Thermoplastic Matrix Phase Transitions in a Carbon Fiber Composite, Studied by Contact Electrical Resistivity Measurement of the Interface Between Two Unbonded Laminae

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Measurement of the contact electrical resistivity of the interface between two unbonded laminae of a continuous carbon fiber thermoplastic (nylon-6) matrix composite during heating provides a method of thermal analysis that is sensitive to the glass transition and melting of the thermoplastic matrix. The phase transitions result in peaks in the resistivity, due to matrix molecular movement.

INTRODUCTION

A thermoplastic material undergoes phase transitions, such as the glass transition and melting, upon heating (1-6). Such transitions affect not only the properties of the polymer, but also those of the corresponding polymer-matrix composite.

Of particular interest are structural composites involving continuous carbon fibers as the reinforcement, as these composites exhibit high strength, high modulus and low density, thus making them useful for lightweight structures. Moreover, thermoplastic-matrix composites are advantageous compared to thermoset-matrix composites in their toughness.

Based on the correlation between calorimetry and electrical resistivity results, we have reported that the phase transitions (glass transition and melting) of a thermoplastic matrix are accompanied by molecular movements that disturb the carbon fibers, thereby increasing the volume electrical resistivity of the carbon fiber thermoplastic-matrix composite in the fiber direction (7, 8). In other words, the resistivity measurement provides a means of detecting the phase transitions. The method involves simple equipment and is applicable to large composite components.

In this paper, the work was extended by measuring the contact electrical resistivity of the interface between two unbonded laminae, rather than the volume resistivity of a lamina in the fiber direction. The contact resistivity is governed by the number of contacts between fibers of adjacent laminae. The phase transitions of the thermoplastic matrix are expected to affect significantly the number of contacts, thereby allowing the contact resistivity to be a sensitive indicator of the occurrence of a phase transition.

Previous work on the measurement of the contact electrical resistivity of composite laminae was limited to the bonded interface, namely, that in a carbon fiber epoxy-matrix composite after composite fabrication by lamination (9, 10). The contact resistivity was observed to decrease reversibly with increasing temperature, owing to the activation energy involved in the jump of an electron from one lamina to another. However, because the epoxy used was a thermoset, no phase transition occurred as the temperature was varied. In contrast, this work investigates the unbonded interface for the purpose of thermal analysis.

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°C–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 and after annealing in air at 100°C, 180°C and 200°C for 5 h, followed by furnace cooling to room temperature. Two to three specimens were tested for each annealing condition, using the testing method described below, in order to ensure reproducibility of the results reported here.

Prepreg strips of length 5 cm and width 1 cm 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 1 cm × 1 cm, as shown in *Fig. 1*. A pressure of 4.4 ×

10^3 Pa was applied through a 3-cm-long cross-shaped steel plate, which was electrically insulated from the prepregs by a PTFE film. The strips were not bonded together.

An electrical contact in the form of silver paint in conjunction with copper wire was applied at each of the four legs of the crossed prepreg strips (*Fig. 1*). Two of the electrical contacts (A and D in *Fig. 1*) are for passing current; the remaining two contacts (B and C) are for measuring voltage. The current flowed from current probe A along one lamina, turned to the through-thickness direction and flowed through the junction from one lamina to the other, and then turned direction again to flow along the other lamina toward current probe D. The voltage between probes B and C gave the voltage across the junction. The potential at B was higher than that of C since the current flowed from A to D. The voltage divided by the current gives the contact resistance of the junction. The contact resistance multiplied by the junction area gives the contact resistivity. This constitutes the four-probe method of DC electrical resistance measurement. A Keithley 2001 multimeter was used.

During the electrical resistance measurement, samples as illustrated in *Fig. 1* were heated from 25°C to 350°C at a heating rate of 0.5°C/min, while a constant pressure of 4.4×10^3 Pa was applied. The heating was not for bonding, but for thermal analysis in the form of electrical resistance measurement. However, after the heating (up to 350°C), bonding was found to have occurred.

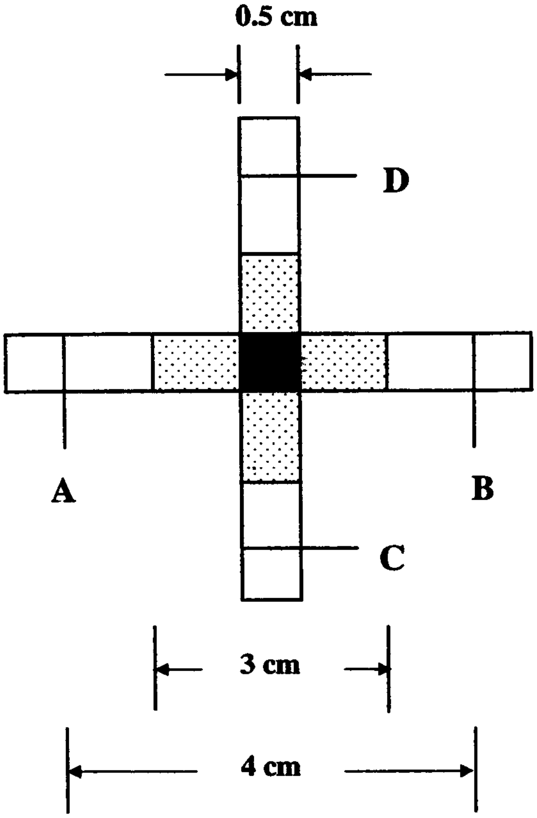

Fig. 1. Sample configuration. The dotted cross-shaped region is where pressure was applied. The square shaded region is the interface under examination.

RESULTS AND DISCUSSION

Figure 2 shows the fractional change in contact resistivity for the as-received prepreg during heating. Two peaks were observed. The onset temperature of the first peak was 50°C and that of the second peak was 215°C. Both temperatures were lower than the corresponding temperatures of 80°C and 220°C obtained from volume resistance measurement in the fiber direction (7). As in Ref. 7 (which showed the correlation between resistance and differential scanning calorimetry results), the first peak is attributed to matrix molecular movement above T_g; the second peak is attributed to matrix molecular movement above T_m. Because the molecular movement above T_g is less drastic than that above T_m, the first peak is much smaller than the second one. Since T_g is known to be 40°C–60°C for nylon-6, the contact resistance measurement of this work allows more accurate determination of T_g than the volume resistance measurement of Ref. 7.

In *Fig. 2*, the contact resistivity baseline decreased with increasing temperature. This is attributed to the gradual process of bonding, which occurs during heating. In contrast, the baseline of the volume resistance in the fiber direction does not change much with temperature (7).

Figures 3–5 show the effect of the annealing temperature. After annealing at 100°C for 5 h (*Fig. 3*), the height of the peak due to molecular movement above T_g decreased. This is attributed to the increase of the degree of crystallinity due to annealing. Because the crystalline portion has constraint on the molecular mobility, the higher the degree of crystallinity, the less is the possibility of molecular movement above T_g. Annealing at 100°C for 5 h had little effect on the melting behavior of the nylon-6 matrix; this is consistent with the DSC results (7). When the annealing temperature was increased to 180°C (*Fig. 4*), the peak due to molecular movement above T_g disappeared and the height of the peak due to molecular movement above T_m decreased. When the annealing temperature was further increased to 200°C (*Fig. 5*), the height of the peak due to molecular movement above T_m decreased even further. This is attributed to the increase of the extent of thermal degradation due to annealing at a high temperature (≥ 180°C). The degradation resulted in less molecular movement above T_m.

CONCLUSION

Measurement of the contact electrical resistivity of the interface between two unbonded laminae of a continuous carbon fiber thermoplastic (nylon-6) matrix composite during heating provides a method of thermal analysis which is sensitive to T_g and T_m of the

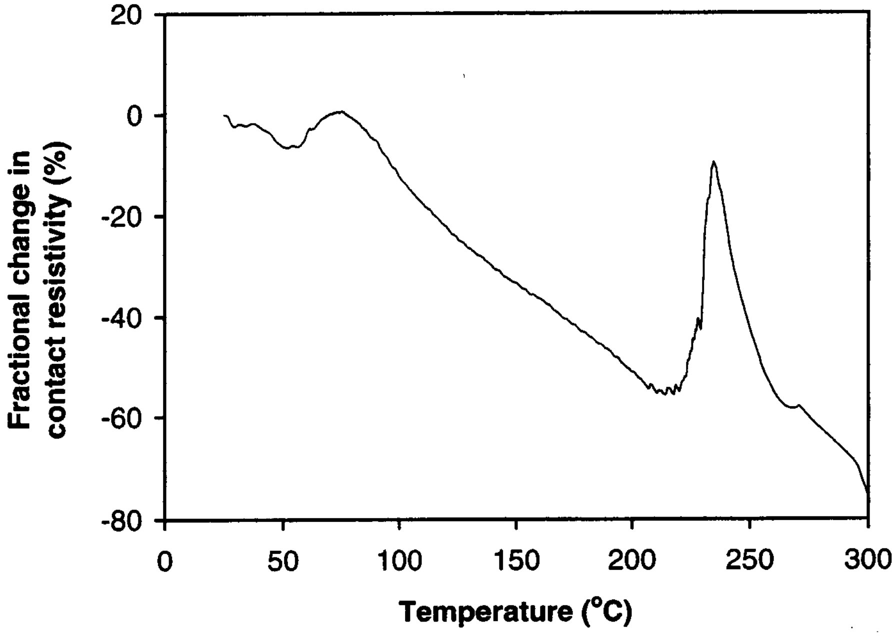

Fig. 2. Fractional change in contact resistivity vs. temperature during heating for as-received prepregs.

thermoplastic matrix. Both phase transitions of the matrix result in peaks in the plot of resistivity vs. temperature, due to the matrix molecular movement causing the number of contacts between fibers of the adjacent laminae to decrease. The T_m peak is larger than the T_g peak. This method gives more accurate determination of T_g than the method involving measurement of the volume resistivity of a lamina in the fiber direction. However, the contact resistivity baseline decreases significantly with increasing temperature, owing to the gradual occurrence of bonding. In contrast, the volume resistivity baseline does not change much with temperature.

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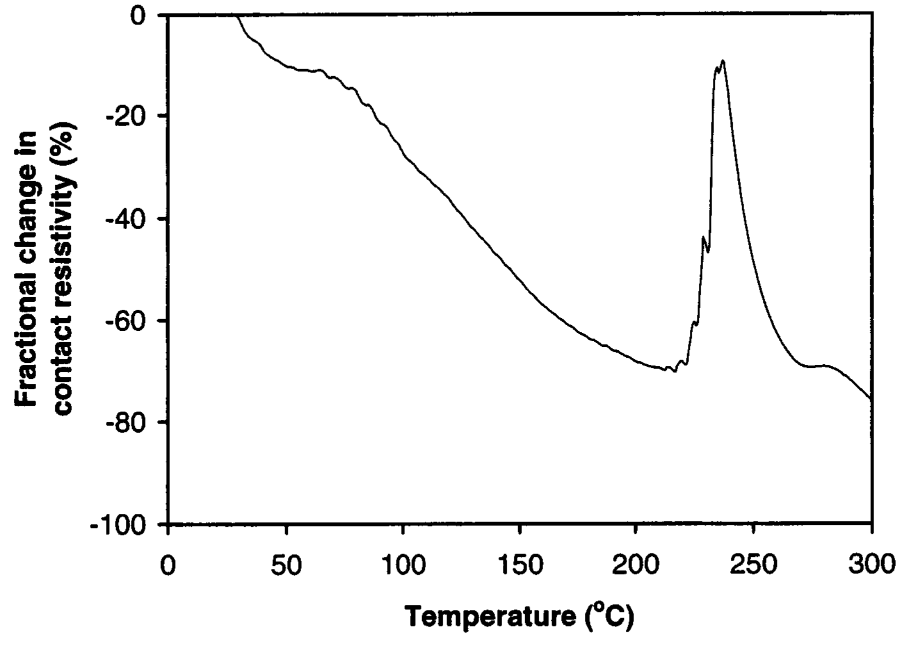

Fig. 3. Fractional change in contact resistivity vs. temperature during heating for prepregs that had been annealed at 100°C for 5 h.

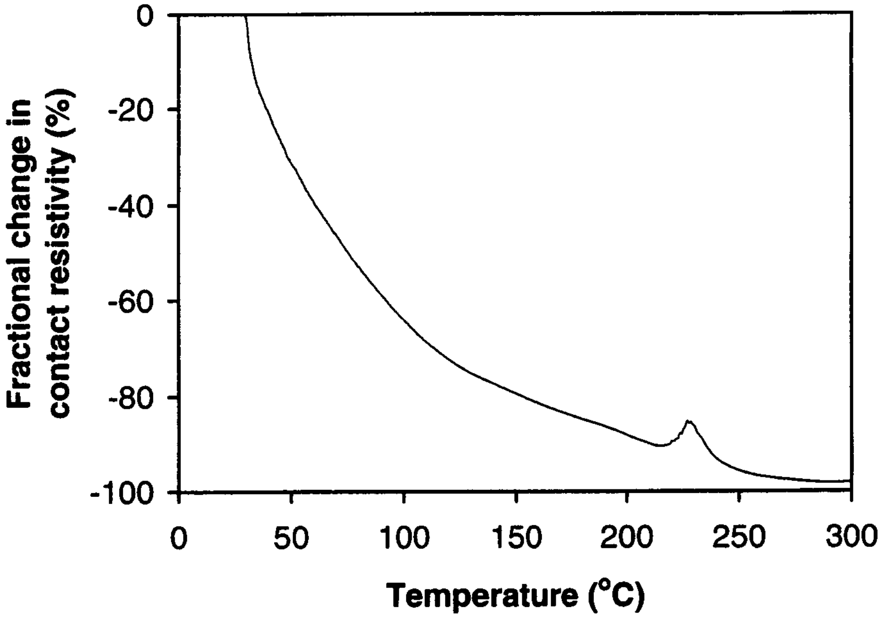

Fig. 4. Fractional change in contact resistivity vs. temperature during heating for prepregs that had been annealed at 180°C for 5 h.

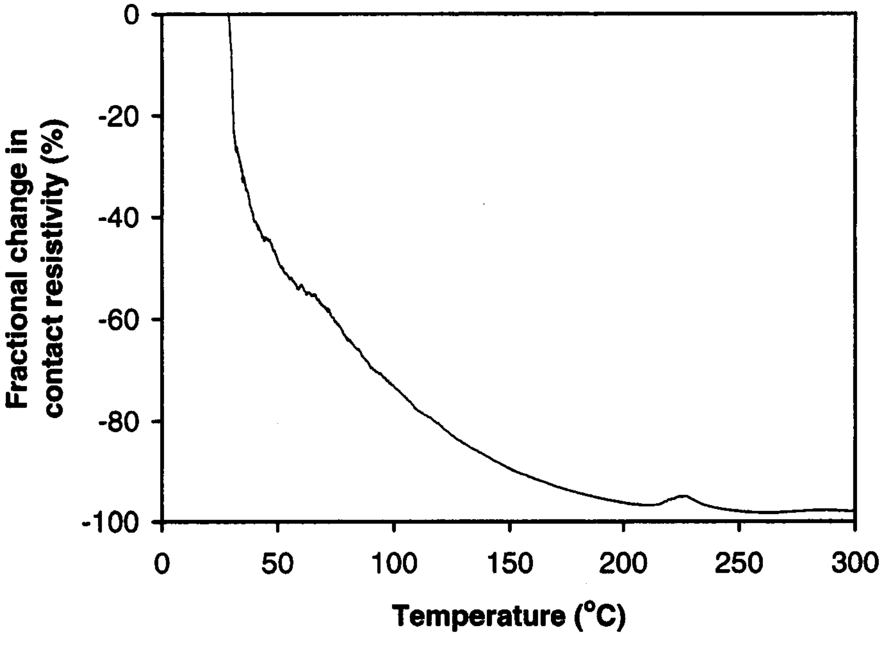

Fig. 5. Fractional change in contact resistivity vs. temperature during heating for prepregs that had been annealed at 200°C for 5 h.

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