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Interlaminar damage in carbon fiber polymer-matrix composites, studied by electrical resistance measurement

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Abstract

Interlaminar thermal damage in continuous carbon fiber polymer-matrix composites was monitored in real time during thermal cycling by measurement of the contact electrical resistivity of the interlaminar interface. Damage was accompanied by an abrupt increase of the resistivity for a thermoset-matrix composite, and by an abrupt decrease of the resistivity for a thermoplastic-matrix composite. Both phenomena are due to the effect of matrix damage on the chance of fibers of one lamina touching those of an adjacent lamina. The damage involved matrix molecular movement in the thermoplastic case, but not in the thermoset case.

Keywords: A. Epoxy; B. Composite; Damage; Interlaminar; Electrical resistance; Polymer; Thermoplastic; PPS; Carbon fiber

1. Introduction

Polymer-matrix composites containing continuous carbon fibers are widely used for lightweight structures (e.g., aircraft, rotating machinery, missiles, sporting goods, etc.), due to their combination of high strength, high modulus and low density. Because of the importance of safety in aircraft and other strategic applications, even minor damage of these structural composites is of concern. The damage is most commonly interlaminar, i.e., occurring between the fiber layers or laminae. Fiber breakage is a more drastic and less common type of damage.

Although nondestructive methods such as ultrasonic testing can reveal damage, they tend to be insufficiently sensitive to minor damage. For example, ultrasonic methods allow detection of defects (e.g., cracks) of size at least equal to the wavelength of the ultrasonic wave. Interlaminar damage can be much more subtle than a well-developed crack of sufficient size. It can be in the form of fiber-matrix debonding, matrix molecular movement (in the case of a thermoplastic matrix), matrix damage, and microscopic cracks in the matrix. The measurement of the contact electrical resistivity of the interlaminar interface is shown in this work to be effective for studying the interlaminar damage in carbon fiber polymer-matrix composites with thermoplastic and thermoset matrices. The technique can be used in real time during damage infliction, so that the nature and cause of the damage can be studied.

This work used the contact resistance technique to study thermal damage during temperature variation, as temperature excursions can occur during the use of a composite and the mismatch of the coefficient of thermal expansion (CTE) between carbon fiber and polymer matrix aggravates the tendency for thermal fatigue upon thermal cycling [1–6].

The volume electrical resistance in the through-thickness direction of a laminate includes the volume resistance of each lamina and the contact resistance of each interlaminar interface. Although measurement of the volume resistivity in the through-thickness direction has been previously used to observe interlaminar damage in a carbon fiber polymer-matrix composite during mechanical damage [7], the contact resistivity of the interlaminar interface provides a more direct indication of the quality of the interface. This quantity has been previously measured during interlaminar shear [8].

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The objective of this work is not only damage detection, but also damage mechanism characterization. Due to the difference in thermal and mechanical properties between a thermoplastic and a thermoset, the damage mechanism is quite different between a thermoplastic-matrix composite and a thermoset-matrix composite. This work used polyphenylene sulfide (PPS) as the thermoplastic matrix and epoxy as the thermoset matrix.

The measurement of the contact electrical resistivity of the interlaminar interface of a thermoset-matrix composite has been previously used to monitor the temperature, as the resistivity decreases reversibly with increasing temperature [9,10]. In other words, the interlaminar interface is a thermistor. The phenomenon is due to the local direct contacts between fibers of adjacent laminae (as a consequence of the movement of the matrix or the matrix precursor) and the fact that an activation energy is involved in the jump of an electron from one lamina to an adjacent one across a contact. In this work, the contact resistivity is used to indicate simultaneously both the temperature and thermal damage. This dual capability adds to the attractiveness of the resistivity technique, as it facilitates identification of the damage mechanism.

2. Experimental methods

The damage revealed by resistance measurement was subtle, in contrast to damage in the form of well-defined delamination cracks or debonded regions at the fiber-matrix interface. Therefore, correlation of the resistance change with microscopic observation of damage was impossible.

The thermal cycling used in this work involved two modes. In one mode, the temperature amplitude (i.e., the peak temperature of a cycle) was fixed as cycling progressed. In the other mode, the temperature amplitude was gradually increased cycle by cycle and then decreased cycle by cycle back to the initial low-temperature amplitude. The group of cycles in which the temperature amplitude increased and then decreased is hereby referred to as a group. The first mode was useful for thermal fatigue study; the second mode was useful for studying the effect of temperature and for distinguishing between reversible and irreversible effects.

This work involved two types of continuous carbon fiber polymer-matrix composites, namely a thermoset-matrix composite with epoxy as the matrix, and a thermoplastic-matrix composite with polyphenylene sulfide (PPS) as the matrix. Both composites were fabricated from fiber prepregs by lamination. Each composite consisted of two laminae in a crossply configuration.

2.1. Thermoset-matrix composite

The thermoset matrix was epoxy. Two laminae of unidirectional carbon fiber epoxy-matrix prepregs (provided by Cape Composites Inc., San Diego, CA) (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 (3.7 mm × 3.7 mm; the dimensions were not critical) of the two laminae by applying pressure (0.33 MPa) and heat to the overlapping region (without a mold). The pressure was provided by a weight. 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 121±2°C at the rate of 2°C/min. Then it was cured at that temperature for 3 h and subsequently furnace cooled to room temperature.

Thermal cycling was conducted after curing and subsequent cooling of the composite by using a small resistance heater for heating and using compressed air

Table 1
Carbon fiber and epoxy matrix properties (according to Cape Composites Inc., San Diego, CA)

Fortafil 555 continuous carbon fiber	
Diameter	6.2 μm
Density	1.8 g/cm^3
Tensile modulus	231 GPa
Tensile strength	3.80 GPa
Cape C2002 epoxy	
Processing temperature	121°C
Flexural modulus	99.9 GPa
Flexural strength	1.17 GPa
T_g	129°C
Density	1.15 g/cm^3

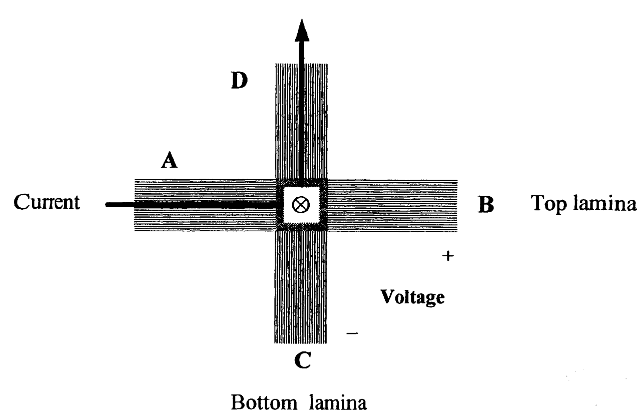

Fig. 1. Composite configuration for testing contact resistivity as a function of temperature.

and a copper tubing with flowing water for cooling. For the thermal cycling mode in which the temperature amplitude was fixed, the time per cycle was 30 s, such that the temperature increase portion took 13 s and the temperature decrease portion took 17 s. For the thermal cycling mode in which the temperature amplitude increased and then decreased, the time per cycle was 60 s, such that the temperature increase portion took 15 s and the temperature decrease portion took 45 s (actually 15 s followed by 30 s of a tail of temperature vs. time).

All the time, the contact electrical resistance and the temperature of the sample were measured, respectively, by a Keithley (Keithley Instruments, Inc., Cleveland, OH) 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 (i.e., from A to the junction along the top lamina, down from the top lamina to the bottom lamina across the junction, and then from the junction to D along the bottom lamina), 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.

2.2. Thermoplastic-matrix composite

The PPS thermoplastic matrix material had a glass transition temperature (T_g) of 90°C and a melting temperature (T_m) of 280°C. The material was in the form of continuous unidirectional carbon fiber prepreg, supplied by Quadrax Corp. (Portsmouth, Rhode Island; Product QLC4164). The thickness of the prepreg was 250 μm. The carbon fiber was AS-4C, from Hercules Advanced Materials and Systems Company (Magna, Utah), with a diameter of 8 μm. The fiber weight fraction in the prepreg was 64%.

The prepreg was used as-received. Prepreg strips 50 mm in length and 5 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 5 mm × 5 mm, as shown in Fig. 1. During formation of the interlaminar interface at the overlap area, the temperature was raised from 20°C to 320°C (T_m= 280°C) at a heating rate of 5°C/min and then held at 320°C for 30 min. After that, the specimen was furnace cooled to room temperature. Throughout the heating and cooling, pressure (2.1×10^5 Pa, 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). Prior to this, the matrix at the ends of each prepreg strip had not been burned out, as this step was found to be not necessary for making a good electrical contact. A Keithley 2001 multimeter was used.

For investigation of the effect of thermal fatigue, the contact resistivity was continuously measured while the temperature was cycled between 25°C and 80°C (below T_g) by using a small resistance heater for heating and using compressed air and a copper tubing with flowing water for cooling. Each cycle took 15 s, as shown in Fig. 2. No pressure was applied during the thermal testing.

For investigation of the effect of the temperature on thermal damage, the contact resistivity was continuously measured while the temperature was cycled such that the maximum temperature of a cycle increased in two steps and then decreased in two steps. Within a group, the minimum temperature was 22°C; the maximum temperature was, cycle by cycle, 65°C, 85°C, 117°C, 85°C, and then 65°C.

3. Results and discussion

Although the results shown below for thermal fatigue are for a single specimen in the thermoset-matrix composite case and for a single specimen in the thermoplastic-matrix composite case, multiple specimens were tested for each case and the reproducibility of the general behavior was observed for each case.

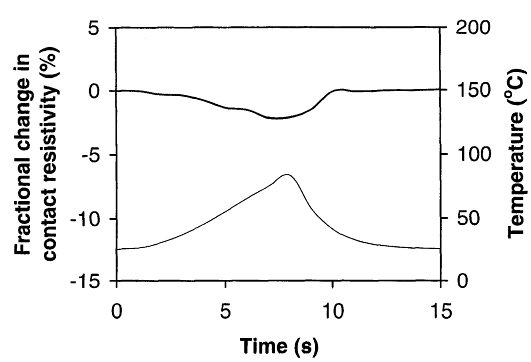

Fig. 2. Variation of the contact electrical resistivity (thick line) with time and of the temperature (thin line) with time in Cycle No. 1 for thermoplastic-matrix composite.

3.1. Thermoset-matrix composite

Fig. 3 shows the variation of the contact resistivity with temperature during thermal cycling. The temperature was repeatedly increased to various levels. Fig. 3(a) shows the results of the first 10 groups, while Fig. 3(b) shows the first group only. The contact resistivity decreased upon heating in every cycle of every group. At the highest temperature (150°C) of a group, a spike of resistivity increase occurred, as shown in Fig. 3(b). This spike was observed similarly in other groups. It is attributed to damage at the interlaminar interface. In addition, the baseline resistivity (i.e., the top envelope) gradually and irreversibly shifted downward as cycling progressed, as shown in Fig. 3(a). The baseline decrease is probably due to matrix damage within a lamina and the resulting decrease in modulus and hence decrease in residual stress; it is not due to thermal fatigue, since the damage was most significant in the early cycles and incremental damage diminished upon thermal cycling.

Fig. 4 shows similar results for a case of more severe damage occurring at the highest temperature (170°C) of a group. The damage resulted in a large spike of resistivity increase at the highest temperature, in addition to a partially reversible upward shift of the baseline resistivity immediately after the spike. The extent of upward shift decreased rapidly from cycle to cycle during the two cycles immediately following the spike.

Fig. 5 shows similar results for a case of even more severe damage. A spike of resistivity increase occurred at the peak temperature of a cycle for quite a few cycles in a group (not just for the cycle with the highest peak temperature), such that the spike became larger as the peak temperature increased. The lowest peak temperature at which a spike was observed was 110°C (below the composite processing temperature of 121°C). Furthermore, a partially reversible upward shift of the baseline resistivity occurred immediately after the spike at the highest temperature (200°C) of the group. This shift is more severe than that in Fig. 4.

The greater the damage (related to interlaminar interface damage), the more severe is the spike or contact resistivity increase and the greater is the partially reversible baseline resistivity increase following the spike (Figs. 3–5). As expected, the higher the

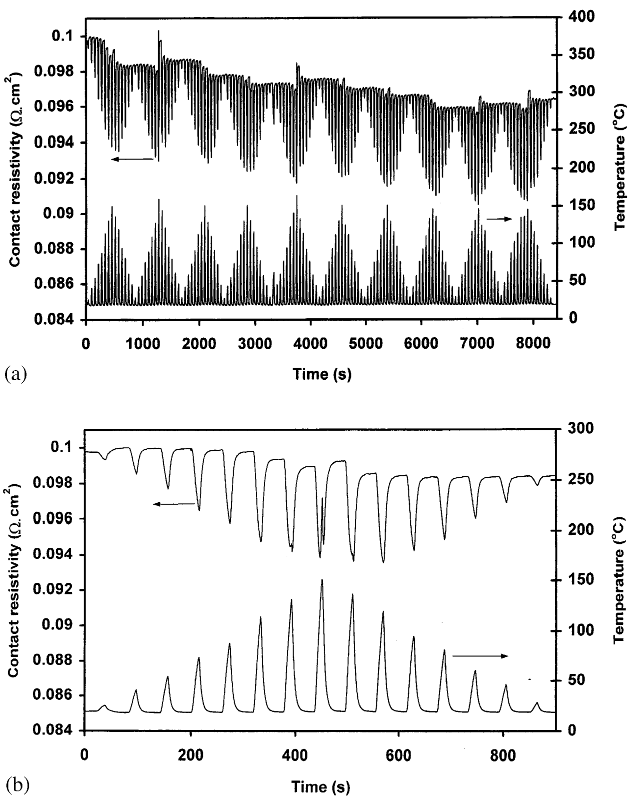

Fig. 3. (a) Variation of the contact electrical resistivity with time and of the temperature with time during thermal cycling for thermoset-matrix composite. (b) is the magnified view of the first 900 s of (a).

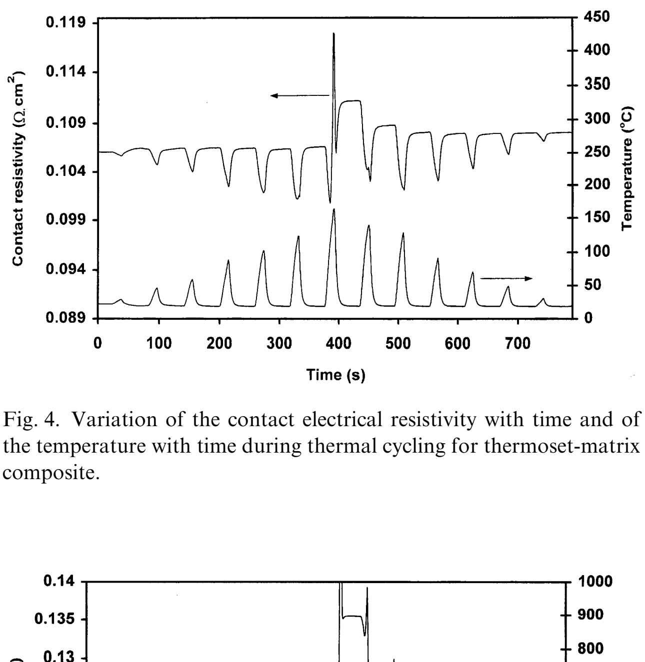

Fig. 4. Variation of the contact electrical resistivity with time and of the temperature with time during thermal cycling for thermoset-matrix composite.

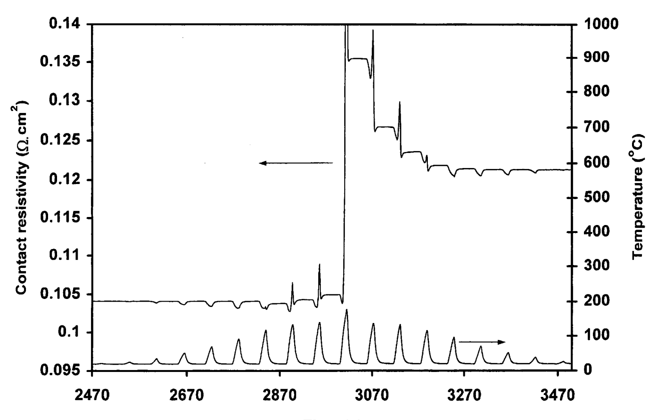

Fig. 5. Variation of the contact electrical resistivity with time and of the temperature with time during thermal cycling for thermoset-matrix composite.

temperature, the more is the extent of damage. In addition, minor damage (probably related to matrix damage) occurred gradually as cycling progressed, leading to the gradual and irreversible decrease of the baseline resistivity.

The spike of contact resistivity increase is particularly sensitive to damage, even to small damage occurring at 110°C. The size of the spike indicates the extent of damage. The time of the spike is the time of the damage occurrence. The partially reversible baseline resistivity increase following a relatively large spike is an additional indicator, which is sensitive to only relatively large extents of damage. Both the spike and the partially reversible baseline resistivity increase following the spike are valuable for monitoring damage in real time. On the other hand, the gradual and irreversible baseline resistivity decrease that occurs as cycling progresses is useful for condition monitoring, whether in real time or not. It is particularly valuable for monitoring minor damage which is not accompanied by a partially reversible baseline resistivity increase following a spike. As shown in Fig. 3(b), the gradual and irreversible baseline decrease starts to occur at lower temperatures than the spike.

Fig. 6 shows the variation of the contact resistivity with temperature during initial thermal cycling. The general decrease of the resistivity baseline is as in Fig. 3.

Fig. 7 shows that a small spike of contact resistivity increase occurred at the maximum temperature of a cycle from Cycle No 13,481 onward. The increase was partly reversible and is attributed to thermal fatigue damage of the interlaminar interface. The damage may be a form of delamination and increased the contact resistivity.

Fig. 8 shows another result of thermal fatigue, which occurred later in the fatigue life. It involved an abrupt increase of the contact resistivity baseline. The abrupt increase, which occurred more than once, also indicates damage of the interlaminar interface—perhaps more serious damage than that indicated by the spikes which occurred earlier in the fatigue life.

3.2. Thermoplastic-matrix composite

Figs. 2 and 9 show the fractional change in contact resistivity during initial thermal cycling. Fig. 2 shows Cycle 1 only; Fig. 9 shows Cycles 1–40. The resistivity decreased reversibly upon heating in every cycle. As cycling progressed, the baseline resistivity decreased continuously and then leveled off after about 135 cycles. The baseline decrease is probably because the thermal cycling damaged the matrix, thereby decreasing the modulus of the laminae, lowering the thermal stress, and decreasing the contact resistivity, as in the case of a thermoset-matrix composite (Fig. 5). This damage is not really due to thermal fatigue, since the damage was most significant in the first cycle and incremental damage diminished upon thermal cycling.

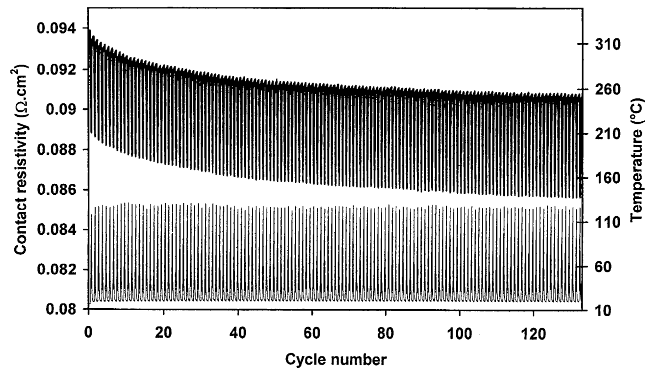

Fig. 6. Variation of the contact electrical resistivity (thick line) with cycle number and of the temperature (thin line) with cycle number during the first 133 thermal cycles for thermoset-matrix composite.

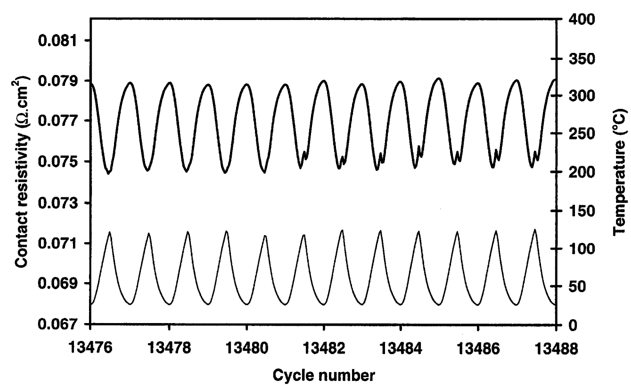

Fig. 7. Variation of the contact electrical resistivity (thick line) with cycle number and of the temperature (thin line) with cycle number from Cycle No. 13,476 to Cycle No. 13,487 for thermoset-matrix composite. The spike started to appear at Cycle No. 13,481 and continued thereafter.

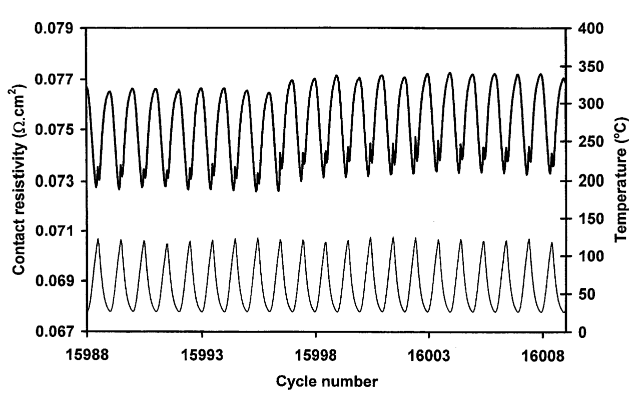

Fig. 8. Variation of the contact electrical resistivity (thick line) with cycle number and of the temperature (thin line) with cycle number from Cycle No. 15,988 to Cycle No. 16,008 for thermoset-matrix composite. An abrupt increase in the baseline of the contact electrical resistivity occurred at cycle No. 15,996.

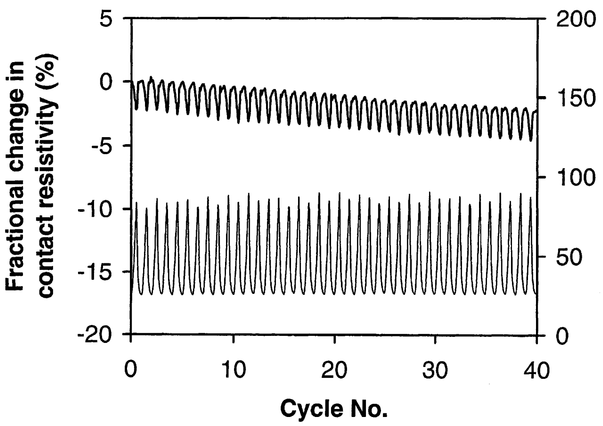

Fig. 9. Variation of the contact electrical resistivity (thick line) with Cycle No. and of the temperature (thin line) with Cycle No. during initial thermal cycling for thermoplastic-matrix composite.

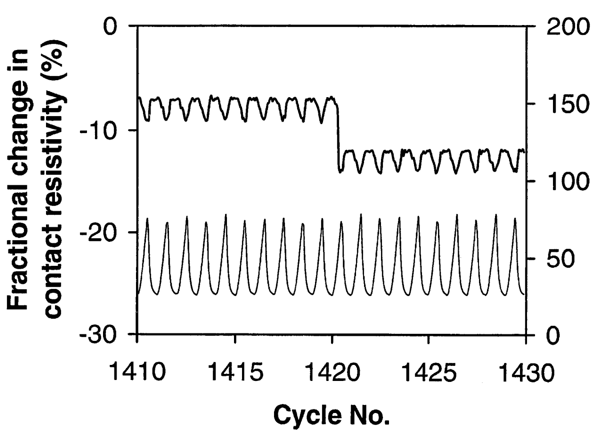

Fig. 10. Variation of the contact electrical resistivity (thick line) with Cycle No. and of the temperature (thin line) with Cycle No. from 1410 to 1430 for thermoplastic-matrix composite. An abrupt and irreversible decrease of the contact electrical resistivity occurred at Cycle No. 1421.

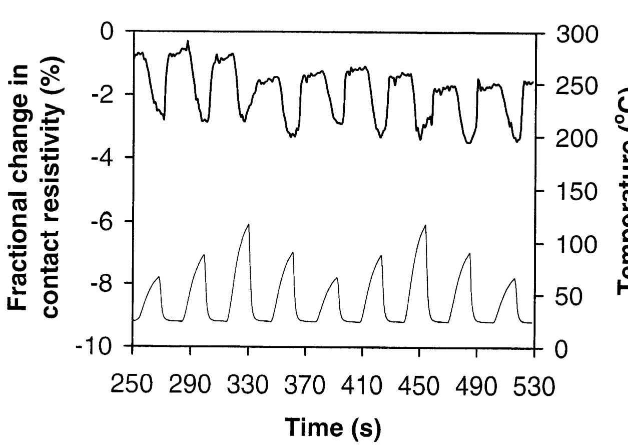

Fig. 11. Variation of the contact electrical resistivity (thick line) with time and of the temperature (thin line) with time for Groups 3 and 4 for thermoplastic-matrix composite.

Fig. 10 shows a result of thermal fatigue, which occurred later in the fatigue life. It involved an abrupt and irreversible decrease of the resistivity at Cycle 1421. The decrease occurred almost at the peak temperature of a cycle. Such abrupt decreases were observed for multiple times (e.g., at Cycles 1421, 1489 and 1557) during the course of thermal cycling. It is attributed to matrix molecular movement and the consequent increase in the chance for fibers of one lamina to touch those of an adjacent lamina.

Fig. 11 shows the thermal damage that occurred at the maximum temperature of a group. Groups 3 and 4 are shown. The damage resulted in an irreversible decrease in the baseline resistivity, as in Fig. 10, which is for the case of thermal fatigue.

Fig. 12 shows more extensive thermal damage, which occurred at the maximum temperature of Group 37. The irreversible decrease in the baseline resistivity is more than that in Fig. 11.

3.3. Comparison of thermoset-matrix and thermoplastic-matrix composites

The abrupt and irreversible resistivity decrease observed for the thermoplastic-matrix composite is in contrast to the abrupt and partly reversible resistivity increase observed in the case of the thermoset-matrix composite. The contrast is due to the difference in mechanism. The matrix molecular movement (i.e., local plastic deformation of the matrix), which is irreversible and is a consequence of fiber-matrix bond degradation, does not occur for the thermoset case (as the chains are fixed in place by crosslinks), but occurs for the thermoplastic case (as the chains can slip past each other freely under conditions of heat and/or pressure). The reversibility in the thermoset case is probably due to the contact between fibers of adjacent laminae being lost locally and reversibly.

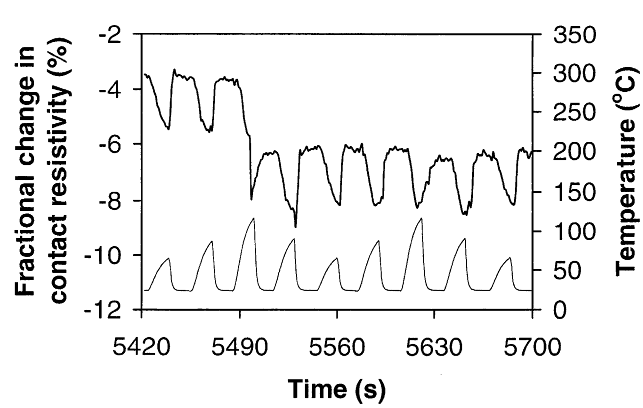

Fig. 12. Variation of the contact electrical resistivity (thick line) with time and of the temperature (thin line) with time for Groups 37 and 38 for thermoplastic-matrix composite.

The gradual decrease of the resistivity baseline in the early cycles was observed for both thermoset-matrix and thermoplastic-matrix composites. It is attributed to minor damage of the matrix—probably in the form of a decrease in the modulus.

4. Conclusion

Thermal damage in continuous carbon fiber polymer-matrix composites was monitored in real time during thermal cycling by measurement of the contact electrical resistivity of the interlaminar interface. Simultaneous to monitoring damage was the monitoring of the temperature by the same resistivity measurement, as the resistivity decreased reversibly upon heating in each thermal cycle, due to the energy barrier for electron jumping from one lamina to the other. For both thermoset-matrix and thermoplastic-matrix composites, the initial stage of damage was characterized by gradual decrease of the resistivity baseline, probably due to matrix modulus decrease. The second stage of damage was characterized by an abrupt increase of the resistivity for the thermoset (epoxy)-matrix composite, and by an abrupt decrease of the resistivity for the thermoplastic (PPS)-matrix composite; both phenomena are due to the effect of matrix damage on the chance of fibers of one lamina to touch those of an adjacent lamina. For the case of the thermoplastic matrix, matrix molecular movement accompanied damage, thereby increasing this chance. For the case of the thermoset matrix, matrix molecular movement did not occur while damage occurred, thereby decreasing this chance.

References

[1] Herokovich CT, Hyer MQ. Eng Fract Mech 1985;25(5–6):779–91.
[2] Assix O, Bahlouli N, Cluzel C, Perret L. Compos Sci Technol 1996;56(7):883–8.
[3] Allix O, Bahlouli N, Ladeveze P, Perret L. Damage Mech Compos, Am Soc Mech Eng 1994;185:21–35.
[4] Huang X, Gillespie Jr JW, Eduljee FR. Compos Part B: Eng 1997;28B(4):419–24.
[5] Crasto AS, Kim RY. J Reinforced Plastics Compos 1993;12(5):545–58.
[6] Dutta PK. Proceedings International Offshore and Polar Engineering Conference, vol. 4, Golden, CO, 1997. p. 672–76.
[7] Wang X, Chung DDL. Polym Compos 1997;18(6):692–700.
[8] Wang S, Chung DDL. Compos Interfaces 1999;6(6):507–18.
[9] Wang S, Chung DDL. Compos Interfaces 1999;6(6):497–506.
[10] Wang S, Chung DDL. Compos: Part B 1999;30(6):591–601.