The table 1 shows the thermoelectric properties of 100 mesh chitosan-bismuth composite TE film.

Table 1. Electrical conductivity, Seebeck coefficient, and power factor for composite TE films

Thermoelectric material	Wt. ratio (binder: particle)	Particle mesh size	Applied pressure (MPa)	Electrical conductivity (S/cm)	Seebeck coefficient (μV/K)	Power factor (μW/mK^2)	Thermal conductivity (W/mK)	Figure of merit
Bismuth	1:2000	100	300	7372±522	-73.4±3.3	4006±391	4.4±0.7	0.273

CONCLUSION

We successfully fabricated chitosan-bismuth composite films with high ZT. The chitosan was novel and excellent binder for the TE ink and the small amount of chitosan binder provided sufficient adhesive strength for the TE particles. The external applied pressure not only coalesced the bismuth particles well but also eliminated the need for a high energy intensive curing process. The chitosan-bismuth composite films were fabricated with relatively low temperature (120 -130 °C), shorter duration of time (15 minutes), and using external pressure (200-300 MPa). Pressing on relatively ductile bismuth material coalesced the bismuth particles to each other well, which provide the chitosan-bismuth composite film a high electrical conductivity. The highest performing composite film was obtained with the conditions of 1:2000 binder to 100 mesh bismuth weight ratio and 300 MPa of pressure. The value of electrical conductivity, seebeck coefficient, and power factor achieved from this study, were comparable to the value of bulk bismuth. However, the thermal conductivity was about half of the bulk material. Therefore, the figure of merit of 0.27 was obtained from the chitosan-bismuth composite films which is higher than the ZT value of bismuth bulk (0.16).

Notes

The authors declare no competing interest

Author Contributions

Conceptualization: Deepa Madan;
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Software: Insuck Baek;
Formal Analysis: Eunhwa Jang, Priyanshu Banerjee, Rudolph Holley, John Gaskins, Md Shafkat Bin Hoque, Patrick Hopkins;
Investigation: Jiyuan Huang, Priyanshu Banerjee, Eunhwa Jang;
Resources: Deepa Madan.;
Data Curation: Eunhwa Jang;
Writing – Original Draft Preparation: Eunhwa Jang , Jiyuan Huang;
Writing – Review & Editing: Eunhwa Jang , Priyanshu Banerjee , Jiyuan Huang, Deepa Madan;
Visualization: Eunhwa Jang.;

Supervision: Deepa Madan.;
Project Administration: Deepa Madan;
Funding Acquisition: Deepa Madan

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