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Apparent negative electrical resistance in carbon fiber composites

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Abstract

Apparent negative electrical resistance was observed, quantified, and controlled through composite engineering. Its mechanism involves electrons traveling in the unexpected direction relative to the applied voltage gradient, due to backflow across a composite interface. The observation was made in the through-thickness direction of a continuous carbon fiber epoxy–matrix two-lamina composite, such that the fibers in the adjacent laminae were not in the same direction and that the curing pressure during composite fabrication was unusually high (1.4 MPa). At a usual curing pressure (0.13 MPa), the resistance was positive. At an intermediate curing pressure (0.33 MPa), the apparent resistance was either positive or negative, depending on the current direction, due to non-uniformity in the thickness within a junction. The magnitude of the apparent negative resistance decreased with increasing temperature. Appropriate apparent negative and positive resistances in series, as provided by more than two laminae, allowed tailoring of the total apparent resistance. Apparent negative resistance was also observed in carbon fiber cement-matrix composites and in bare carbon fibers held together by pressure. Relevant applications are electrical, optical, structural and electrochemical.

Keywords: A. Carbon fibre; Polymer

1. Introduction

Because an electron, being negatively charged, drifts toward the positive end of a voltage gradient, the electrical resistance of a material is positive (i.e. the greater the voltage gradient, the higher the current). For a simple conductor under a voltage gradient which is not excessive, the current is proportional to the voltage—a relationship known as Ohm's Law.

Negative resistance means that the more positive is the voltage, the more negative is the current, i.e. the current–voltage characteristic is a straight line of negative slope through the origin. In this paper, negative resistance does not mean differential negative resistance (the more positive is the voltage, the less positive is the current). Negative resistance in the latter sense over a limited range of the voltage away from zero voltage has been previously observed for a number of materials, including polymer films [1,2] and metal films [3]; and was explained in terms of the effect of voltage or current on the conduction mechanism. True negative resistance in the former sense is not possible due to energy consideration. However, apparent negative resistance in the former sense is reported here. Although the negative resistance is apparent, its mechanism resembles that of true negative resistance, i.e. the electrons traveling in the unexpected direction relative to the applied voltage gradient. The apparent negative resistance phenomenon provides the basis for an electronic device that can be used in electronic circuits.

In this paper, we report an apparent negative resistance phenomenon in which the entire current–voltage characteristic is a straight line of negative slope through the origin. We observed this phenomenon in composites containing continuous carbon fibers, such that the pressure during composite fabrication is unusually high, as explained in the next section. As such a composite is a structural material, a negative resistance device in the form of this material is mechanically rugged. Further, a structure made out of this composite is itself an electronic device, thus providing smartness to the structure.

In a companion paper, we have reported that this composite, when made with the usual curing pressure, is semiconducting in its temperature dependence of the electrical resistivity and exhibits the usual positive resistance [4]. The semiconducting behavior stems for the need for the electrons to jump from one lamina to the adjacent one (across an activation energy) in order to contribute to electrical conduction [4]. The apparent negative resistance

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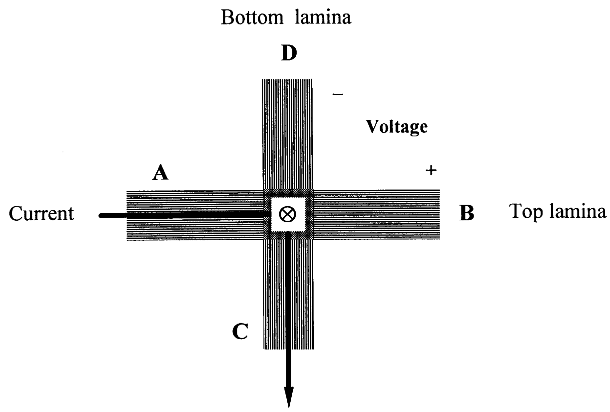

Fig. 1. Composite configuration for electrical measurement.

behavior reported in this paper adds to the variety of electronic devices that can be in the form of a structural composite. Such electronic devices that are made from structural materials constitute a new field of electronics called structural electronics. The attractions of structural electronics compared to conventional silicon electronics include low cost, mechanical ruggedness and space saving (the electronics vanished into the structure).

2. Apparent negative resistance

Apparent negative resistance in the sense of the current–voltage characteristic being a straight line of negative slope through the origin was observed in this work in the through-thickness direction of a continuous two-lamina crossply carbon fiber epoxy–matrix composite (Fig. 1) that had been fabricated with an unusually high curing pressure, which resulted in an unusually large number of fiber–fiber contacts at the junctions of crossply fibers of adjacent laminae. Direct fiber–fiber contacts exist in epoxy–matrix composites, even for those made at a usual curing pressure, because the epoxy resin that coats each fiber prior to composite fabrication flows during composite fabrication [5]. In Fig. 1, the top lamina is AB and the bottom lamina is CD. Current is passed from A to C, while voltage is measured between B and D. Resistance is voltage divided by current. The fiber ends at A are electrically shorted; similarly at B, C and D. As a result, the electrons travel at the surface of each lamina at the interface side. When there are sufficient fiber–fiber contacts between the laminae, the measured resistance is negative; otherwise, it is positive.

A mechanism for the apparent negative resistance, as suggested by the experimental results, is given below. Upon application of a current from A to C (positive end of the applied voltage at A, the top lamina) between two crossply laminae, electrons drift from the bottom lamina to the top lamina through the fiber–fiber contacts, though the drift requires the jumping of electrons across the interface between the laminae through activation to overcome the associated energy barrier. After jumping across the interface through drift, the electrons may travel along the top lamina away from the AC quadrant of the interface that is exposed most strongly to the applied current and then, due to entropy (i.e. diffusion), flow back to the bottom lamina at the fiber–fiber contacts. The backflow current overshadows the drift current in its influence on the measured voltage between B and D, because the backflow occurs away from the AC quadrant, mainly at the BD quadrant. Therefore, the measured voltage corresponds to the electrons going from top to bottom laminae, or, in other words, down the applied voltage gradient. The drift of the electrons up the voltage gradient is necessary to supply the electrons, which subsequently flow back. Consequently, the greater the voltage gradient, the greater the drift current and hence the greater the backflow current. Therefore, though backflow itself does not require a voltage gradient, the backflow current increases with the voltage gradient. The free energy that drives the backflow current is derived from the energy of the drift current and the entropy increase associated with the backflow.

If the curing pressure during composite fabrication is not high enough, there are not enough fiber–fiber contacts, so the electrons spread out at the bottom lamina at the interface and drift across the entire interface to the top lamina. As a result, there is no backflow current and the measured voltage is positive, corresponding to a positive resistance.

At the borderline curing pressure, the observed resistance is either negative or positive, depending on the electrical contact configuration (i.e. current from A to C versus current from A to D), due to non-uniformity in the interface.

3. Experimental

This section gives the experimental support of the phenomenon of apparent negative resistance (when the curing pressure is high enough) and that of positive resistance (when the curing pressure is not high enough). Three cases are described. They are: (i) high curing pressure (1.4 MPa); (ii) low curing pressure (0.13 MPa); and (iii) borderline curing pressure (0.33 MPa). However, the pressure range for each case has not been determined.

3.1. Experimental method

Composite samples were made from two layers of unidirectional carbon fiber prepreg tapes manufactured by ICI Fiberite (Tempe, AZ). The product used was Hy-E 1076E, which consisted of a 976 epoxy–matrix and 10E carbon fibers. The fiber diameter was 7 μm; the tensile modulus of the fiber was 221 GPa; the tensile strength of the fiber was 3.1 GPa; the density of the fiber was 1.76 g/cm^3. Two 6 mm wide strips of carbon fiber were pressed together in a crossply configuration to form a 6 mm × 6 mm junction (Fig. 1).

Pressure (0.13, 0.33 or 1.4 MPa) on the junction was

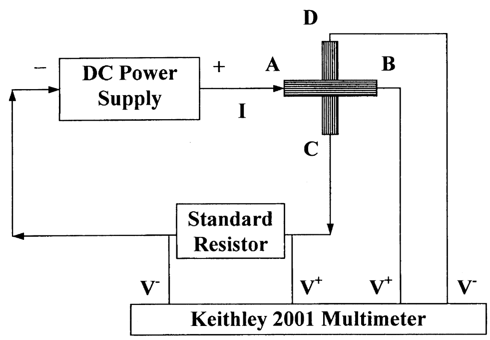

Fig. 2. Experimental set-up for obtaining current–voltage characteristics.

provided by a steel weight. A glass fiber–epoxy composite spacer was placed between the weight and the junction to make sure that the weight was applied to the junction only. The fiber volume fractions for different curing pressures were determined by measuring the density of each composite (6 mm × 6 mm, 10 laminae) and calculation using the known densities of the fibers and the matrix. The samples were put between the two heating platens of a Carver hot press, where they were cured at 175 ± 2°C for 10 h. The heating rate was 2.5°C/min. After curing, the samples were cooled to room temperature at a rate of 0.18°C/min. In order to study the situation of apparent negative and positive resistances in series, a four-lamina [0/90/0/90] crossply composite with a junction area of 6 mm × 6 mm was made by the same curing procedure and under a pressure of 1.4 MPa. The apparent negative resistance was contributed by the contact resistances at the interlaminar interfaces, while the positive resistance was contributed by the volume resistances of the laminae. All resistances were in the direction perpendicular to the laminae.

The epoxy at the ends of each prepreg strip was burned out to expose the carbon fibers for the purpose of making electrical contacts. These exposed fibers were wrapped by pieces of copper foil, with silver paint between the copper and the fibers. In other words, the fibers of each strip were electrically shorted at each end.

A DC power supply was employed to provide the current through the junction. A standard resistor was connected in series to the junction, as shown in Fig. 2. The current was scanned from − 1 to + 1 A at the rate of 0.02 A/s. At the same time, the voltage difference between the two laminae of the junction and that between the two terminals of the standard resistor were measured using a Keithley 2001 multimeter. The electrical current was calculated by Ohm's Law, i.e.

$$\text{Current} = \frac{\text{Voltage difference between the two terminals of the standard resistor}}{\text{Resistance of the standard resistor}}.$$

As the fibers were electrically shorted at each end of a strip, the applied current in Fig. 1 flows from A along the fibers at the bottom of the top lamina, goes down in the direction perpendicular to the interlaminar interface and then flows along the fibers at the top of the bottom lamina to C. The measured voltage between B and D divided by this applied current gives the apparent contact resistance of the interface. Air was blown to the junction to remove the heat caused by the current. The temperature change of the junction, which was monitored by a K-type thermocouple attached to it, was thus in a range of 1–5°C. The apparent contact resistance R_c was obtained through linear regression of current–voltage characteristic within the linear range (R_c is the reciprocal of the slope of the current–voltage characteristic). The apparent contact resistivity (ρ_c) was calculated by the equation $\rho_c = R_c A$, where A is the contact area of the junction. For each sample, the current and voltage for

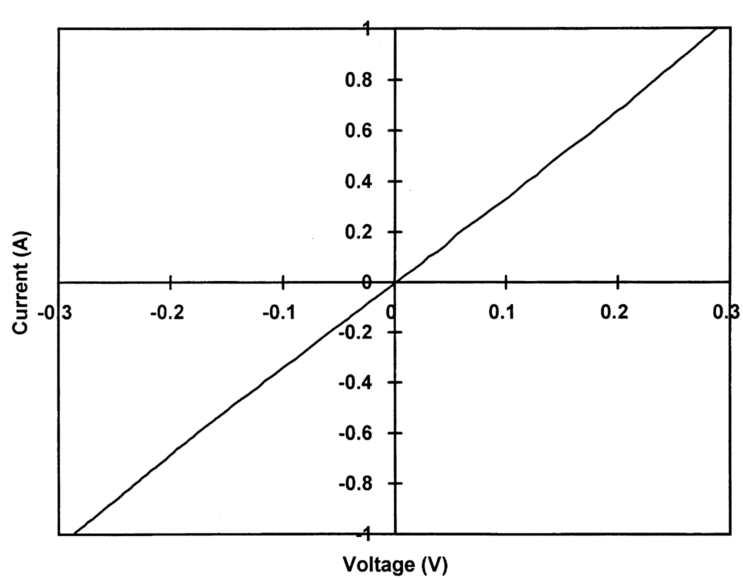

Fig. 3. A typical current–voltage characteristic for sample cured at 0.13 MPa.

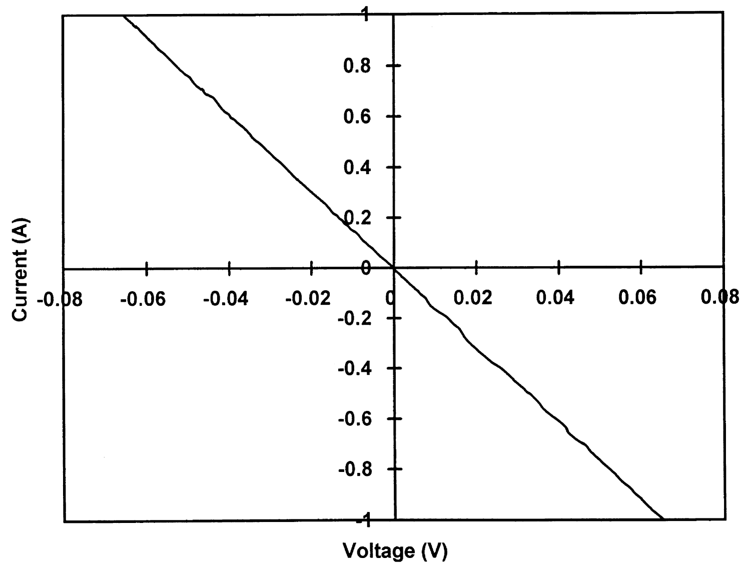

Fig. 4. A typical current–voltage characteristic for sample cured at 1.4 MPa.

each of the four ways of passing the current (i.e. from A to C, A to D, B to D and B to C, Fig. 1) were measured.

In order to study the semiconducting behavior for the case of negative resistance, the sample with the curing pressure of 1.4 MPa was reheated to 150 ± 2°C and then cooled to 50 ± 2°C while the resistance was monitored. Both the reheating and the subsequent cooling were at a controlled rate of 0.15°C/min.

3.2. Results and discussion

Fig. 3 shows a typical current–voltage characteristic for a sample cured at 0.13 MPa. It is quite linear and has a positive slope. Fig. 4 shows that for a sample cured at 1.4 MPa. It is also quite linear but has a negative slope, which means that the contact resistance is negative. For an intermediate curing pressure of 0.33 MPa, two types of current–voltage characteristics were observed, as shown in Fig. 5(a), which gives a negative resistance, and Fig. 5(b), which gives a positive resistance. In both Fig. 5(a) and (b), the current–voltage characteristic is not very linear, especially when the current is relatively high. The deviation from linearity is such that the resistance becomes more negative or less positive, probably due to the enhancement of the drift current.

The contact resistivities for different current directions, curing pressures and fiber volume fractions are shown in Table 1. It can be seen that the apparent contact resistivities for the sample with the lowest curing pressure (0.13 MPa) are all positive, those for the sample with the highest curing pressure (1.4 MPa) are all negative, and those for the sample with the intermediate curing pressure (0.33 MPa) are partly positive (in the A to C and B to D directions) and partly negative (in the A to D and B to C directions). These behaviors are consistent with Figs. 3–5.

For all the samples cured at 1.4 and 0.33 MPa, the contact resistivities in the A to C and B to D directions are quite close and those in the A to D and B to C directions are also quite close, whereas the resistivities in the A to C (or B to D) and B to C (or A to D) directions are quite different, as shown in Table 1 for representative samples. In contrast, for all the samples cured at 0.13 MPa, all four resistivities are close. Table 1 also shows the thickness of each two-lamina composite. Half of this thickness is the thickness of a lamina. For the samples cured at 1.4 and 0.33 MPa, a more negative apparent resistivity is associated with a lower thickness of the composite at the corner (quadrant) of the junction close to the current contacts; the thicknesses were measured by a micrometer. A lower local thickness is probably caused by the flow of epoxy during curing. Hence, the variation of the apparent resistivity with the current direction is attributed to non-uniformity in the thickness within a junction. A low thickness favors a negative resistance, akin to a high curing pressure favoring a negative apparent resistance. For a low curing pressure (the 0.13 MPa case), the flow of epoxy is probably less and a positive resistance apparently depends on thickness less than a negative apparent resistance, so the resistivity does not vary with the current direction. Thus, the composites cured at 1.4 or 0.33 MPa are four-terminal electrical devices with asymmetric current–voltage characteristics, whereas those cured at 0.13 MPa are devices with symmetric characteristics.

Fig. 6 shows the resistance of a junction at a constant pressure of 0.13 MPa during curing. As the temperature was increased, the epoxy resin melted and flowed. Under the pressure, the resin was squeezed, resulting in consolidation of the fiber layers and the fiber layers becoming closer together. As a result, the resistance dropped during curing. In Fig. 6, the resistance was positive throughout the curing

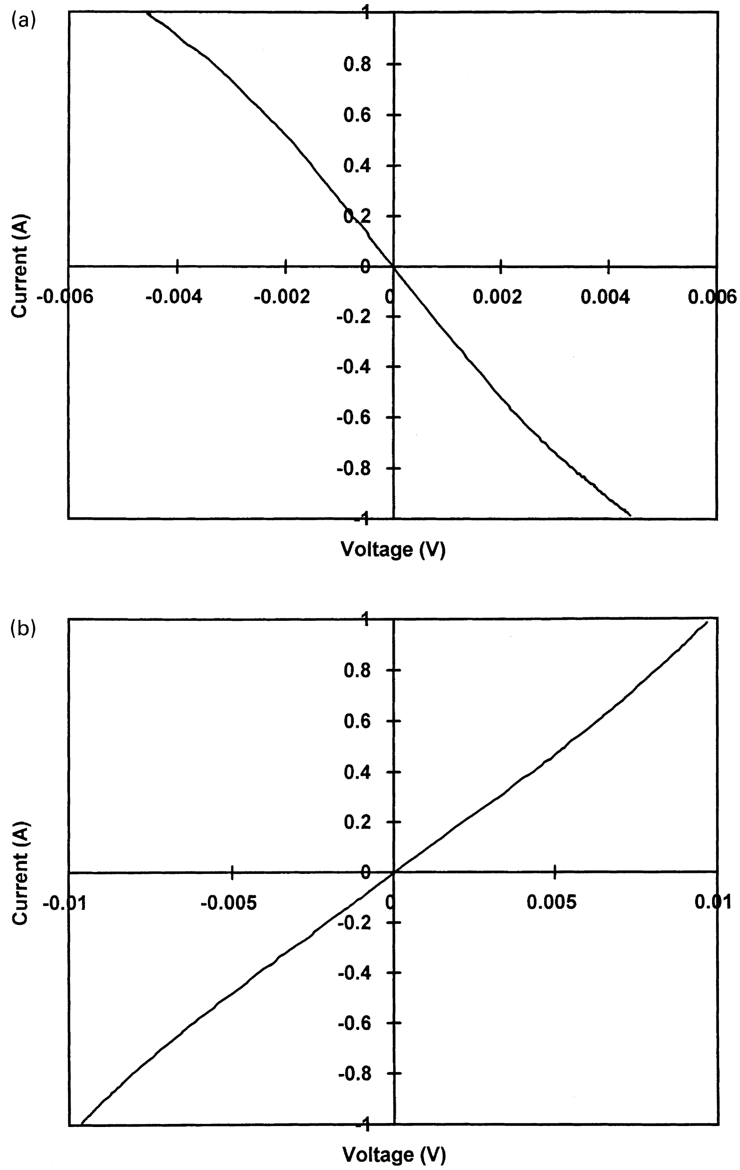

Fig. 5. Two types of current–voltage characteristics for sample cured at 0.33 MPa. (a) Negative slope. (b) Positive slope.

process and leveled off at a positive value at the end of curing.

Fig. 7 shows the resistance (with the current from A to C) of a junction at a constant pressure of 1.4 MPa during curing. The apparent resistance is negative throughout the curing process, though it becomes more negative as the temperature increases toward the curing temperature. This trend is due to the increase in the amount of fiber–fiber contacts as consolidation occurs and the consequent increase in the backflow current. After curing and subsequent cooling, the resistances are -0.0297, -0.0306, -0.0309 and $-0.0296\ \Omega$ in the AC, AD, BC and BD directions, respectively. As in Table 1, two of these resistances (AC and BD) are close, and the other two (AD and BC) are also close. Although the absolute value of these resistances varies from sample to sample, the fact that all four resistances are negative and that two (AC and BD) are close and the other two (AD and BC) are close, is a behavior that is observed in every sample with two crossply laminae cured at 1.4 MPa.

For a two-lamina sample, the measured resistance in the through-thickness direction is the apparent contact resistance of one interlaminar interface. For a three-lamina sample, the through-thickness resistance is the sum of the apparent contact resistances of the two, interlaminar interfaces and the volume resistance in the through-thickness direction of one lamina. Thus, by having more than two laminae, the apparent negative resistance due to the contact resistance and the positive resistance due to the volume resistance are in series.

Four laminae stacked in a crossply [0/90/0/90] configuration were subjected to a pressure of 1.4 MPa during curing.

Table 1
The relationship among apparent contact resistivity, curing pressure, fiber volume fraction and current direction

Curing pressure (MPa)	Fiber volume fraction	Thickness at center (mm)	Direction of current	Thickness at corner (mm)[a]	Apparent contact resistivity (Ω cm^2)	Current range for resistivity calculation (A)
1.4	0.58	0.236	A to C	0.246	− 0.0423	0 − 1
			A to D	0.234	− 0.0487	0 − 1
			B to C	0.226	− 0.0483	0 − 1
			B to D	0.226	− 0.0425	0 − 1
0.33	0.52	0.284	A to C	0.284	0.00511	0 − 0.4
			A to D	0.274	− 0.00187	0 − 0.4
			B to C	0.277	− 0.00268	0 − 0.4
			B to D	0.282	0.00532	0 − 0.4
0.13	0.50	0.315	A to C	0.325	0.121	0 − 1
			A to D	0.310	0.121	0 − 1
			B to C	0.307	0.125	0 − 1
			B to D	0.269	0.120	0 − 1

[a] "Corner" refers to the quadrant of the square junction that is closest to both current contacts, which are A and C, A and D, B and C, or B and D.

As the volume resistance within each lamina in the through-thickness direction is positive, the total (series) apparent through-thickness resistance of the stack (Fig. 8) is not as negative as a single interlaminar junction (Fig. 7). At the beginning of the heating of the stack, the apparent resistance is positive. As the temperature increases, the resistance becomes less positive, goes through zero and then becomes negative. After curing and subsequent cooling, the resistance remains negative, at −0.0261, −0.0087, −0.0090 and −0.0262 Ω for current directions AC, AD, BC and BD, respectively.

Three laminae stacked in a crossply [0/90/0] configuration were within the four-lamina stack mentioned above. After curing at 1.4 MPa and subsequent cooling, the apparent through-thickness resistances of the three-lamina stack are + 0.0007, − 0.0771, − 0.0771 and + 0.0007 Ω for the four directions of current flow. In another three-lamina stack within the four-lamina stack mentioned above, the apparent resistances after 1.4 MPa curing and cooling are + 0.0024, − 0.0713, − 0.0712 and + 0.0024 Ω for the four directions of current flow. Thus, by tailoring the stack and using the appropriate direction of current flow, the resistance can be close to zero (e.g. + 0.0007 Ω). Another way to attain zero apparent resistance is to adjust the curing pressure, as suggested by Table 1. However, this route has not been used in this work.

Upon heating the sample of Fig. 7 (cured at 1.4 MPa), the apparent resistance became less negative, but remained negative even at the maximum temperature of 150°C. Upon subsequent cooling, the apparent resistance returned

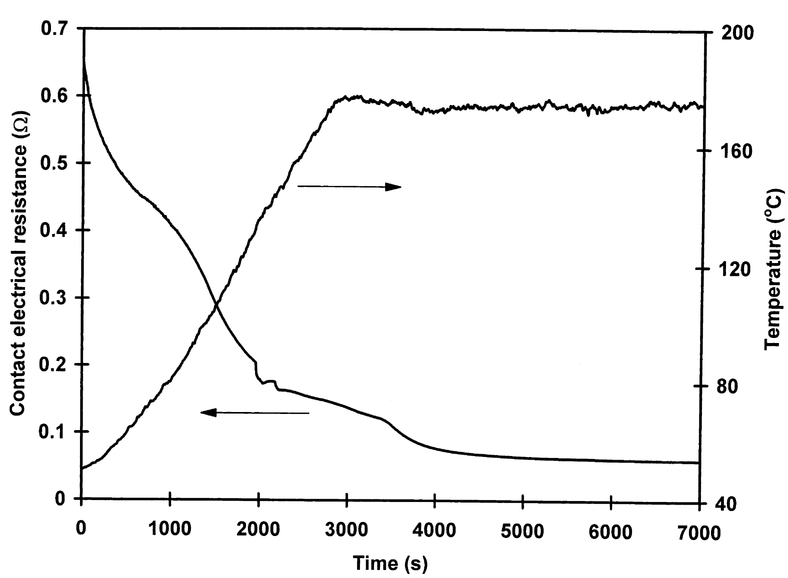

Fig. 6. Variation of apparent resistance during curing at 0.13 MPa of a two-lamina crossply sample.

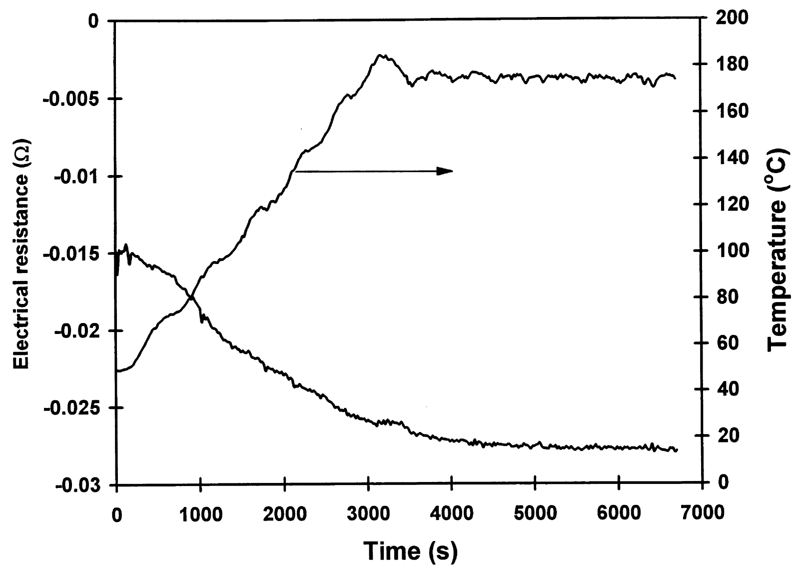

Fig. 7. Variation of apparent resistance during curing at 1.4 MPa of a two-lamina crossply sample.

to the initial more negative value. This trend indicates that this composite is semiconducting. Fig. 9 shows the Arrhenius plot of the logarithm (to the base 10) of the contact conductivity (absolute value; conductivity equals the reciprocal of the resistivity) versus inverse absolute temperature within the temperature range of 75–125°C (during cooling), in which the temperature change was linear with time, for the sample with the curing pressure of 1.4 MPa and a negative apparent contact resistance. In Fig. 9, σ stands for the absolute value of apparent contact conductivity, i.e. $\sigma = |1/(R_c A)|$, where R_c and A are the apparent contact resistance and the contact area, respectively. The Arrhenius plot is quite linear, though more noisy compared with those for the samples with lower curing pressures and positive contact resistances [4]. The activation energy E, calculated from the following equation:

$$\text{Slope of Arrhenius plot} = -\frac{E}{2.3\mathrm{k}},$$

where k is the Boltzmann's constant, is 2.1×10^{-3} eV, one or two orders of magnitude smaller than those in the cases of lower curing pressure and positive contact resistances [4]. The higher noise in the Arrhenius plot may be because of the smaller absolute value of the apparent contact resistance. In the case of composites exhibiting positive resistance, the activation energy increases with increasing curing pressure [4]. In spite of the high curing pressure for the composites exhibiting negative resistance, the activation energy is low. For both positive and negative apparent resistance cases, the activation energy is that for electrons to jump from one

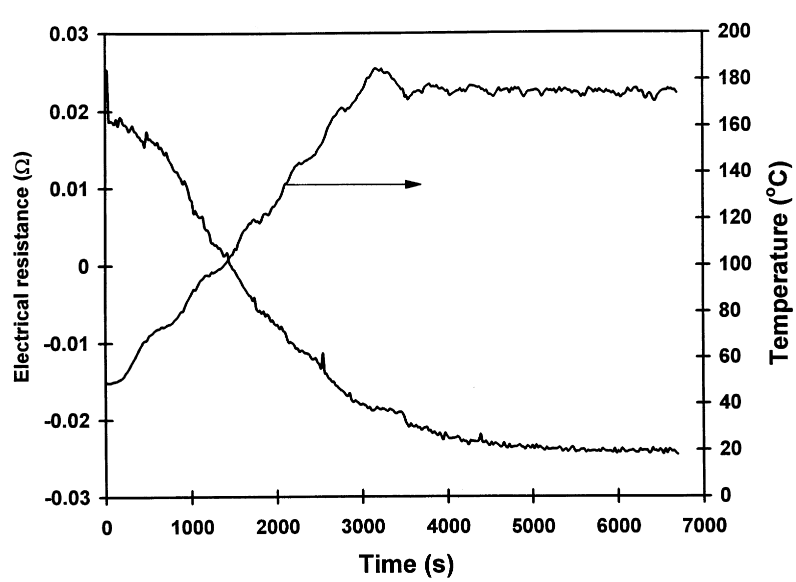

Fig. 8. Variation of apparent resistance during curing at 1.4 MPa of a four-lamina crossply sample.

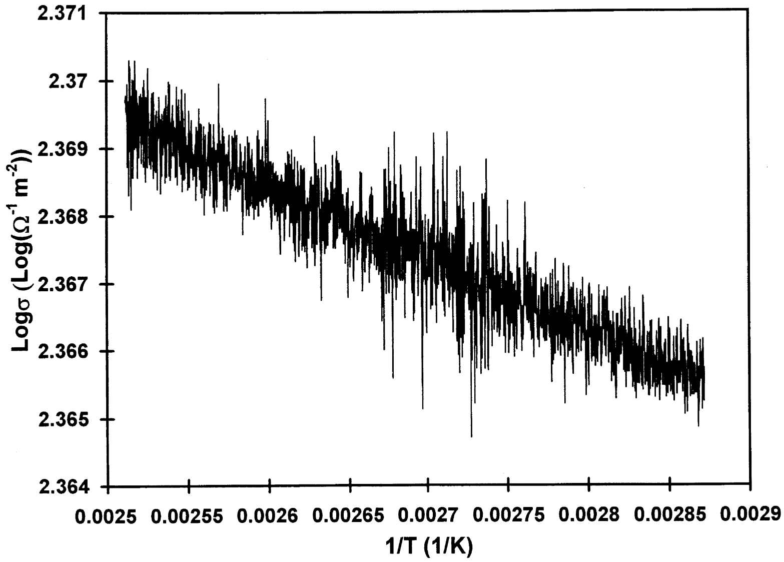

Fig. 9. Arrhenius plot of the logarithm (to the base 10) of the apparent conductivity versus the inverse absolute temperature for sample cured at 1.4 MPa during cooling.

lamina to the adjacent one. The unusually low activation energy for the negative apparent resistance case may stem from the unusually high number of fiber–fiber contacts between adjacent laminae. From a mechanism viewpoint, it is probably due to the temperature dependence of the forward flow dominating over that of the backflow and the two flows subtracting from one another.

Consistent results were obtained for junctions that were formed by laminae (strips) at 30, 45, 60 and 90° from one another, by laminae (strips) of different widths and by interior and edge portions of laminae. In particular, a junction of a smaller area gave a higher magnitude of the apparent resistance, whether negative or positive, as shown by measurement on 2×2, 4.5×4.5 and $7 \times 7\ mm^2$ junctions. Further, for a given junction area, the greater the magnitude of positive apparent resistance (as obtained at a low curing pressure), the greater the magnitude of negative apparent resistance (as obtained at a high curing pressure). The apparent negative resistance observation did not require a 90° crossply configuration and was not restricted to a 6 mm × 6 mm junction, although these were the conditions under which most results presented here were obtained.

For crossply laminae which had no polymer matrix, i.e. bare fibers (pitch-based, Thornel P-25, 2000 fibers per lamina, no sizing, no twist, from Amoco Performance Products, Inc., Ridgefield, CT), the contact resistivity (junction size 4.6 mm × 4.4 mm, as measured after loading and subsequent unloading) was positive at zero, pressure and

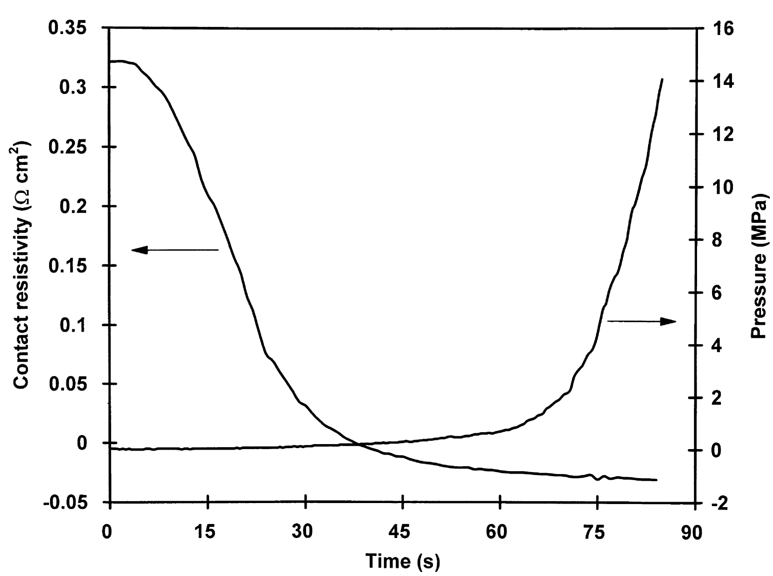

Fig. 10. Variation of apparent resistivity and of pressure with time during compressive loading of crossply laminae having no matrix.

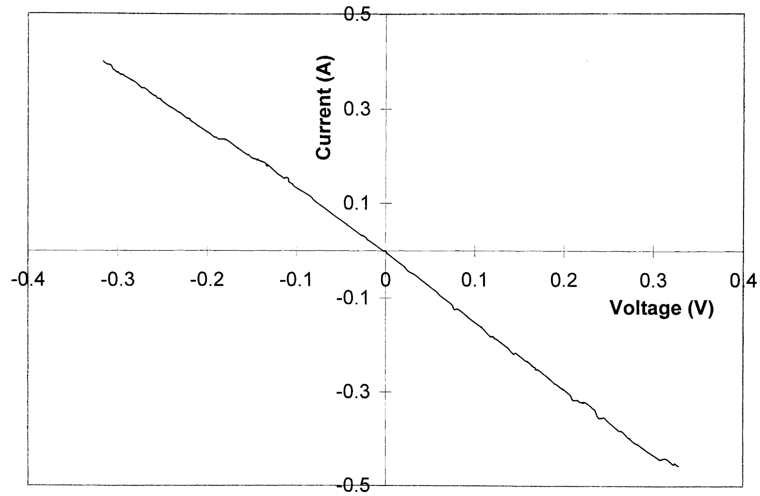

Fig. 11. A typical current–voltage characteristic for cement–matrix composite.

decreased with increasing pressure (continuously varied by using a screw-action mechanical testing system, Sintech 2/D), such that it crossed zero resistivity at a pressure of 0.15 MPa and then became negative (leveling off at $-0.03\ \Omega\ \mathrm{cm}^2$) at higher pressures (Fig. 10). This negative resistance value is comparable to those obtained above for the case of fiber prepregs (with epoxy) rather than bare fibers (Table 1). The reason why the apparent contact resistance of the crossply laminae consisting of bare fibers changes with pressure is that only a portion of fibers is at the interface, i.e. in contact with the other lamina, and this portion increases with increasing pressure. The minimum pressure required for the resistance to be negative in the bare fiber case (0.15 MPa) is smaller than the minimum curing pressure for the resistance to be negative in the fiber prepreg case (0.33–1.4 MPa). This difference is attributed to the relative ease of attaining a sufficient number of fiber–fiber contacts between the laminae when the polymer matrix is absent. Upon subsequent unloading, the resistance remained negative (although the data during unloading are not shown in Fig. 10), because the fibers remained stuck together after unloading. Similar negative resistance results were obtained by using 20 fibers instead of 2000 fibers per lamina. The use of one fiber instead of 20 or 2000 failed to give a measurable resistance, partly due to the very high value of the positive resistance and partly due to the tendency of the fiber to break under compression. Thus the investigation of the case of one fiber crossing one other fiber was conducted by using metal fiber (more ductile than carbon fiber), as described below.

The use of bare metal fibers (silver coated copper, 100 μm diameter) instead of carbon fibers failed to give an apparent negative resistance for the case of a single fiber crossing another, but for the case of 14 fibers crossing another 14 fibers, apparent negative resistance was observed upon compression. However, the magnitude of the apparent negative resistance was much smaller than those involving carbon fibers and the positive resistance observed at pressures below that required for the apparent resistance to be negative was also much smaller than those involving carbon fibers. These much smaller magnitudes of both apparent negative resistance and positive resistance result from the much better contact quality between metal fibers than that between carbon fibers. As a consequence, the voltage drops associated with both the drift current and the backflow current are relatively small.

The absence of apparent negative resistance for a single fiber (whether metal or carbon) crossing another single fiber is consistent with the mechanism of apparent negative resistance, as the very small junction size does not allow the mechanism to occur.

For crossply laminae with a cement (Portland cement, Type I, at a high water–cement ratio of 2.0) matrix instead of a polymer matrix, prepared by impregnating bare carbon fiber tows (Thornel P-25) with cement paste, laying up the tows to form a 13.54 mm × 13.44 mm seven-lamina crossply stack, compressing the stack in a mold at 3.20 MPa for 24 h, demolding, and then curing for 28 days in a moist chamber at a relative humidity of 100%. After curing, four electrical contacts were made with silver paint applied around the whole perimenter of the stack of four 0° laminae that protruded from the junction and around the whole perimeter of the stack of three 90° laminae that protruded from the junction, akin to Fig. 1. Hence, the measured resistance is the contact resistances of six interlaminar interfaces in parallel, i.e. the contact resistance of one interface is six times the measured resistance. The fiber volume fraction in the seven-lamina stack (i.e. the junction) after curing was 60%. Fig. 11 shows the resulting current–voltage characteristic, which is a straight line of negative slope going through the origin. The contact resistivity (junction size 13.54 mm × 13.44 mm) was $-8.0\ \Omega\ \mathrm{cm}^2$—more negative than the case of no matrix or the case of a polymer matrix. This behavior is attributed to the fact that the cement matrix is slightly conducting, whereas the polymer matrix is

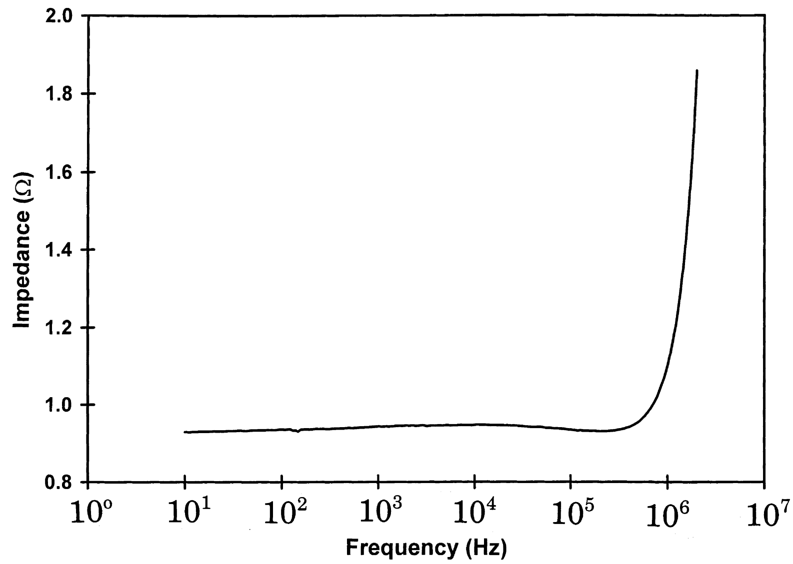

Fig. 12. Plot of apparent impedance magnitude versus frequency for carbon fiber cement–matrix composite.

insulating. The conducting matrix enhances the chance of electrical contact between fibers of one lamina and those of an adjacent lamina and, based on the results for the case of a polymer matrix, a large number of fiber–fiber contacts is necessary for negative resistance to occur. The pressure (3.20 MPa) used for making the cement–matrix composite is higher than the curing pressure (1.4 MPa) used for making the polymer–matrix composite exhibiting negative resistance. This is because of the high viscosity of the cement paste (in spite of the high water–cement ratio) compared to that of the epoxy resin.

Apparent negative resistance was not observed in carbon fiber thermoplast–matrix composites (10 mm × 10 mm junctions) made from carbon fiber thermoplast prepregs with polyphenylenesulfide (PPS) as the thermoplast. The thermoplast matrix did not flow as much as epoxy or cement matrices during composite fabrication below the melting temperature of the thermoplast, so the contact resistivity was high ($\geq 0.1\ \Omega\ \mathrm{cm}^2$) in the thermoplast–matrix composite and the amount of fiber–fiber contacts between laminae was insufficient for the occurrence of apparent negative resistance.

Although all the results given above were on the DC resistance, AC impedance measurement of the cement–matrix composite using a QuadTech 7600 RLC meter up to 2 MHz showed that the magnitude of the impedance was the same as that of the apparent negative DC resistance and it essentially did not change with frequency up to 1 MHz (Fig. 12).

Long-term continuous passing of current through a composite with apparent negative resistance for over 24 h did not cause any change in the apparent negative resistance, as shown by an epoxy–matrix composite.

The passing of current through a composite with an apparent negative resistance caused heating, just like that through a composite with a positive resistance, as shown by the epoxy–matrix composites.

4. Mechanism of apparent negative resistance

Measurement of the true contact resistance at the interlaminar interface of a carbon fiber epoxy–matrix composite made at a curing pressure of 1.4 MPa was conducted by using a four-lamina [0/90/0/90] crossply laminate (6 mm × 6 mm) with the topmost and bottommost laminae extending out of the stack to serve as current leads and the two inner laminae extending out to serve as voltage probes. This is a more classical four-probe configuration than that in Fig. 1. The contact resistance is 0.059 Ω (positive). In contrast, the apparent contact resistance ($-0.13\ \Omega$) is negative for this curing pressure (Table 1).

In order to address the mechanism of the apparent negative resistance, a single layer of Grafoil (flexible graphite, EGC Enterprises, Inc., Mentor, OH) of thickness 0.41 mm and in-plane electrical resistivity $7.5 \times 10^{-4}\ \Omega$ cm was cut into the shape of a cross of dimensions 6 mm × 6 mm at the junction (the two-dimensional shape of Fig. 1) and the electrical measurement depicted in Fig. 1 was conducted on it. The measured resistance was $-0.0044\ \Omega$. This negative value is due to the current path from A to C laterally across the junction area causing the voltage at D to be higher than that at B. In contrast, the apparent negative resistance for the carbon fiber epoxy–matrix composite case is $-0.13\ \Omega$. Considering the difference in volume resistivity and thickness between the Grafoil and composite, the normalized magnitude of the apparent negative resistance of the composite was still five times that of Grafoil. The large magnitude of the apparent negative resistance of the composite suggests that the interlaminar interface contributed to it. Similar measurement on copper foil in place of Grafoil gave, after normalization with respect to volume resistivity and thickness, similar magnitude of the apparent negative resistance as Grafoil.

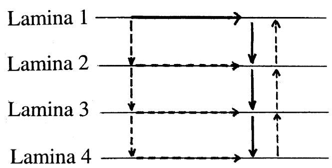

Fig. 13. Schematic of a four-lamina composite illustrating current flows resulting in zero apparent resistance. The flow indicated by solid arrows occurs because of the volume resistance within a lamina in the through-thickness direction making this flow more favorable than in the case of a two-lamina composite exhibiting apparent negative resistance. The flow indicated by upward dashed arrows is the backflow.

A simple equivalent circuit analysis shows that, for a two-lamina junction, the magnitude of the apparent negative resistance increases with junction area, if the mechanism of the apparent negative resistance is due to the lateral current path causing the voltage to be higher at D than at B. Moreover, Grafoil of a single layer cut into crosses of junction areas ranging from 2×2 to $6 \times 6\ \mathrm{mm}^2$ showed negligible (if any) effect of junction size on the apparent negative resistance. In contrast to these theoretical and experimental results for the case of the apparent negative resistance being due to the lateral current path, the carbon fiber epoxy–matrix two-lamina composites of a similar range of junction sizes showed that the magnitude of the apparent negative resistance decreased substantially with increasing junction size. This means that the mechanism of apparent negative resistance associated with the lateral current path is not the dominant mechanism for the composite case. Rather, the mechanism for the composite case involves the backflow of electrons across the interlaminar interface, as described earlier in this paper. The backflow mechanism is consistent with the observed symmetry in that the apparent negative resistance is similar for two opposite quadrants (i.e. AC and BD quadrants are similar and AD and BC quadrants are similar) (Table 1). This symmetry suggests that, when the applied current flows from A to C, the backflow primarily occurs in the BD quadrant and, when the applied current flows from B to D, the backflow primarily occurs in the AC quadrant; the two flow paths are essentially the same across the interlaminar interface except for a reversal in direction. The backflow mechanism is also consistent with the correlation of high magnitudes of positive and negative apparent resistances for the same junction area.

For a four-lamina stack exhibiting an apparent zero resistance, the apparent zero resistance is due to the balance between the backflow current and the forward flowing current in the quadrant near the voltage probes, as illustrated in Fig. 13.

5. Significance

Although the negative resistance reported here is apparent rather than true, its mechanism resembles that of true negative resistance (which actually does not occur due to energetics) in that the electrons flow in the unexpected direction relative to the applied current/voltage. Although electrons flowing one way in a part of a circuit and another way in another part of a circuit is common, the occurrence of backflow and forward flow of electrons in the same piece of material such that the backflow and forward flow can be distinctly and reproducibly detected and be controlled makes the apparent negative resistance phenomenon technologically attractive. Moreover, the relative amounts of these flows can be tailored through composite design (e.g. the number of laminae) and fabrication (e.g. the curing pressure). This adds versatility to the design of structural electronics as well as conventional electronics that use the apparent negative resistance device as a circuit element.

The observation of electron backflow is the scientifically most interesting aspect of this work. The backflow occurs due to the nature of the interface between fiber layers. This interface is geometrically complex (due to the multiplicity of fibers) and not uniform, but is reproducible and controllable. Both the interface and the material on either side of the interface can be engineered so as to control the extent of electron backflow. The tailorability is in contrast to similar electron backflow that can occur in monolithic anisotropic materials, such as graphite, where there is relatively little tailorability in terms of both the interface structure and the number of interfaces encountered by the electrons. The tailorability contributes much to the technological significance. The engineered interface between fiber layers, together with the ability of the fiber layers to serve as electrical leads, enable separate detection (hence quantification) of the backflow current. This is a situation, which is difficult to attain in a monolithic anisotropic material.

The control of the relative amounts of the backflow and forward flow means the control of the total apparent resistance. In the situation of zero apparent resistance, the two flows are nonzero but balanced, such that the voltage across the flow region (right portion of Fig. 13) is zero. The current loops in this region suggest the possibility of interesting magnetic and electromagnetic effects. Even when the apparent resistance is negative rather than zero currents loops occur due to the presence of backflow and forward flow currents, so the magnetic/electromagnetic effects may occur in this situation as well.

Because apparent negative resistance is not true negative resistance, it has escaped the attention of scientists, both in terms of the mechanism and the applications. The mechanism of apparent negative resistance in the case of carbon fiber composites is quite rich, due to the involvement of electron backflow. Further, the magnitude of apparent negative resistance in the case of carbon fiber composites is quite large, due to the fact that the resistance is associated with the interface between fiber layers. The apparent negative resistance phenomenon also occurs in other materials and for other conducting configurations, but the richness and magnitude may be small compared to the case of carbon fibers in the crossply configuration.

From an application viewpoint, the case of carbon fiber composites is particularly attractive due to the importance of these composites in structures (e.g. aerospace, automobile, sporting goods, machinery and other structures) and electrochemical electrodes. The electrode application is particularly interesting, as the two directions of current flow perpendicular to the electrode surface suggest the possibility of electrochemical effects that are useful for batteries and electrochemical processing.. The structure application relates to smart structures that use the apparent negative resistance phenomenon for switching and to low-observable aircrafts that use the phenomenon for electromagnetic radiation absorption.

The electron backflow is expected to affect the local affinity of the composite to charged particles. At a high AC frequency, the oscillation of the electrons may lead to radiation emission. These effects are potentially valuable for the use of the composite for imaging and for adaptive optics, as a crossply composite comprises a two-dimensional array of junctions. In addition, the interaction of electromagnetic radiation with the backflow electrons provides a mechanism for the use of the composite for radiation detection.

The combined use of carbon fibers and metal fibers for the purpose of using the metal fibers to connect to electrical circuits that utilize the apparent negative resistance phenomenon is possible, though investigation is still needed.

6. Conclusion

Apparent negative electrical resistance in the sense of a current–voltage characteristic of negative slope through the origin was observed, quantified and controlled through composite engineering. The observation was made in the through-thickness direction of a continuous carbon fiber epoxy–matrix two-lamina composite, such that the fibers in the adjacent laminae were crossply and the curing pressure during composite fabrication was unusually high (1.4 MPa). At a usual curing pressure (0.13 MPa), the resistance was positive. At an intermediate curing pressure (0.33 MPa), the apparent resistance was either positive or negative, depending on the current direction, due to nonuniformity in the thickness within a junction. The current–voltage characteristic was a straight line of negative slope for the case of apparent negative resistance (high curing pressure) and a straight line of positive slope for the case of positive resistance (low curing pressure). For the intermediate pressure case, the current–voltage characteristic deviated from being a straight line when the current was relatively high. The magnitude of the apparent negative resistance decreased with increasing temperature.

Apparent negative and positive resistances in series, as provided by a stack of more than two crossply laminae, gave a total apparent resistance that was intermediate between the apparent negative and positive resistances. Zero apparent resistance was observed during consolidation of the fiber layers. Apparent negative resistance was observed in carbon fiber epoxy–matrix and cement–matrix composites and in bare carbon fibers held together by pressure.

The mechanism of apparent negative resistance involves the backflow of electrons in the unexpected direction relative to the applied voltage gradient. The extent of backflow increases with the extent of contact between fibers of the adjacent laminae. Relevant applications are electrical, optical, structural and electrochemical.

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