Letters

Enhancement of the absolute thermoelectric power of carbon fiber polymer–matrix composite in the through-thickness direction

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Abstract—The absolute thermoelectric power of a continuous carbon fiber polymer–matrix structural composite in the through-thickness direction was increased from 0.5 to 22 μV/°C by adding tellurium particles (7.3 vol%) as an interlaminar filler. The effect was small when bismuth was used instead of tellurium. The effect of tellurium was much less in the longitudinal direction than in the through-thickness direction.

Keywords: Composite; polymer; thermoplastic; nylon; carbon fiber; thermoelectric; Seebeck.

1. INTRODUCTION

Thermoelectric behavior pertains to the conversion between thermal and electrical energy. In particular, the Seebeck effect is a thermoelectric effect in which a voltage results from a temperature gradient, which causes the movement of charge carriers from the hot point to the cold point. This voltage (Seebeck voltage) is useful for temperature sensing and pertains also to the generation of electrical energy. The negative of the change in Seebeck voltage (hot minus cold) per degree Celsius temperature rise (hot minus cold) is called the thermoelectric power, the thermopower, or the Seebeck coefficient.

Polymer–matrix composites with continuous carbon fibers as the reinforcement are important for lightweight structures such as aircraft. A structure during use often encounters a temperature difference between its interior side and its exterior side. Such is the case of aircraft, ships, armors, skis, ocean platforms, etc. The use of this temperature gradient (in the through-thickness direction of the composite laminate)

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to generate a voltage is attractive, as it allows temperature sensing as well as electric power generation.

Previous work on the Seebeck effect in carbon fiber polymer–matrix composites is limited to that in the longitudinal (fiber) direction. Although the interface between adjacent laminae (referred to as the interlaminar interface) of dissimilar fibers serves as a thermocouple junction, the Seebeck effect utilized is that in the longitudinal direction [1]. By using intercalated carbon fibers, the magnitude of the Seebeck effect is greatly increased, due to the holes provided by intercalation with an acceptor or the electrons provided by intercalation with a donor [1]. In contrast, and due to the common occurrence of a temperature gradient along the through-thickness direction during use, this work is focused on the Seebeck effect in this direction and its enhancement by using interlaminar thermoelectric particulate additives. These additives are bismuth and tellurium, which are well-known as thermoelectric materials. Their thermoelectric power is high: -72 $\mu V/°C$ for Bi and $+70$ $\mu V/°C$ for Te [2].

Although the polymer matrix is electrically insulating, the electrical resistivity is never infinity in the through-thickness direction [3]. This is due to the occurrence of direct contact between fibers of adjacent laminae. The contact results from the movement of the resin or polymer during composite fabrication and is also related to the waviness of the fibers.

The Seebeck coefficient is relatively low in many metals (e.g. -0.20 $\mu V/°C$ for aluminum), but is relatively high in many semiconductors (e.g. -210 $\mu V/°C$ for germanium). On the other hand, metals are more conductive electrically than semiconductors. This means that attaining a large Seebeck effect is not simply a matter of increasing the carrier concentration or mobility. A low thermal conductivity helps, as it enables a steep temperature gradient to occur. This supports the use of bismuth and tellurium for this work, as their thermal conductivity is low (8 w/mK for Bi and 3 w/mK for Te) and their electrical resistivity is high ($1.1 \times 10^{-6} \Omega$ m for Bi and $2.5 \times 10^{-4} \Omega$ m for Te) [2].

The electrical behavior of continuous carbon fiber polymer–matrix composites is highly anisotropic, as the fibers are far more conducting than the polymer matrix, which is usually insulating. Hence, both the electrical conductivity and the thermal conductivity of a composite are much higher in the fiber (longitudinal) direction than in the through-thickness direction. The Seebeck coefficient in the fiber direction can be positive or negative, depending on the carbon fiber type [1]. The Seebeck coefficient of the highest magnitude attained in the fiber direction is -7 $\mu V/°C$ when pristine (not intercalated) fibers are used, and is -50 $\mu V/°C$ when intercalated fibers are used [1].

The continuous carbon fiber polymer–matrix composite of this work is to be distinguished from the discontinuous carbon fiber polymer–matrix composites [4] and cement–matrix composites [5–8] of previous work in relation to the thermoelectric behavior. The essentially random orientation of the discontinuous fibers is in contrast to the aligned arrangement of the continuous fibers.

The Seebeck effect in the through-thickness direction is not amenable to exploitation for thermocouples, due to the inaccessibility of the thermocouple junction of two dissimilar composites that are in contact on the plane of the junction. In contrast, the Seebeck effect in the longitudinal direction is amenable to exploitation for a two-dimensional array of thermocouples [1]. Nevertheless, the Seebeck effect in the through-thickness direction can be used for sensing the temperature difference between the two surfaces of a composite.

The electrical conduction behavior in the through-thickness direction of a continuous carbon fiber polymer–matrix composite is different between unidirectional and crossply configurations. The contact electrical resistivity of the interlaminar interface is lower and the activation energy for conduction is higher for the crossply configuration [9], due to the larger number of contacts among fibers of adjacent laminae and the greater residual stress in the crossply case. This work addresses the thermoelectric behavior in the through-thickness direction for a unidirectional composite.

Although this work addresses the Seebeck effect only, the Peltier effect, which is useful for heating and cooling, is related. The Peltier effect involves two dissimilar materials in electrical contact and the passing of an electrical current through the electrical contact. The two dissimilar materials may both be continuous carbon fiber polymer–matrix composites, such that the two composites differ, say, in the fiber type.

2. EXPERIMENTAL METHODS

The thermoplastic polymer was nylon-6 (PA) in the form of unidirectional carbon fiber (CF) prepregs supplied by Quadrax Corp. (Portsmouth, Rhode Island; QNC 4162). The fibers were 34-700 from Grafil, Inc. (Sacramento, California). The fiber diameter was 6.9 μm. The fiber weight fraction in the prepreg was 62%. The glass transition temperature (T_g) was 40–60°C and the melting temperature (T_m) was 220°C for the nylon-6 matrix. The prepreg thickness was 250 μm.

The bismuth particles were from Baker Chemical Co. (Phillipsburg, NJ). Leico Industries Inc. (New York, NY) supplied the tellurium particles. In both cases, the particles had a maximum size of 45 μm, as obtained by sieving.

Four sets of composite specimen sets were obtained. Each specimen was made by stacking eight plies of the prepreg in the unidirectional configuration. For the first set of specimens, no interlaminar particle was used. For the other three sets, bismuth or tellurium particles were spread out manually on each ply as they were laid up. By using a hydraulic hot press, the stacks obtained were subjected to a pressure of 2 MPa, heated to 260°C at a rate of 5°C/min and then held at the temperature and pressure for 30 min.

Two types of specimens were obtained by cutting a laminate. The first type, with a nominal size of 15 × 12 mm, was used to determine the absolute thermoelectric

power in the through-thickness direction. The second type, with a nominal size of 35 × 6 mm, was used to determine the value in the longitudinal direction.

To generate a temperature gradient in the through-thickness direction, a specimen of the first type was placed between a hot plate and a cold plate, both lined with an electrically insulating film. For the purpose of voltage measurement, copper wire was laid up on both of the 15 × 12 mm surfaces, and then covered with copper foil. A layer of silver paint was applied between the foil and the sample surface. Both the silver paint and the copper foil helped to enhance the thermal contact.

To obtain a temperature gradient in the longitudinal direction, one of the ends of a specimen of the second type was placed on a hot plate and the other on a cold plate. For voltage measurement, copper wire was wrapped around the perimeter at each end of the specimen and then covered with copper foil, with silver paint between them the foil and the specimen surface.

In both cases, the temperature of the hot plate was increased by using a temperature controller, which enabled heating to be conducted at a rate of 0.5°C/min. The temperatures of the hot and cold surfaces of the sample were simultaneously measured by two T-type thermocouples. The voltage difference between them was measured with a Keithley 2001 multimeter. Three specimens of each type were tested.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show plots of the measured voltage difference *vs.* the temperature difference obtained during heating for the composites used in this work. In all the cases, the data points fall on a nearly straight line through the origin, and the curves for heating and cooling are similar. The slope of the line in a figure gives the value for the Seebeck coefficient relative to copper. This Seebeck coefficient plus the absolute thermoelectric power of copper ($+1.94$ $\mu V/°C$ at 300 K) [10] is the absolute thermoelectric power of the sample. Table 1 shows the absolute thermoelectric power obtained in the through-thickness and longitudinal directions for the composites investigated.

As can be seen, even though the sign of the absolute thermoelectric power is different in the directions considered, the addition of the interlaminar thermoelectric particles tends to make it more positive in both cases. The effect is larger in the through-thickness direction than in the longitudinal direction. The thermoelectric behavior of the composite material is influenced by the reinforcing fibers and the interlaminar interfaces. While the fibers govern the behavior in the longitudinal direction, the interlaminar interfaces are encountered in the through-thickness direction. As a result, the effect of the interlaminar particles on the thermal or electrical conduction is expected to be larger in the through-thickness direction than in the longitudinal direction.

The use of tellurium particles is more effective than the use of bismuth in making the absolute thermoelectric power more positive, particularly in the through-
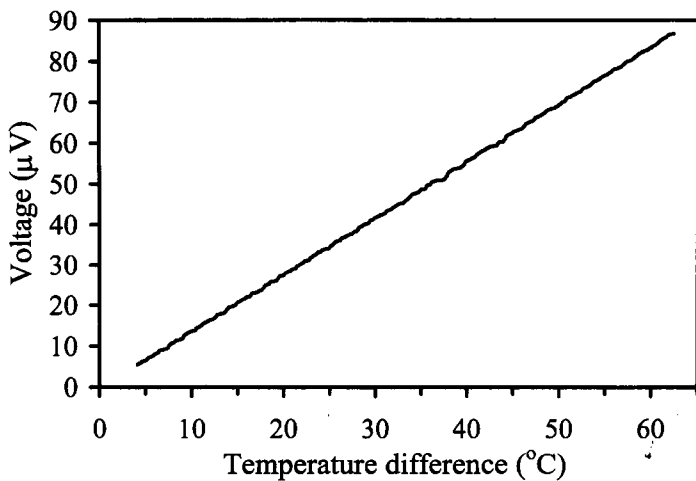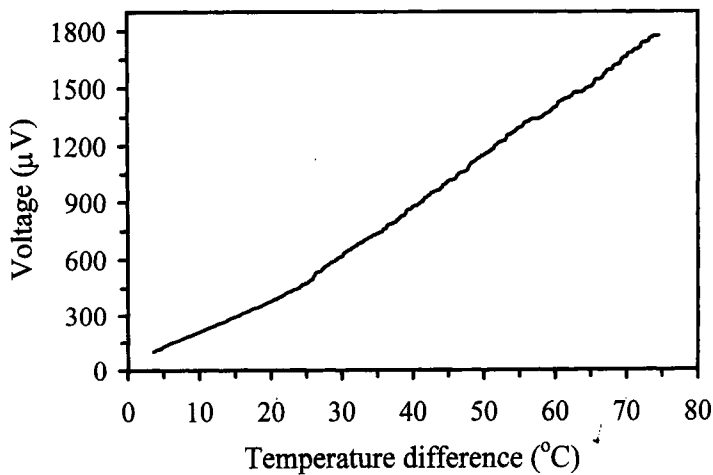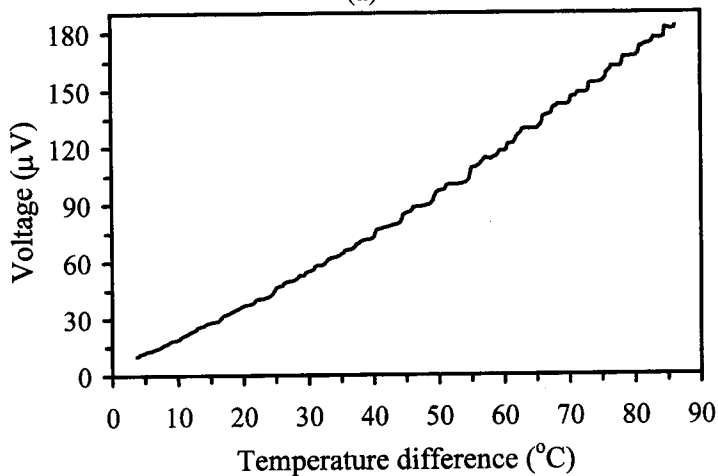
(a)
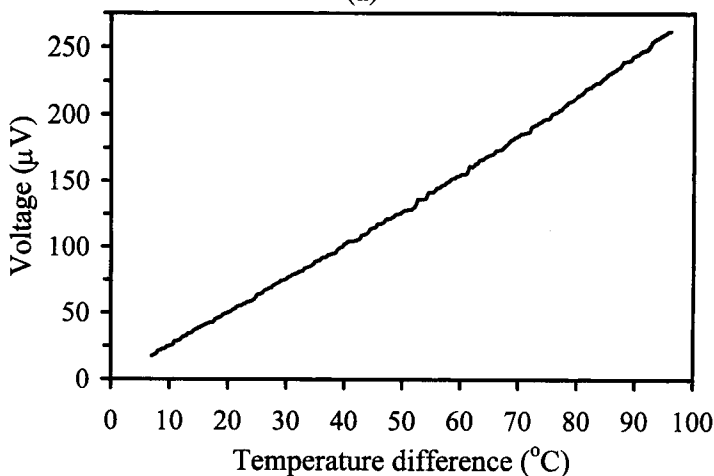
(b)

Figure 1. Seebeck voltage (relative to copper) *versus* the temperature difference for a carbon fiber polymer–matrix composite without interlayer during heating (a) in the through-thickness direction (b) in the longitudinal direction.

thickness direction. This is because in this direction the sign of the absolute thermoelectric power is the same (positive) for the carbon fiber polymer–matrix composite without interlayer and for tellurium, and this is a favorable condition for the enhancement of the thermoelectric effect in composite thermoelectrics [11]. Further research is needed to understand the cause of the large effect of tellurium on the through-thickness absolute thermoelectric power.

The thermoelectric effect of the composite in the through-thickness direction is potentially useful for temperature sensing in aircraft structures, marine structures, skis and other components which encounter a temperature gradient in the through-

Figure 2. Seebeck voltage (relative to copper) *versus* the temperature difference for a carbon fiber polymer–matrix composite with a tellurium interlayer during heating (a) in the through-thickness direction (b) in the longitudinal direction.

Table 1.
Density, interlayer particle volume fraction and absolute thermoelectric power of various thermoplastic–matric composites

Set	Density (g/cm^3)	Particle material	Volume fraction particles (%)	Absolute thermoelectric power (μV/°C)	
				Through-thickness	Longitudinal
1	1.4±0.2	None	0	0.5±0.1	−0.7±0.1
2	1.8±0.2	Bismuth	4.5 ± 0.5	0.6±0.1	−0.9±0.1
3	2.3±0.2	Bismuth	10.5 ± 0.5	1.2±0.1	−0.3±0.1
4	1.8±0.2	Tellurium	7.3 ± 0.5	22.3±0.2	−0.1±0.1

thickness direction of the composite. Although the absolute thermoelectric power is low, the use of the structural material itself for sensing eliminates or reduces the need for embedded or attached sensors. Embedded sensors are intrusive. Attached sensors are poor in durability.

4. CONCLUSION

The through-thickness absolute thermoelectric power of a continuous carbon fiber polymer–matrix structural composite was increased from 0.5 to 22 $\mu V/°C$ by adding tellurium particles (7.3 vol%) as an interlaminar filler. The enhancement is due to the high positive absolute thermoelectric power of tellurium and presumably also due to the influence of the tellurium interlayer on the thermal and electrical conduction in the through-thickness direction. The effect was much less in the longitudinal direction, which was dominated by the fibers and was associated with small negative values of the absolute thermoelectric power. The effect in the through-thickness direction was small when bismuth was used instead of tellurium.

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