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Interlaminar interface relaxation upon heating carbon fiber thermoplastic-matrix composite, studied by contact electrical resistivity measurement

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Abstract—The interlaminar interface of a crossply carbon fiber thermoplastic-matrix composite was found to relax upon heating at and above the glass transition temperature of the matrix. The relaxation caused the contact electrical resistivity of the interface to increase gradually and irreversibly.

Keywords: Composite; polymer; thermoplastic; nylon; carbon fiber; electrical resistivity; contact resistivity; interlaminar.

1. INTRODUCTION

A structural polymer-matrix composite typically contains continuous fibers as reinforcement. The fibers are often in the form of laminae, which are consolidated to form a laminate. The interface between adjacent laminae (referred to as the interlaminar interface) is the weak link where damage most often occurs.

The structure and properties of the interlaminar interface are affected by the composite fabrication conditions. For example, it has been shown that the contact electrical resistivity of the interface decreases with increasing pressure used in composite fabrication for the case of a crossply carbon fiber composite with an epoxy (a thermoset) matrix [1]. This effect is due to the increased extent of squeezing of the resin out of the laminate as the composite curing pressure increases, and the consequent increased degree of contact between fibers of adjacent laminae. In the case of a thermoplastic-matrix composite, resin squeezing does not occur, since a resin is not involved. However, a thermoplastic matrix softens upon heating, due to the glass transition. Thus, heating can affect the interlaminar interface of a thermoplastic-matrix composite. Although the thermal degradation [2–6] and thermal analysis [7–9] of polymer-matrix composites have been topics of numerous studies, the effect of the glass transition on the interlaminar interface of a thermoplastic-matrix composite has received little prior attention, if any. This is because of the difficulty of examining the interface in real time during temperature variation.

The interlaminar interface is conventionally studied by measuring the interlaminar shear strength (ILSS) using techniques such as the short-beam method [10], the Iospiescu method [11] and other methods [12]. 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. The anisotropy is severe when the fibers in the adjacent laminae are in different 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 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 [13].

The contact electrical resistivity of the interlaminar interface can be used as a quantity to describe the structure of the interlaminar interface, as shown for an epoxy-matrix carbon fiber composite [1]. 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 $\Omega \cdot \mathrm{cm}$ whereas the contact resistivity has the unit $\Omega \cdot \mathrm{cm}^2$.

For a composite with electrically conducting fibers, such as carbon fibers, and an electrically insulating matrix, such as a polymer, 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 is the contact conductivity.

By using contact electrical resistivity measurement to monitor the interlaminar interface in real time during temperature variation, this paper provides the observation that the interlaminar interface of a thermoplastic-matrix composite relaxes upon heating at and above the glass transition temperature. The relaxation causes the contact resistivity to increase irreversibly.

2. EXPERIMENTAL METHODS

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

The prepreg was used as-received. Prepreg strips 3 mm in width were placed on one another at an angle of 90° in a cross-shaped steel mold cavity lined with a PTFE film for electrical insulation, so that the overlap area was 3 × 3 mm, as shown in Fig. 1. During formation of the interlaminar interface at the overlap area, the temperature was raised from 20 to 260°C (T_m = 220°C) at a heating rate of 5°C/min and then held at 260°C for 30 min. After that, the specimen was furnace cooled to room temperature. Throughout the heating and cooling, pressure (0.89, 1.33 and 1.78 MPa, as provided by steel plates of known weights) was applied through a 3-cm long cross-shaped steel plate, which was electrically insulated from the prepreg strips by a PTFE film.

An electrical contact in the form of silver paint in conjunction with copper wire was applied to each of the four legs of the crossed prepreg strips (Fig. 1). In the

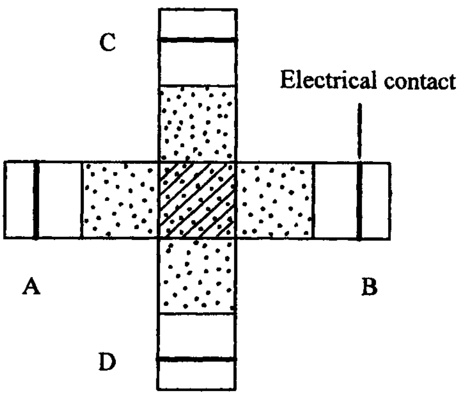


Figure 1. Sample configuration. The dotted cross-shaped region is where pressure was applied during composite fabrication. The square shaded region is the interlaminar interface.

four-probe method of DC electrical resistance measurement, two of the electrical contacts (A and D in Fig. 1) were for passing current; the remaining two contacts (B and C) were for measuring voltage. The voltage divided by the current gave the contact resistance of the joint. The resistance multiplied by the contact area gave the contact resistivity. A Keithley 2001 multimeter was used.

During the contact electrical resistivity measurement, the specimen was heated and cooled between room temperature and 95°C at a rate of 0.25°C/min. Four specimens were tested for each composite fabrication pressure.

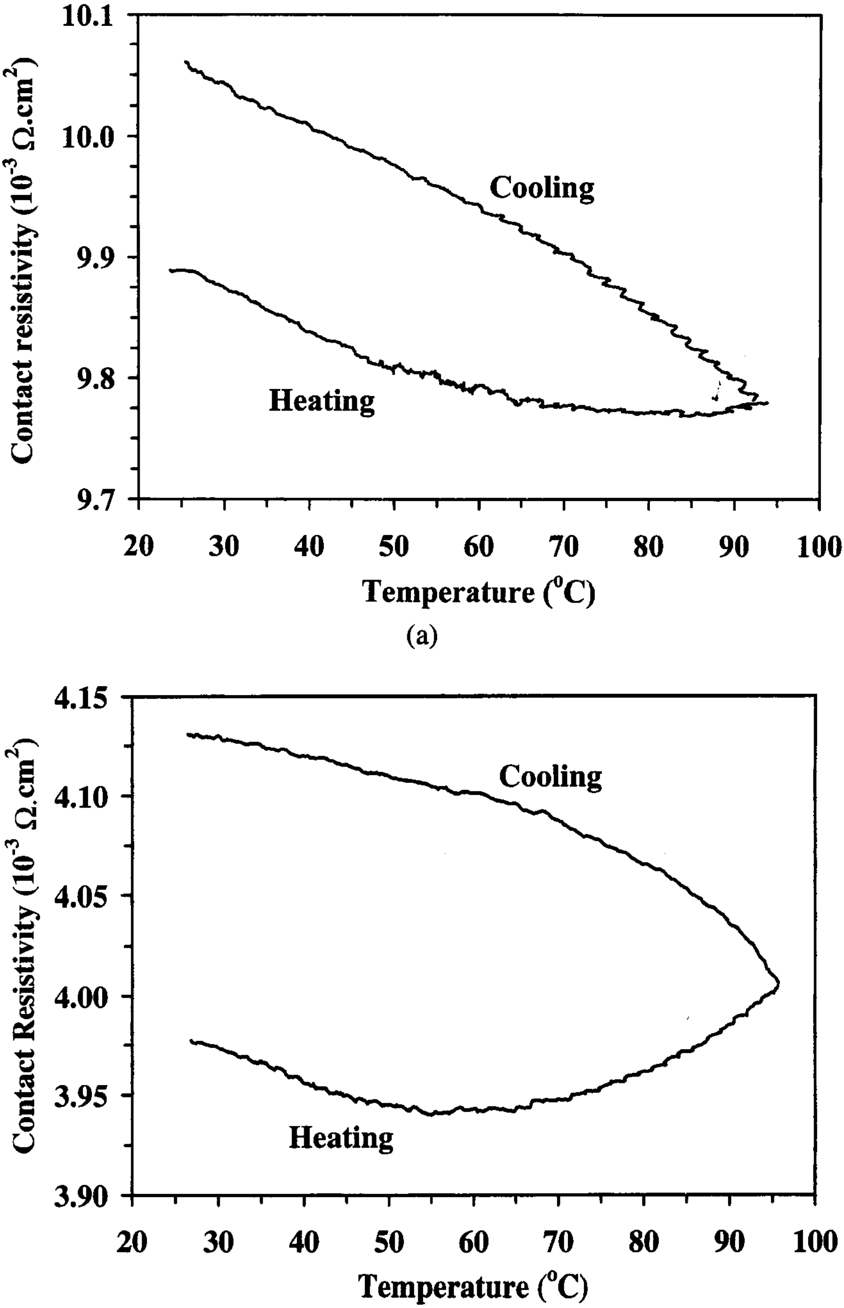
To investigate the effect of the composite fabrication pressure on a property of the composite at room temperature, the coefficient of thermal expansion (CTE) was measured in the through-thickness direction of a 16-ply crossply composite fabricated as described above. The measurement was performed using a thermomechanical analyzer (TMA7, Perkin-Elmer Corp., Norwalk, CT). The temperature was varied from 25 to 45°C at a rate of 1°C/min. The specimen size was 6 × 3 mm. Three specimens were tested for each composite fabrication pressure.

3. RESULTS AND DISCUSSION

The current–voltage characteristic is linear for all samples studied. Figure 2 shows the variation of the contact resistivity with temperature during heating and subsequent cooling for different composite fabrication pressures. The contact resistivity decreases with increasing temperature, such that the decrease becomes more gradual as the temperature increases past about 40°C. There is even a tendency for the resistivity to increase with temperature, as clearly shown by the composite fabricated at the high pressure of 1.78 MPa. This effect is attributed to relaxation of the interlaminar interface. Upon subsequent cooling, the resistivity increases further; the increase upon cooling is more abrupt in the high temperature regime, due the continuation of the relaxation phenomenon, which starts in the heating portion. Hence, the resistivity increase during heating is irreversible, indicating the irreversibility of the relaxation phenomenon that occurs above the glass transition temperature. This phenomenon is absent in the epoxy matrix case [1], due to the absence of a glass transition.

Because of the combined effects of the interface relaxation phenomenon, which causes the resistivity to increase upon heating, and the electron jump activation phenomenon, which causes the resistivity to decrease upon heating, the Arrhenius plots of log conductivity versus reciprocal absolute temperature are far from being linear and the activation energy cannot be determined.

The contact resistivity before heating is $(9.90 \pm 0.15) \times 10^{-3}$, $(4.90 \pm 0.15) \times 10^{-3}$ and $(4.0 \pm 0.2) \times 10^{3}$ $\Omega \cdot \mathrm{cm}^{-2}$ for composite fabrication pressures of 0.89, 1.33 and 1.78 MPa, respectively. This means that an increase in fabrication pressure causes the extent of contact between fibers of adjacent laminae to increase. As a consequence, the effect of interface relaxation on the contact resistivity is larger when the fabrication pressure is higher.



(b)

Figure 2. Variation of the contact electrical resistivity with temperature during heating and subsequent cooling for composites fabricated at (a) 0.89 MPa and (b) 1.78 MPa.

The thermal expansion increases linearly with temperature and the CTE is the same during heating and cooling. The CTE is $(8.6 \pm 0.3) \times 10^{-5}$, $(7.4 \pm 0.3) \times 10^{-5}$ and $(6.9 \pm 0.3) \times 10^{-5}/°C$ for composite fabrication pressures of 0.89, 1.33 and 1.78 MPa, respectively. This trend means that an increase in the extent of contact between fibers of adjacent laminae is associated with a decrease in the CTE. Thus, the structure of the interlaminar interface affects the through-thickness CTE of the composite.

The relaxation of the interlaminar interface occurs at temperatures at and above the glass transition temperature of the thermoplastic matrix. It results in the decrease of the number of contacts between fibers of adjacent laminae, and thus an irreversible increase in the contact electrical resistivity of the interface. This relaxation phenomenon takes time, as shown by its continuation during cooling subsequent to heating at 0.25°C/min.

4. CONCLUSION

The interlaminar interface of a crossply carbon fiber thermoplastic-matrix composite was found to relax upon heating at and above the glass transition temperature of the matrix. The relaxation caused the contact electrical resistivity of the interface to increase gradually and irreversibly, due to the decrease in the extent of contact between fibers of adjacent laminae. A higher composite fabrication pressure caused the extent of contact to be higher, thereby increasing the extent of contact resistivity increase upon relaxation.

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REFERENCES

1. S. Wang and D. D. L. Chung, *Compos Interfaces* **6** (6), 497 (1999).
2. C. T. Herokovich and M. Q. Hyer, *Engineering Fracture Mechanics* **25** (5–6), 779 (1985).
3. O. Allix, N. Bahlouli, P. Ladeveze and L. Ferret, *Damage Mechanics in Composites: American Society of Mechanical Engineers* **185**, 21 (1994).
4. X. Huang, J. W. Gillespie, Jr. and F. R. Eduljee, *Composites Part B: Engineering* **28B** (4), 419 (1997).
5. S. Wang, Z. Mei and D. D. L. Chung, *Int. J. Adh. Adh.* **21** (ER6), 465 (2001).
6. S. Wang and D. D. L. Chung, *Polym. Polym. Compos.* **9** (2), 135 (2001).
7. D. D. L. Chung, *Thermochim. Acta* **364**, 121 (2000).
8. Z. Mei and D. D. L. Chung, *Polym. Polym. Compos.* **8** (5), 319 (2000).
9. Z. Mei and D. D. L. Chung, *Thermochim. Acta* **369** (2), 135 (2001).
10. ASTM Standard, D 2344-84, 43 (1995).
11. G. Zhou, E. R. Green and C. Morrison, *Compos. Sci. Tech.* **55** (2), 187 (1995).

12. S. L. Iyer, C. Sivaramakrishnan and C. Young, in: *Proc. 34th Int. SAMPE Symp.* SAMPE, Covina, CA, p. 2172 (1989).
13. X. Wang and D. D. L. Chung, *Polym. Compos.* **18** (6), 692 (1997).