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Electrical behavior of carbon fiber polymer-matrix composites in the through-thickness direction

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The electrical behavior of continuous carbon fiber epoxy-matrix composites in the through-thickness direction was studied by measuring the contact electrical resistivity (DC) of the interlaminar interface in the through-thickness direction. The contact resistivity was found to decrease with increasing curing pressure and to be higher for unidirectional than crossply composites. The lower the contact resistivity, the greater was the extent of direct contact between fibers of adjacent laminae. The activation energy for electrical conduction in the through-thickness direction was found to increase with increasing curing pressure and to be lower for unidirectional than crossply composites. The higher the activation energy, the greater was the residual interlaminar stress. 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).

1. Introduction

A structural composite in the form of laminae of continuous fibers (e.g., carbon fibers) bound by a matrix (e.g., a polymer such as epoxy) is strong in the fiber direction (in the plane of the laminae), but is weak in the through-thickness direction. As a result, delamination is a common form of damage and studies of the interlaminar interface and of the properties of the composite in the through-thickness direction are of interest.

Considerable attention has been given to the mechanical behavior of composites. Mechanical testing during compression in the fiber direction and during flexure gives information which relates to the through-thickness behavior. Measurement of the interlaminar shear strength (ILSS) by techniques such as the short-beam method [1], the Iospiescu method [2] and other methods [3] is also relevant. In the case of the fibers being electrically conducting (e.g., carbon fibers) and the matrix being insulating (e.g., epoxy), or the case of the fibers being much more conducting than the matrix, electrical testing can be revealing, though relatively little attention has been given to it [4–8]. This paper is focused on the electrical behavior in the through-thickness direction.

If the matrix is insulating and completely covers every fiber in the composite, the volume electrical resistivity should be infinite in the through-thickness direction. However, it is not. This means that there are direct contacts between the fibers of adjacent laminae due to the flow of the resin during composite fabrication. Previous work on the electrical behavior has emphasized the modeling of the through-thickness volume resistivity in terms of the number of fiber-fiber contacts and other microstructural parameters and comparison of the calculated and measured resistivity values [4–8]. Previous work has also used the through-thickness resistivity as an indication of the extent of delamination, as delamination decreases the number of fiber-fiber contacts, thereby increasing this resistivity [9]. The effect of longitudinal strain (in the fiber direction) on the through-thickness resistivity has also been reported [9]. This effect is due to the effect of longitudinal strain on the number of fiber-fiber contacts.

Because the volume electrical resistance in the through-thickness direction is the sum of the volume resistance of each lamina in this direction and the contact resistance of each interlaminar interface in the composite, direct measurement of the contact resistivity is more suitable than measurement of the volume resistivity of the composite for the purpose of understanding the through-thickness electrical behavior, which is governed by the interlaminar interface. Therefore, this paper provides measurement of the contact resistivity and a study of the effects of temperature and curing pressure on this resistivity.

The volume electrical resistivity is a geometry-independent quantity that describes the resistivity of a three-dimensional material in a particular direction and has the unit Ω m, whereas the contact electrical resistivity is a geometry-independent quantity that describes the resistivity of an interface in the direction perpendicular to the interface and has the unit Ω m^2. For a composite with electrically conducting fibers, such as carbon fibers, and an electrically insulating matrix, such as epoxy, the contact resistivity can be conveniently measured, since the fibers serve as electrical leads. The greater the extent of direct contact between fibers of adjacent laminae, the lower is the contact resistivity. The jumping of the electrons from one lamina to another is a thermally activated process, so the higher the temperature, the higher is the contact conductivity. The activation energy of the process can be determined by measuring the temperature dependence of the contact resistivity, as it is related to the slope (negative) of the Arrhenius plot of the logarithm of the contact conductivity (conductivity being the reciprocal of the resistivity) versus the inverse of the absolute temperature. The contact resistivity and the activation energy are quantities determined in this paper for the purpose of characterizing the interlaminar interface.

TABLE I Carbon fiber and epoxy matrix properties (according to ICI Fiberite)

10E-Torayca T-300 (6K) untwisted, UC-309 sized	
Diameter	7 μm
Density	1760 kg/m^3
Tensile modulus	221 GPa
Tensile strength	3.1 GPa
976 Epoxy	
Process temperature	177 °C
Maximum service temperature	177 °C dry 121 °C wet
Flexural modulus	3.7 GPa
Flexural strength	138 MPa
T_g	232 °C
Density	1280 kg/m^3

2. Experimental methods

Two laminae of unidirectional carbon fiber epoxy-matrix prepregs (Table I) in the form of strips crossing one another, with one strip on top of the other (Fig. 1), were fabricated into a composite at the overlapping region (6 × 6 mm) of the two laminae by applying pressure and heat to the overlapping region (without a mold). The pressure was provided by a weight, which was varied in order to vary the pressure. A glass fiber epoxy-matrix composite spacer was placed between the weight and the junction (the overlapping area region of the two strips). The heat was provided by a Carver hot press. A Watlow model 981C-10CA-ARRR temperature controller was used to control the temperature and the ramping rate. Each of the samples was put between the two heating platens of the hot press and heated linearly up to 175 ± 2 °C at the rate of 2.5 °C/min. Then it was cured at that temperature for 10 h and subsequently cooled linearly to 50 ± 2 °C at the rate of 0.18 °C/min. After that, the sample was reheated up to 150 ± 2 °C and then cooled back to 50 ± 2 °C. Both the reheating and the subsequent cooling were linear and at the rate of 0.15 °C/min. Still after that, the sample was heated linearly up to 150 ± 2 °C again at the rate of 1 °C/min and then cooled linearly back to 50 ± 2 °C at the rate of 0.15 °C/min. All the time, the contact electrical resistance and the temperature of the sample were measured respectively by a Keithley 2001 multimeter and a T-type thermocouple, which was put just beside the junction. Electrical contacts were made to the four ends of the two strips, so as to measure the contact electrical resistivity (resistance multiplied by contact area, which is the area of the overlapping region) between the two laminae in the composite, using the four-probe method (Fig. 1). 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 foil and the fibers. The electric current flowed from A to D, such that the dominant resistance was the contact resistance, as the volume resistance of the strips was negligible in comparison. The voltage between B and C is the voltage between the two laminae.

A four-lamina [0/90/0/90] crossply composite with a junction area of 6 × 6 mm was made by the same curing procedure and under a pressure of 1.4 MPa.

A DC power supply was employed to provide the current through the junction. A standard resistor was

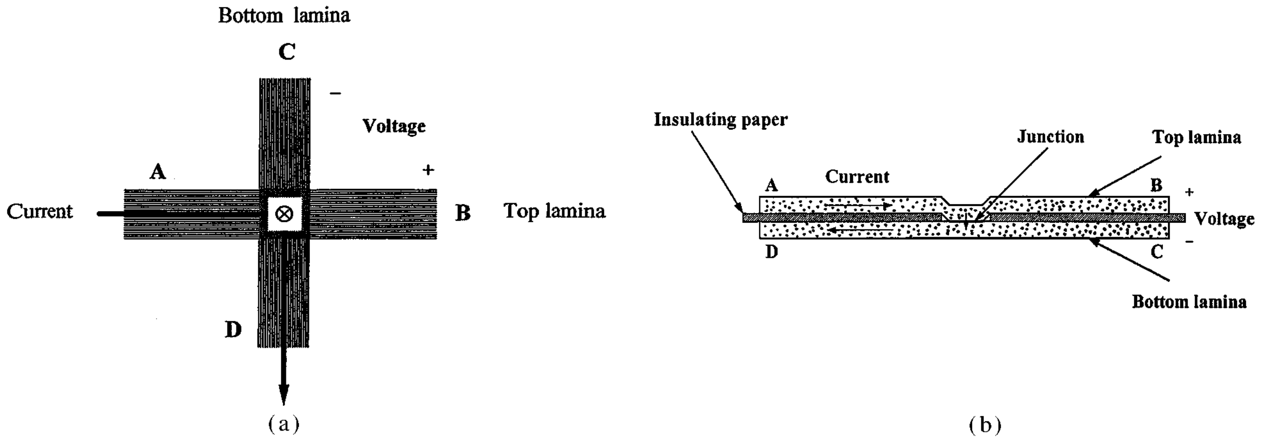

Figure 1 Composite configurations for testing contact resistivity as a function of temperature. (a) Crossply. (b) Unidirectional.

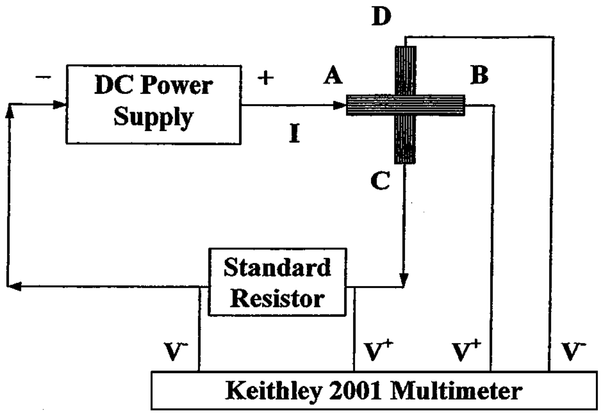

Figure 2 Experimental set-up for obtaining current-voltage characteristics.

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.,

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

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 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 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 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.

3. Results and discussion

Fig. 3 shows the variation of the contact resistivity ρ_c with temperature during reheating and subsequent cooling, both at 0.15 °C/min, for samples cured at 0 and 0.33 MPa. The corresponding Arrhenius plots of log contact conductivity (inverse of contact resistivity) versus inverse absolute temperature during heating are shown in Fig. 4. From the slope (negative) of the Arrhenius plot, which is quite linear, the activation energy can be calculated. The linearity of the Arrhenius plot means that the activation energy does not change throughout the temperature variation. This activation energy is the energy for electron jumping from one lamina to the other. Electronic excitation across this energy enables conduction in the through-thickness direction.

Although the Arrhenius plots are essentially linear, they have a slightly concave shape during heating as well as cooling (Fig. 4). This shape means that the activation energy increases slightly with increasing temperature. On the other hand, the interlaminar thermal stress decreases with increasing temperature, as explained in the next paragraph. Thus, this curvature cannot be explained by considering the effect of the thermal stress on the activation energy. The curvature is probably because of the change in the moisture content, which decreases with increasing temperature. Moisture makes the epoxy matrix dilate slightly, thus diminishing the

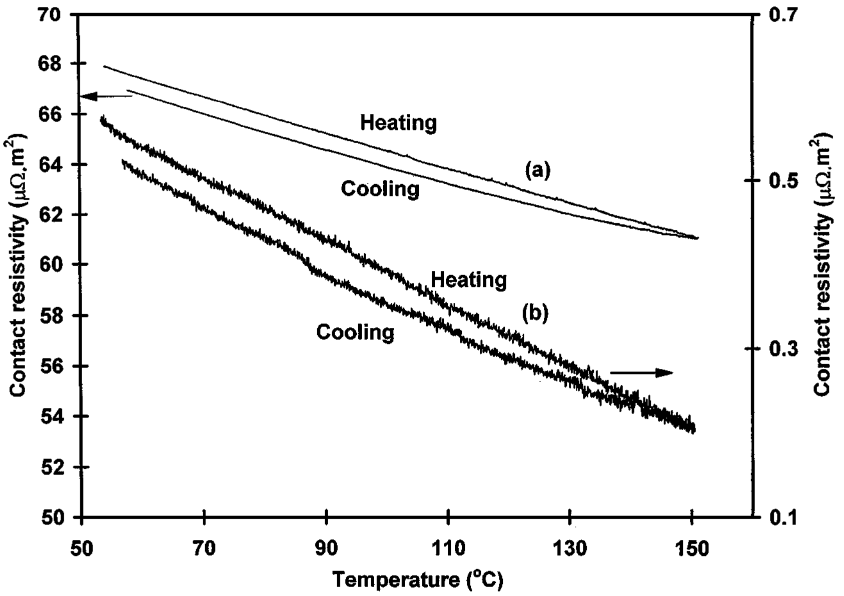

Figure 3 Variation of contact electrical resistivity with temperature during heating and cooling at 0.15 °C/min (a) for epoxy-matrix composite made without any curing pressure and (b) for epoxy-matrix composite made with a curing pressure 0.33 MPa.

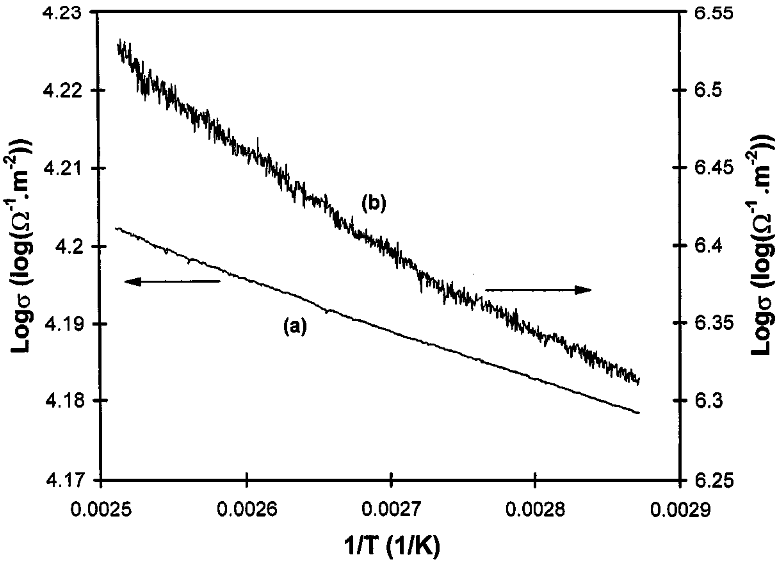

Figure 4 Arrhenius plot of log contact conductivity vs. inverse absolute temperature during heating at 0.15 °C/min (a) for epoxy-matrix composite made without any curing pressure and (b) for epoxy-matrix composite made with curing pressure 0.33 MPa.

proximity among the fibers and decreasing the contact conductivity of the interface. As a consequence, a moisture content decrease causes the conductivity to increase.

The activation energies, thicknesses and room temperature contact resistivities for samples made at different curing pressures and composite configurations are shown in Table II. All the activation energies were calculated based on the data at 75–125 °C. In this temperature regime, the temperature change was very linear and well controlled. From Table II it can be seen that, for the same composite configuration (crossply), the higher the curing pressure, the smaller was the composite thickness (because of more epoxy being squeezed out), the lower was the contact resistivity, and the higher the activation energy. A smaller composite thickness corresponds to a higher fiber volume fraction in the composite. During curing and subsequent cooling, the matrix shrinks. For carbon fibers, the modulus in the longitudinal direction is much higher than that in the transverse direction. Moreover, the carbon fibers are continuous in the longitudinal direction. Thus, the overall shrinkage in the longitudinal direction tends to be less than that in the transverse direction. In other words, there is a CTE difference between the longitudinal and transverse directions and hence a CTE mismatch between any two crossply layers. Therefore, there will be a residual interlaminar stress in the two crossply layers. The stress is compressive in the longitudinal direction and tensile in the transverse direction. This stress accentuates the barrier for the electrons to jump from one lamina to the other. After curing and subsequent cooling, heating will decrease the thermal stress. Both the thermal stress and the curing stress contribute to the residual interlaminar stress. Therefore, the higher the curing pressure, the larger the fiber volume fraction, the greater the CTE mismatch between the crossply laminae, the greater the residual interlaminar stress, and the higher is the activation energy, as shown in Table II. Besides the residual stress, thermal expansion can also affect contact resistance by changing the contact area. However, calculation shows that the contribution of thermal expansion is less than one-tenth of the observed change in contact resistance with temperature. The effect of the extent of cure on the activation energy has not been investigated.

TABLE II Activation energy for various carbon fiber epoxy-matrix composites. The standard deviations are shown in parentheses

Composite configuration	Curing pressure (MPa)	Composite thickness (mm)	Contact resistivity ρ_{co} (Ω m^2)	Activation energy (kJ/mol)		
				Heating at 0.15 °C/min	Heating at 1 °C/min	Cooling at 0.15 °C/min
Crossply	0	0.36	7.3×10^{-5}	1.26 (2×10^{-3})	1.24 (3×10^{-3})	1.21 (8×10^{-4})
	0.062	0.32	1.4×10^{-5}	1.26 (4×10^{-3})	1.23 (7×10^{-3})	1.23 (4×10^{-3})
	0.13	0.31	1.8×10^{-5}	1.62 (3×10^{-3})	1.57 (4×10^{-3})	1.55 (2×10^{-3})
	0.19	0.29	5.4×10^{-6}	2.14 (3×10^{-3})	2.15 (3×10^{-3})	2.13 (1×10^{-3})
	0.33	0.26	4.0×10^{-7}	11.4 (4×10^{-2})	12.4 (8×10^{-2})	11.3 (3×10^{-2})
Unidirectional	0.42	0.23	2.9×10^{-5}	1.02 (3×10^{-3})	0.82 (4×10^{-3})	0.78 (2×10^{-3})

The electron jump primarily occurs at points where direct contact occurs between fibers of the adjacent laminae. The direct contact is possible due to the flow of the epoxy resin during composite fabrication and due to the slight waviness of the fibers, as explained in Ref. 9 in relation to the through-thickness volume resistivity of a carbon fiber epoxy-matrix composite. For a thermoplastic (polyphenylenesulfide, or PPS) matrix carbon fiber composite, the matrix flow during composite fabrication (below the melting temperature of the thermoplastic) was less than that of the epoxy, so the amount of fiber-fiber contacts between laminae was relatively low and the contact resistivity was relatively high [10].

The activation energy increased gradually with increasing curing pressure from 0 to 0.19 MPa, but increased abruptly from 2.14 to 11.4 kJ/mol (0.02 to 0.12 eV) when the curing pressure was increased from 0.19 to 0.33 MPa. The abrupt increase at high pressure is probably not totally due to the interlaminar stress abruptly increasing, but is partly due to another phenomenon that occurred at the high curing pressure of 0.33 MPa. This phenomenon has not been thoroughly investigated, but one possibility is that the pressure greatly increased the proximity of the fibers, as suggested by the abrupt drop in contact resistivity when the curing pressure was increased from 0.19 to 0.33 MPa (Table II). The proximity may allow tunneling of the electrons across the epoxy between fibers of adjacent laminae, at least at certain points with sufficient proximity. Another possibility is the pressure increasing the anisotropy of the matrix and thereby accentuating the barrier for electron jumping from one lamina to the other.

The curing pressure for the sample in the unidirectional composite configuration was higher than that of any of the crossply samples (Table II). Consequently, the thickness was the lowest. As a result, the fiber volume fraction was the highest. However, the contact resistivity of the unidirectional sample was the second highest rather than being the lowest, and its activation energy was the lowest rather than the highest. The low activation energy is consistent with the fact that there was no CTE or curing shrinkage mismatch between the two unidirectional laminae and, as a result, no interlaminar stress between the laminae. This low value supports the notion that the interlaminar stress is important in affecting the activation energy. The high contact resistivity for the unidirectional case can be explained in the following way. In the crossply samples, the pressure during curing forced the fibers of the two laminae to press on to one another and hence contact tightly. In the unidirectional sample, the fibers of one of the laminae just sank into the other lamina at the junction, so pressure helped relatively little in the contact between fibers of adjacent laminae. Moreover, in the crossply situation, every fiber at the lamina-lamina interface contacted many fibers of the other lamina, while, in the unidirectional situation, every fiber had little chance to contact the fibers of the other lamina. Therefore, the number of contact points between the two lamina was less for the unidirectional sample than the crossply samples. Fig. 3 also shows a small irreversible decrease in the room temperature contact resistivity after a heating-cooling cycle. This is mainly due to the decrease in moisture content during heating, as shown by testing specimens having various moisture contents, as attained by allowing the specimens to sit in air for different lengths of time. The irreversibility vanished when the temperature change was small (e.g., temperature changing from 20 to 100 °C). The larger the temperature change, the more significant the irreversibility. The slight irreversibility is consistent with the fact that the activation energy obtained during cooling was slightly less than that obtained during heating (Table II). Table II also shows that the heating rate essentially did not affect the activation energy.

Electrical resistance is the slope of the voltage-current curve. If this slope is negative, the resistance, at least apparently, is negative. We call this kind of resistance apparent negative resistance. Fig. 5a shows a typical current-voltage characteristic for a sample cured at 0.13 MPa. It is quite linear and has a positive slope. Fig. 5b shows that for a sample cured at 1.4 MPa. It is also quite linear but has a negative slope. For an intermediate curing pressure of 0.33 MPa, two types of current-voltage characteristics were observed (Fig. 6).

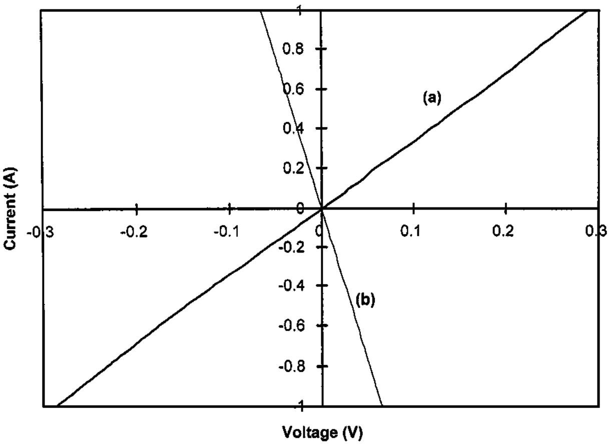

Figure 5 Typical current-voltage characteristics for epoxy-matrix composite cured at (a) 0.13 MPa (thick line), (b) 1.4 MPa (thin line).

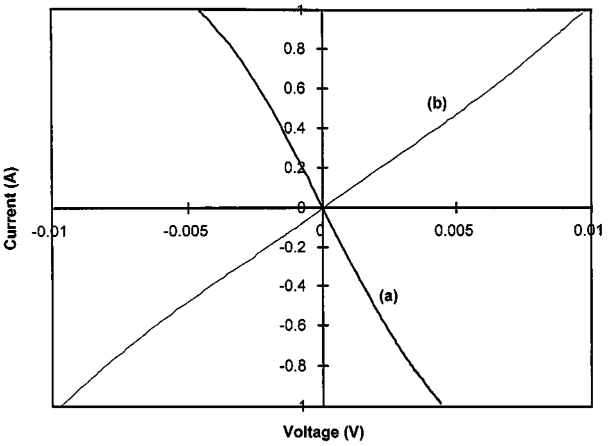

Figure 6 Two types of current-voltage characteristics for epoxy-matrix composite cured at 0.33 MPa. (a) Negative slope (thick line). (b) Positive slope (thin line).

TABLE III The relationships among apparent contact resistivity, curing pressure and current direction for carbon fiber epoxy-matrix composites

Curing pressure (MPa)	Thickness at center (mm)	Direction of current	Thickness at corner[a] (mm)	Apparent contact resistivity (Ω m^2)	Current range for resistivity calculation (A)
1.4	0.236	A to C	0.246	-4.23×10^{-6}	0–1
		A to D	0.234	-4.87×10^{-6}	0–1
		B to C	0.226	-4.83×10^{-6}	0–1
		B to D	0.226	-4.25×10^{-6}	0–1
0.33	0.284	A to C	0.284	5.11×10^{-7}	0–0.4
		A to D	0.274	-1.87×10^{-7}	0–0.4
		B to C	0.277	-2.68×10^{-7}	0–0.4
		B to D	0.282	5.32×10^{-7}	0–0.4
0.13	0.315	A to C	0.325	1.21×10^{-5}	0–1
		A to D	0.310	1.21×10^{-5}	0–1
		B to C	0.307	1.25×10^{-5}	0–1
		B to D	0.269	1.20×10^{-5}	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.

The deviation from linearity in Fig. 6 is such that the apparent resistance becomes more negative or less positive when the current is high, probably due to the enhancement of the drift current.

The apparent contact resistivities for different current directions and curing pressures are shown in Table III. 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-C and B-D directions) and partly negative (in the A-D and B-C directions). These behaviors are consistent with Figs 5 and 6.

Another interesting fact from Table 3 is that, for the samples cured at 1.4 and 0.33 MPa, the apparent contact resistivities in the A-C and B-D directions are quite close and those in the A-D and B-C directions are also quite close, whereas the resistivities in the A-C (or B-D) and B-C (or A-D) directions are quite different. For the sample cured at 0.13 MPa, all four resistivities are close. Table III 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 resistivity with the current direction is attributed to non-uniformity in the thickness within a junction. A low thickness favors an apparent negative resistance, akin to a high curing pressure favoring an apparent negative 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 an apparent negative resistance, so the resistivity does not vary with the current direction.

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. After curing and subsequent cooling, the apparent resistances are −0.0297, −0.0306, −0.0309 and −0.0296 Ω in the AC, AD, BC and BD directions respectively. As in Table III, two of these resistances (AC and BD) are close, and the other two (AD and

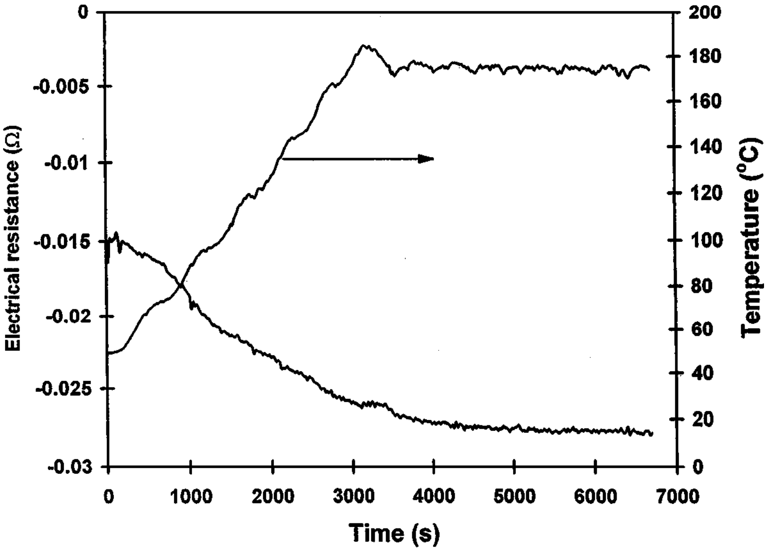

Figure 7 Variation of resistance during curing at 1.4 MPa of a two-lamina crossply epoxy-matrix composite.

BC) are also close. Though the absolute value of these resistances vary from sample to sample, that all four resistances are negative and that two (AC and BD) are close and the other two (AD and BC) are close is behavior 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. Since the volume resistance within each lamina in the through-thickness direction is positive, the total (series) through-thickness apparent 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, it becomes less positive, goes through zero and then becomes negative. After curing and subsequent cooling, it 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 through-thickness apparent 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 apparent resistance can be close to zero (e.g, $+0.0007$ Ω). Another way to attain apparent zero resistance is to adjust the curing pressure, as suggested by Table I. 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 resistance returned to the initial more negative value. Fig. 9 shows the Arrhenius plot of the logarithm (to the base 10) of the apparent 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 an apparent negative contact resistance. In Fig. 9, σ stands for the absolute value of the 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. The activation energy (energy gap) E is 0.20 kJ/mol (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. 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. In spite of the high curing pressure for the composites exhibiting apparent negative resistance, the activation energy is low. For both positive and negative resistance cases, the activation energy is that for electrons to jump from one lamina to the adjacent one. The unusually low activation energy for the negative resistance case may stem from the unusually high number of fiber-fiber contacts between adjacent laminae.

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.

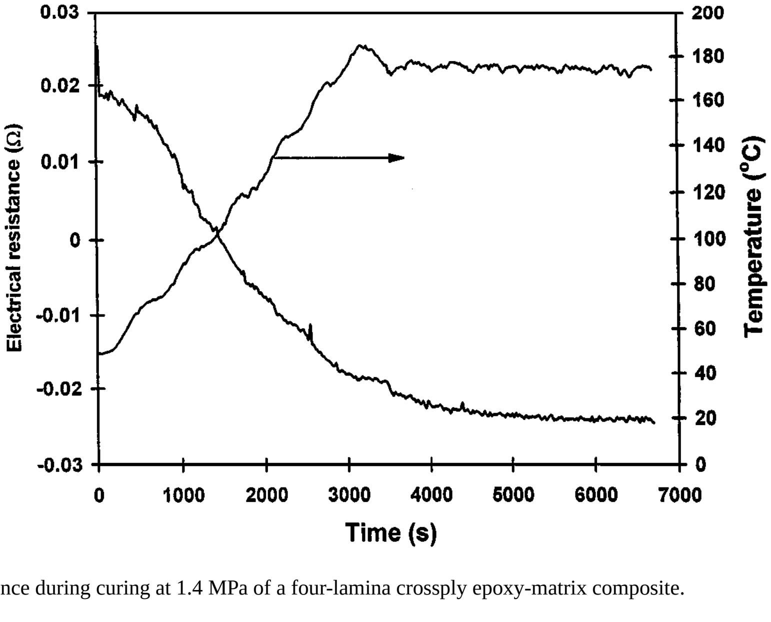

Figure 8 Variation of resistance during curing at 1.4 MPa of a four-lamina crossply epoxy-matrix composite.

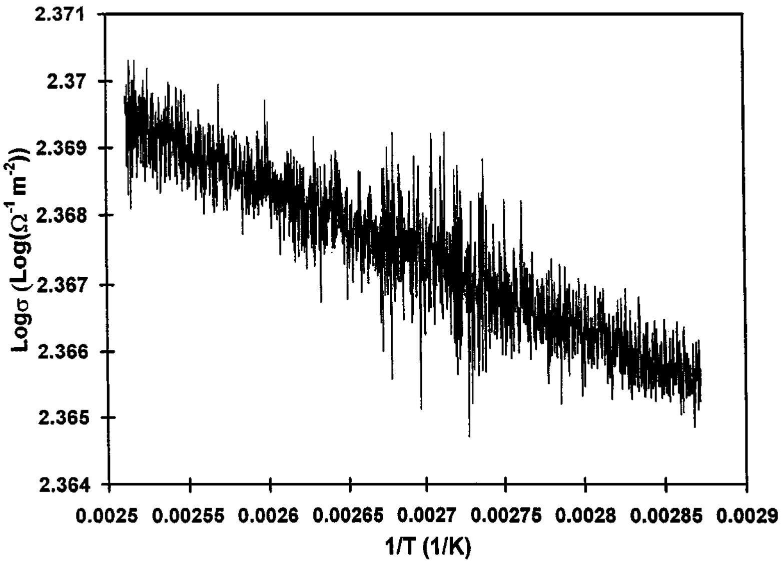

Figure 9 Arrhenius plot of the logarithm (to the base 10) of the contact conductivity versus the inverse absolute temperature for epoxy-matrix composite cured at 1.4 MPa during cooling.

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 7×7 mm junctions. Furthermore, 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 6×6 mm junction, although these were the conditions under which most results presented here were obtained.

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 (6×6 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. 1a. The contact resistance is 0.059 Ω (positive). In contrast, the apparent contact resistance (−0.13 Ω) is negative for this curing pressure (Table III).

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 7.5×10^{-8} Ω m was cut into the shape of a cross of dimensions 6×6 mm at the junction (the two-dimensional shape of Fig. 1a) and the electrical measurement depicted in Fig. 1a was conducted on it. The measured resistance was −0.0044 Ω. 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 Ω. 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.

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 6×6 mm 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. 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 III). 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.

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. If the epoxy matrix is replaced by a thermoplastic (PPS) matrix, the amount of fiber-fiber contacts is insufficient for the occurrence of apparent negative resistance [10].

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. 10.

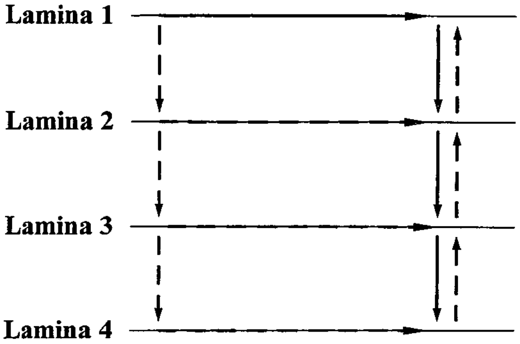

Figure 10 Schematic of a four-lamina composite illustrating current flows resulting in zero apparent resistance. The flow indicated by solid arrows occurs because of the volume resistance within a lamina in the through-thickness direction making this flow more favorable than in the case of a two-lamina composite exhibiting apparent negative resistance. The flow indicated by upward dashed arrows is the backflow.

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).

4. Applications

The decrease in resistivity with increasing temperature, as observed for crossply composites (cured at a usual pressure) in the through-thickness direction, allows the composites to serve as temperature sensors. Since a crossply two-lamina composite is a two-dimensional array of junctions, the composite is a temperature sensor array that allows the sensing of the temperature distribution. While the junctions serve as sensors, the crossply fibers serve as an x-y grid of electrical interconnections. Hence, both sensors and interconnections are built-in to the composite.

For composites cured at a high pressure, the combination of forward flow and backflow of electrons provides a current loop. An application of the current loop is in self-induction, which means that a composite laminate serves as an inductor. As inductors are important in electric circuits, the ability of a composite laminate to provide inductance adds to the versatility of structural electronics, which refer to electronics made from structural materials.

Structural electronics enable structures to be intrinsically smart, i.e., smartness attained without embedding devices in the structures. Compared to conventional electronics, structural electronics are attractive in the low materials and processing costs, mechanical ruggedness, space saving (electronics "vanished" into the structure), and absence of problems associated with heat dissipation (since electronics are spread out in the structure). Sensing and electronic circuitry are both aspects of structural electronics.

5. Conclusion

The electrical behavior of continuous carbon fiber epoxy-matrix composites in the through-thickness direction was studied by measuring the contact electrical resistivity (DC) of the interlaminar interface in the through-thickness direction, with emphasis on the effects of temperature and curing pressure.

The contact resistivity was found to decrease with increasing curing pressure and to be higher for unidirectional than crossply composites. This is because the extent of direct contact between fibers of adjacent laminae increases with increasing curing pressure and, at the same curing pressure, the fibers of adjacent laminae press on to one another much more strongly for crossply than unidirectional composites. The lower the contact resistivity, the greater is the extent of direct contact between fibers of adjacent laminae.

The activation energy for electrical conduction in the through-thickness direction was found to increase with increasing curing pressure and to be lower for unidirectional than crossply composites. This is because (i) the residual interlaminar stress increases with increasing CTE mismatch between the crossply laminae, (ii) the CTE match increases with increasing fiber volume fraction, which increases with increasing curing pressure, and (iii) the residual interlaminar stress is higher for crossply than unidirectional composites. The higher the interlaminar stress, the greater is the activation energy.

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 non-uniformity 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.

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.

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