N86-11283

EFFECTS OF REAL-TIME THERMAL AGING ON GRAPHITE/POLYIMIDE COMPOSITES*

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As part of a program to evaluate high-temperature advanced composites for use on supersonic cruise transport aircraft, two graphite/polyimide composites have been aged at elevated temperatures for times up to 5.7 years. Work on the first, HT-S/710 graphite/polyimide, was started in 1974. Evaluation of the second polyimide, Celion 6000/LARC-160, began in 1980. Baseline properties are presented, including unnotched and notched tensile data as a function of temperature, compression, flexure, shear, and constant-amplitude fatigue data at R = 0.1 and R = −1.

Tensile specimens were aged in ovens where pressure and aging temperatures were controlled for various times up to and including 50,000 hours. Changes in tensile strength were determined and plotted as a function of aging time. The HT-S/710 composite aged at 450F and 550F is compared to the Celion 6000/LARC-160 composite aged at 350F and 450F. After tensile testing, many of the thermal aging specimens were examined using a scanning electron microscope. Results of these studies are presented, and changes in properties and degradation mechanisms during high-temperature aging are discussed and illustrated using metallographic techniques.

INTRODUCTION

Advanced composites will play a key role in the technology emerging for the design and fabrication of future supersonic vehicles.

Research and development during recent years has led to advances in fabrication techniques and characterization of short-time properties and has provided limited supersonic flight experience for these materials.

However, information on the effects of long-time exposure to service environments representative of supersonic cruise aircraft on composite materials has not generally been available. An extensive program to generate such information has been in progress at General Dynamics Convair Division under NASA Contract NAS1-12308 since 1973 (Ref. 1).

Figure 1 illustrates the overall NASA study from which the material for this paper was taken. Changes in mechanical properties that occur over very long periods of time are being determined for ambient and thermal aging conditions and for random cyclic loading with cyclic temperature variations. These latter tests, the flight simulation exposures, are intended to provide data on the effect of 10,000, 25,000 and 50,000 hours of simulated supersonic flight service on residual properties of the composites. The purpose of the thermal aging study (conducted at constant temperature without load) was to assist in understanding the results of the more complex flight simulation program. While flight simulation tests are still in progress, the original thermal aging specimens have completed the required 50,000 hours of exposure, and the residual strength data is now available. The second polyimide, introduced later in the program, has completed thermal aging tests out to 10,000 hours.

This paper presents the results of these aging tests for two graphite/polyimide systems. Earlier work on thermal aging of HT-S/710 (Ref. 2) is compared to more recent work on Celion 6000/LARC-160. All exposures were conducted at ambient pressure. Previous work had shown a direct correlation of thermal aging and oxygen pressure on residual strength of resin-matrix composites (Ref. 1). In this paper, ambient pressure was

* *Sponsored by the National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia, under Contract NAS 1-12308, monitored by Mr. Bland A. Stein.*

chosen to compare the two systems, since most of the data has been generated at ambient pressure.

In actual use, a supersonic cruise vehicle would be at a very high altitude during much of the time at which the structure has reached its maximum temperature. Thus, if reduced oxygen pressure were taken into account, the composite materials could likely be used at high temperatures for longer periods of time.

EXPERIMENTAL

The graphite/polyimide composite systems employed in this program were HT-S/710 and Celion 6000/LARC-160. Six- and twelve-ply [0° ± 45] crossplied laminates of each system were fabricated by Convair Division from vendor-supplied prepreg material using conventional autoclave processing methods. Quality assurance testing was conducted on both the as-received prepreg and the fabricated laminates. These acceptance tests included fiber, resin, and volatile contents, resin flow, and process gel for the prepreg material and ultrasonic C-scan, fiber content, specific gravity, and metallographic examinations for the panels. Table 1 lists information for the two composites.

Test specimens were cut from the panels using a diamond impregnated saw. Details of the specimen configurations for the various types of tests are presented in Table 2. Polyimide-quartz doublers were bonded to all but the flexure and short beam shear specimens using HT-424, a modified epoxy-phenolic film adhesive with an aluminum filler. For the thermal aging specimens, the doublers were attached after exposure.

Conventional test methods were used for the tensile, compression, flexure, and shear tests. The notched tensile specimens contained a center hole 0.25 inch in diameter, giving a theoretical stress concentration (K_t) of 2.43. Compressive strength

Table 1. Material systems.

Material System	Celion 6000/LARC-160	HT-S/710
Vendor	Fiberite	Hercules
Orientation	$[0° \pm 45°]_s$ $[0° \pm 45°]_{s2}$	$[0° \pm 45°]_s$ $[0° \pm 45°]_{s2}$
Fiber Content	67%	70%
Specific Gravity	1.56	1.48

was determined using a Celanese-type test fixture with an 18-ply specimen prepared by bonding together three six-ply panels. A similar 18-ply specimen was also used for the short beam shear tests.

Constant-amplitude fatigue tests were conducted at a constant frequency of 30 Hz. For elevated temperature tests, clamshell and ring furnaces were used. Temperature was monitored by a thermocouple attached to the specimen at the center of the gage section. A total of nine specimens was used to obtain an S-N curve for any given set of conditions. Test conditions were:

- Cycles: 10^3 to 10^7
- R values: − 1 and 0.1
- Temperature: 75 and 350 or 450F
- Specimen configuration: unnotched and notched

Thermal aging exposures were conducted in specially constructed aging furnaces similar to the sketch in Figure 2. The heater plates consist of insulated wire sandwiched between two thin aluminum plates. All furnace temperatures were equilibrium-controlled; i.e., a constant amount of power was supplied to the heaters. The various aging temperatures were generally maintained to ± 5F with infrequent excursions to a maximum of ± 10F.

Table 2. Details of test specimens

Specimen Type	Length (in.)	Width (in.)	Plies	Doublers Required
Unnotched Tensile	9	0.5	6	Yes
Notched Tensile	9	1	6	Yes
Compressive	5.5	0.25	18	Yes
Unnotched Fatigue	9	0.5	6 and 12	Yes
Notched Fatigue	9	1.0	6 and 12	Yes
Flexure	3	0.5	12	No
Short Beam Shear	0.6	0.25	18	No
Thermal Aging	9	0.5	6	Yes

The aging temperatures were: Celion 6000/LARC-160, 350F and 450F; and HT-S/710, 450 and 550F.

The procedure followed for the exposures was to cut the specimen blanks to final size, heat at 250F for 24 hours to remove absorbed moisture, and load into the aging furnaces. The specimens were supported at their ends by narrow strips of stainless steel so that almost the entire surface was exposed to the air atmosphere within the furnaces. At the required time intervals, the ovens were shut down, opened, and the specimens removed and stored in a desiccator until doubler bonding and tensile testing. Residual strength testing was performed at 350F for the Celion 6000/LARC-160 and at 450F and 550F for the HT-S/710. The data points shown in the residual strength-versus-time plots are averages obtained from three tensile specimens per test condition.

After tensile testing, many of the thermal aging specimens were sectioned and mounted for study using a scanning electron microscope. These studies were intended to detect changes that occurred in the composites during exposure to assist in identifying degradation mechanisms.

A more detailed account of the fabrication, quality assurance, baseline testing, and thermal aging procedures can be found in Reference 1.

RESULTS AND DISCUSSION

To establish sufficient baseline data, a number of tensile tests were performed. In Figures 3 and 4, the tensile properties for the two polyimide composites are shown for both the unnotched and notched configurations. Tests were performed at a number of temperatures between −67 and 650F. Each data point represents the average of at least three tests. A regression line was fitted to the data, as shown in Figures 3 and 4. Each set of data points was superpositioned to 350F; the resulting Weibull distribution fit is shown in Figures 5 and 6. Each polyimide is compared for both the unnotched and notched conditions. The Weibull and normal distribution parameters for each of the four curves are listed in Table 3.

The data was pooled in this manner to provide the maximum use of the tensile data in setting load levels for the flight simulation tests shown in Figure 1. The loads in Table 3 can be converted to stress by dividing by the laminate thickness (approximately 0.03 inch).

Other baseline properties are given in Table 4. The data given compares flexural strength, shear strength, and compressive strength and modulus of HT-S/710 and Celion 6000/LARC-160. As was the case for tensile strength, the Celion 6000/LARC-160 composite is considerably stronger.

Results of the fatigue testing portion of the program are presented in Figures 7 through 10. These S-N plots compare the effects of stress ratio, R, notch configuration, and temperature on the fatigue strength of the two graphite/polyimide systems.

The data shows the fatigue life for a stress ratio of $R = -1$ to be much lower than for $R = 0.1$. The effect of test temperature or the presence of a center notch (hole with $K_t = 2.43$) was slight compared to the stress ratio effect.

Table 4. Baseline mechanical property data.

	HT-S/710		Celion 6000/LARC-160	
	(0-deg ± 45)	(0-deg)	(0-deg ± 45)	(0-deg)
Flexural strength (ksi)				
75F	94	171	137	196
350F	79	127	124	145
Shear strength (ksi)				
75F	5.4	7.0	8.8	9.0
350F	—	—	7.5	8.8
Compressive strength (ksi)				
75F	55	—	85	—
Compressive modulus (msi)				
75F	6.7	—	7.5	—

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Table 3. Comparison of Weibull and normal distribution parameters for tensile loads of two polyimide composites.

Material & Specimen Configuration	Weibull α	Weibull β (lb/in.)	Standard Deviation	Average (lb/in.)	Coef. of Variation	No. of Data Points
Celion 6000/LARC-160 Unnotched	28	3,245	147	3,180	0.046	35
Celion 6000/LARC-160 Notched	14	2,377	192	2,290	0.083	35
HT-S/710 Unnotched	13	2,396	237	2,301	0.103	26
HT-S/710 Notched	12	1,675	145	1,611	0.090	29

The lines on each of the four graphs are regression lines drawn by computer. Differences in slope or slight changes in position are not considered significant. As for the mechanical properties, in general, the Celion 6000/LARC-160 S-N curves are about 25% higher than those for HT-S/710.

Residual tensile strength of the HT-S/710 system is plotted as a function of aging time in Figure 11. Curves for aging at 450 and 550F in 14.7 psi air are included. The material aged at 450F showed very little change in tensile strength for times up to 25,000 hours. However, when the aging temperature was raised to 550F, significant strength decreases were observed after 5,000 hours of exposure. After 50,000 hours, almost no resin was left in the specimens, only graphite fibers. The specimens were badly warped and delaminated, and were no longer suitable for tensile testing. All tensile tests were performed at 350F after the indicated aging times. Each point consists of the average of three tensile coupons.

Residual tensile strength of the Celion 6000/LARC-160 system is plotted as a function of aging time in Figure 12 for ambient air pressure. As in the case of the HT-S/710, each point represents the average of three tensile tests. Aging temperatures were reduced for the second polyimide to 350 and 450F. There was not enough difference in the data for the two temperatures to draw separate curves. As shown in Figure 12, there is some loss in strength for aging times as short as 500 hours. After 10,000 hours of exposure at 450F, a comparison of the two graphite/polyimide systems shows that each has about the same residual tensile strength. Based on the shape of the aging curves, however, the HT-S/710 system would appear to be superior for time periods greater than 10,000 hours.

Scanning electron microscope photomicrographs in Figures 13 through 15 show results of metallographic examination of the graphite/polyimide aging specimens. For the HT-S/710 system (Figure 13), specimens aged at 450F exhibited no oxidation or matrix degradation effects for the first 25,000 hours. After 50,000 hours, relief polishing around the graphite fibers, increased porosity, and more fiber-matrix separation were observed. Raising the aging temperature to 550F greatly increased the degree of matrix degradation of the HT-710 system. Figure 13 shows that, in one-atmosphere air, 10,000 hours at 550F has a slightly greater effect on the microstructure than 50,000 hours at 450F.

For the Celion 6000/LARC-160 system, metallographic effects were much more evident for the thermal aging specimens. At lower magnifications, the degree of microcracking and relief polishing was found to be related to both the temperature and length of time of aging. This can be seen in Figure 14. As pointed out earlier, however, the results of the tensile tests did not indicate a significant temperature effect for at least 10,000 hours of exposure. At higher magnification, evidence of oxidation, similar in nature to that first observed in the A-S/3501 graphite/epoxy system (Ref. 3) was found. Figure 15 shows the results of the higher-magnification examinations. When the polyimide resin matrix oxidized, it was more prone to crumble and resulted in an increased amount of relief polishing around the individual fibers. After 10,000 hours of aging at both temperatures, considerable oxidation has occurred in the outer plies but almost none in the center plies. This would be expected for an oxidation mechanism where attack begins at the outer surfaces and proceeds inward. Careful examination of Figure 15 also reveals an effect of temperature on oxidation where the degree of relief polishing around the graphite fibers is slightly greater at 450F than at 350F.

CONCLUSIONS

The mechanical properties of the Celion 6000/LARC-160 system were, in general, at least 25% stronger than the HT-S/710 system. The fiber-dominated properties of the two polyimides were nearly independent of temperature for the region examined. The matrix-dominated properties showed a slight decrease in strength as the temperature was increased.

The fatigue results clearly show that the strength at 10^7 cycles for a stress ratio of $R = -1$ is 50% of that for $R = 0.1$. Differences between room and elevated temperature S-N curves were not statistically significant. Also, notching had little effect on the fatigue results.

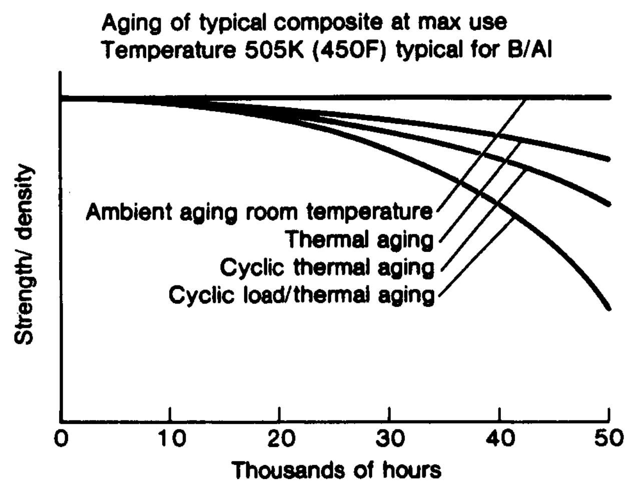
During thermal aging of HT-S/710 at 450F in an air atmosphere, there was little change in tensile strength for times out to 25,000 hours. At 550F, the strength was reduced significantly by 5,000 hours. Aging of Celion 6000/LARC-160 at both

350F and 450F resulted in a 20% loss in strength after 5,000 hours and a 30% loss after 10,000 hours. Tests on these specimens are being continued to 25,000 hours.

Metallographic studies have shown an increase in microcracking with aging time for the Celion 6000/LARC-160 system. These examinations have also revealed evidence of conventional oxidation damage to the matrix with the effect initiating at the surface and progressing inward with time. A similar effect had been observed earlier for A-S/3501 graphite/epoxy. For the HT-S/710 system, metallographic examinations showed very little during the early stages of exposure. For the longer times, increased porosity and fiber-matrix separation accompanied by numerous fine cracks at the fiber-matrix interface were revealed. However, visual effects starting at the edges and moving inward as seen in the Celion 6000/LARC-160 and A-S/3501 systems were not observed.

REFERENCES

1. Kerr, J.R. and Haskins, J.F., "Time-Temperature-Stress Capabilities of Composite Materials for Advanced Supersonic Technology Application," General Dynamics Convair Division, Report No. NASA CR-159267 (GDC-MAP-80-001), Prepared for NASA-Langley Research Center, April 1980.
2. Kerr, J.R. and Haskins, J.F., "Effects of 50,000 Hours of Thermal Aging on Graphite/Epoxy and Graphite/Polyimide Composites," AIAA/ASME/ASCE/AHS 23rd Structures, Structural Dynamics, and Materials Conference, New Orleans, Louisiana, May 1982.
3. Haskins, J.F., Kerr, J.R., and Stein, B.A., "Flight Simulation Testing of Advanced Composites for Supersonic Cruise Aircraft Applications," AIAA/ASME 18th Structures, Structural Dynamics, and Materials Conference, San Diego, California, March 1977.



Test environments
218K (−67K) to 700K (800F)
Single-variable tests
Multiple-variable tests
Materials
Proven composite systems
Tested in severe supersonic environment
B/E, G/E, B/PI, G/PI, B/Al
Types of tests
Laboratory tests
Tensile-fatigue-creep-aging
Flight simulation
Temp profile-random loading
Analysis
Lamination theory
Wearout model
Damage assessment
Data base
Existing
Extending
Confidence

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Figure 1. Characterization of composite material for up to 50,000 hours of supersonic cruise aircraft environment.

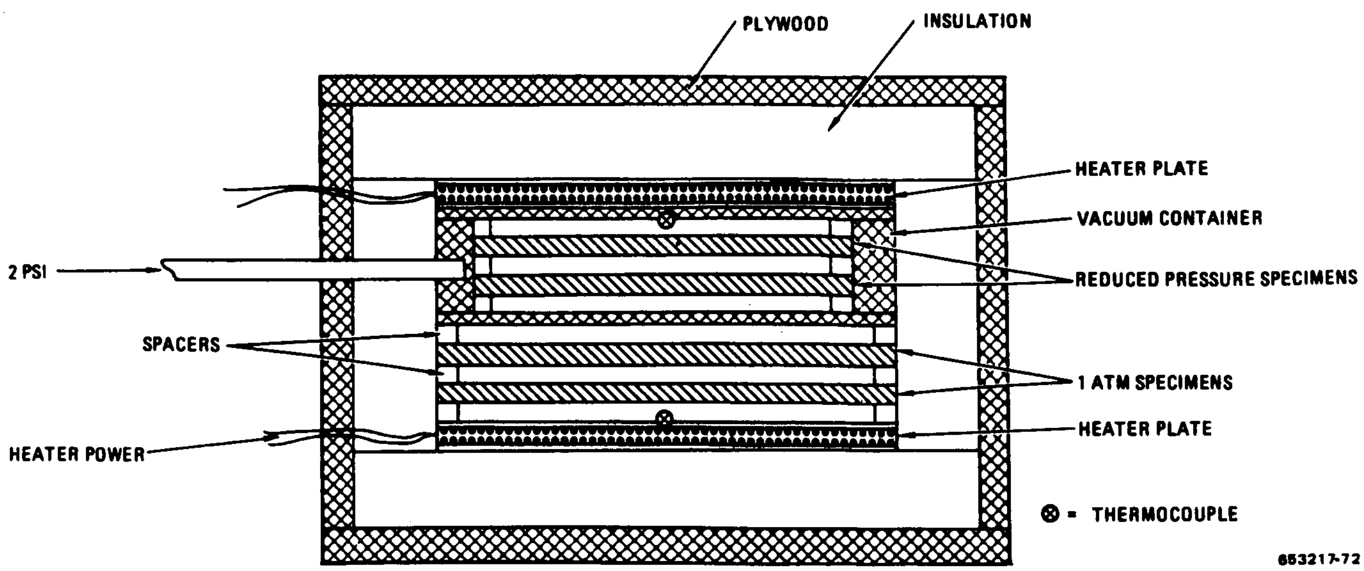


Figure 2. Thermal aging furnace configuration.

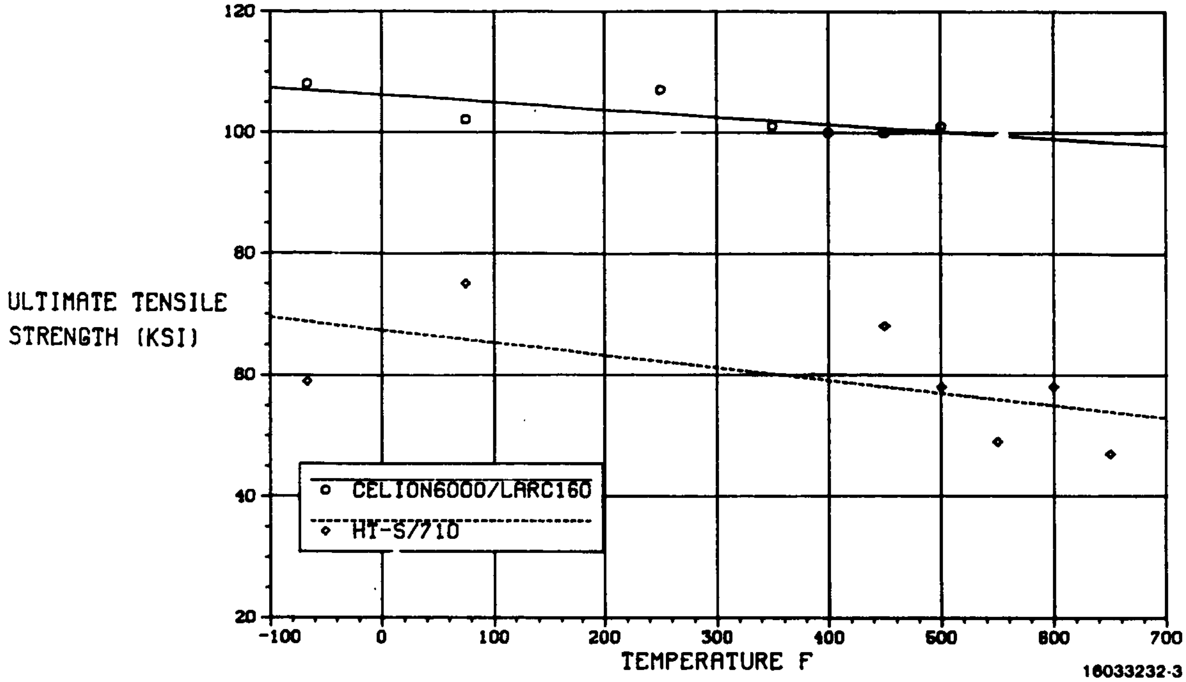


Figure 3. Baseline tensile results comparing unnotched Celion 6000/LARC-160 and HT-S/710 $(0 \pm 45)_S$ polyimide composites.

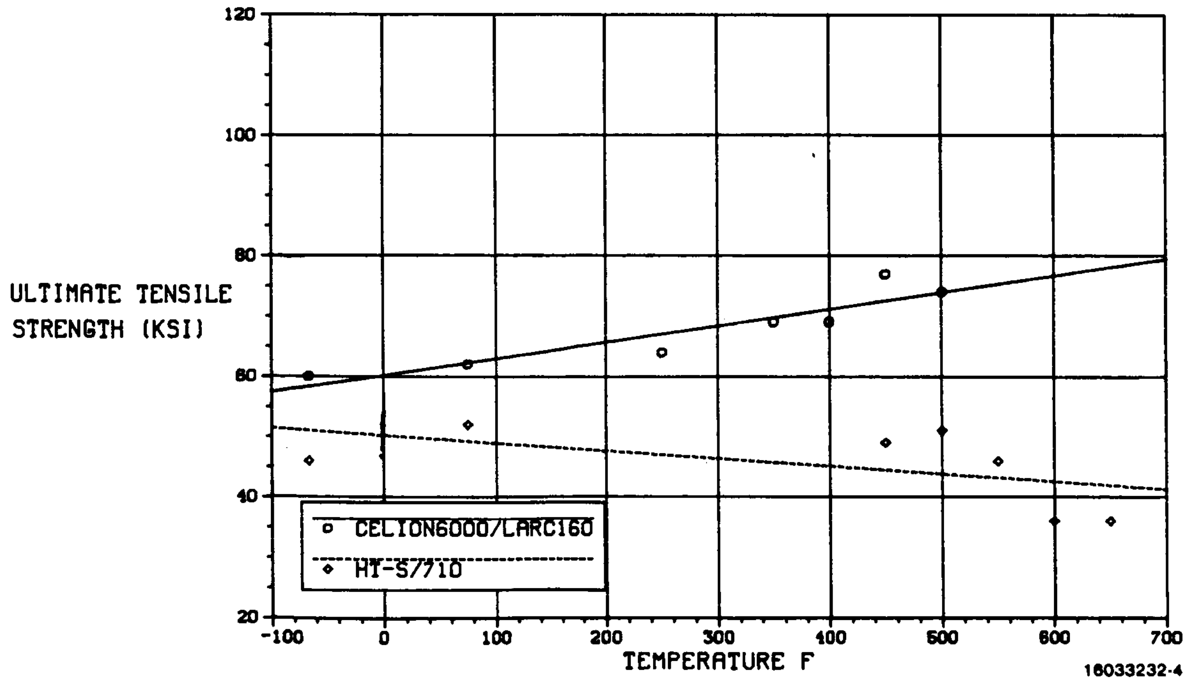


Figure 4. Baseline tensile results comparing notched Celion 6000/LARC-160 and HT-S/710 $(0 \pm 45)_S$ polyimide composites.

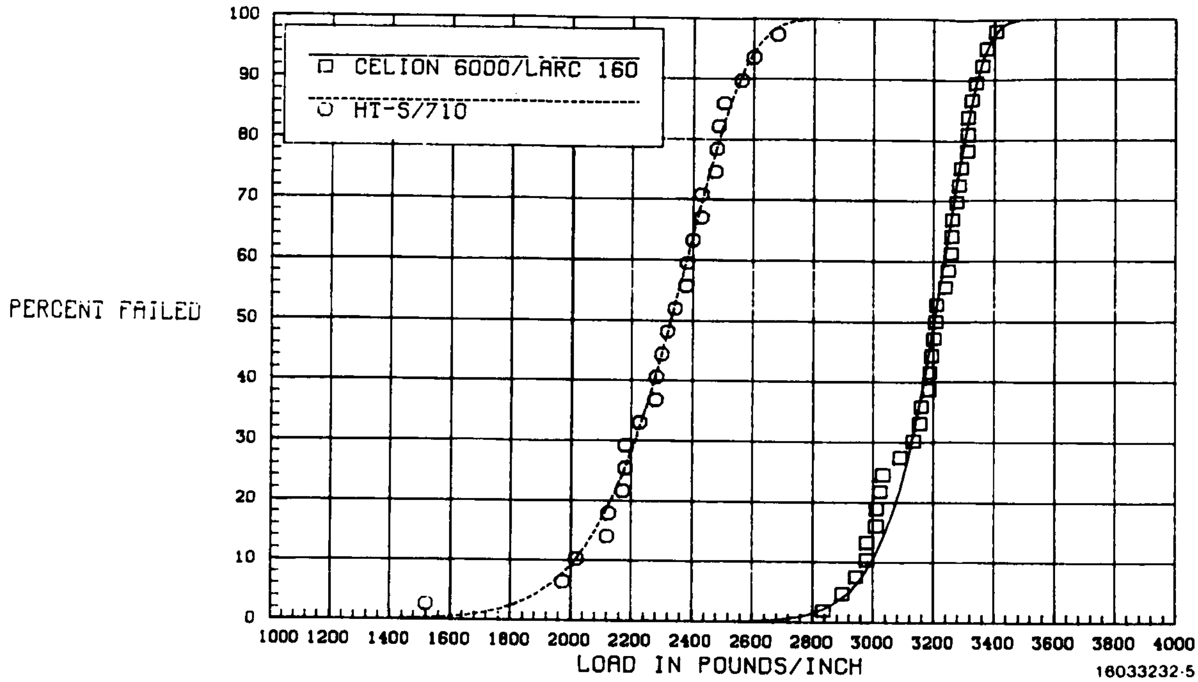


Figure 5. Comparison of unnotched tensile data for HT-S/710 and Celion 6000/LARC-160 (0 ± 45)$_S$ (test points superpositioned to 350F for pooling).

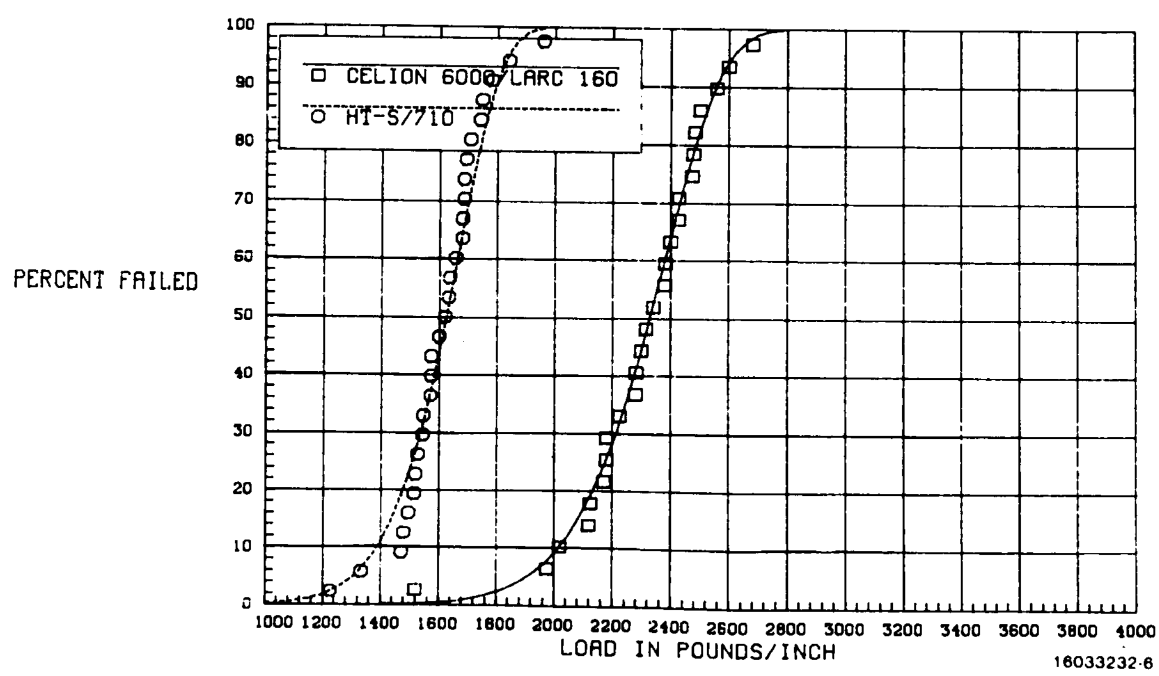


Figure 6. Comparison of notched tensile data for HT-S/710 and Celion 6000/LARC-160 (0 ± 45)$_S$ (test points all superpositioned to 350F for pooling).

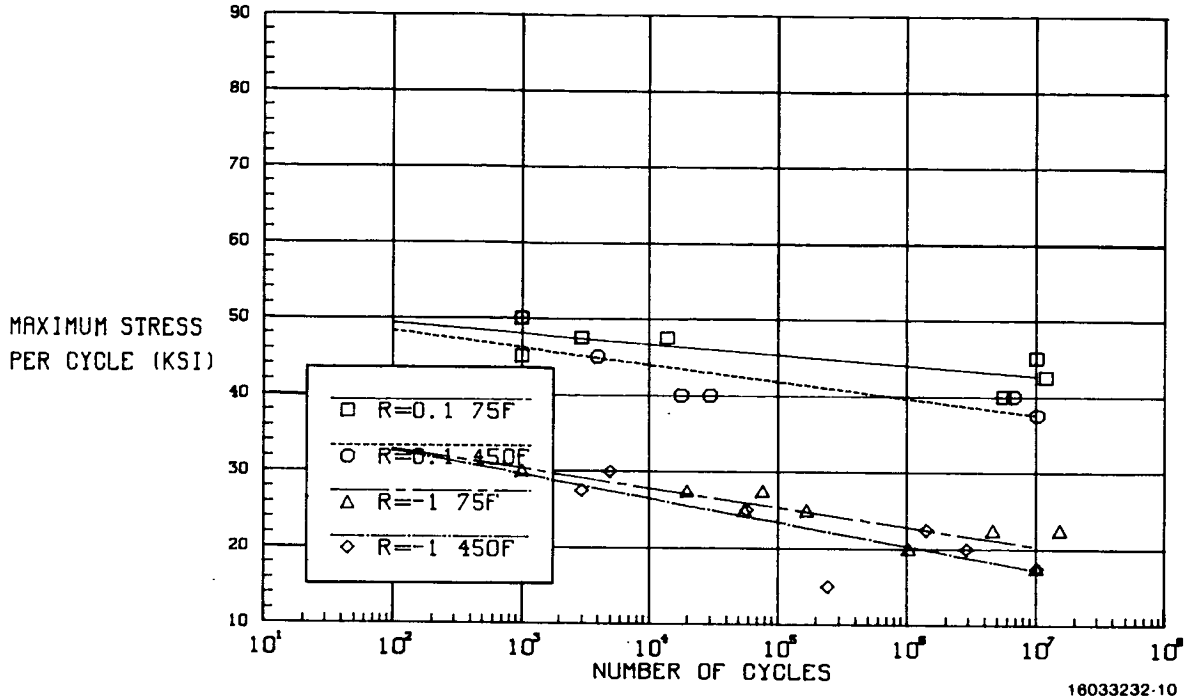


Figure 7. Axial fatigue data for HT-S/710 $(0\pm45)_S$ G/PI, unnotched, $R=0.1$, $R=-1$.

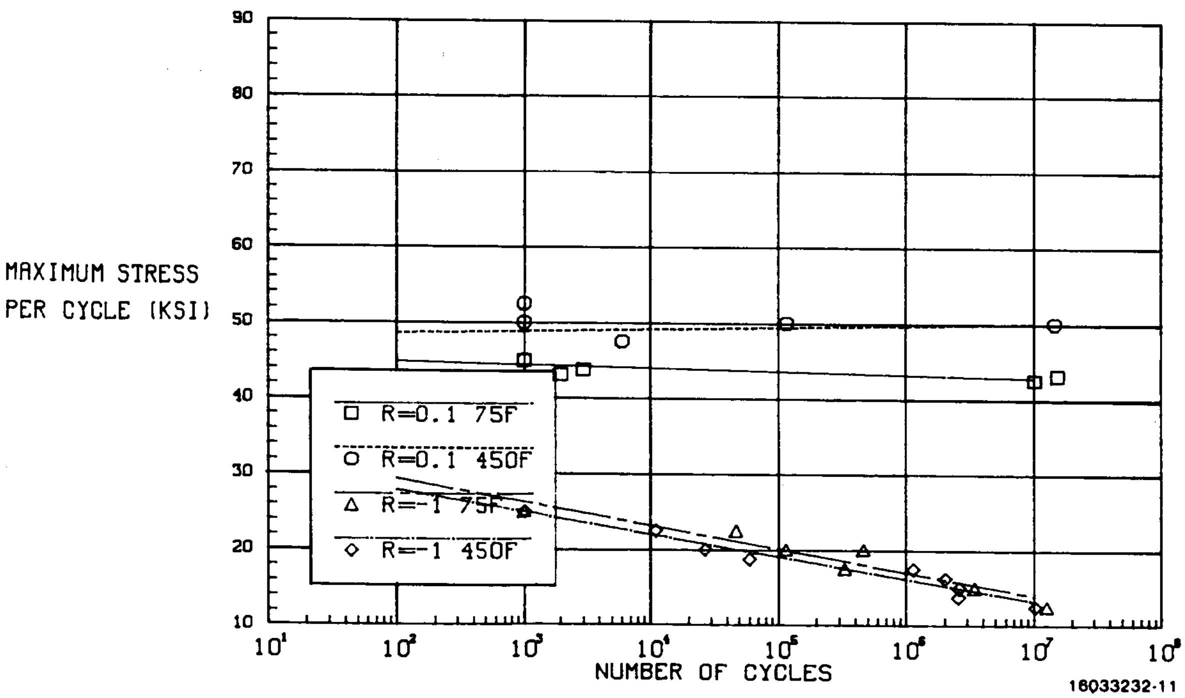


Figure 8. Axial fatigue data for HT-S/710 $(0\pm45)_S$ G/PI, notched, $R=0.1$, $R=-1$.

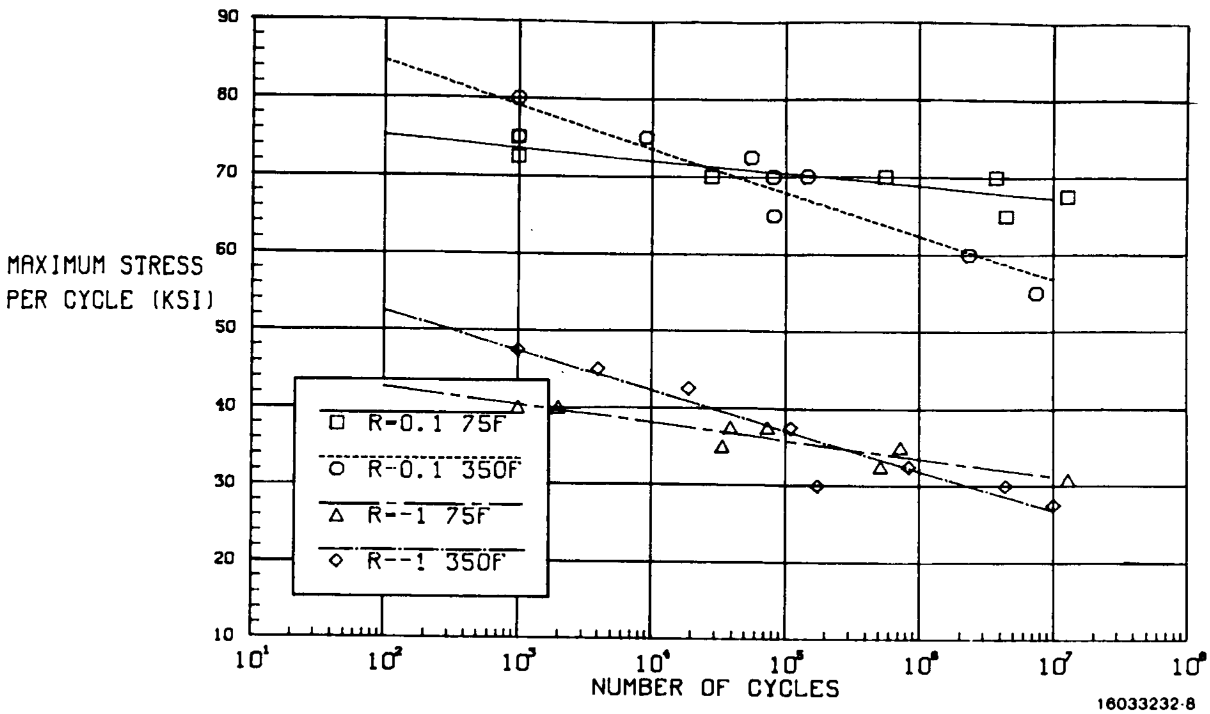


Figure 9. Axial fatigue data for Celion 6000/LARC-160 $(0\pm45)_S$ G/PI, unnotched, R = 0.1, R = −1.

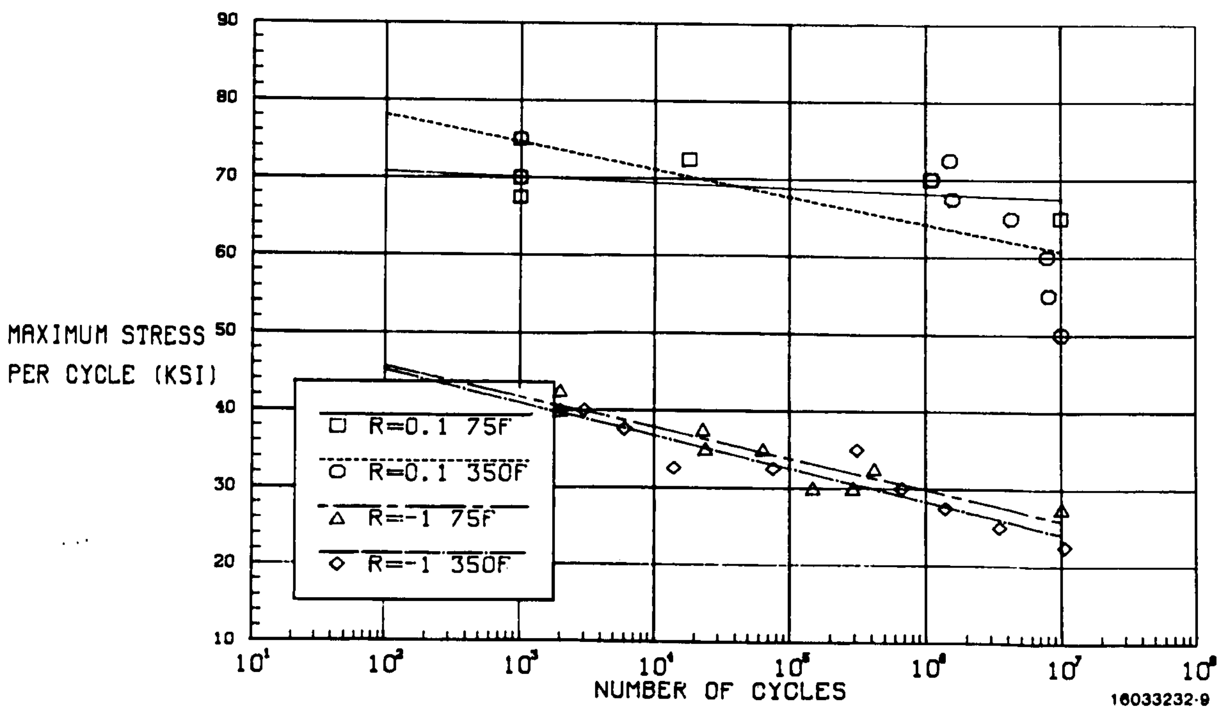


Figure 10. Axial fatigue data for Celion 6000/LARC-160 $(0\pm45)_S$ G/PI, notched, R = 0.1, R = −1.

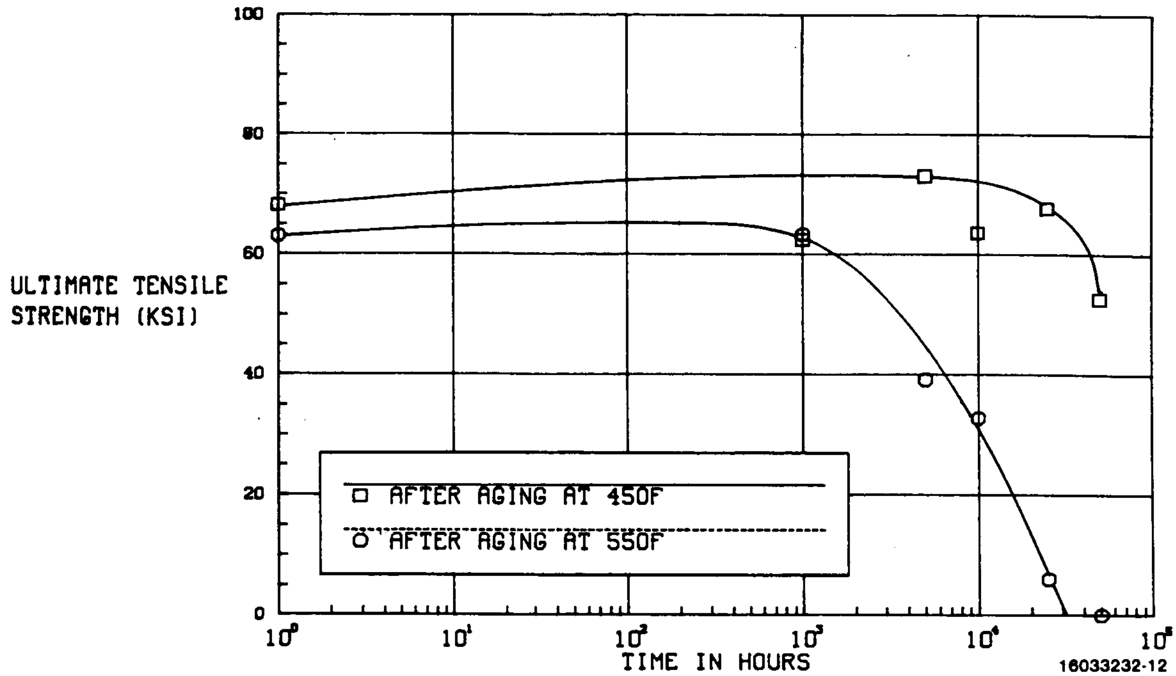


Figure 11. Tensile strength at aging temperature of HT-S/710 (0 ± 45)$_S$ G/PI after thermal aging in 14.7 psi air at indicated temperatures.

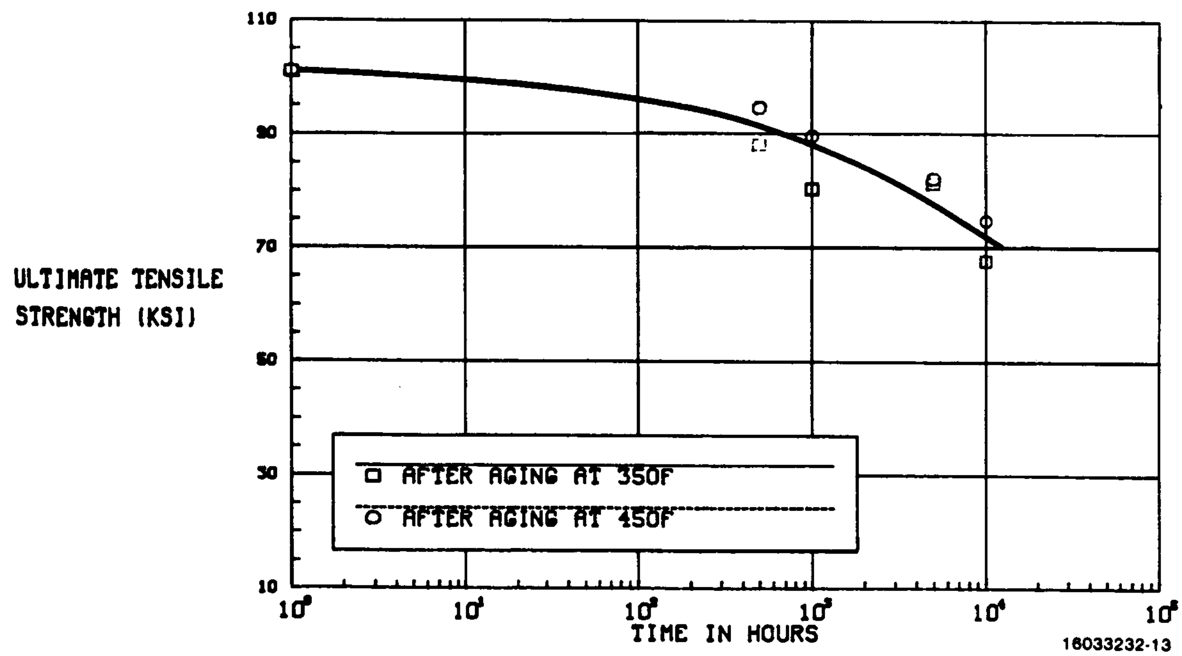


Figure 12. Tensile strength of Celion 6000/LARC-160 (0 ± 45)$_S$ G/PI at 350F after thermal aging in 14.7 psi air at the indicated temperatures.

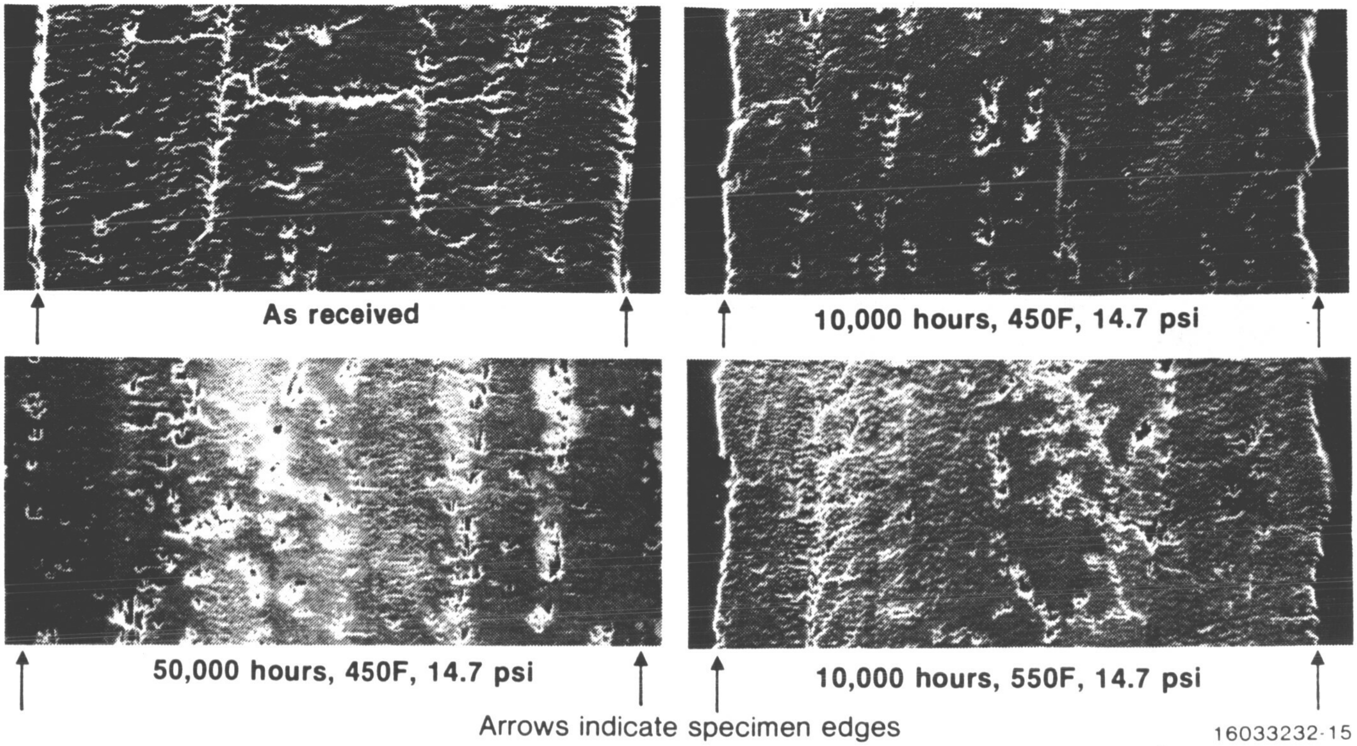


Figure 13. HT-S/710 graphite/polyimide after thermal aging at indicated conditions (100×).

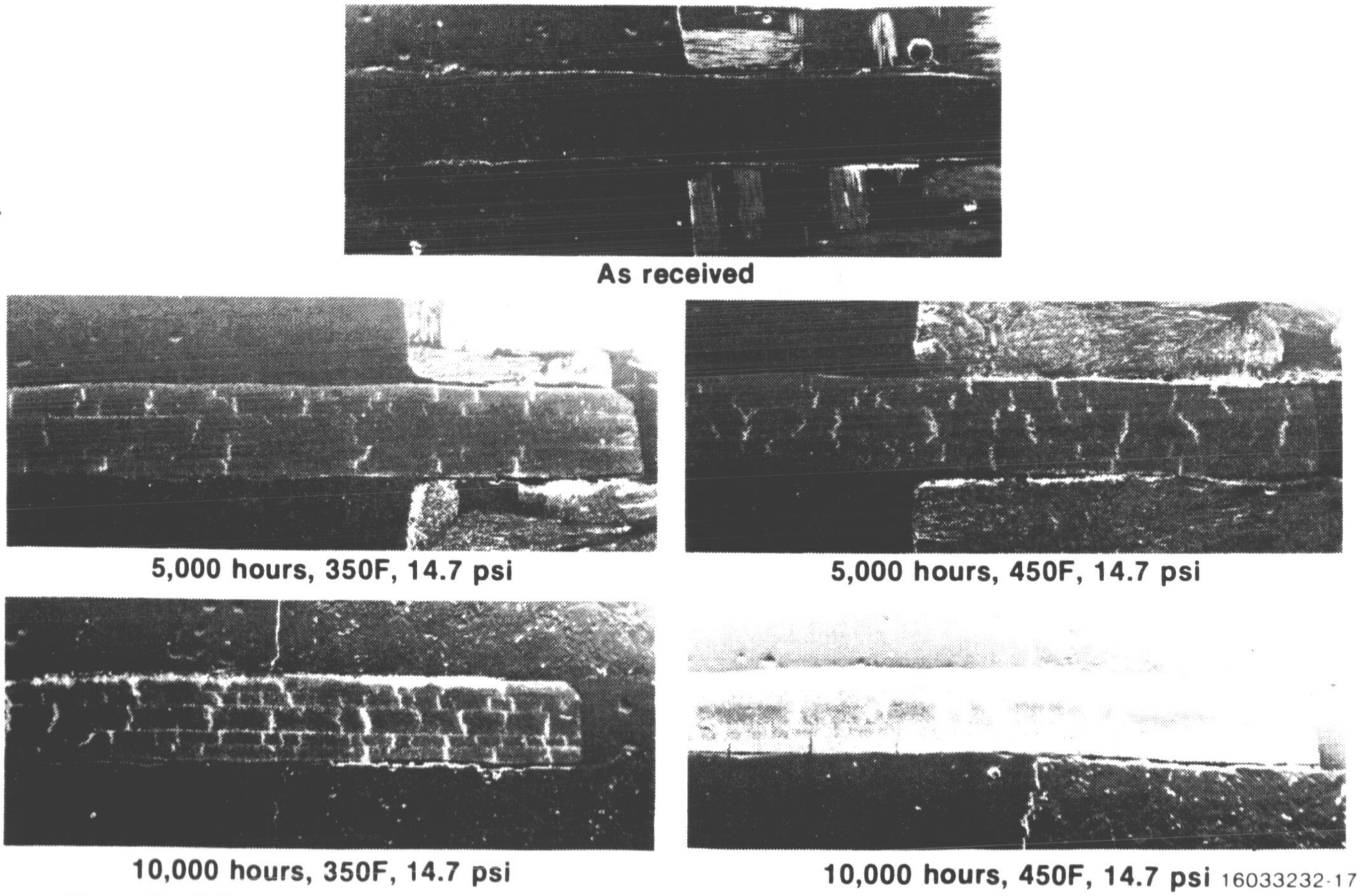
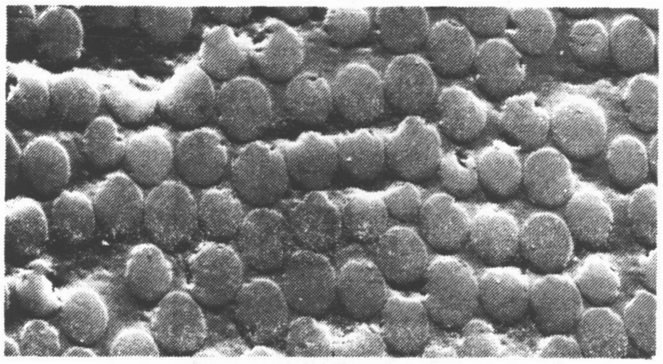
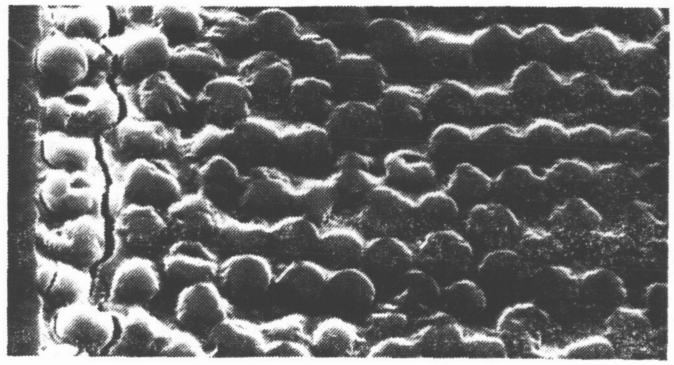


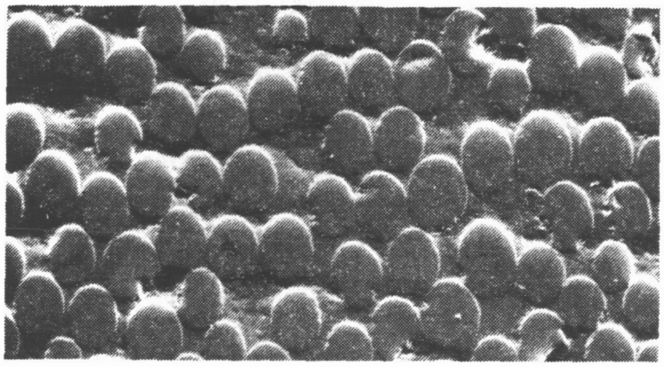
Figure 14. Celion 6000/LARC-160 graphite/polyimide after thermal aging at indicated conditions (13×).



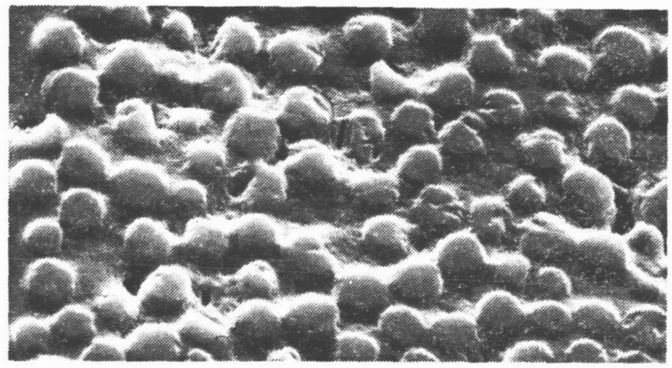
10,000 hours, 350F, 14.7 psi
Inner ply



10,000 hours, 350F, 14.7 psi
Outside ply



10,000 hours, 450F, 14.7 psi
Inner ply



10,000 hours, 450F, 14.7 psi
Outside ply

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Figure 15. Celion 6000/LARC-160 graphite/polyimide after thermal aging at indicated conditions (1000×).