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Carbon fiber polymer-matrix composite interfaces as thermocouple junctions

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Abstract—Thermocouples made from dissimilar continuous carbon fibers in the form of epoxy-matrix composite, using the interlaminar interface as the thermocouple junction, were found to exhibit thermocouple sensitivity that is close to the difference between the Seebeck coefficients of the two partners of the thermocouple. The highest thermocouple sensitivity of 82 μV/°C was obtained by using Thornel P-100 carbon fibers that had been intercalated with bromine and sodium. The thermocouple sensitivity was the same for unidirectional and crossply junctions. Two crossply laminae comprising dissimilar carbon fibers provided an array of junctions, each of which was a thermocouple, thus allowing temperature distribution sensing.

Keywords: Composite; carbon fiber; polymer; epoxy; intercalation; thermopower; Seebeck; thermocouple.

1. INTRODUCTION

Thermoelectric phenomena involves the transfer of energy between electric power and thermal gradients. They are widely used for cooling and heating, including air conditioning, refrigeration, thermal management and the generation of electrical power from waste heat.

A thermocouple is a thermoelectric thermometric device that involves a junction between two dissimilar materials. The voltage between the two dissimilar materials at the ends away from the junction relates to the temperature difference between the junction and these ends. The physics relies on the Seebeck effect, i.e. the movement of the mobile charge carriers from the hot point to the cold point of each dissimilar material and the consequent voltage difference between the hot and cold points of each dissimilar material.

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The dissimilar materials used for thermocouples are conventionally metals. This paper provides thermocouples in the form of continuous carbon fiber polymer–matrix composites. Carbon fibers are used because of their electrical and thermal conductivity. The interlaminar interface (i.e. interface between adjacent laminae in a composite) serves as the junction in the thermocouple. The dissimilar materials are laminae with different types of carbon fibers (fibers that differ in carrier type and/or concentration).

The advantages of fiber composite thermocouples compared to conventional thermocouples are low cost, mechanical ruggedness, processability into various shapes and sizes, and that the thermocouple is itself the structure. The last advantage means that the structure is itself a thermocouple, thus making the structure able to monitor its temperature without the need for embedded or attached devices. This leads to low cost, high durability, large sensing volume and absence of mechanical property degradation (which occurs in the case of embedded sensors).

The Seebeck effect involving a single type of material rather than dissimilar materials has been reported in carbon fibers (no matrix) [1–3] and in carbon fiber composites [4, 5]. The use of dissimilar materials allows the voltage measurement to be made only at one end (say the end at room temperature) of the dissimilar materials, thus making thermocouples convenient to use. Furthermore, appropriate selection of the dissimilar materials can make the change in measured voltage per unit rise in temperature (i.e. thermocouple sensitivity) larger than the Seebeck coefficient of a single type of material.

Carbon fibers can be n-type or p-type even without intercalation. Intercalation greatly increases the carrier concentration, thus making the fibers strongly n-type or strongly p-type, depending on whether the intercalate is an electron donor or an electron acceptor. Although there had been study of the thermopower of intercalated carbon fibers [3], n-type and p-type forms of carbon fibers have not been exploited as dissimilar materials for thermocouples. This work shows that such thermocouples are particularly sensitive.

One of the drawbacks of intercalated graphite is the instability over time, either due to intercalate desorption or reaction with environmental species. For the case of bromine (acceptor) as the intercalate, the instability due to desorption can be overcome by the use of a residue compound, i.e. a compound that has undergone desorption as much as possible so that the remaining intercalate is strongly held, thereby making the compound stable. The stability of bromine intercalated carbon fibers has been previously demonstrated [6–8]. For the case of an alkali metal such as sodium (donor) as the intercalate, the instability due to reactivity with moisture can be overcome by the use of an alkali metal hydroxide (with the alkali metal ions in excess) as the intercalate [9]. Therefore, this paper uses bromine as the acceptor intercalate and sodium hydroxide (with Na^+ ions in excess) as the donor intercalate.

Although considerable attention has been given to intercalated carbon fibers, little attention has been given to composites that involve these fibers [10–12]. Previous work on these composites has been focused on the electrical conductivity, due to the relevance to electromagnetic interference shielding and other applications. In contrast to previous work, this paper addresses the thermoelectric behavior of the composites, particularly composites involving dissimilar carbon fibers that meet at a junction to form a thermocouple.

2. EXPERIMENTAL

The carbon fibers used were Thornel P-25, P-100 and P-120 2K pitch-based fibers (Amoco Performance Products, Alpharetta, GA) and T-300 PAN-based fibers (in the form of 976 epoxy unidirectional fiber prepregs, Hy-E 1076E, ICI Fiberite, Tempe, AZ).

Intercalation was carried out only for P-100 and P-120 fibers, due to their relatively high crystallinity. Bromine intercalation involved exposure to bromine vapor in air at room temperature for 10 days, followed by desorption in a fume hood at room temperature for several months. Sodium hydroxide intercalation involved immersion of the fibers in a liquid solution of NaOH and molten sodium contained in a nickel crucible. The atomic ratio of Na to NaOH was 1 : 100. The procedure is described below. The crucible was placed in a small furnace, which was purged with argon gas. After the furnace had reached 350°C, sodium metal was added to the molten NaOH in the crucible. Then the fibers (protected by a nickel spring) were immersed in the liquid solution. The furnace was covered and the temperature of 350°C was maintained for 4 h. After that, the fibers were removed and allowed to cool. Then the fibers (still protected by a nickel spring) were washed by flowing water for 12 h in order to remove the NaOH on the fiber surface. After this, the fibers were dried in a vacuum oven.

Thermocouple junctions were epoxy-matrix composite interlaminar interfaces. In this study, a junction was formed by allowing two laminae to overlap partially and then curing the stack under heat and pressure, as required for the curing of the epoxy matrix. The overlap region served as the junction; the remaining regions served as thermocouple wires. Those junctions involving T-300 fibers used the epoxy in the prepreg as the bonding agent for the junction. Those not involving T-300 fibers used epoxy resin 9405 and curing agent 9470 from Shell Chemical Co. (Houston, TX) as the epoxy matrix as well as bonding agent. Curing of the epoxy in the T-300 prepreg was conducted by heating in a hydraulic hot press at a rate of 2.5°C/min and then maintaining the temperature for 2 h. The curing temperature was 175°C for the epoxy in the T-300 prepregs and was 150°C for the other epoxy. The curing pressure was 18 MPa for unidirectional junctions (i.e. the fibers in the two laminae oriented in the same direction) and 16 MPa for crossply junctions (i.e. the fibers in the two laminae oriented at 90°) involving the epoxy in the T-300 prepregs. For junctions involving the other epoxy, the curing pressure was 0.02 MPa. A sample with six crossply junctions of P25 and T-300 (Fig. 1) was made to measure the temperature distribution. The curing procedure of the sample was the same as that

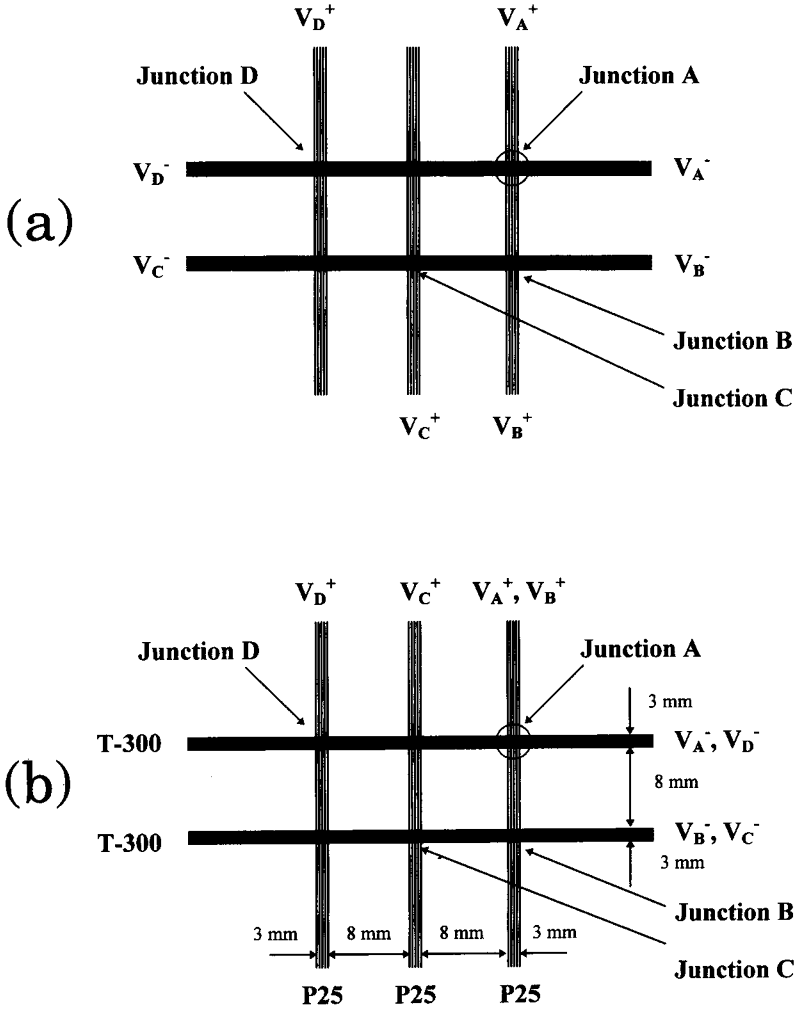

Figure 1. A six-junction sample for temperature distribution sensing, each of the junctions comprising pristine P-25 and pristine T-300. The center of the light spot was at junction A. (a) Voltage probe configuration I. (b) Voltage probe configuration II.

of the single junctions involving T-300 prepreg except that the curing pressure was 0.25 MPa.

Thermopower measurement was performed on the fibers (P-25, P-100 and P-120 fiber bundles without matrix, and T-300 prepreg with epoxy matrix) and on the epoxy-matrix composite junctions involving dissimilar fibers (one being p-type and other being n-type). The measurement in the former case involved attaching the two ends of a fiber bundle or prepreg to copper foils using a silver-epoxy conducting adhesive, maintaining one copper foil at a controlled high temperature (up to 200°C) by using a furnace, and maintaining the other copper foil at a temperature near room temperature. A copper wire was soldered at its end to each of the two copper foils. The copper wires were fed to a Keithley 2001 multimeter for measuring the voltage. T-type thermocouples were used for measuring the temperatures of the hot and cold ends. Voltage and temperature measurements were done simultaneously using the multimeter. The voltage difference divided by the temperature difference yielded the Seebeck coefficient with copper as the reference, since the copper wires at the two ends of a sample were at different temperatures. This Seebeck coefficient plus the absolute thermoelectric power of copper ($+2.34\ \mu V/^{\circ}C$) [13] is the absolute thermoelectric power of the carbon fiber. The thermopower measurement in the latter case involved the same configuration, except that the junction was at the hot point and the two ends of the sample away from the junction were attached using silver-epoxy onto two copper foils, which were both at a temperature near room temperature.

In the case of pristine P-25 fibers without matrix, thermopower measurement was also made using fixed temperatures at the hot (100°C, boiling water) and cold (0°C, ice water) points and using four methods of attaching the sample ends to the copper foils (namely silver epoxy, silver paint, solder and brass clips). Results (Seebeck coefficient) obtained using these variations in methods are consistent with that obtained using the method described in the last paragraph, thus confirming the validity of the method used in this paper.

In the case of the junction between pristine P-25 and pristine T-300 fibers in either unidirectional or crossply configuration, thermopower measurement was performed during the curing heating cycle as well as during subsequent heating and cooling.

For the six-junction sample (Fig. 1), an incandescent light was used to heat the junctions. The center of the light spot was at junction A. At the same time, the voltages of junctions A, B, C, and D were measured simultaneously with a Keithley 2001 multimeter. Then four T-type thermocouples were attached to the centers of junctions A, B, C and D to measure the temperature changes and the temperature distribution during the light shining. Two kinds of voltage probe configurations, labeled I and II and shown in Fig. 1a and Fig. 1b respectively, were tested. Configuration I (Fig. 1a) involves the probes positioned in closest proximity to the junction under measurement, so that the interference of other junctions on the junction under measurement is minimized. Configuration II (Fig. 1b) involves probes that are positioned on the same side for different junctions, so that interference among junctions occurs.

3. RESULTS AND DISCUSSION

Table 1 shows the Seebeck coefficient and the absolute thermoelectric power of carbon fibers and the thermocouple sensitivity of epoxy-matrix composite junctions. A negative value of the absolute thermoelectric power indicates p-type behavior; a positive value indicates n-type behavior. Pristine P-25 is slightly n-type, pristine T-300 is strongly n-type. A junction comprising pristine P-25 and pristine T-300

Table 1.
Seebeck coefficient (μV/°C) and absolute thermoelectric power (μV/°C) of carbon fibers and thermocouple sensitivity (μV/°C) of epoxy-matrix composite junctions. All junctions are unidirectional unless specified as crossply. The temperature range is 20–110°C

	Seebeck coefficient with copper as the reference (μV/°C)	Absolute thermoelectric power (μV/°C)	Thermocouple sensitivity (μV/°C)
P-25*	−0.8	+1.5	
T-300*	+5.0	+7.3	
P-25* + T-300*			+5.5
P-25* + T-300* (crossply)			+5.4
P-100*	+1.7	+4.0	
P-120*	+3.2	+5.5	
P-100 (Na)	+48	+50	
P-100 (Br_2)	−43	−41	
P-100 (Br_2) + P-100 (Na)			+82
P-120 (Na)	+42	+44	
P-120 (Br_2)	−38	−36	
P-120 (Br_2) + P-120 (Na)			+74

* Pristine (i.e. not intercalated).

has a positive thermocouple sensitivity that is close to the difference of the Seebeck coefficients (or the absolute thermoelectric powers) of T-300 and P-25, whether the junction is unidirectional or crossply. Pristine P-100 and pristine P-120 are both slightly n-type. Intercalation with sodium causes P-100 and P-120 to become strongly n-type. Intercalation with bromine causes P-100 and P-120 to become strongly p-type. A junction comprising bromine intercalated P-100 and sodium intercalated P-100 has a positive thermocouple sensitivity that is close to the sum of the magnitudes of the absolute thermoelectric powers of the bromine intercalated P-100 and the sodium intercalated P-100. Similarly, a junction comprising bromine intercalated P-120 and sodium intercalated P-120 has a positive thermocouple sensitivity that is close to the sum of the magnitudes of the absolute thermoelectric powers of the bromine intercalated P-120 and the sodium intercalated P-120. Figure 2 shows the linear relationship of the measured voltage with the temperature difference between hot and cold points for the junction comprising bromine intercalated P-100 and sodium intercalated P-100.

A junction comprising n-type and p-type partners has a thermocouple sensitivity that is close to the sum of the magnitudes of the absolute thermoelectric powers of the two partners. This is because the electrons in the n-type partner as well as the holes in the p-type partner move away from the hot point toward the corresponding cold point. As a result, the overall effect on the voltage difference between the two cold ends is additive.

By using junctions comprising strongly n-type and strongly p-type partners, a thermocouple sensitivity as high as +82 μV/°C was attained. Semiconductors are

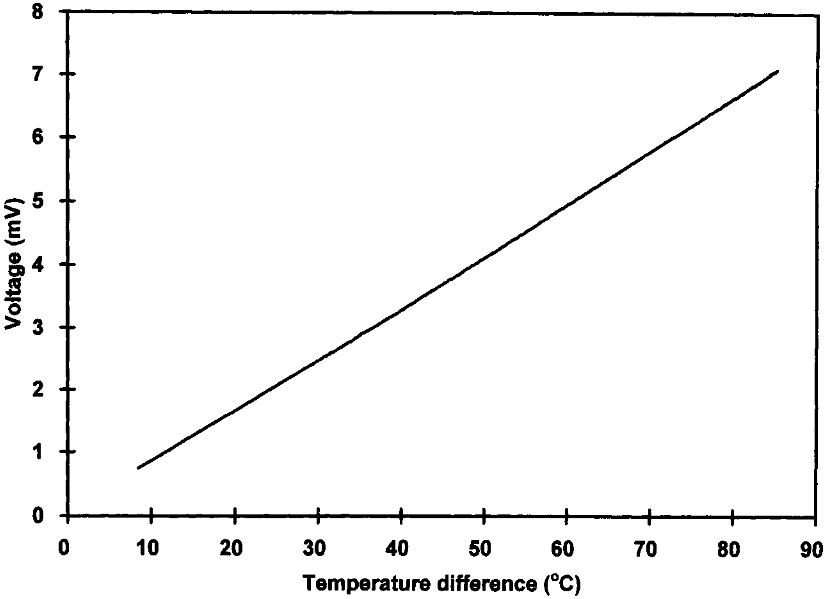

Figure 2. Variation of the measured voltage with the temperature difference between hot and cold points for the epoxy-matrix composite junction comprising bromine intercalated P-100 and sodium intercalated P-100.

known to exhibit much higher values of the Seebeck coefficient than metals, but the need to have thermocouples in the form of long wires makes metals the main materials for thermocouples. Intercalated carbon fibers exhibit much higher values of the Seebeck coefficient than metals. Yet, unlike semiconductors, their fiber form and fiber composite form make them convenient for practical use as thermocouples.

The Seebeck coefficient of HNO_3-intercalated CVD carbon fibers is 15 μV/°C at 300 K [3]. Extrapolation of the data of [3] to 500 K gave a value of less than 20 μV/°C. The values obtained in this work for intercalated fibers are considerably higher in magnitude.

Figure 3 shows the relationship between the measured voltage and the temperature difference between hot and cold points for the junction comprising pristine P-25 and pristine T-300, as obtained during the curing heating cycle. Even though the junction is essentially not cured during heating in the curing cycle and is cured during cooling in the curing cycle, the curves during heating and cooling overlap. This means that the thermocouple sensitivity is independent of the nature of the interface. The curves for unidirectional and crossply configurations essentially overlap. The results obtained during subsequent heating and cooling are essentially the same as those in Fig. 3. The curves in Fig. 3 deviate positively from linearity, in contrast to the linearity in Fig. 2. A positive deviation from linearity is quite common among commercial thermocouples, such as T-type thermocouples.

That the thermocouple sensitivity of the carbon fiber epoxy-matrix composite junctions is independent of the extent of curing and is the same for unidirectional

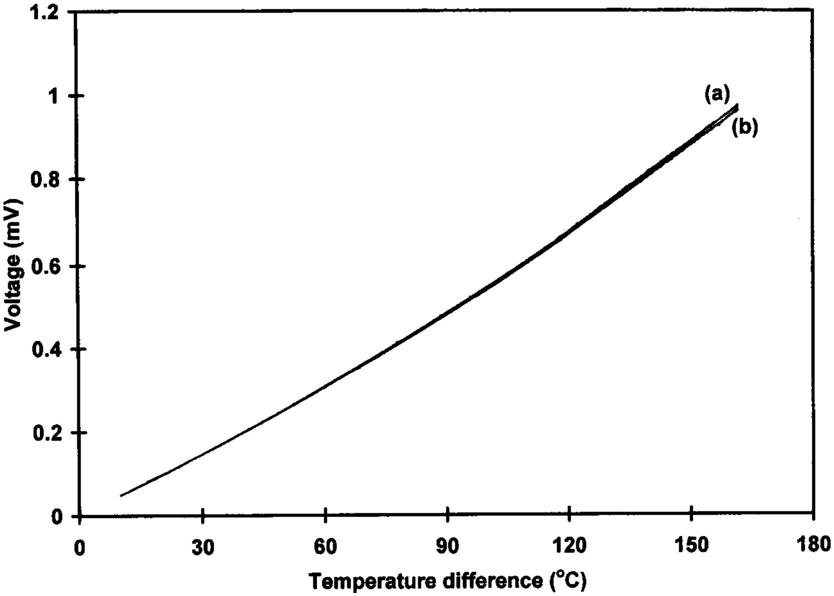

Figure 3. Variation of the measured voltage with the temperature difference between hot and cold points for the epoxy-matrix composite junction comprising pristine P-25 and pristine T-300, as obtained in the curing heating cycle. (a) Unidirectional configuration. (b) Crossply configuration.

and crossply junctions (Table 1 and Fig. 3) is consistent with the fact that the thermocouple effect hinges on the difference in the bulk properties of the two partners, and is not an interfacial phenomenon. This behavior means that the interlaminar interfaces in a fibrous composite serve as thermocouple junctions in the same way, irrespective of the lay-up configuration of the dissimilar fibers in the laminate. As a structural composite typically has fibers in multiple directions, this behavior facilitates the use of a structural composite as a thermocouple array.

The six-junction sample (Fig. 1) can be used as a simple thermocouple array. Each of the junctions is a thermocouple, thus allowing temperature distribution sensing. Figure 4 shows the temperature distribution during light shining measured by conventional thermocouples. The temperature decreases from junction A to D, for the distance to the center of the light spot increases from A to D. Corresponding to the temperature distribution, we have the voltage distributions, as shown in Fig. 5. Figure 5a shows the voltage distribution for voltage probe configuration I. It is quite consistent with the temperature distribution, since configuration I minimizes the influences of the other junctions on the voltage of the junction to be measured. However, the voltage distribution measured by configuration II (Fig. 5b) is less consistent with the temperature distribution, especially for junctions C and D. This is because of the mutual influences of the junctions. Both configurations I and II indicate correctly the junction with the highest temperature.

It is important to note that the thermocouple junctions do not require any bonding agent other than the epoxy, which serves as the matrix of the composite and does

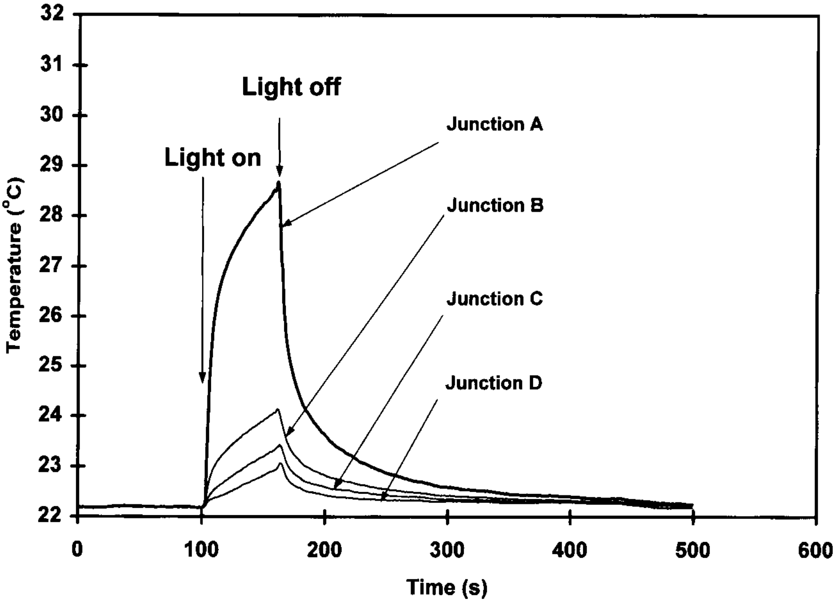

Figure 4. Variation of the temperatures of junctions A, B, C and D of the six-junction sample during light shining. The center of the light spot was at junction A.

not serve as an electrical contact medium (since it is not conducting). In spite of the presence of the epoxy matrix in the junction area, direct contact occurs between a fraction of the fibers of a lamina and a fraction of the fibers of the other lamina, thus resulting in a conduction path in the direction perpendicular to the junction. This conduction path is indicated by direct measurement of the electrical resistance of the junction [14] and enables an electrical contact to be made across the junction. The use of silver paint as an additional bonding agent did not give better result, as we found experimentally. That the bonding agent did not affect the result is also consistent with the fact that the thermocouple effect is not an interfacial phenomenon. That an additional bonding agent is not necessary facilitates the use of a structural composite as a thermocouple array, as a typical structural composite does not have any extra bonding agent at the interlaminar interface.

The thermocouple effect can be used for converting thermal energy to electrical energy. To make the voltage generated of practical significance, a large number of thermocouples can be connected in series. In other words, the laminae configuration in the composite can be designed so as to provide a large number of thermocouples that are connected in series. Hence, the structural composite is an electric power generator, which is valuable for providing a part of the electric power needed by aircraft made with composites.

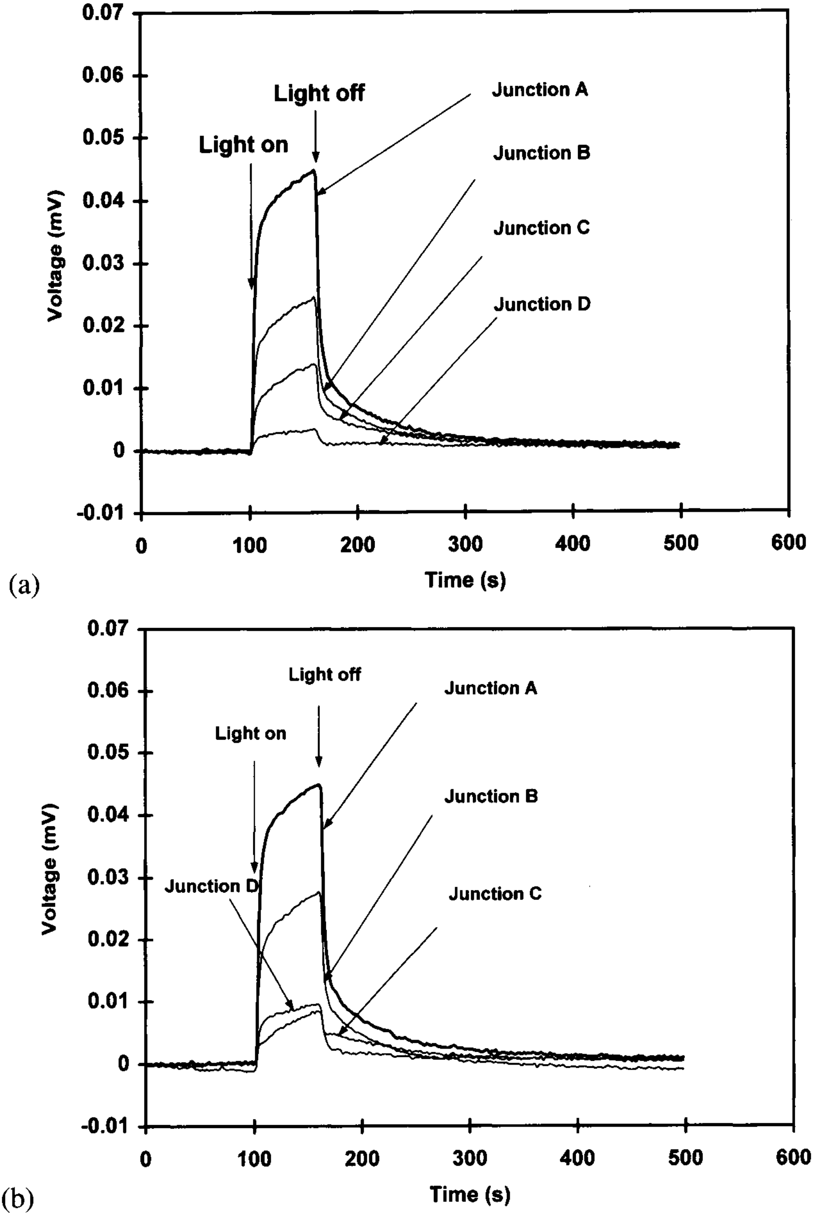

Figure 5. Variation of the voltages of junctions A, B, C and D of the six-junction sample during light shining. (a) Voltage probe configuration I. (b) Voltage probe configuration II.

4. CONCLUSION

Thermocouples made from n-type carbon fibers (e.g. sodium intercalated P-100 fibers) and p-type carbon fibers (e.g. bromine intercalated P-100 fibers) in the form of epoxy-matrix composites, using the interlaminar interface as the thermocouple junction, were found to exhibit thermocouple sensitivity up to 82 μV/°C — close to the sum of the magnitudes of the Seebeck coefficients of the two partners of the thermocouple. Bromine intercalation changed the Seebeck coefficient (with copper as the reference) of P-100 fibers from +1.7 to −43 μV/°C. Sodium intercalation changed it from +1.7 to +48 μV/°C. Similarly large effects were observed for intercalated P-120 fibers. Pristine fibers gave similar junctions, but with a much smaller value of the thermocouple sensitivity. The thermocouple sensitivity was the same for unidirectional and crossply junctions. Two crossply laminae comprising dissimilar carbon fibers provided an array of junctions, each of which was a thermocouple, thus allowing temperature distribution sensing.

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