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Interlaminar interface in carbon fiber polymer-matrix composites, studied by contact electrical resistivity measurement

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Abstract—The interlaminar interface in carbon fiber (continuous) epoxy-matrix composites was studied by measuring the contact electrical resistivity of this interface. 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 the residual interlaminar stress.

Keywords: Polymer-matrix composites; carbon fiber; interlaminar; electrical resistivity; electrical resistance; contact resistance; interface; epoxy.

1. INTRODUCTION

A polymer-matrix composite comprising layers (laminae) of continuous fibers tends to be mechanically weakest at the interface between the laminae. As a result, delamination is a common mechanism of failure in the composites. The study of the interlaminar interface has been previously performed by measuring the interlaminar shear strength (ILSS) by techniques such as the short-beam method [1], the Iospiescu method [2] and other methods [3]. Although ILSS is a valuable quantity that describes the mechanical property of the joint between laminae, it gives little information on the interfacial structure, such as the extent of direct contact (without the polymer matrix in between) between fibers of adjacent laminae and the residual interlaminar stress resulting from the anisotropy between adjacent laminae. The anisotropy is severe when the fibers in the adjacent laminae are in different

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directions, since the fibers and polymer matrix differ greatly in modulus and thermal expansion coefficient. Direct contact between fibers of adjacent laminae occurs due to the flow of the matrix during composite fabrication and the waviness of the fibers. Direct contact means that the thickness of the matrix between the adjacent fibers is so small (say, a few Å) that electrons can tunnel or hop from one fiber to the other. The presence of direct contact has been shown by the fact that the volume electrical resistivity of carbon fiber epoxy-matrix composites in the through-thickness direction is finite, even though the epoxy matrix is electrically insulating [4].

In contrast to previous work, this paper uses the contact electrical resistivity of the interlaminar interface as a quantity to describe the structure of this interface. Note that the volume electrical resistivity is a geometry-independent quantity that describes the resistivity of a three-dimensional material in a particular direction. For example, the volume resistivity of a composite in the through-thickness direction reflects both the volume resistance within each lamina in the through-thickness direction and the contact resistance at each interlaminar interface. Hence, the volume resistivity does not simply relate to the structure of the interlaminar interface. However, the contact resistivity does, since it is a geometry-independent quantity that describes the resistivity of a plane in the direction perpendicular to the plane. The volume resistivity has the unit Ω cm, whereas the contact resistivity has the unit $\Omega\,\mathrm{cm}^2$. Although previous attention has been given to the volume resistivity in the through-thickness direction [4], no previous attention has been given to the contact resistivity. 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 contact resistivity is lower when the extent of direct contact between fibers of adjacent laminae is greater. However, the contact resistivity also depends on the nature of each direct contact. This nature is reflected by the activation energy for electrons to jump from one lamina to an adjacent one. This activation energy is expected to increase when the interlaminar stress is higher. It 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 jumping of the electrons from one lamina to another is a thermally activated process, so the higher is the temperature, the higher the contact conductivity. The contact resistivity and the activation energy are quantities determined in this paper for the purpose of characterizing the interlaminar interface. These quantities have not been used previously for studying the interlaminar interface of any composite.

2. EXPERIMENTAL

Two laminae of unidirectional carbon fiber epoxy-matrix prepregs (Table 1) 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 mm × 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. After the reheating and cooling, 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

Table 1.
Carbon fiber and epoxy matrix properties (according to ICI Fiberite)

10E-Torayca T-300 (6K) untwisted, UC-309 sized	
Diameter	7 μm
Density	1.76 g/cm^3
Tensile modulus	221 GPa
Tensile strength	3.1 GPa
976 Epoxy	
Process temperature	350°F (177°C)
Maximum service temperature	350°F (177°C) dry 250°F (121°C) wet
Flexural modulus	3.7 GPa
Flexural strength	138 MPa
T_g	232°C
Density	1.28 g/cm^3

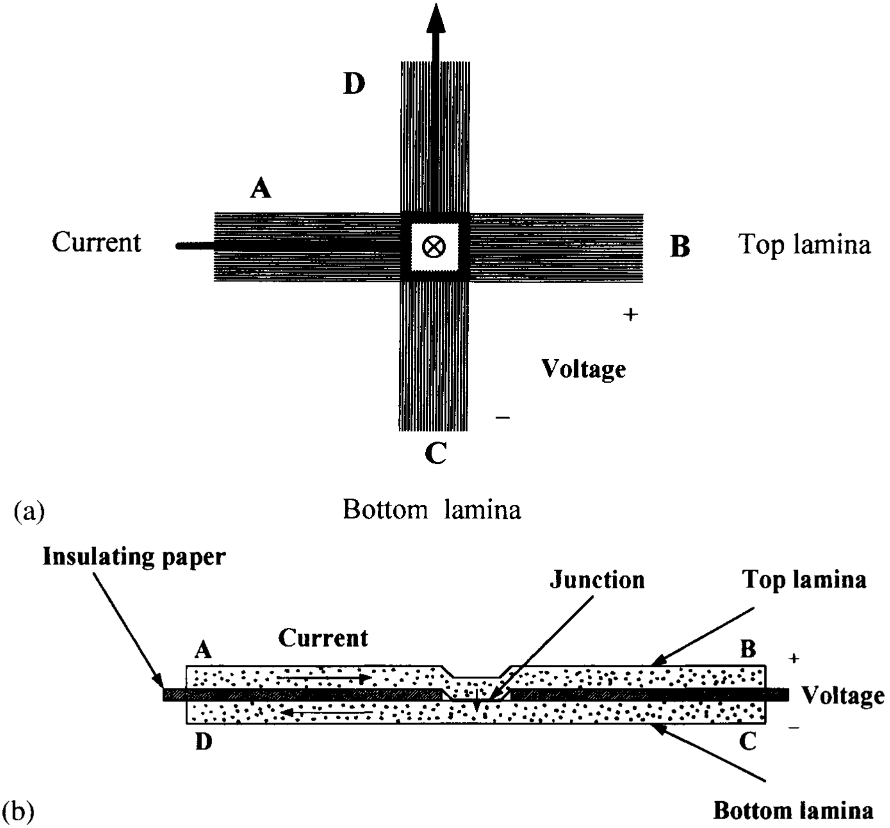

Figure 1. Composite configurations for testing contact resistivity as a function of temperature. (a) Crossply. (b) Unidirectional.

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.

3. RESULTS AND DISCUSSION

The current–voltage characteristic is linear for all samples studied. Figure 2 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. 3. From the slope (negative) of the Arrhenius plot, which is quite linear, the activation energy can be calculated by using the equation

$$\text{slope} = -\frac{E}{2.3k}, \tag{1}$$

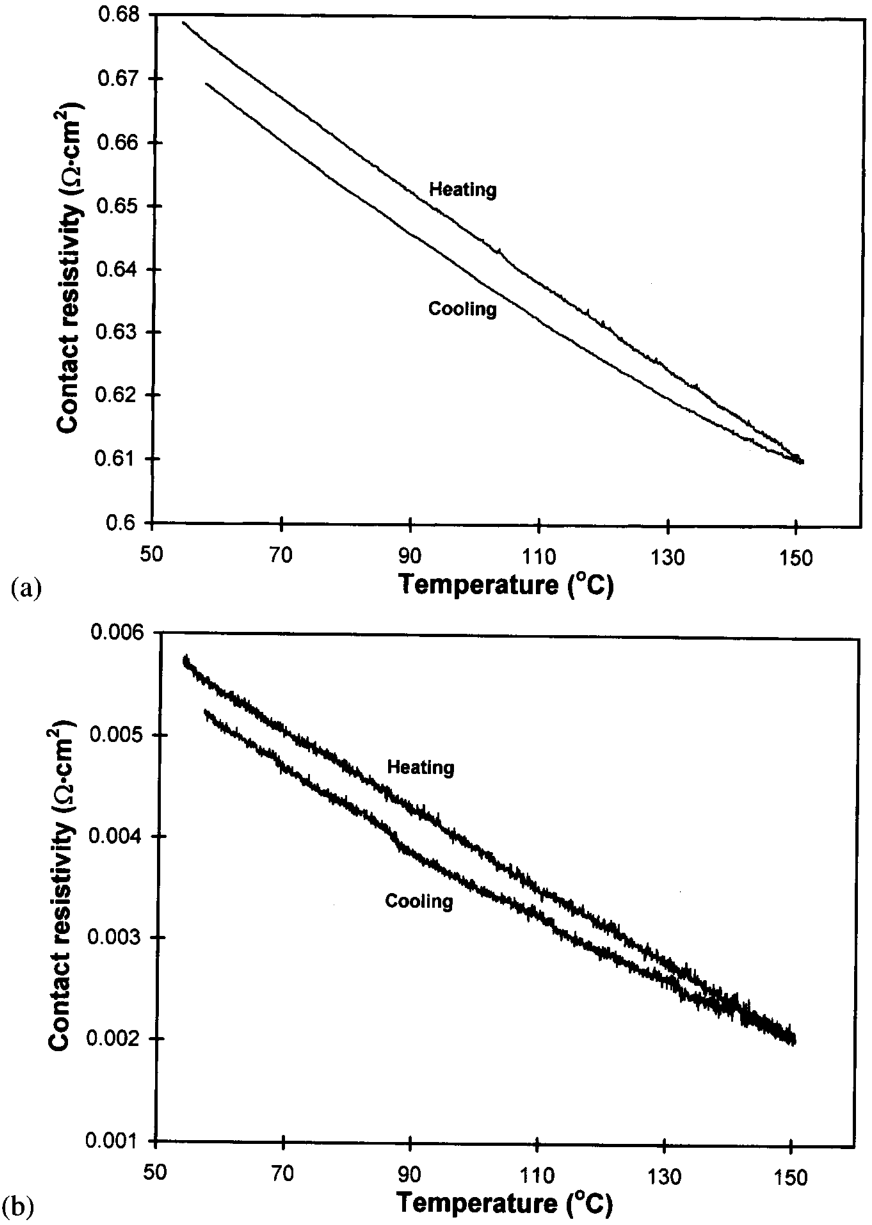

Figure 2. Variation of contact electrical resistivity with temperature during heating and cooling at 0.15°C/min (a) for sample made without any curing pressure and (b) for sample made with a curing pressure 0.33 MPa.

where k is the Boltzmann's constant, T is the absolute temperature (in K), and E is the activation energy. 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 an electron jumping from one lamina to the other. Electronic

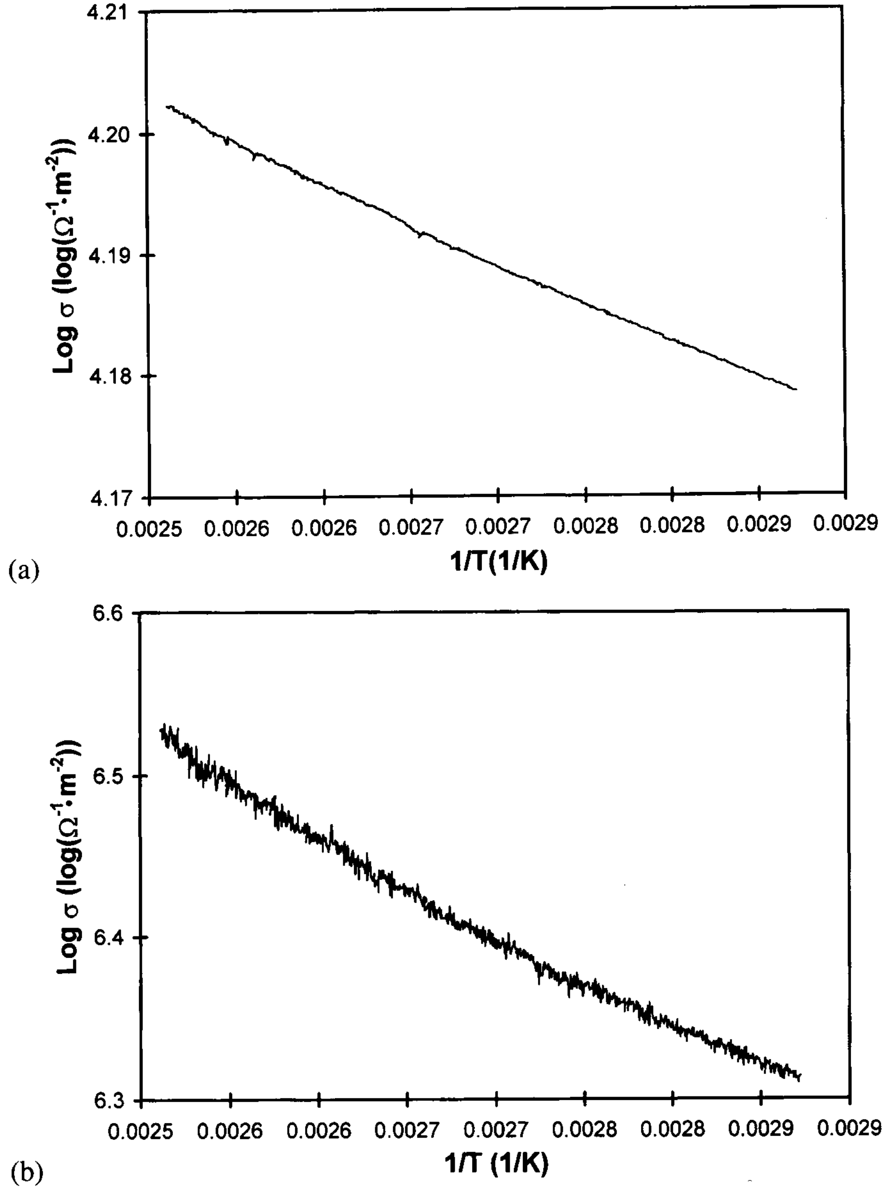

Figure 3. Arrhenius plot of log contact conductivity *vs.* inverse absolute temperature during heating at 0.15°C/min (a) for sample made without any curing pressure and (b) for sample made with curing pressure 0.33 MPa.

excitation across this energy enables conduction in the through-thickness direction. This activation phenomenon is common in the electrical conduction of composite materials with an insulating matrix and an electrically conducting filler (whether particles or fibers). Based on volume resistivity measurement, an activation energy in the range from 0.060 to 0.069 eV has been previously reported for short carbon fiber polymer-matrix composites [5]. Direct measurement of the contact resistivity is impossible for the short fiber composites.

A slightly concave shape is present in the Arrhenius plots obtained during heating as well as cooling (Fig. 3). 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 origin of the curvature is presently not clear.

The activation energies, thicknesses and room temperature contact resistivities for samples made at different curing pressures and composite configurations are shown in Table 2. 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 2 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 while the carbon fibers essentially do not, so a longitudinal compressive stress will develop in the fibers. For carbon fibers, the modulus in the longitudinal direction is much higher than that in the transverse direction. Thus, the overall shrinkage in the longitudinal direction tends to be less than that in the transverse direction. Therefore, there will be a residual interlaminar stress in the two crossply layers in a given direction. This stress accentuates the barrier for the electrons to jump from one lamina to the other. The greater the residual interlaminar stress, the higher the barrier, which is the activation energy. After curing and subsequent cooling, heating will decrease the thermal stress, due to the CTE (coefficient of thermal expansion) mismatch between fibers and matrix. 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 residual interlaminar stress, and the higher the activation energy, as shown in Table 2.

The activation energy increased gradually with increasing curing pressure from 0 to 0.19 MPa, but increased abruptly from 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 due to the interlaminar stress abruptly increasing, but is probably due to another phenomenon that occurred at the high curing pressure of 0.33 MPa. This phenomenon has not been investigated, but one 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 2). 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

Table 2.
Activation energy for various composites. The standard deviations are shown in parentheses

Composite configuration	Curing pressure (MPa)	Composite thickness (mm)	Contact resistivity ρ_{co} ($\Omega\,cm^2$)	Activation energy (eV)		
				Heating at 0.15°C/min	Heating at 1°C/min	Cooling at 0.15°C/min
Crossply	0	0.36	0.73	0.0131 (2×10^{-5})	0.0129 (3×10^{-5})	0.0125 (8×10^{-6})
	0.062	0.32	0.14	0.0131 (4×10^{-5})	0.0127 (7×10^{-5})	0.0127 (4×10^{-5})
	0.13	0.31	0.18	0.0168 (3×10^{-5})	0.0163 (4×10^{-5})	0.0161 (2×10^{-5})
	0.19	0.29	0.054	0.0222 (3×10^{-5})	0.0223 (3×10^{-5})	0.0221 (1×10^{-5})
	0.33	0.26	0.0040	0.118 (4×10^{-4})	0.129 (8×10^{-4})	0.117 (3×10^{-4})
Unidirectional	0.42	0.23	0.29	0.0106 (3×10^{-5})	0.0085 (4×10^{-5})	0.0081 (2×10^{-5})

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. Figure 2 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 2). Table 2 also shows that the heating rate essentially did not affect the activation energy.

4. CONCLUSION

The interlaminar interface in carbon fiber (continuous) epoxy-matrix composites was studied by measuring the contact electrical resistivity of this interface.

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 the residual interlaminar stress increases with increasing fiber volume fraction, which increases with increasing curing pressure, and the residual interlaminar stress is higher for crossply than unidirectional composites. The higher the activation energy, the greater is the interlaminar stress.

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