NASA Technical Memorandum 85763

NASA-TM-85763 19840013599

EDGE CRACK GROWTH IN THERMALLY AGED GRAPHITE/POLYIMIDE COMPOSITES

James B. Nelson

MARCH 1984

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

18 1 1 RN/NASA-TM-85763

DISPLAY 18/2/1

84N21667*# ISSUE 12 PAGE 1789 CATEGORY 24 RPT*: NASA-TM-85763 NAS 1.15:85763 84/03/00 22 PAGES UNCLASSIFIED DOCUMENT

UTTL: Edge crack growth of thermally aged graphite/polyimide composites

AUTH: A/NELSON, J. B.

CORP: National Aeronautics and Space Administration. Langley Research Center, Hampton, Va. AVAIL.NTIS SAP: HC A02/MF A01

MAJS: /*AGING (METALLURGY)/*CRACK PROPAGATION/*FRACTURES (MATERIALS)/* GRAPHITE-POLYIMIDE COMPOSITES/*HEAT TREATMENT/*LAMINATES/*MICROCRACKS/* SURFACE DEFECTS/*X RAY ANALYSIS

MINS: / CRACK GEOMETRY/ DIES/ FLEXING/ LOADING MOMENTS/ SHEARING/ THERMAL DEGRADATION

ABA: M.A.C.

ABS: Laminates of Celion 6000/LARC-160 and Celion 6000/PMR-15 graphite/polyimide composite materials were aged in air at temperatures of 202, 232, 260 and 288 C for various times up to 15,000 hours. Three unidirectional specimen types were studied: short beam shear (SBS), flexure, and 153 mm square panels. The interior region of the square panels exhibited little or no property degradation, whereas both laminate materials degraded and cracked preferentially at the specimen edge perpendicular to the fibers. Using a dye penetrant, the specimens were X-rayed and the crack depth measured as a function of time and temperature. A time temperature superposition of the crack data was

ENTER:

EDGE CRACK GROWTH IN THERMALLY AGED GRAPHITE/POLYIMIDE COMPOSITES

James B. Nelson

NASA Langley Research Center

Hampton, Virginia 23665

SUMMARY

Celion®6000/LARC-160 and Celion 6000/PMR-15 graphite/polyimide composite materials were aged in air at temperatures of 202, 232, 260 and 288°C for various times up to 15,000 hours. Three unidirectional specimen types were studied: short beam shear (SBS), flexure, and 153 mm square panels. The interior region of the square panels exhibited little or no property degradation, whereas both laminate materials degraded and cracked preferentially at the specimen edge perpendicular to the fibers. Using a dye penetrant, the specimens were x-rayed and the crack depth measured as a function of time and temperature. A time-temperature superposition of the crack data was successfully performed using an Arrhenius form for the shift factor. A direct correlation was found for edge crack depth and SBS strength for Celion/LARC-160 but not for Celion/PMR-15.

®Celion is a registered trademark of Celanese Corporation.

INTRODUCTION

There have been numerous studies reported on microcracking phenomena in fiber reinforced laminates (ref. 1 to 3). Usually this cracking is observed in cross-plied laminates subjected to external loads. Cracking has been observed for laminates subjected to only internal curing stresses and internal stresses due to the adsorption and desorption of moisture. In a previously reported study by this author (ref. 4), unidirectional graphite/polyimide laminates aged with no external load at temperatures from 202 to 288°C for up to 15,000 hours exhibited microcracking on the laminate edges that appeared to be the controlling influence in the observed property degradation. In this report, an analysis of the cracked specimens aged in reference 4 is described.

EXPERIMENTAL

Materials and Fabrication

The graphite/polyimide laminate materials tested were Celion® 6000/LARC-160 and Celion 6000/PMR-15. The continuous filament Celion 6000 fiber was sized by the manufacturer with a polyimide material based on DuPont NR-150B.* The two matrix resins are similar polyimides, differing primarily in the aromatic diamines used. PMR-15 is a monomeric mixture of

®Celion is a registered trademark of Celanese Corporation.

*NR150B is the trade name of polyimide precurser solutions manufactured by the DuPont Company.

4,4'-methylenedianiline (MDA) and the methyl ester-acids of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and nadic anhydride (NA) (ref. 5). LARC-160 is a solventless resin system based on the ethyl ester-acids of BTDA and NA, and Jeffamine AP-22 aromatic amine mixture (ref. 6).

PMR-15 prepreg was prepared by conventional solvent impregnation of Celion 6000 fiber during drum winding. Unidirectional layups of 11 and 22 plies, approximately 610 mm x 610 mm, were autoclave processed to a maximum temperature of 330°C according to the cure cycle reported in reference 7. The LARC-160 laminates were fabricated from a commercial hot-melt impregnated tape.* Unidirectional layups of 12 and 24 plies (more plies used due to thinner prepreg), approximately 1270 mm x 660 mm, were autoclave processed to a maximum temperature of 330°C as detailed in reference 4.

After fabrication, the laminates were subjected to ultrasonic C-scan inspection. The acceptable laminates were cut into square panels, short beam shear (SBS) and flexure specimens. Specimen dimensions are shown in figure 1.

Experimental

The specimens and panels were isothermally aged in forced convection air ovens at 204°C, 232°C, 260°C and 288°C. At predetermined intervals up to 15,000 hours, specimens were removed for weight loss determination and mechanical testing. SBS specimens were machined from the aged square panels as shown in figure 1. A corner specimen was retained from each square panel for microscopic and radiographic analysis. The two outside edges of each of

*Hexcel Company in Dublin, CA.

the radiographic specimens were treated with an x-ray absorber solution (zinc iodide solution) to penetrate any cracks and delaminations. Excess solution was wiped clean and the specimens placed in a Faxitron Model 804D x-ray chamber (Field Emission Industries) for exposure on a Polaroid film sheet in contact with the specimens. Crack depth was determined directly from the radiographs.

RESULTS AND DISCUSSION

Edge Cracking

In the aging study reported in reference 4, the edge cracking of these unidirectional laminates was observed to occur primarily on the panel edges normal to the fiber (°0 edge). Low magnification scanning electron microscope photographs of the edge surfaces of an unaged and an aged Celion 6000/PMR-15 panel (15,000 hours at 232°C) are shown in figure 2. The low magnification photomicrographs of the unaged specimen reveal no obvious cracks. Indeed, the unaged specimens were carefully examined at magnifications up to 5000x but no cracking was observed. The edge cracks were observed after as few as 75 hours of aging at 232°C. Figures 3(a), 3(b), 3(c) and 3(d) show a series of SEM photographs of a typical 0° edge of a 75 hour aged Celion 6000/PMR-15 panel. The initial degradation pattern is evident in figure 3(a); the resin-rich areas have been oxidized or degraded leaving shallow trenches scattered across the edge surface. This process is observed almost immediately on aging. In addition, this figure shows the cracks that appeared, generally in the fiber-rich areas, after 75 hours.

The horizontal crack near the center of figure 3(a) is further examined in figures 3(b), 3(c) and 3(d). This crack has propagated into a resin rich area where the effect of the crack on the matrix material can be seen. These figures show the large amount of polymer stretching that takes place around the fibers as the crack opens up.

When SBS specimens were cut from the 153 mm square coupons, it was observed that the shear strengths of the specimens taken from the 0° ends of the coupons were significantly lower (fig. 4) than for the other specimens. A direct relationship between coupon weight loss and the relative surface area of the 0° edges was observed and reported in reference 4. These factors suggested that the cracks were propagating deeper into the specimens with continued thermal aging. The dye penetrant x-ray method permitted the measurement of the average crack growth depth of each of the aged laminates. The gradual crack growth of PMR-15 laminates aged at 232°C can be seen in figure 5.

Crack Growth Analysis

Crack depth variation with aging time for LARC-160 and PMR-15 laminates aged of 204°C to 288°C are shown in figures 6 and 7. Both materials exhibit a strong relationship between crack depth and both aging time and aging temperature. This suggests that the crack growth might follow a rate equation of the Arrhenius type, e.g.:

$$\frac{dC}{dt} = A\, e^{-B/T} \qquad (1)$$

where C = crack depth

T = Temperature, K

t = time, hrs

A & B constants

Equation (1) may be integrated for the isothermal $(\frac{dT}{dt} = 0)$ case:

$$C = A\, e^{-B/T}\, t \tag{2}$$

If a time-temperature superposition of the crack depth curves in figures 6 and 7 is attempted, each of the curves is shifted along the time axis into a single master curve. Each curve is shifted according to

$$\tau = \alpha t \tag{3}$$

where τ = shifted time, hrs

t = measured time, hrs

α = shift factor

Often shift factors are determined by trial and error. However, an expression for the shift factor can be derived from equation (2).

$$\alpha = e^{-B\left(\frac{1}{T} - \frac{1}{Tr}\right)} \tag{4}$$

where T_r = reference temperature, K (arbitrary)

To evaluate equation (4), the constant B was determined graphically for both materials. Using equations (3) and (4), master crack depth curves were constructed as shown in figures 8 and 9, for LARC-160 and PMR-15 laminates. These master crack depth curves can be used to estimate crack growth for any

time and temperature. It was speculated in reference 4 that edge cracking was the primary factor in the measured mechanical property degradation. To test this hypothesis, the room temperature SBS data for all four aging temperatures of each of the composite materials were plotted versus the measured crack depth. A least-squares fit of the shear strength to crack depth of aged LARC-160 laminates is shown in figure 10. This plot suggests that the shear strength of specimens machined from the exposed 0° edge of a panel of Celion 6000/LARC-160 is controlled by the edge cracking behavior regardless of aging time or temperature. In contrast, the shear strength of PMR-15 laminates (0° edge), shown in figure 11, does not appear to be as directly dependent on crack depth. Only two data points (the lowest SBS values at 204°C and 288°C) prevent a single curve, similar to LARC-160, to be fitted. Of course, these materials are affected by thermal aging in a variety of ways: thermal degradation of the bulk matrix resin, thermooxidative degradation at the surface, stress cracking, etc. At any given time during aging, at each location within a composite panel there probably will exist a balance of degradative modes that is unique to that specific location. Although both of these laminate materials experience apparently similar cracking behavior at the 0° edges, only the LARC-160 laminates show a true direct, unambiguous correlation between crack depth and shear strength. If comparison of mechanical properties was made with material taken away from the panel edges, a more accurate assessment of the

material's actual performance for a structural application could probably be made. These considerations are very important in analysis of data from aging studies of small specimens, such as SBS specimens. Any edge effect will influence measured differences between materials in ways that are irrelevant to larger panels.

CONCLUSIONS

The cracks found in the 0° edge of aged PMR-15 and LARC-160 unidirectional graphite fiber reinforced laminates were formed during aging, at temperature/time combinations as low as 232°C/75 hours. The resin-rich areas of the 0° edges were severely degraded before the cracks formed in the fiber-rich areas. The crack growth of both LARC-160 and PMR-15 laminates exhibited an Arrhenius type relationship with aging temperature. A direct correlation between crack growth and measured SBS strength was demonstrated for the LARC-160 laminates. However, the correlation appears more complex for the PMR-15 laminates.

REFERENCES

1. Mills, J. Steven; Herakovich, Carl T.; and Davis, John G., Jr.: Transverse Microcracking in Celion 6000/PMR-15 Graphite/Polyimide. Report No. VPI-E-79-35, Virginia Polytechnic Institute and State University, 1979.

2. Hahn, H. Thomas: Residual Stresses in Polymer Matrix Composite Laminates. J. Composite Materials, vol. 10, Oct. 1976, pp. 266-278.

3. Wang, A. S. D.; and Crossman, F. W.: Initiation and Growth of Transverse Cracks and Edge Delamination in Composite Laminates Parts 1 and 2. J. of Composite Materials Supplement, vol. 14, 1980, pp. 71-108.

4. Nelson, James B.: Thermal Aging of Graphite/Polyimide Composites. Long-Term Behavior of Composites, ASTM STP-813, T. K. O'Brien, ed., ASTM, Philadelphia, 1983, pp. 206-221.

5. Serafini, T. T.; Delvigs, P.; and Lightsey, G. R.: Thermally Stable Polyimides from Solutions of Monomeric Reactants. J. Appl. Polym. Sci., vol. 16, No. 4, 1972, pp. 905-915.

6. St. Clair, Terry L.; and Jewell, Robert A.: Solventless LARC-160 Polyimde Matrix Resin. Proceedings, 23rd Nat'l SAMPE Symp., vol. 23, May 1978, pp. 520-527.

7. Baucom, Robert M.: LaRC Fabrication Development. Graphite/Polyimide Composites. NASA CP-2079, 1979, pp. 19-37.

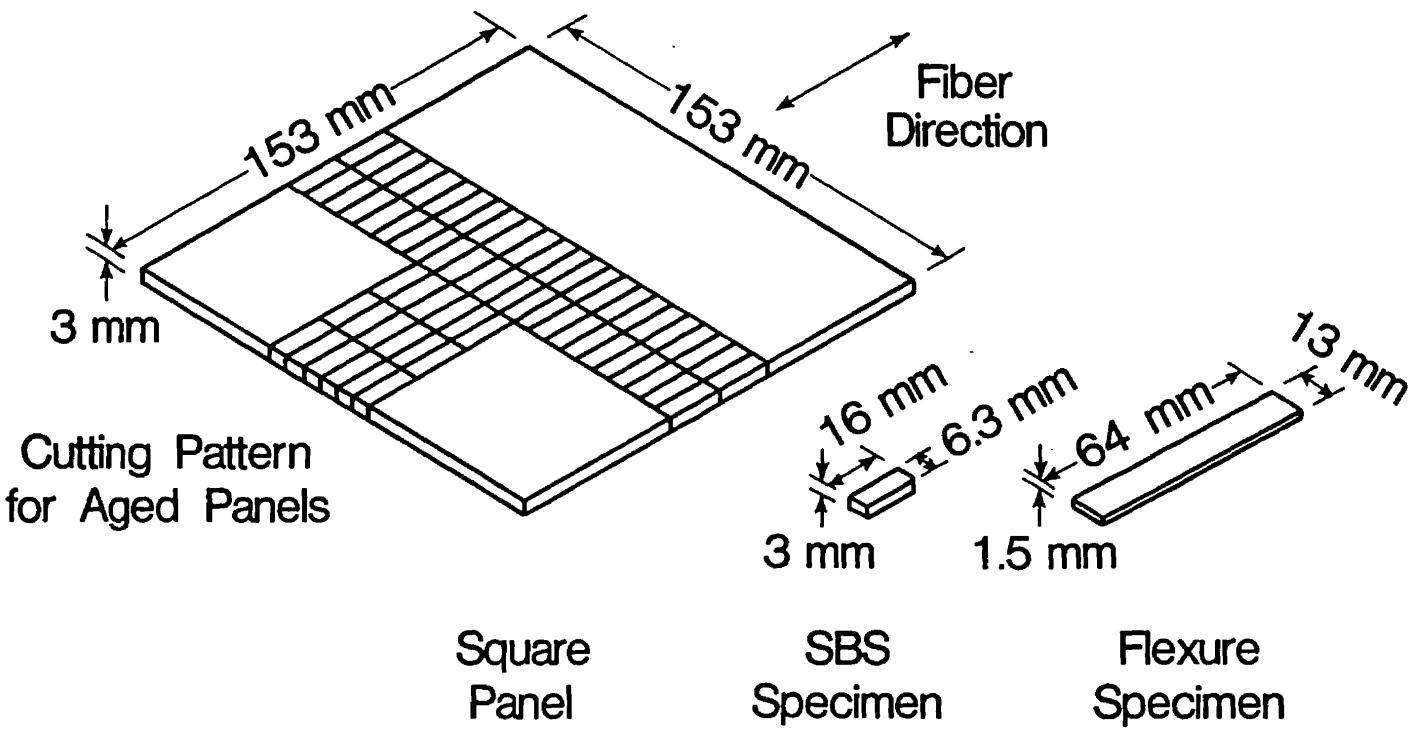


Figure 1 - Test specimen geometry.

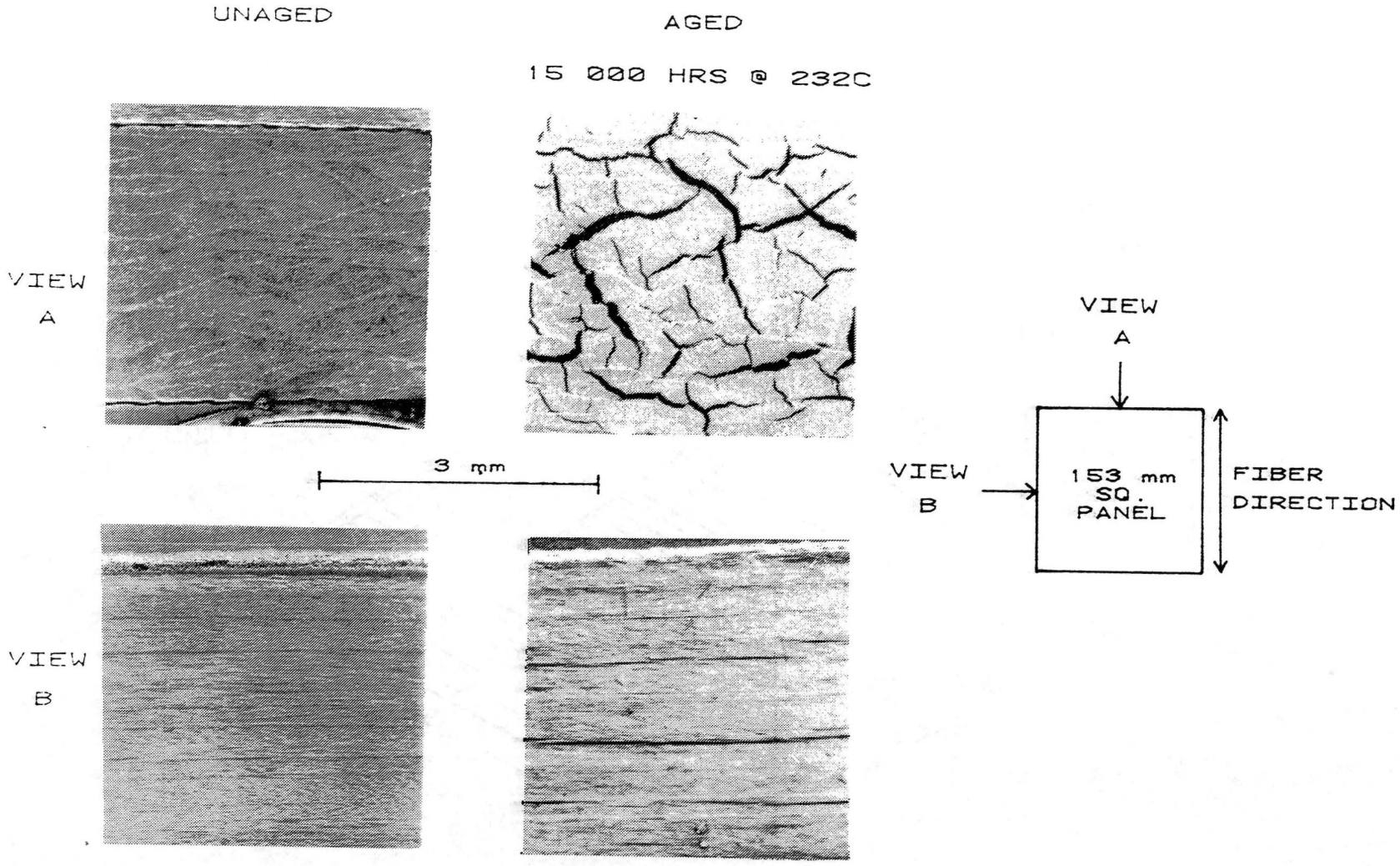
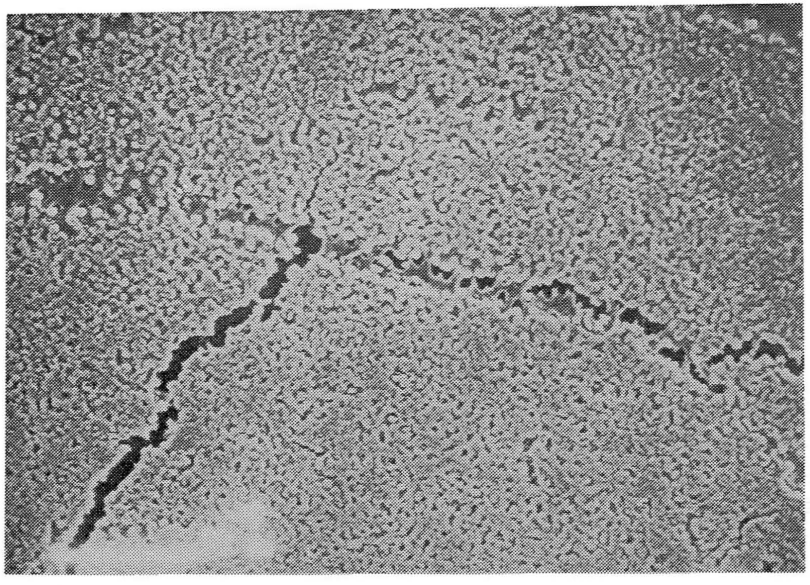
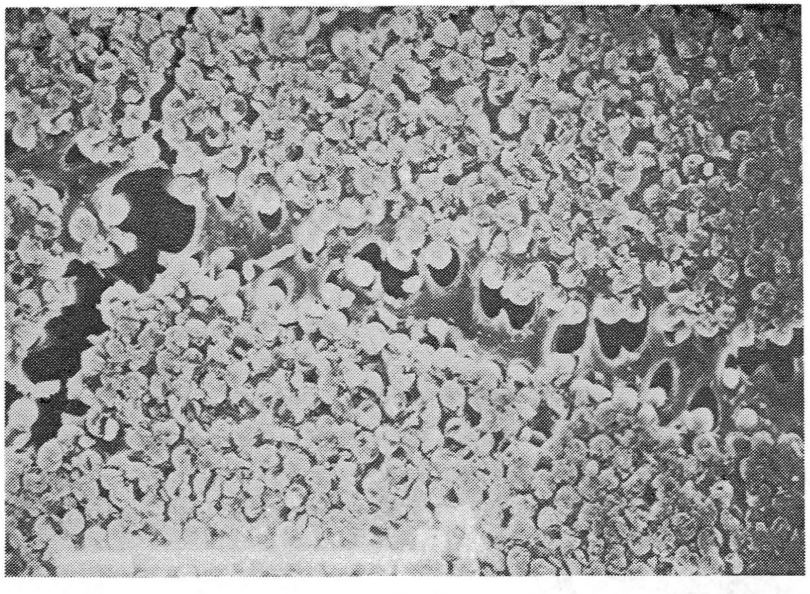


Figure 2 - Photomicrographs of Celion 6000/PMR-15, unaged and aged at 232°c for 15,000 hours.

(a) 50X



(b) 200X



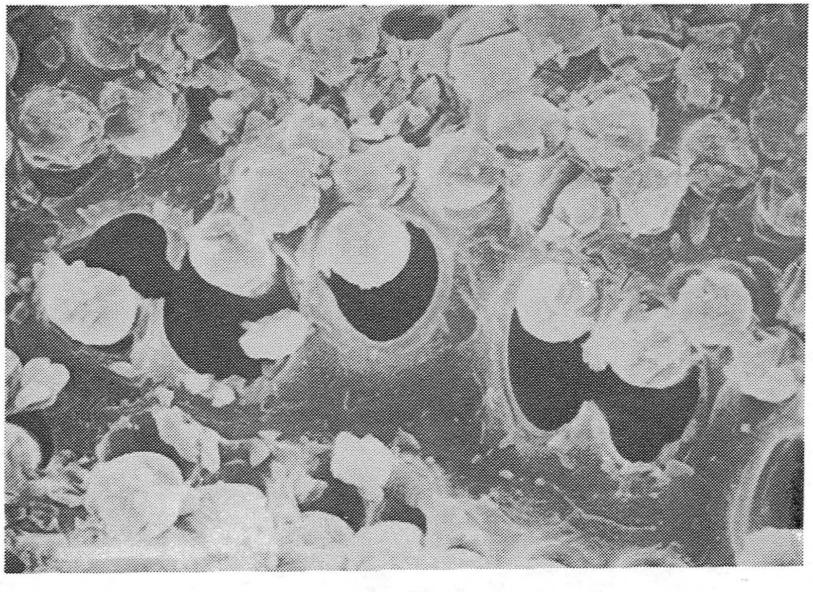


Figure 3 - SEM photographs of 0° edge of Celion 6000/PMR-15 panel aged for 75 hours at 232°C.

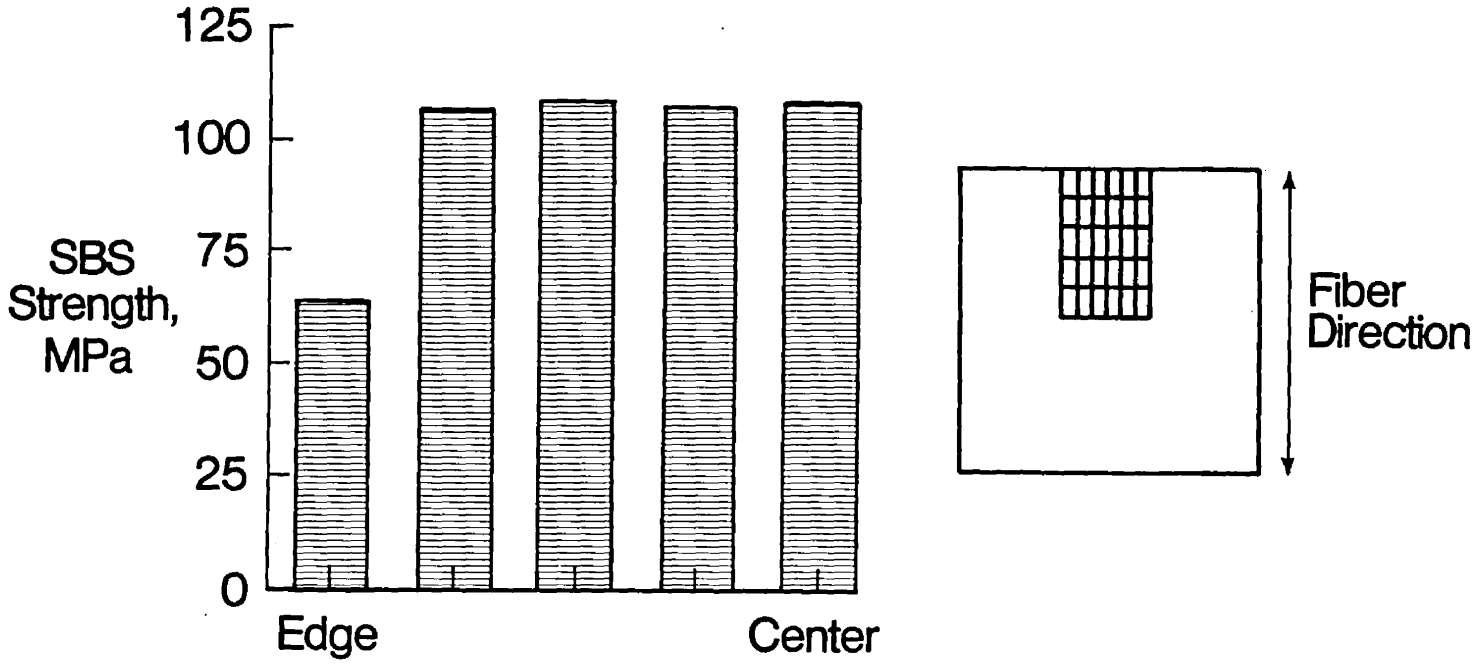


Figure 4 - Room temperature SBS strength retention of specimens machined from a 153 mm square Celion 6000/PMR-15 panel after aging 15,000 hours at 232°C.

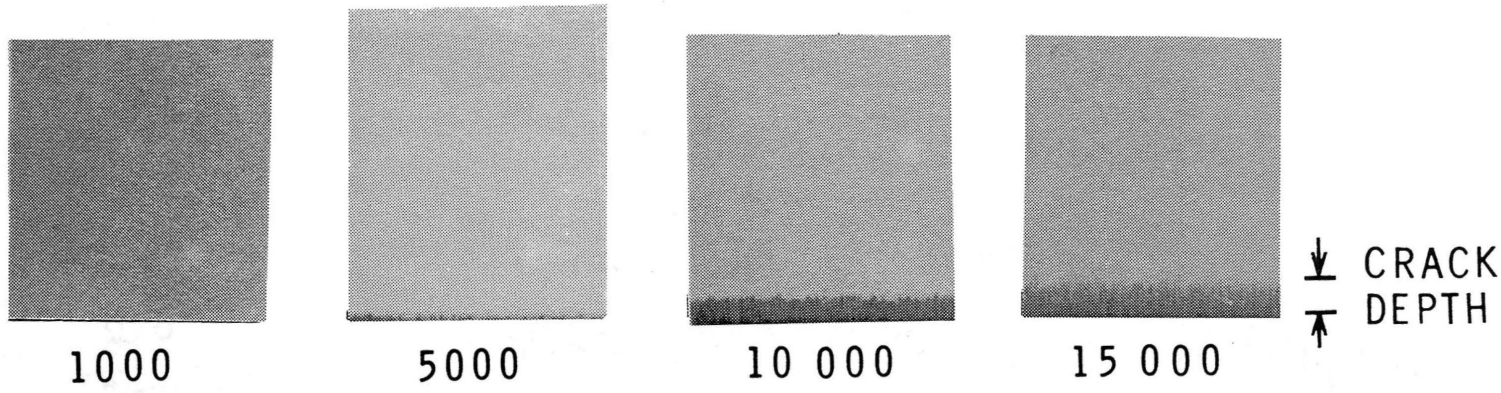


Figure 5 - X-ray photographs of Celion 6000/PMR-15 specimens aged at 232°C.

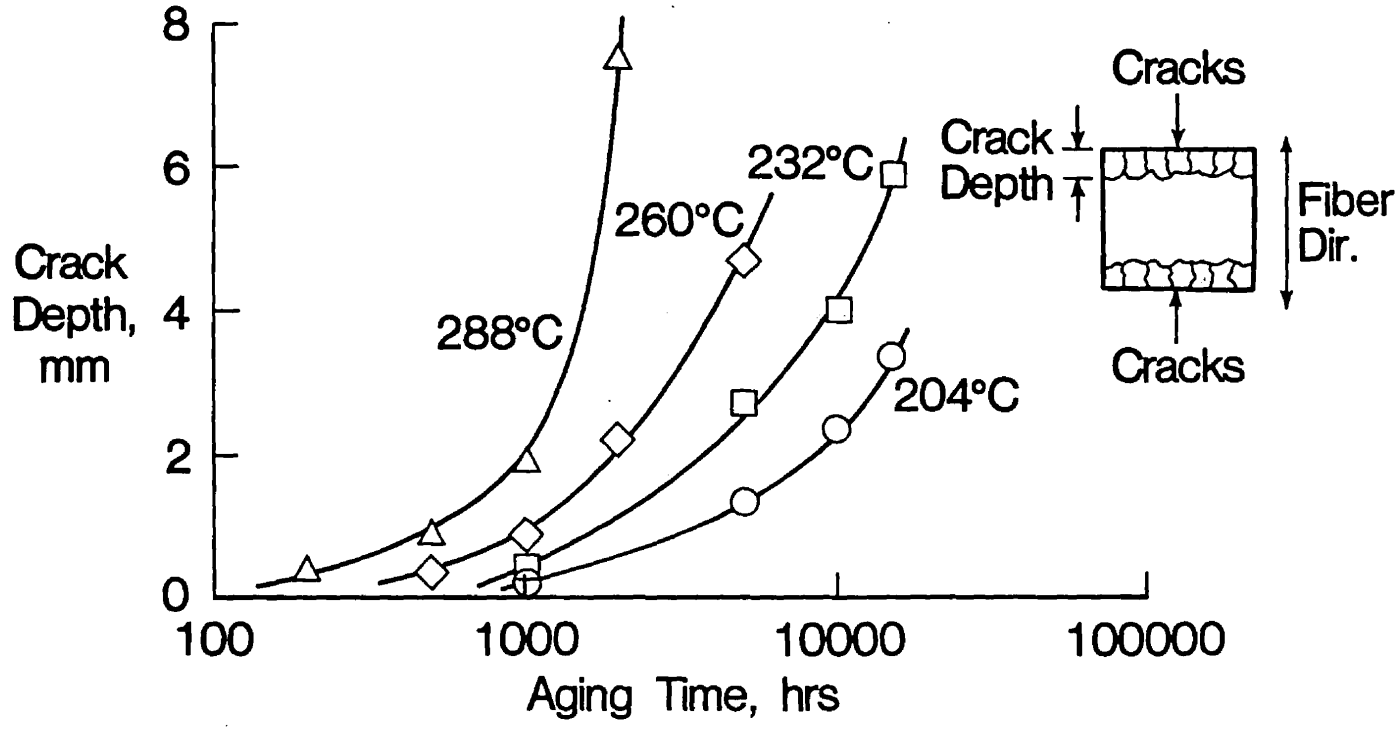


Figure 6 - Edge crack growth of aged Celion 6000/LARC-160 laminates.

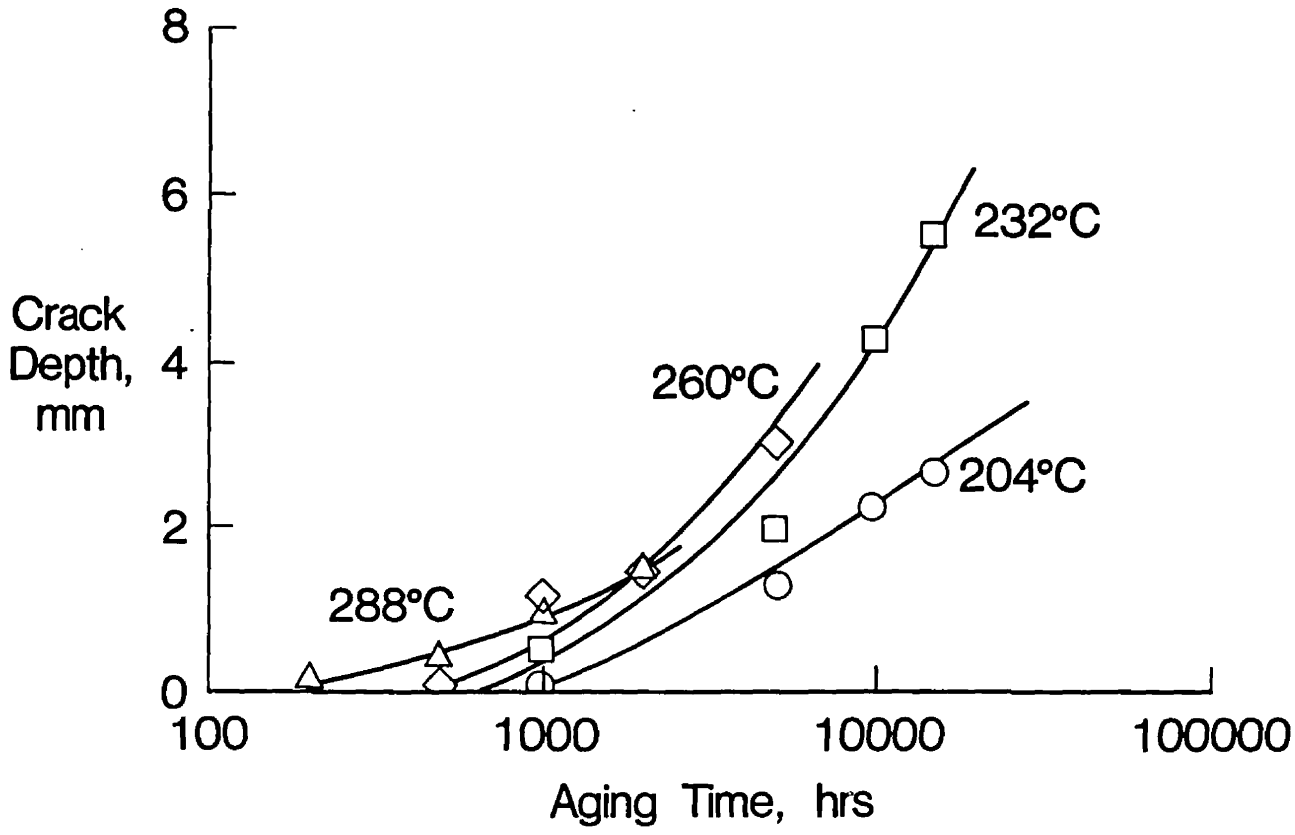


Figure 7 - Edge crack growth of aged Celion 6000/PMR-15.

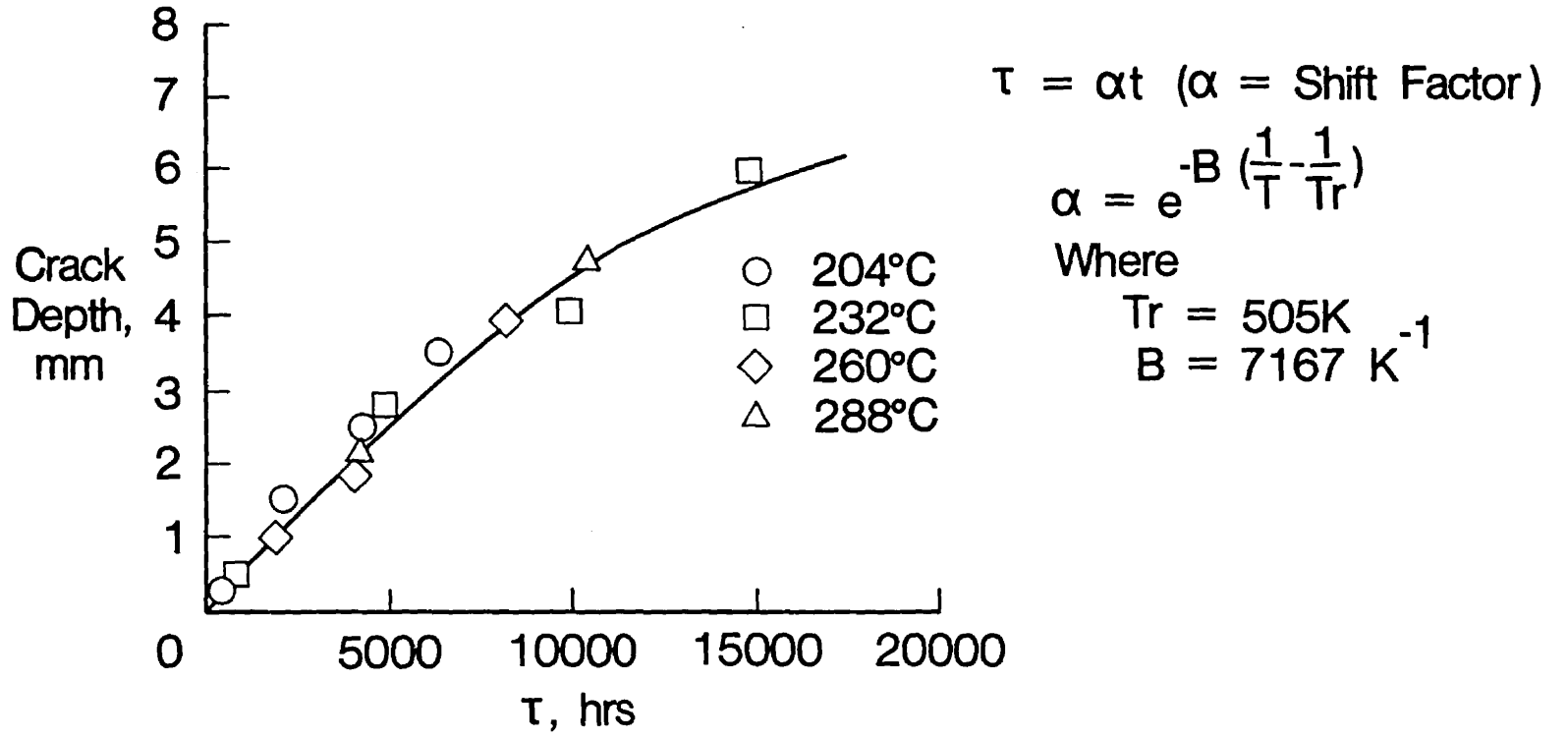


Figure 8 - Time temperature superposition master curve for Celion 6000/LARC-160.

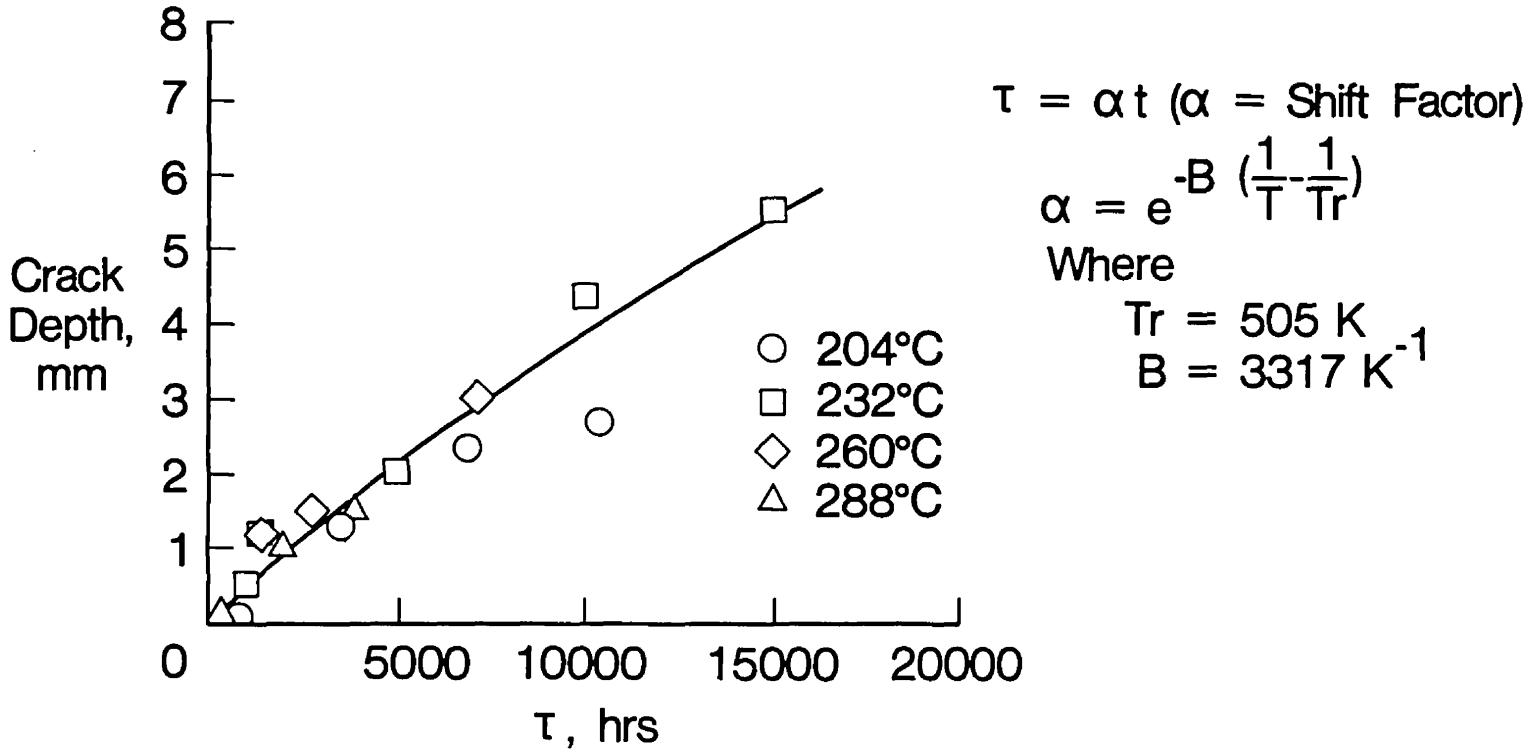


Figure 9 - Time temperature superposition master curve for Celion 6000/PMR-15.

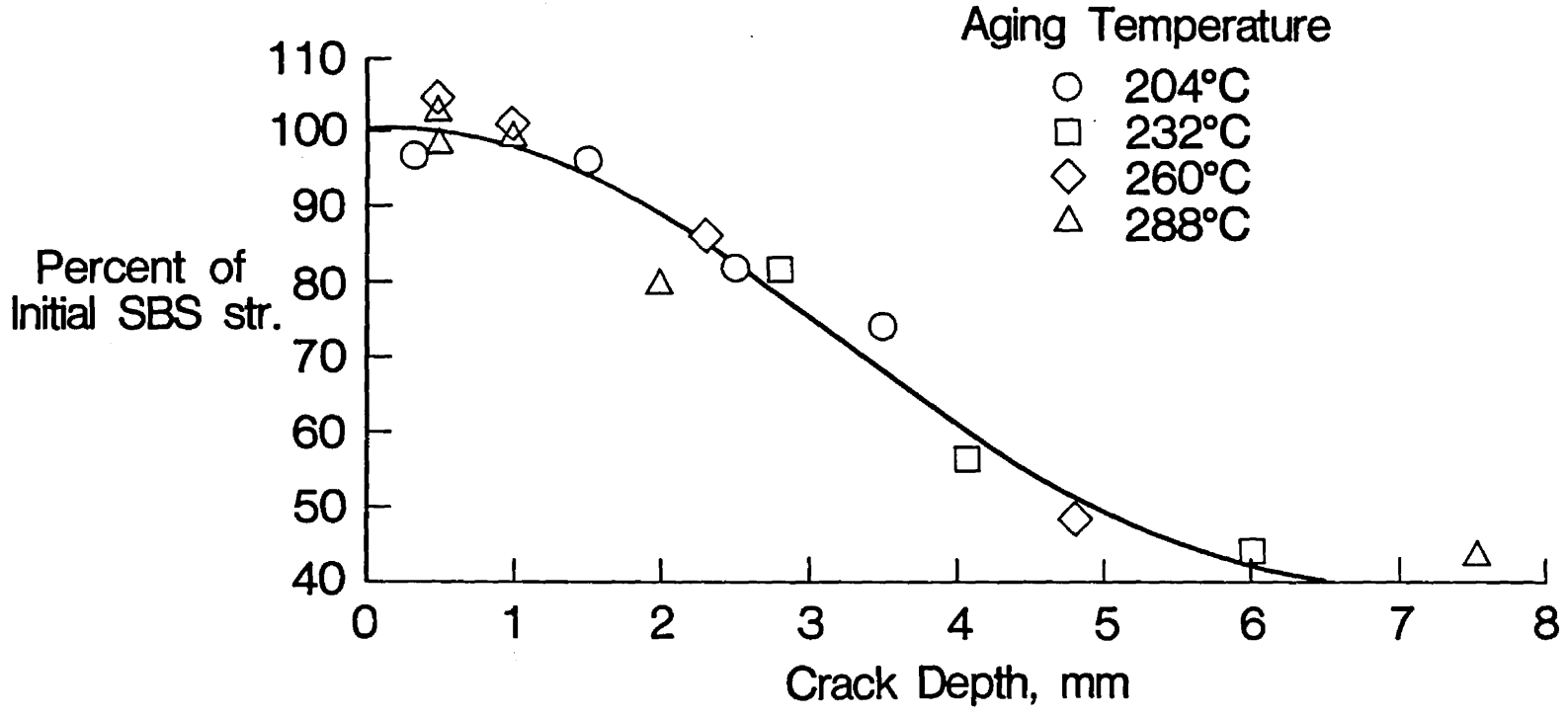


Figure 10 - Correlation of crack depth and shear strength of aged Celion 6000/LARC-160 panels.

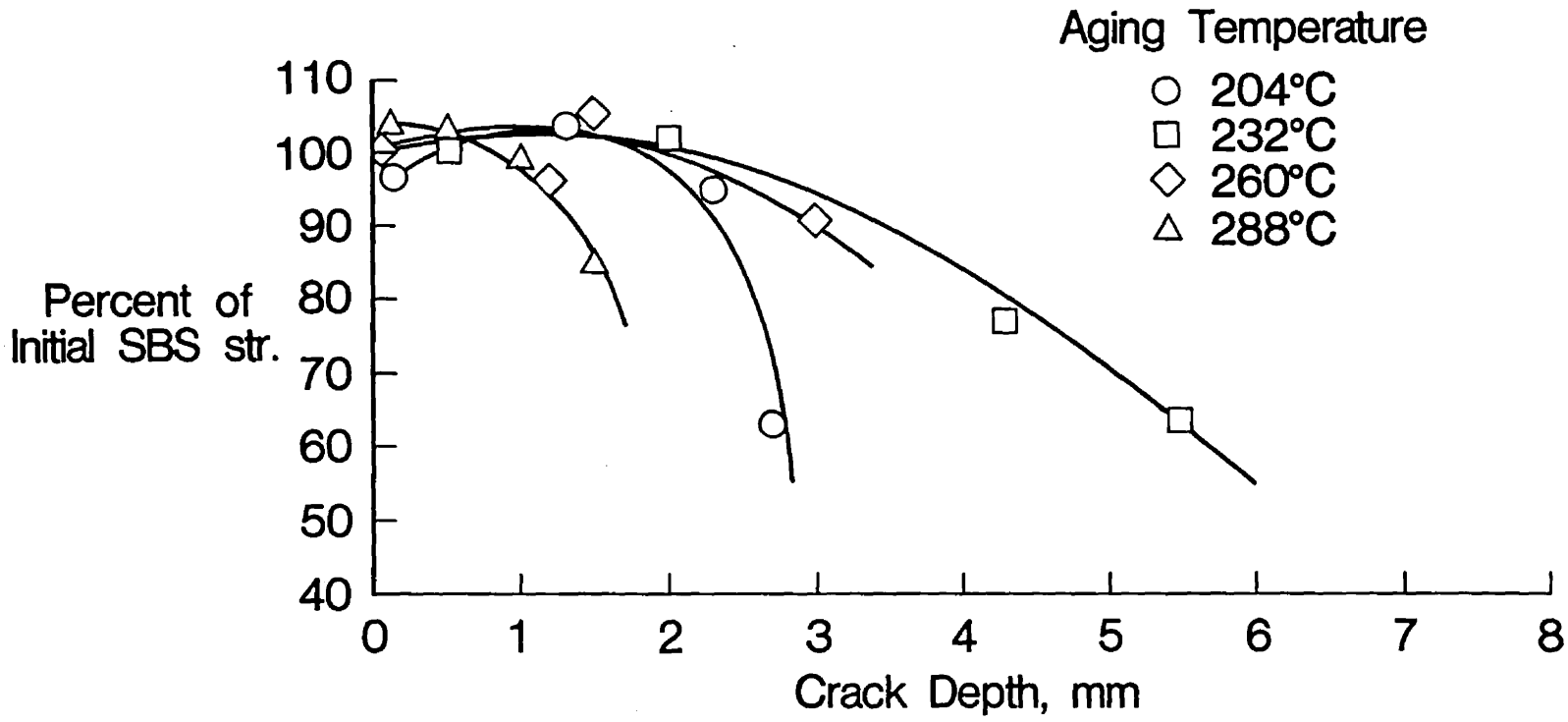


Figure 11 - Correlation of crack depth and shear strength of aged Celion 6000/PMR-15 panels.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-85763		

4. Title and Subtitle	5. Report Date
Edge Crack Growth of Thermally Aged Graphite/Polyimide Composites	March 1984
	6. Performing Organization Code 505-33-33-01
7. Author(s) James B. Nelson	8. Performing Organization Report No.
	10. Work Unit No.
9. Performing Organization Name and Address Langley Research Center National Aeronautics and Space Administration Hampton, VA 23665	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

16. Abstract

Celion®6000 LARC-160 and Celion 6000 PMR-15 graphite/polyimide composite materials were aged in air at temperatures of 202, 232, 260 and 288°C for various times up to 15,000 hours. Three unidirectional specimen types were studied: short beam shear (SBS), flexure, and 153 mm square panels. The interior region of the square panels exhibited little or no property degradation, whereas both laminate materials degraded and cracked preferentially at the specimen edge perpendicular to the fibers. Using a dye penetrant, the specimens were x-rayed and the crack depth measured as a function of time and temperature. A time-temperature superposition of the crack data was successfully performed using an Arrhenius form for the shift factor. A direct correlation was found for edge crack depth and SBS strength for the LARC-160 laminates but the correlation for PMR-15 laminates was more complex.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Graphite/Polyimide, Microcracking, Edge Cracking, X-Ray, Thermal Aging, Composite	Unclassified - unlimited Subject Categories 24 & 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	22	A02

For sale by the National Technical Information Service, Springfield, Virginia 22161