



# Carbon fiber polymer–matrix structural composites exhibiting greatly enhanced through-thickness thermoelectric figure of merit

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## ABSTRACT

The through-thickness thermoelectric behavior of continuous carbon fiber epoxy-matrix composites is greatly improved by adding tellurium particles (13 vol.%), bismuth telluride particles (2 vol.%) and carbon black (2 vol.%). The thermoelectric power is increased from 8 to 163  $\mu\text{V}/\text{K}$ , the electrical resistivity is decreased from 0.17 to 0.02  $\Omega\cdot\text{cm}$ , the thermal conductivity is decreased from 1.31 to 0.51  $\text{W}/\text{m}\cdot\text{K}$ , and the dimensionless thermoelectric figure of merit  $ZT$  at 70  $^{\circ}\text{C}$  is increased from  $9 \times 10^{-6}$  to  $9 \times 10^{-2}$ . Tellurium increases the thermoelectric power greatly. Bismuth telluride decreases the electrical resistivity and thermal conductivity. Carbon black decreases the electrical resistivity.

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## 1. Introduction

### 1.1. Thermoelectric energy generation

Energy harvesting refers to the conversion to electricity of various forms of energy (mechanical, thermal, light, etc.) that is present in the environment anyway. The efficiency and cost of the energy conversion and the abundance of the particular form of energy determine the practicality of large-scale energy harvesting, which is an avenue to alleviate the energy crisis and reduce the negative environmental impact of the burning of fossil fuels. This paper is concerned with thermoelectric conversion of thermal energy to electricity.

Thermal energy is commonly available in the environment due to waste heat from various devices (e.g., engines, hot gas exhausts, reactors, furnaces, heaters, boilers, hot water pipes, friction sources, machinery, integrated circuits, lights and lasers) and due to natural heating by the sun. These sources of energy are little used in practice, due to the shortcomings and limitations of conventional technologies for the required energy conversion. The conversion of thermal energy to electricity provides clean energy and can use thermal energy that is largely untapped.

The conversion of thermal energy to electricity is commonly conducted by using the thermoelectric effect, in which a temperature gradient in a material results in a voltage difference between the points in the material that are at different temperatures. The effect is also known as the Seebeck effect. The severity of this effect is described by the thermoelectric power (also known as the Seebeck coefficient), which is defined as the voltage difference per unit temperature difference between two points in the material. In general, the negative end of the voltage difference can be at the hot point or the cold point of the temperature gradient. A material that exhibits a substantial thermoelectric effect is known as a thermoelectric material. Examples of thermoelectric materials are bismuth, tellurium, bismuth telluride, lead telluride, zinc antimonide, germanium and silicon.

The effectiveness of a thermoelectric material for energy conversion requires the combination of high thermoelectric power, low electrical resistivity and low thermal conductivity. A low electrical resistivity is needed for a substantial current to pass through the thermoelectric material as the material provides electricity. A low thermal conductivity is needed to provide a substantial temperature gradient in the material.

The figure of merit ( $Z$ ) of a thermoelectric material is given by

$$Z = S^2 / (\rho k), \quad (1)$$

where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity and  $k$  is the thermal conductivity. The unit of  $Z$  is  $\text{K}^{-1}$ . The dimensionless figure of merit ( $ZT$ ) is given by the product of  $Z$  and the temperature  $T$  in K, where  $T$  is the average temperature in the presence of a temperature gradient. The  $ZT$  value relates to the thermodynamic efficiency.

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State-of-the-art thermoelectric materials in bulk form have  $ZT$  values about 1.2 at room temperature. Thin-film thermoelectric materials can reach higher  $ZT$  values, because thin films can allow quantum confinement of the carrier, thereby obtaining an enhanced density of states near the Fermi energy. In addition, thin films can allow structures in the form of superlattices with interfaces that block phonons but transmit electrons. For practical application, bulk thermoelectric materials are needed, since the thickness of a thin film is too small to support a substantial temperature difference. Thus, the state of the art of thermoelectric materials is not adequate for practical large-scale conversion of thermal energy to electrical energy.

Prior work [1–13] used various techniques to raise  $ZT$ , with particular attention given to the decrease of both the thermal conductivity and the electrical resistivity. The techniques include the formation of thermoelectric materials in the form of alloys (e.g., PbTe–Ge [1], La-doped PbTe [2],  $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te}$  [3], nanocrystalline compounds (e.g.,  $\text{Bi}_2\text{Te}_3$  [4]), nanostructured alloys (e.g., bismuth–antimony–tellurium [5] and silicon–germanium [6]), oxides (e.g., perovskites [7] and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Mn}_x\text{O}_3$  [8]), skutterudites [9], AgTlTe [10], half-Heusler compounds [11], composites (e.g.,  $\text{ZrO}_2/\text{CoSb}_3$  [12]) and copolymers [13]. In particular, interfaces have been used to reduce the thermal conductivity.

For large-scale thermoelectric energy conversion, it is important to have thermoelectric materials that can be formed into large bulk cost-effective devices, as needed to capture a large amount of thermal energy in practical cost-effective implementation of the energy harvesting technology. As the electrical resistance is inversely proportional to the area perpendicular to the resistance direction, a large area of the thermoelectric material in the plane perpendicular to the temperature gradient is valuable for providing a small resistance and hence a high electric power. A large area and a high  $ZT$  value are both valuable. Prior work has focused on raising  $ZT$ , with little attention on increasing the area. All the techniques mentioned in the last paragraph suffer from problems associated with one or more of the following: high costs of materials and processing, thermoelectric material size limitation, production scale-up difficulty, insufficiently high  $ZT$  values, inadequate mechanical performance, and implementation difficulty. In particular, many of the techniques involve thermoelectric materials in the form of films, which are not suitable for practical use.

### 1.2. Structures capable of energy harvesting

An energy harvesting approach that differs that those of prior work [1–13] involves modification of a structural material that is not capable of energy harvesting but is widely available in large scale, such that the modification renders the material energy harvesting ability. This approach results in a multifunctional structural material that can provide both structural and thermoelectric functions. Such a multifunctional material enables self-powered structures, i.e., structures that generate electric power. Self-powering is attractive for structures for which the use of batteries is not desired, structures to which power transmission lines cannot reach, and strategic structures that require back-up energy.

The rendering of the energy harvesting function to a structure by using a structural material that has this inherent ability is to be distinguished from the rendering that involves embedded or attached devices. The latter method [14] suffers from high cost, poor durability (particularly for attached devices), mechanical property loss (in case of device embedment) and limited functional volume.

The developing of structural materials that have the inherent ability to harvest energy is challenging from a scientific viewpoint, since the structural material needs to be modified in such a way as to provide this function. In addition, for structural performance, the mechanical properties should not be degraded by the modification.

In case of structural materials in the form of composites with continuous fiber reinforcement, the volume fraction of the continuous fibers in the composite must be sufficiently high after the modification, since the fibers are the load-bearing component. Furthermore, for good mechanical performance, the bond between fiber and polymer matrix must be sufficient after the modification.

### 1.3. Carbon fiber polymer–matrix structural composites

Continuous carbon fiber epoxy-matrix composites are widely used for aircraft, satellites, missiles, windmills and other light-weight structures. A carbon fiber polymer–matrix composite commonly comprises layers of fibers that are in one or more directions that are all in the plane of each layer. Each layer has a large number of fibers in the plane of the layer and there are a substantial number of fibers within the thickness of a layer. Each fiber layer is known as a lamina or a ply. Due to the in-plane orientation of the fibers, the in-plane electrical conductivity of the composite is much higher than that in the direction perpendicular to the laminae. The direction perpendicular to the laminae is known as the through-thickness direction of the composite.

Although polymers that are inherently conductive in the absence of fillers are available, most cost-effective polymers are not conductive. Due to (i) the slight waviness of the fibers in a typical carbon fiber composite, and (ii) the incomplete or imperfect coverage of a fiber by the polymer matrix in a composite, fiber–fiber contact points exist in a composite, thus resulting in electrical conductivity in the through-thickness direction of a conventional carbon fiber polymer–matrix composite, even when the polymer matrix itself is nonconductive. Therefore, the composite is conductive in both in the in-plane direction and the through-thickness direction. In other words, the composite does not have insulating character in any direction.

The interlaminar interface in a continuous fiber composite is the interface between adjacent lamellae in the composite. This interface is particularly distinct when the fibers in the adjacent lamellae are oriented in different directions. Fiber–fiber contact points normally exist across the interlaminar interface. Therefore, in spite of the presence of one or more interlaminar interfaces in a typical carbon fiber composite, the composite is not insulating in the through-thickness direction.

Thermoelectric particles have been incorporated in carbon fiber polymer–matrix composites for enhancing the thermoelectric power [16,17]. The effect of the thermoelectric particle incorporation is much smaller for the thermoelectric power in the longitudinal (fiber) direction than the through-thickness direction of the composite, due to the dominance of the carbon fibers in governing the longitudinal effect [16]. Therefore, this paper is focused on the thermoelectric behavior in the through-thickness direction.

Carbon fiber is an electrical conductor that is very weakly thermoelectric [15]. The incorporation of thermoelectric particles (such as tellurium and bismuth telluride) at the interlaminar interface of a carbon fiber polymer–matrix composite increases the thermoelectric power substantially [16,17]. The incorporation of tellurium particles causes the thermoelectric power to be strongly positive, whereas the incorporation of bismuth telluride particles causes the thermoelectric power to be strongly negative [16,17]. The greater is the tellurium content, the higher is the magnitude of the thermoelectric power [17]. A mixture of tellurium and bismuth telluride particles gives greater enhancement of the thermoelectric power than the use of a single type of thermoelectric particle [16]. The highest value of the absolute thermoelectric power reported for carbon fiber polymer–matrix composites is  $+110 \mu\text{V/K}$ , which is the value for a composite with tellurium as the sole interlaminar filler [17]. However, the  $ZT$  value, the electrical resistivity and the thermal conductivity were not reported in the prior work [16,17].

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