

# Effect of Heating on the Structure of Carbon Fiber Polyphenylenesulfide-Matrix Composite, as Studied by Electrical Resistance Measurement

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Heating and cooling were found to affect the structure of carbon fiber polyphenylenesulfide-matrix composites, as shown by their effects on the DC electrical resistance of the composite in the fiber direction. Matrix flow during first heating above  $T_g$  and thermal stress buildup during cooling in any thermal cycle caused the resistance to increase, whereas isothermal crystallization at 180°C caused the resistance to decrease. Thermal stress buildup was reversible upon thermal cycling. Prior annealing at 180°C diminished the matrix flow because of improved fiber-matrix bond, and it increased the matrix crystallinity. Annealing at 180°C for 15 h or more was sufficient to eliminate the matrix flow.

## INTRODUCTION

Continuous carbon fiber polymer-matrix composites are widely used for lightweight structures due to their high strength, high modulus and low density. The dominant polymer matrix used is epoxy—a thermoset. However, thermoplast matrices are increasingly used, due to their higher ductility compared to thermoset matrices. On the other hand, a thermoplast softens upon heating above the glass transition temperature ( $T_g$ ), whereas a thermoset does not soften upon heating. Thus, the effect of heating on the structure of thermoplast-matrix composites is of concern. The structural aspects of concern include the softening and crystallization of the thermoplast and their effects on the fiber alignment and waviness and on the fiber-matrix interface. Previous work has focused on the use of calorimetry to monitor the progress of crystallization of the thermoplast (1–4, 6), although rheological measurements (3), microscopy (4, 7), infrared spectroscopy (5), X-ray diffraction (5) and electron spin resonance (5) have also been used. Most of these techniques are much more sensitive to the polymer than the fibers. A complementary technique that has not been previously used for this purpose is electrical resistance measurement. Because carbon fibers are much more conductive than the polymer matrix, electrical resistance measurement is more sensitive to the fibers than the polymer matrix. By using this method, we have obtained new information on the effect of heating on the structure of carbon fiber thermoplast-matrix composites.

The thermoplast chosen for this work is polyphenylenesulfide (PPS), because of its combination of excellent environmental, mechanical, and thermal properties (3). Moreover, the tendency of PPS to crystallize (4) adds to the importance of studying the effect of heating.

The experimental observation in this work on carbon fiber PPS-matrix composite using electrical resistance measurement pertains to the flow of PPS during initial temperature increase above  $T_g$ , the crystallization of PPS during isothermal heating, and the reversible reduction in thermal stress at the fiber-matrix interface upon temperature increase.

## EXPERIMENTAL METHODS

The continuous unidirectional carbon fiber PPS-matrix composite was in the form of a single lamina (ply) of prepreg provided by Quadrex Corp. (Portsmouth, R.I.) under the designation QLC4164. The carbon fibers were AS-4C. The prepreg contained 64 wt% carbon fibers. The PPS matrix had  $T_g = 90^\circ\text{C}$  and  $T_m$  (melting temperature) = 280°C.

The samples were cut from a prepreg. Each sample was of length 9 cm in the fiber direction and of width 1 cm in the transverse direction. Samples were tested either as-received or after annealing, which was performed in air at 180°C for 5, 15 or 25 h, followed by furnace cooling to room temperature. During annealing, slight pressure was applied by sandwiching a sample between two horizontal steel plates.

Both as-received and annealed samples were subjected to thermal cycling, while the DC electrical re-

sistance of the sample in the fiber direction between the inner two of four electrical contacts was measured. The four contacts were such that the outer two (3 cm apart) were for passing a current and the inner two (2 cm apart) were for measuring the voltage, in accordance with the four-probe method of electrical resistance measurement. Each contact was in the form of a line drawn by silver paint all the way around the perimeter of the sample in a plane perpendicular to the fiber direction of the composite. The four contacts were positioned around the mid-point of the length of the rectangular sample. A Keithley 2001 multimeter was used for measuring the electrical resistance, which ranged from 0.3 to 3  $\Omega$  in this work.

Thermal cycling was performed such that one cycle involved (i) holding at 90°C for 2 h, (ii) heating to 180 or 235°C at a rate of 0.75°C/min, (iii) holding at 180 or 235°C for either 2 or 10 h, and (iv) cooling to 90°C at a rate of 0.75°C/min. During the thermal cycling, PTFE films were used to sandwich the sample in order to electrically insulate the sample from the surrounding steel mold and resistance heated platens. During thermal cycling, the temperature was measured by a thermocouple.

## RESULTS

### As-Received Composite

Figure 1 shows the fractional change in resistance during the first two cycles of thermal cycling, in which the temperature was held at 235°C for 10 h in each

cycle. The resistance increased abruptly during the first heating. During the subsequent period in which the temperature was held at 235°C, the resistance gradually decreased to levels below the initial resistance. During subsequent cooling, the resistance abruptly increased. During heating in the following cycle, the resistance decreased abruptly. The effect of cooling at the end of the first cycle on the resistance was reversed upon heating at the beginning of the second cycle. In the constant temperature (235°C) period of the second cycle, the resistance gradually decreased, as in the first cycle.

### Composite Annealed at 180°C for 5 h

Figure 2 shows the fractional change in resistance during the first four cycles of thermal cycling, in which the temperature was held at 180°C for 2 h in each cycle. The resistance increased abruptly during the first heating, as in Fig. 1. During the subsequent period in which the temperature was held at 180°C, the resistance decreased to levels below the initial resistance. During subsequent cooling, the resistance increased. In every subsequent cycle, the resistance decreased during heating, decreased further during holding at 180°C to levels below the minimum resistance of the previous cycle, and increased during subsequent cooling. As cycling progressed, the resistance decrease in the 180°C constant temperature period became more and more gradual.

In a separate experiment, the first heating was conducted in an interrupted fashion, i.e., heating from 90

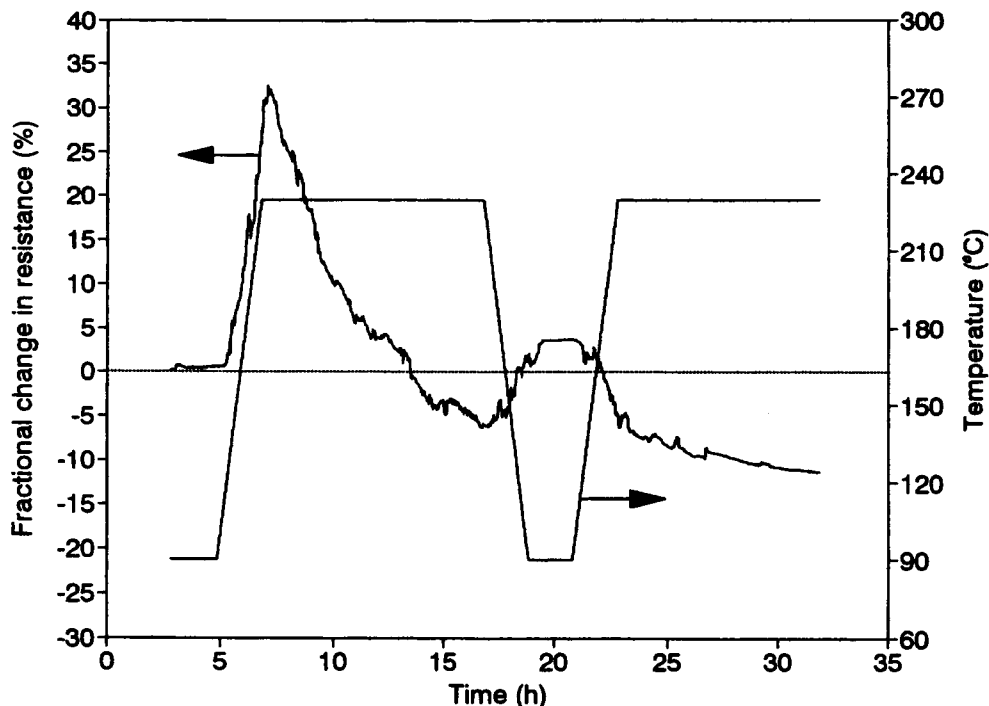


Fig. 1. Fractional change in electrical resistance during the first two cycles of thermal cycling for as-received composite.

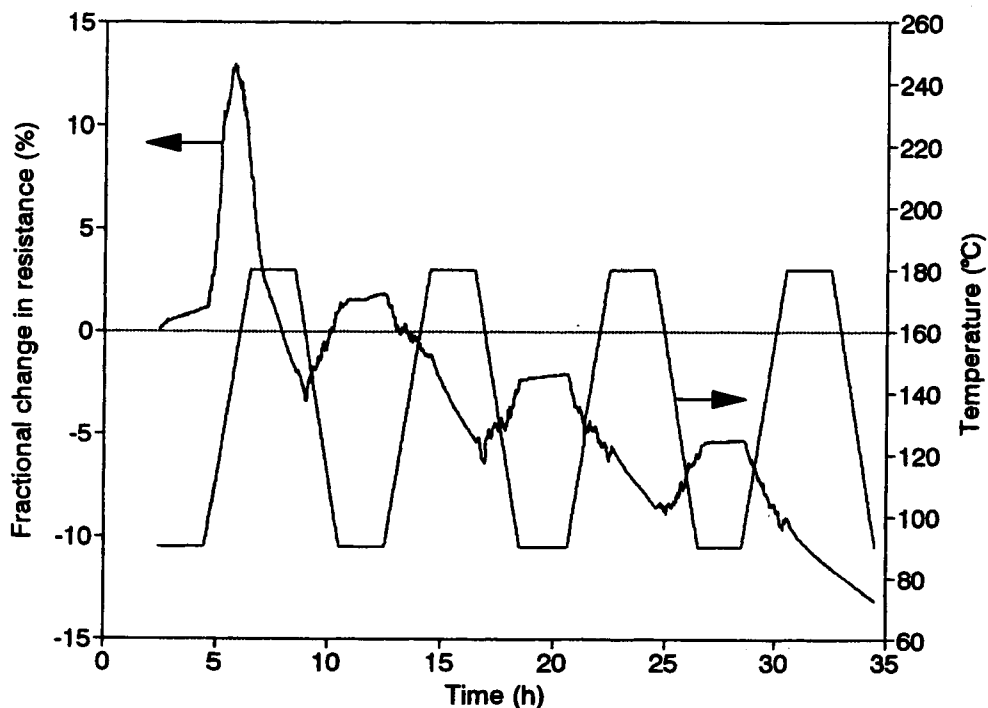


Fig. 2. Fractional change in electrical resistance during the first four cycles of thermal cycling for composite annealed at 180°C for 5 h.

to 135°C at a rate of 0.75°C/min, holding at 135°C for 1 h and then heating from 135 to 180°C at a rate of 0.75°C/min, as shown in Fig. 3. The resistance increased throughout the first heating, even in the 135°C constant temperature period.

**Composite Annealed at 180°C for 15 h**

Figure 4 shows the fractional change in resistance during the first three cycles of thermal cycling, in which the temperature was held at 180°C for 10 h in

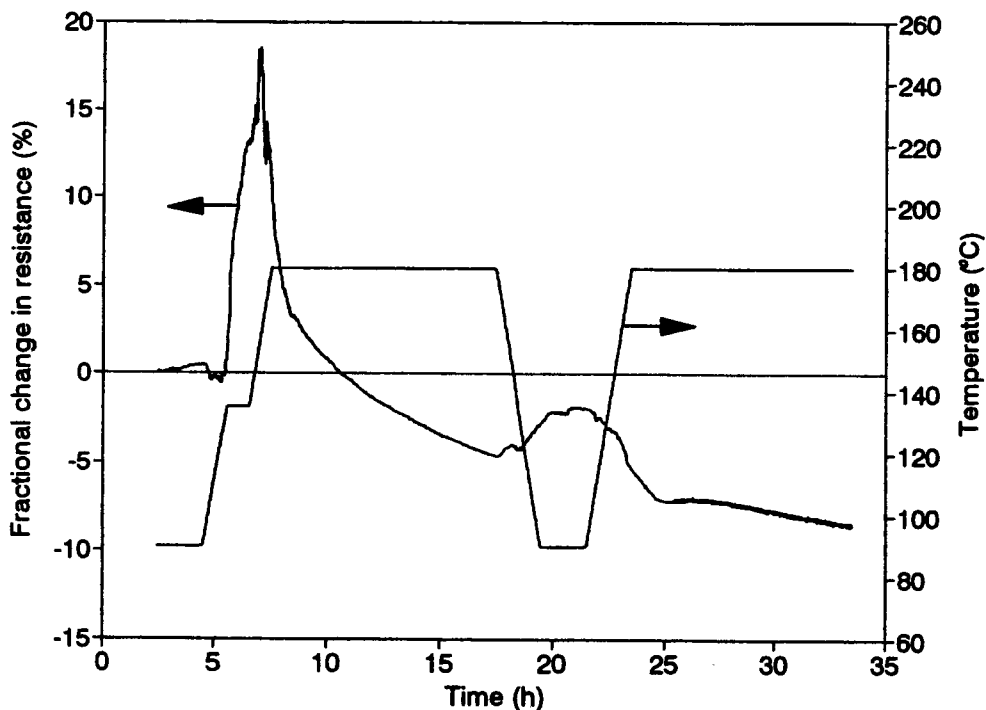


Fig. 3. Fractional change in electrical resistance during the first two cycles of thermal cycling for composite annealed at 180°C for 5 h, such that first heating from 90 to 180°C was interrupted at 135°C.

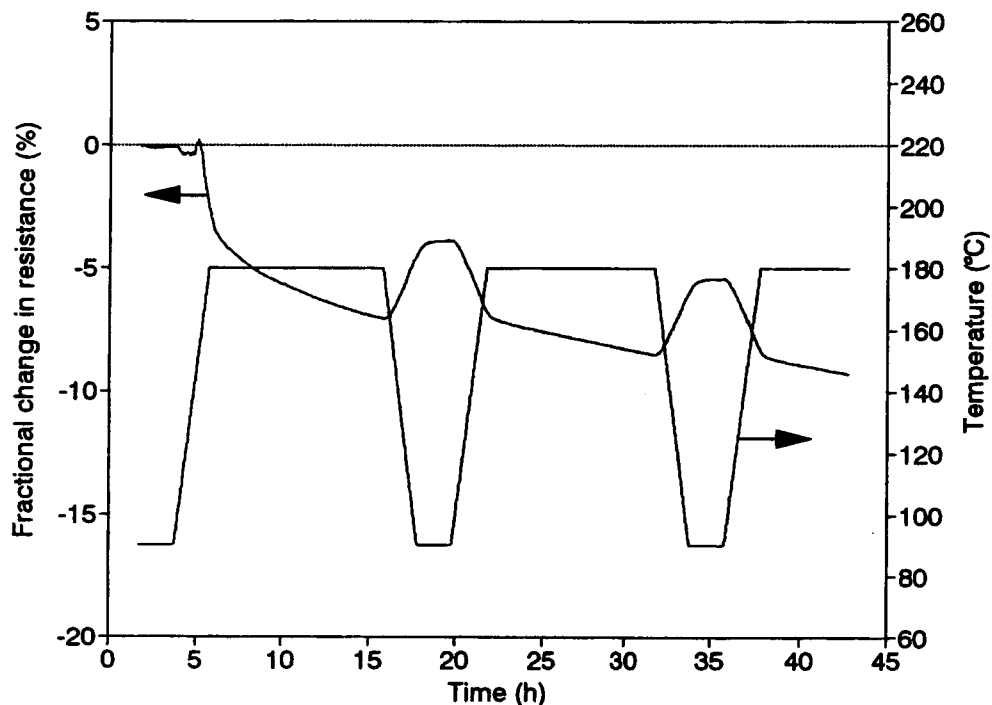


Fig. 4. Fractional change in electrical resistance during the first three cycles of thermal cycling for composite annealed at 180°C for 15 h.

each cycle. The resistance decreased abruptly during the first heating, in contrast to the abrupt increase in Figs. 1-3. Other than this, the pattern of resistance changes in Fig. 4 is the same as that in Figs. 1-3. However, the fractional changes in resistance are smaller in Fig. 4 than in Figs. 1-3.

#### Composite Annealed at 180°C for 25 h

Figure 5 shows the fractional change in resistance during the first three cycles of thermal cycling, in which the temperature was held at 180°C for 10 h in each cycle. The behavior in Fig. 5 is similar to that in Fig. 4 except that (i) the resistance essentially did not change in the 180°C constant temperature period in Fig. 5, but decreased in this period in Fig. 4, and (ii) the amount of resistance change upon heating or cooling increased with further cycling in Fig. 5, but not in Fig. 4.

### DISCUSSION

The abrupt resistance increase during the first heating, observed only for the as-received composite and the composite annealed at 180°C for 5 h, is attributed to the poor bond between fiber and matrix and the resulting flow of the matrix during heating above  $T_g$ . The flow probably led to an increase in the degree of fiber waviness or a decrease in the degree of fiber alignment, thereby resulting in an increase in the resistance in the fiber direction of the composite. Annealing at 180°C for 15 h or more improved the fiber-matrix bond, thereby removing this effect. That this effect is due to matrix flow is also supported by

the observation (Fig. 3) that flow (resistance increase) occurred at a constant temperature of 135°C, in addition to occurring during temperature increase.

The resistance increase during cooling and resistance decrease during subsequent heating (Figs. 1-5) are a reversible effect associated with the build-up of the thermal stress upon cooling and reduction of the thermal stress upon heating. The thermal stress is due to the thermal contraction mismatch between fiber and matrix. (The thermal expansion coefficient is much lower for carbon fiber than polymer.) The thermal stress can lead to an increase in the degree of fiber waviness or a decrease in the degree of fiber alignment, thereby increasing the resistance. The resistance decrease during first heating in Figs. 4 and 5 is also attributed to reduction in thermal stress.

The gradual resistance decrease in the constant high temperature period of each cycle (Figs. 1-5) is attributed to crystallization of the matrix. Crystallization (known as transcrystallization) occurs on the fiber surface (1), thereby tending to decrease the fiber waviness. Hence, the resistance of the composite is decreased. The higher is the degree of crystallinity of the matrix, the lower is the resistance of the composite. Therefore, the minimum resistance of a cycle decreased cycle by cycle (Figs. 2 and 4). On the other hand, annealing at 180°C for 25 h caused the crystallinity to essentially attain its maximum, so the above-mentioned effect due to crystallization essentially vanished in Fig. 5. Annealing at 180°C for 15 h caused some crystallization (though not the maximum), so the above-mentioned effect due to crystallization is smaller in Fig. 4 than Figs. 1-3.

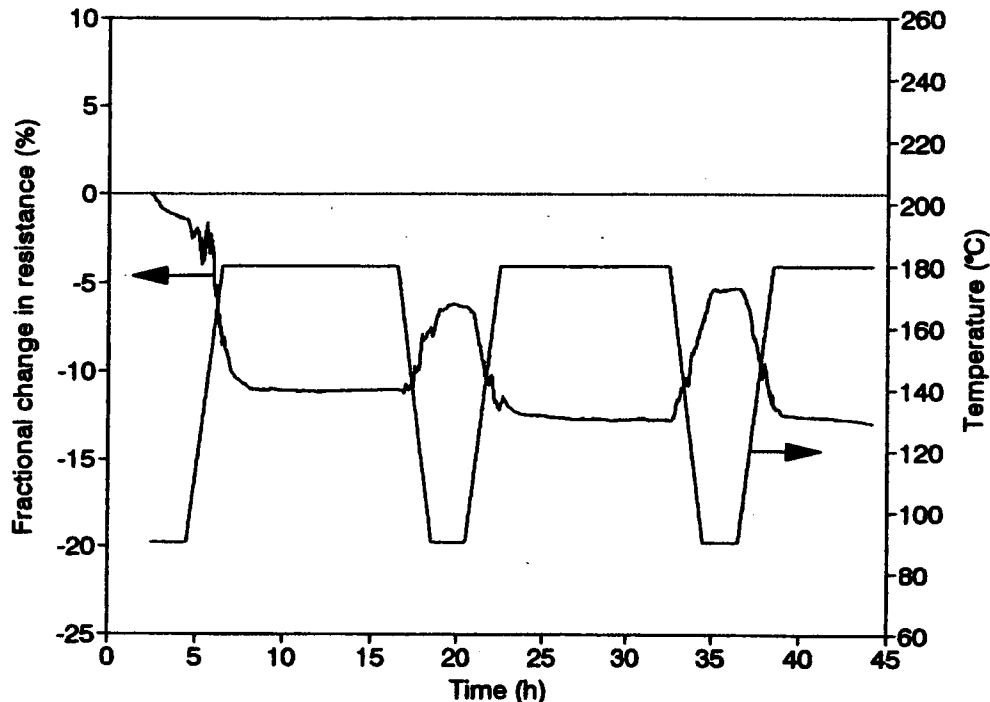


Fig. 5. Fractional change in electrical resistance during the first three cycles of thermal cycling for composite annealed at 180°C for 25 h.

The fact that the peak resistance of a cycle was higher for the third cycle than the second cycle in Fig. 5 is probably due to degradation of the composite (matrix) upon thermal cycling.

### CONCLUSION

Heating and cooling were found to affect the structure of carbon fiber PPS-matrix composites in terms of the flow of the matrix, the thermal stress at the fiber-matrix interface and the crystallinity, as shown by their effects on the electrical resistance of the composite in the fiber direction. The extents of these effects depended on the amount of prior annealing. In particular, annealing at 180°C diminished the matrix flow due to improved fiber-matrix bond, and it increased the matrix crystallinity. Annealing at 180°C for 15 h or more was sufficient to eliminate the matrix flow. Matrix flow during first heating above  $T_g$  and thermal

stress buildup during cooling in any thermal cycle caused the resistance to increase, whereas isothermal crystallization at 180°C caused the resistance to decrease. Thermal stress build-up was reversible upon thermal cycling.

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