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# Long-Term Thermal Aging of Two Graphite/Polyimide Composite Materials

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*Langley Research Center*  
*Hampton, Virginia*

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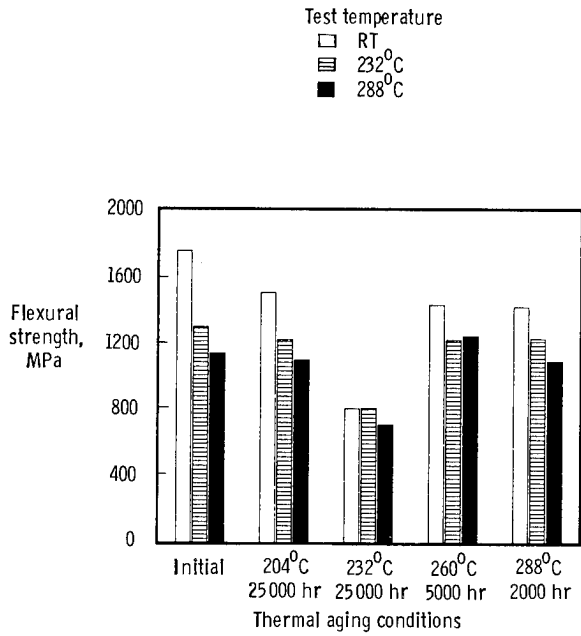


Figure 2. Flexural strengths of unidirectional Celion/LARC-160 composite after aging.

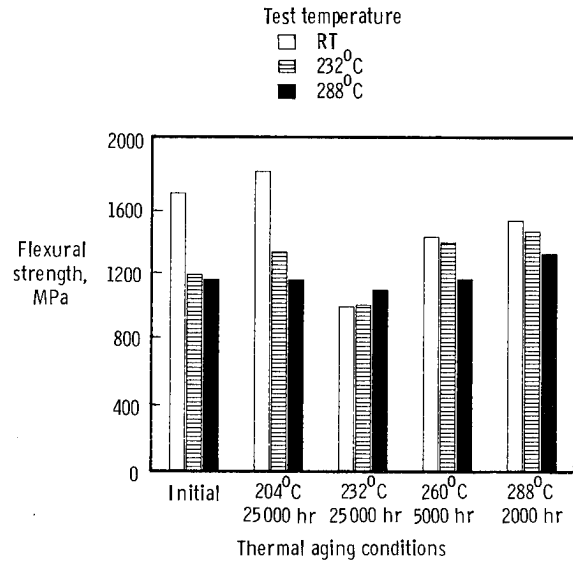


Figure 3. Flexural strengths of unidirectional Celion/PMR-15 composite after aging.

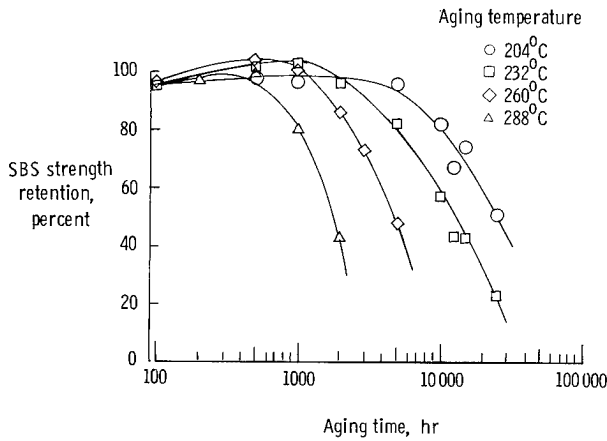


Figure 4. SBS strength retention of Celion/LARC-160 specimens aged at 204°C, 232°C, 260°C, and 288°C. Tested at room temperature.

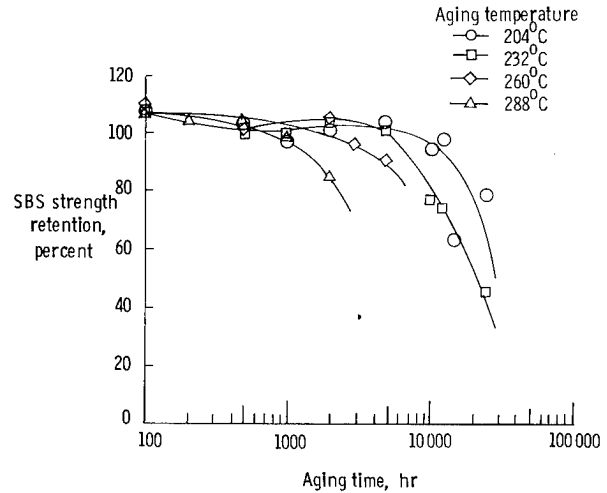


Figure 5. SBS strength retention of Celion/PMR-15 specimens aged at 204°C, 232°C, 260°C, and 288°C. Tested at room temperature.

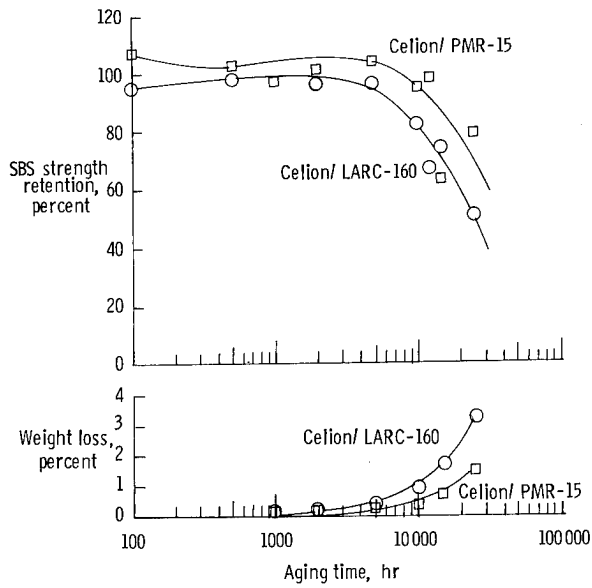


Figure 6. SBS strength retention and weight loss of Celion/LARC-160 and Celion/PMR-15 laminates aged at 204°C. Tested at room temperature.

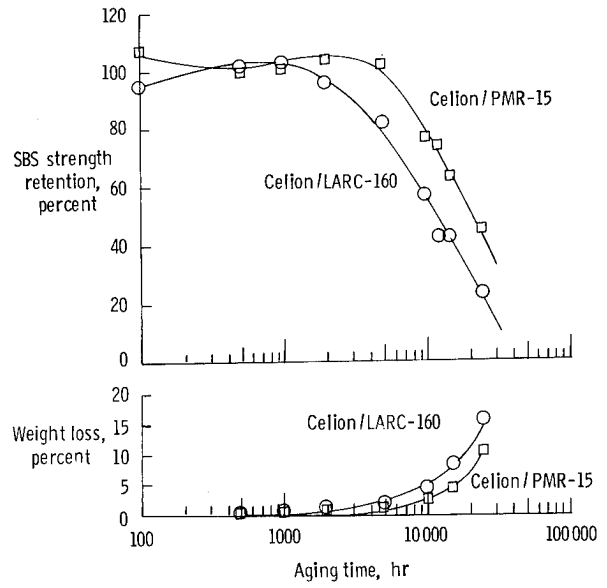


Figure 7. SBS strength retention and weight loss of Celion/LARC-160 and Celion/PMR-15 laminates aged at 232°C. Tested at room temperature.

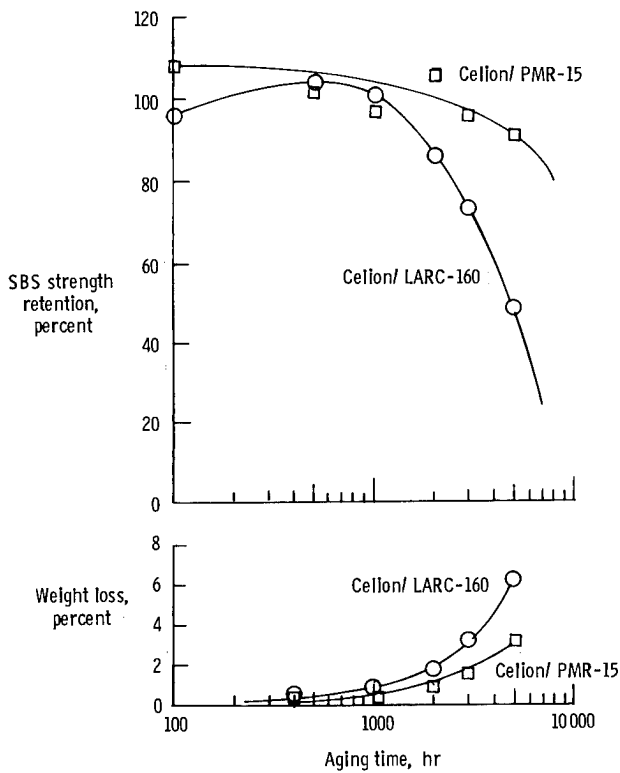


Figure 8. SBS strength retention and weight loss of Celion/LARC-160 and Celion/PMR-15 laminates aged at 260°C. Tested at room temperature.

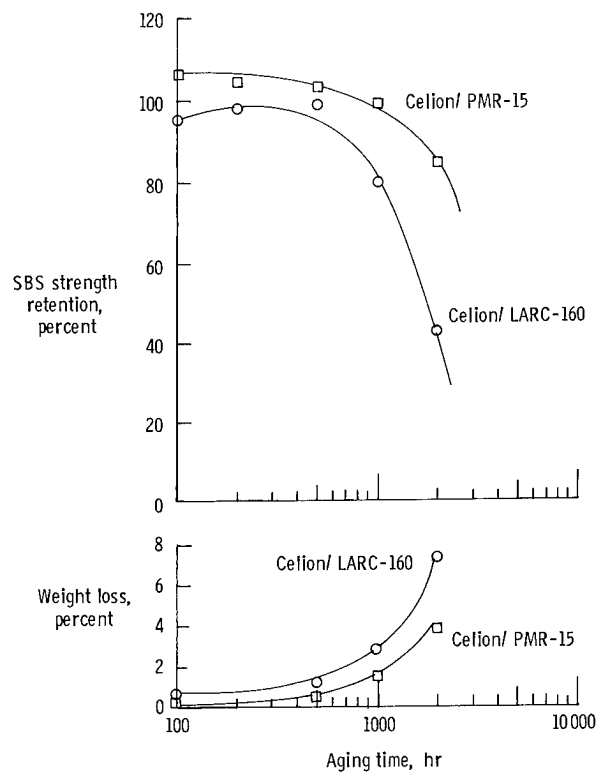


Figure 9. SBS strength retention and weight loss of Celion/LARC-160 and Celion/PMR-15 laminates aged at 288°C. Tested at room temperature.

The flexural moduli of both materials remained essentially constant for the duration of aging. The predominant failure mode in all the flexure tests was tensile failure of the outer fibers. A few of the specimens aged from 10 000 to 25 000 hours and tested at room temperature failed by complete tensile fracture of the specimens. There were no observed shear failures.

Strength retention and weight loss of precut SBS specimens as a function of thermal aging are shown in figures 4 to 9. The curves shown are faired through the data points only to show the trends. The data scatter of each set of specimens, represented by a data symbol, was small. The standard deviations ranged from 1 to 7 percent for all the data shown. Only the room-temperature SBS values are shown. Elevated-temperature SBS strengths were generally lower than room-temperature values, but the room-temperature strengths exhibited the greatest change during aging. The elevated-temperature shear data are detailed in appendix A.

The variation in room-temperature SBS strengths with time and aging temperature for both materials is seen in figures 4 and 5. The LARC-160 laminates show a regular decrease in time required to reach a given degradation level with increasing aging temperature. Although the behavior of the PMR-15 composite specimens is similar, the progression of the aging curves from lower to higher aging temperature is not as regular. These figures suggest that the aging of LARC-160 SBS specimens is dominated by a single degradative mode in this temperature range, whereas the PMR-15 specimens are exhibiting a more complex degradation behavior.

A comparison of weight loss and room-temperature SBS strength retention for PMR-15 and LARC-160 laminates aged at 204°C is shown in figure 6. Neither material shows any significant change in SBS retention on aging at 204°C for less than 5 000 hours. After 25 000 hours PMR-15 retains approximately 80 percent of initial SBS strength and LARC-160 retains about 50 percent. The data show a weight loss of about 1.5 percent for PMR-15 and approximately 3 percent for LARC-160 after 25 000 hours. The general trends in weight loss and SBS strength retention correlate well. However, the 12 000- and 15 000-hour SBS data exhibit somewhat anomalous behavior.

The SBS strength retention and weight loss as a function of aging at 232°C are shown in figure 7 for both materials. These data compare the thermal stability of small specimens of these materials. After 25 000 hours at 232°C, PMR-15 retains 45 percent of SBS strength and has a weight loss of 10 percent, and LARC-160 retains 23 percent of SBS strength and has a weight loss of 16 percent. After 25 000 hours of aging at 232°C, both materials exhibited signs of surface degradation.

Both PMR-15 and LARC-160 specimens had slightly "fuzzy" surfaces by 15 000 hours of aging, and after 25 000 hours, both materials exhibited severe surface degradation with numerous loosely attached fibers. In spite of the apparent surface degradation, there was no indication of compressive failure in the tested SBS specimens.

The relative behavior of these materials after aging at 204°C and 232°C is repeated after aging at 260°C and 288°C (figs. 8 and 9). After 5 000 hours at 260°C or 2 000 hours at 288°C, PMR-15 had a weight loss of 3 to 4 percent and essentially no change in SBS strength; LARC-160 laminates had a weight loss greater than 5 percent and showed about a 50-percent decrease in SBS strength. Thus, the data for precut aged SBS specimens seem discouraging for projecting long-term use (50 000 hours) of these materials in the 204°C to 232°C range. If a 20-percent decrease in RT SBS strength is assumed to be the acceptable limit, the use time at 232°C would be limited to 5 000 hours for LARC-160 and 10 000 hours for PMR-15.

In this investigation, thermal oxidation was presumed to be the dominant degradation mechanism. This type of degradation would be sensitive to specimen surface area and geometry. SBS and flexure specimens are quite small and have large ratios of surface area to volume compared with most structural panels of interest. The square panels were aged to give an indication of the behavior of larger structural composites. SBS-strength-retention values of specimens machined from various locations in a panel of Celion/PMR-15 aged at 232°C for 15 000 hours are shown in figures 10 and 11. Figure 10 shows SBS-strength-retention values of specimens taken on a line across the panel, perpendicular to the fiber direction. Each value represents an average of the strengths of two adjacent SBS specimens. The SBS strengths shown in figure 10 are generally about 5 percent greater than the initial values, probably because of postcuring effect. All the square panels of PMR-15 and LARC-160 aged at the various temperatures and times exhibited similar behavior.

In figure 11 are shown SBS-strength-retention values of specimens machined from the Celion/PMR-15 panel described in the preceding paragraph but taken along the axis parallel to the fibers. Each data point represents an average of six specimens. A marked difference was observed for the specimens machined from the exposed edge (SBS strength retention of 63 percent) as compared with the interior specimens (SBS strength retention of 105 percent). The average SBS strength of the edge specimens is similar to the SBS strength of individually aged specimens. Strength degradation of specimens taken from the 0° edges was typical for panels of both materials aged at the various temperatures and times. A more detailed analysis of strength

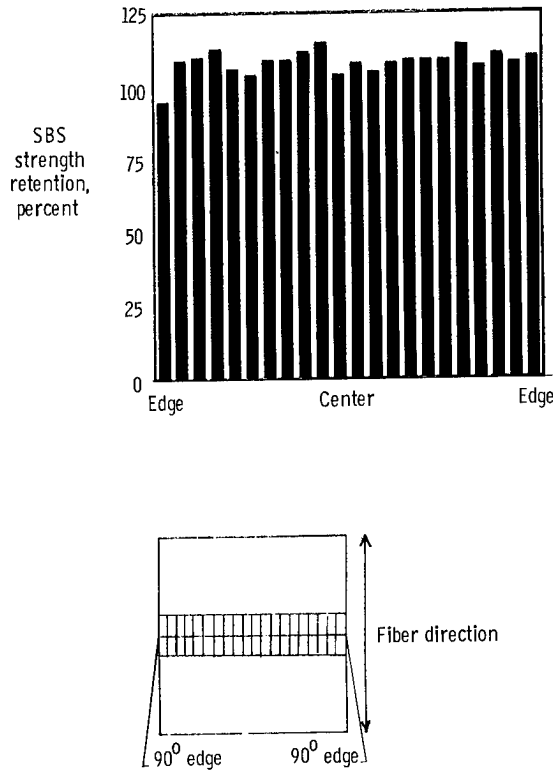


Figure 10. Room temperature SBS strength retention of specimens machined from 153-mm square Celion/PMR-15 panel after aging for 15 000 hours at 232°C. Specimens taken perpendicular to fiber direction.

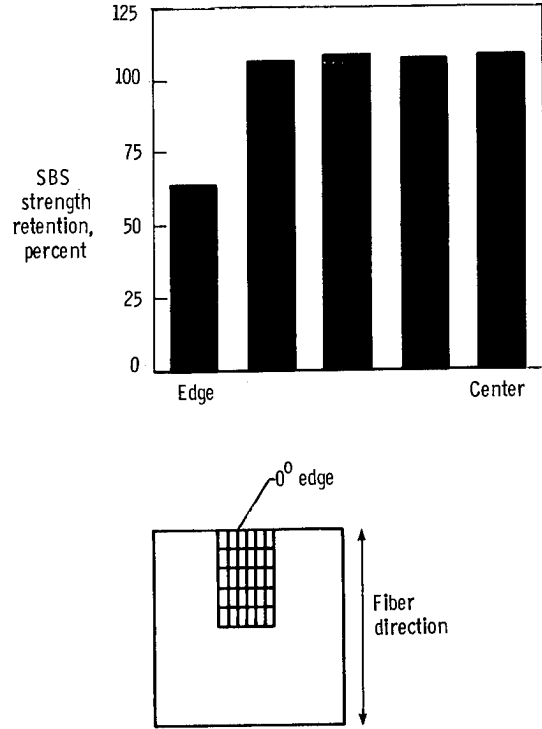


Figure 11. Room temperature SBS strength retention of specimens machined from 153-mm square Celion/PMR-15 panel after aging for 15 000 hours at 232°C. Specimens taken parallel to fiber direction.

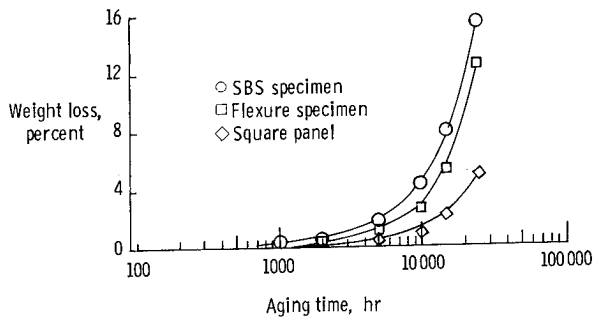


Figure 12. Weight losses of three specimen geometries of Celion/LARC-160 laminates aged at 232°C.

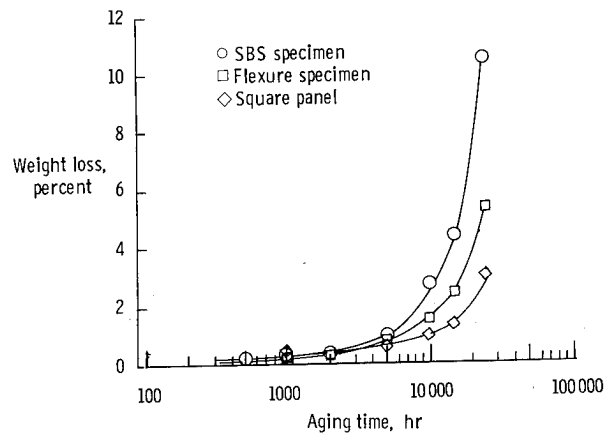


Figure 13. Weight losses of three specimen geometries of Celion/PMR-15 laminates aged at 232°C.

variations in the aged panels is presented in appendix B.

Figures 12 and 13 show weight loss data for the three specimen geometries of LARC-160 and PMR-15 laminates as a function of aging time at 232°C. The aged precut SBS specimens had the greatest percent weight loss; the flexure specimens, an intermediate amount; and the 153-mm square panels, the least. This trend was exhibited by both PMR-15 and LARC-160 laminates at all aging temperatures. Comparison of ratios of surface area to volume shown in table II and the weight loss data in figures 12 and 13 indicates that the specimens have a much higher weight loss than their ratios of surface area to volume indicate. The SBS strength data of the square panels shown in figures 10 and 11 suggest that the 0° edge of the specimen is especially affected by thermal aging. When ratios of surface area to volume were calculated by utilizing only the surface area of the specimen edges perpendicular to the fibers (table II), the relative ranking of the three geometries was the same as the weight loss trends. This observation, considered with the panel data presented in figure 11, suggests that oxidative degradation is occurring preferentially at the fiber ends of the specimens.

TABLE II. RATIOS OF SURFACE AREA TO VOLUME FOR LAMINATES

Specimen	Total surface area per unit volume, mm <sup>-1</sup>	Surface area perpendicular to fibers per unit volume, mm <sup>-1</sup>
SBS	1.109	0.125
Flexure	1.518	.031
Square panels	.693	.013

Scanning electron microscope photographs of the edge surfaces of a Celion/PMR-15 square panel unaged and aged 15 000 hours at 232°C are shown in figure 14. As anticipated, photomicrographs of the unaged specimen indicate no obvious cracks or porosity. After aging, the 0° edge contains a network of sizable cracks. Cracks were observed after less than 100 hours of aging and grew with time at each aging temperature. Similar cracking behavior was observed in the LARC-160 laminates. The 90° view shows a number of cracks in the fiber plane. This type of cracking was observed only in the panels aged for 15 000 to 25 000 hours at 204°C and 232°C.

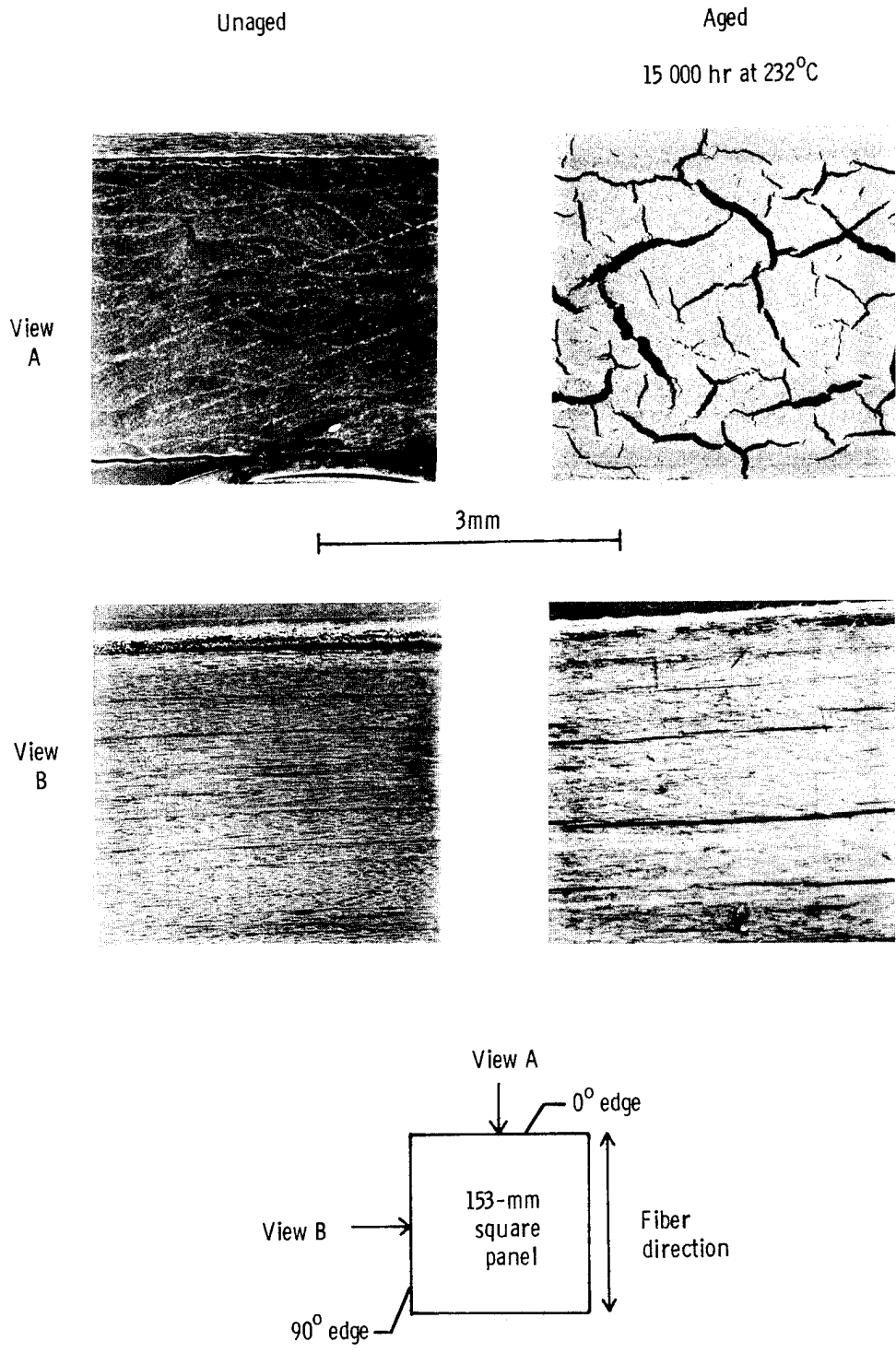
The depth of the cracks was measured by using a dye penetrant X-ray technique (refs. 8 and 9). The measured crack depth versus aging time at each aging temperature for both materials is shown in figures 15

and 16. The shapes and sequences of the crack-growth curves for LARC-160 laminates (fig. 15) have similarities to those for curves showing SBS strength variation with aging (fig. 4). These similarities suggest a causal relationship between crack growth and loss of shear strength in the LARC-160 laminates. To examine this hypothesis, crack-depth data (including all temperatures and times) for all the LARC-160 specimens were combined (fig. 17). A least-squares-fit line was drawn through these data. This figure indicates a strong correlation between these variables for LARC-160. In contrast, the crack-growth/aging curves for PMR-15 (fig. 16) do not exhibit the same regularity as those for LARC-160, and the crack-growth/shear-strength data for PMR-15 cannot be resolved into a single simple relationship (fig. 18). This would indicate that the degradation of the PMR-15 laminates was more complex than that exhibited by LARC-160.

Whatever the mechanism, the dominant degradation mode of small specimens of both PMR-15 and LARC-160 laminates is related to the cracking behavior of the laminate edges. Aging of precut SBS and flexure specimens indicates that PMR-15 laminates have significantly higher thermal stability than the LARC-160 laminates. The individually aged SBS specimens accurately reflect the degradation behavior of the panel edges; however, the relatively minor surface degradation and mechanical property loss occurring in the interior of the larger PMR-15 and LARC-160 panels are probably more indicative of the behavior of large structural panels exposed to the environment used in this work. If the usable life of a composite panel is arbitrarily defined as limited to 70-percent retention of initial strength (panel average), then the panel analysis in appendix B indicates that unidirectional laminates of both of these materials have usable lifetimes of 25 000 hours or greater when aged unstressed at 204°C or 232°C.

## Conclusions

A general conclusion of this study was that thermal aging of small graphite/polyimide composite specimens can yield results quite different from results for larger panels more representative of structural parts. Individually aged short beam shear and flexure specimens exhibited large reductions in strengths after aging; the interior regions of the square panels, on the other hand, exhibited only minor property degradation. Aging of small test specimens indicated that the usable lifetime at 232°C is 10 000 hours for PMR-15 laminates and 5 000 hours for LARC-160 laminates. However, larger panels of both of these materials exhibited usable lifetimes of at least 25 000 hours when aged unstressed at 204°C and 232°C. Unidirectional laminates, large or small, of both LARC-160 and PMR-15 cracked



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Figure 14. Photomicrographs of Celion/PMR-15, unaged and aged at 232°C for 15 000 hours.

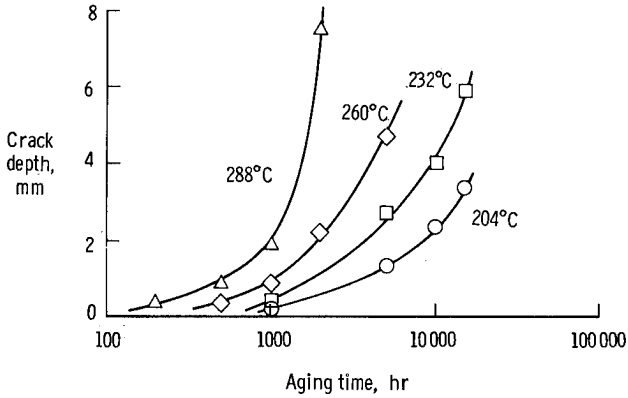
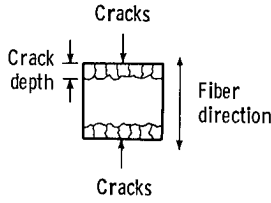


Figure 15. Edge crack growth in aged Celion/LARC-160 laminates.

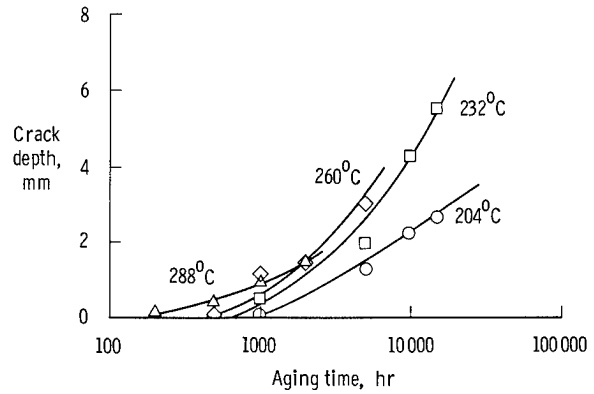


Figure 16. Edge crack growth in aged Celion/PMR-15 laminates.

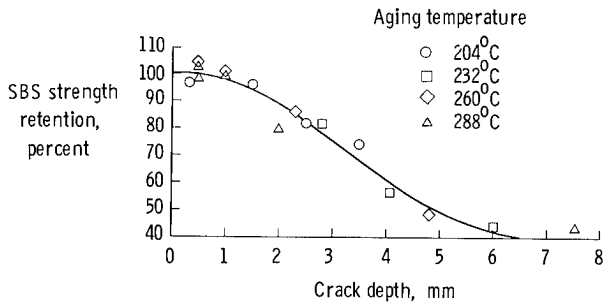


Figure 17. Correlation of crack depth and shear strength retention in aged Celion/LARC-160 panels.

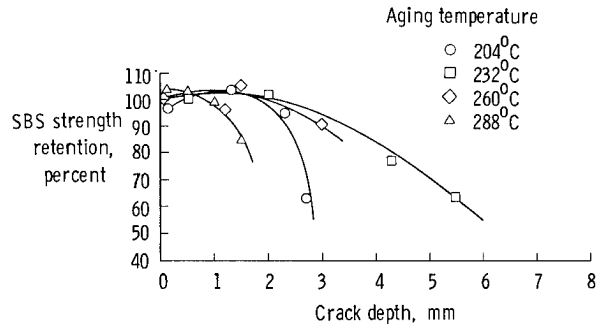


Figure 18. Correlation of crack depth and shear strength retention in aged Celion/PMR-15 panels.

and degraded preferentially at the specimen edge perpendicular to the fibers.

Langley Research Center  
National Aeronautics and Space Administration  
Hampton, VA 23665  
July 19, 1984

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## Appendix A

### Elevated-Temperature Testing of Aged SBS Specimens

The individually aged precut SBS specimens were removed from the aging ovens at periodic intervals, and mechanical testing was performed at room temperature (RT), 204°C, 232°C, 260°C, and 288°C. The RT and elevated-temperature SBS strengths for unidirectional Celion/LARC-160 laminates aged at 204°C, 232°C, 260°C, and 288°C are shown in figures A1 to A4. Each of these curves shows the same general pattern for each aging temperature. The RT and elevated-temperature strength curves are similar but are ar-

ranged in descending order of strength with increasing test temperature for the early portion of the aging. However, at the time when the strengths begin to fall off sharply (5 000 hours at 204°C, 2 000 hours at 232°C, 1 000 hours at 260°C, or 500 hours at 288°C), the RT strengths decrease the most, and all the curves converge to a single line.

The RT and elevated-temperature SBS strengths for the aged Celion/PMR-15 laminates are shown in figures A5 to A8. The PMR-15 laminates exhibit behavior similar to that just described for the LARC-160 laminates, except that the degradation of the PMR-15 laminates has not progressed as far as that of the LARC-160 material.

APPENDIX A

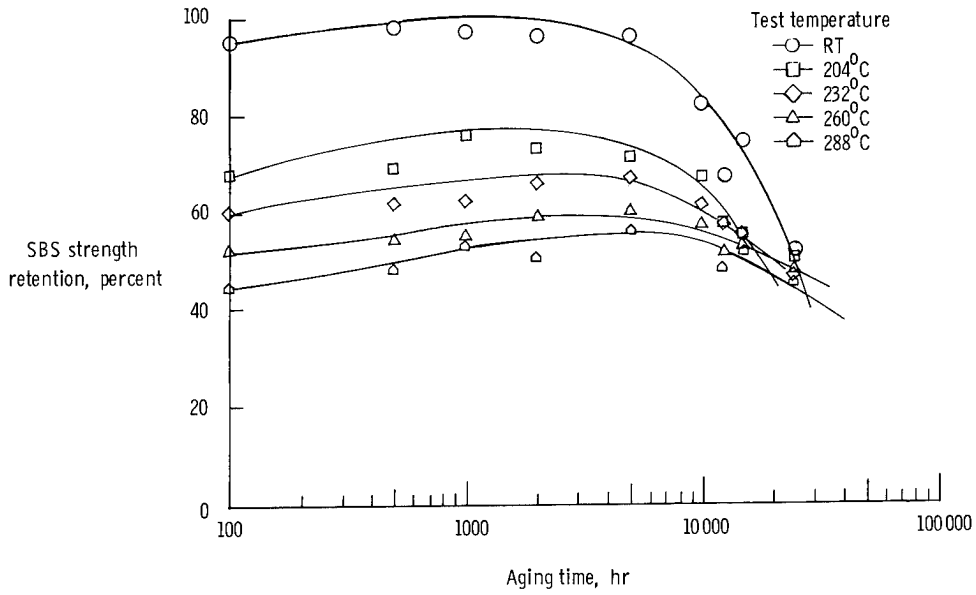


Figure A1. Shear strength retention of Celion/LARC-160 specimens aged at 204°C.

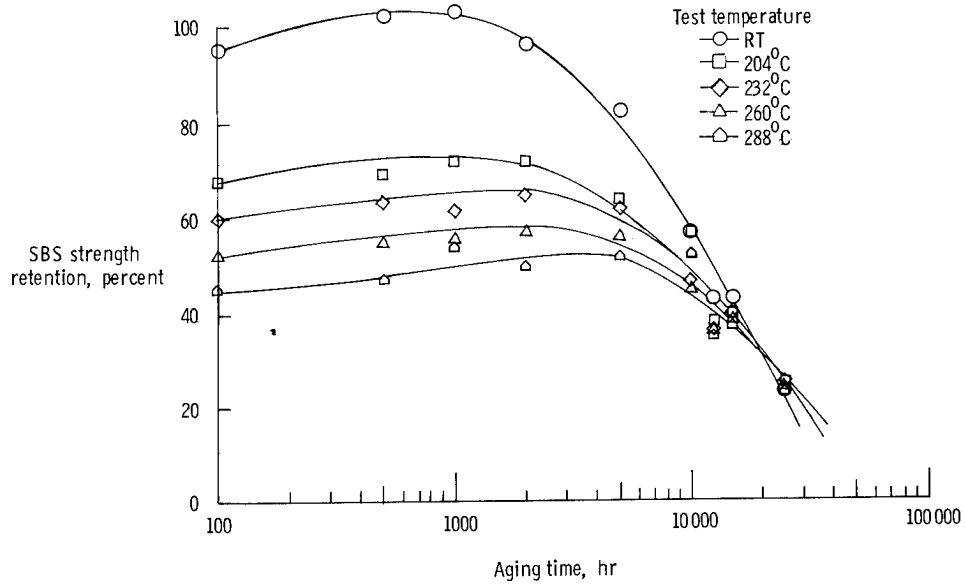


Figure A2. Shear strength retention of Celion/LARC-160 specimens aged at 232°C.

APPENDIX A

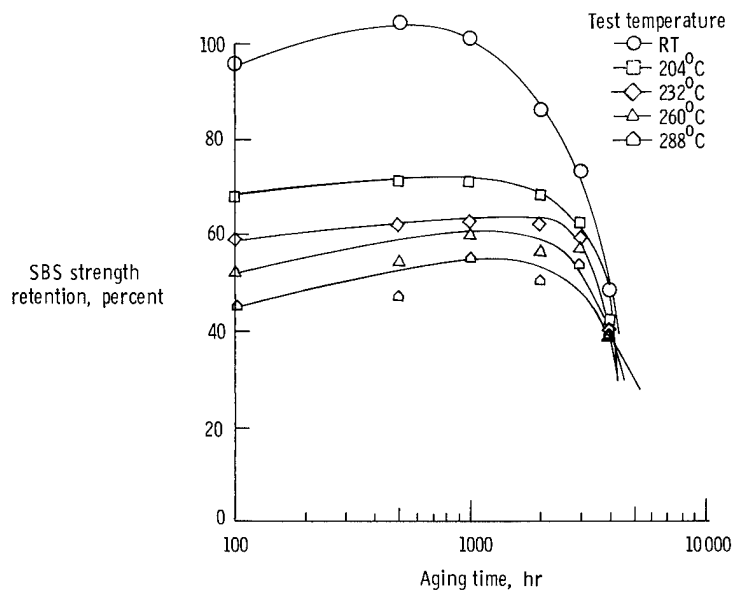


Figure A3. Shear strength retention of Celion/LARC-160 specimens aged at 260°C.

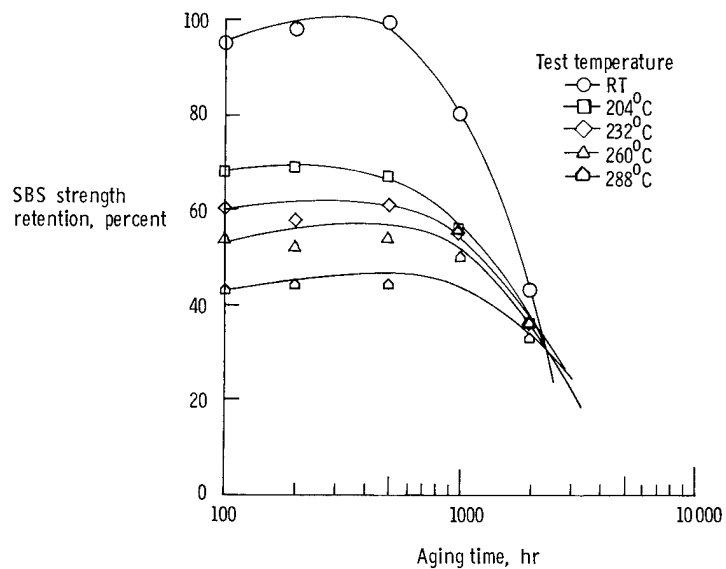


Figure A4. Shear strength retention of Celion/LARC-160 specimens aged at 288°C.

APPENDIX A

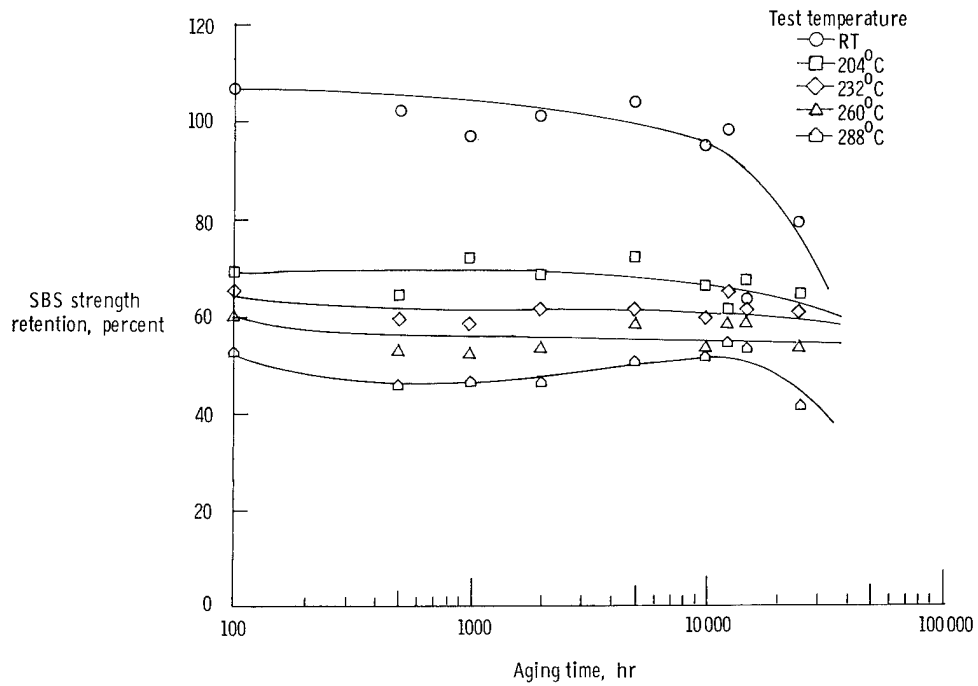


Figure A5. Shear strength retention of Celion/PMR-15 specimens aged at 204°C.

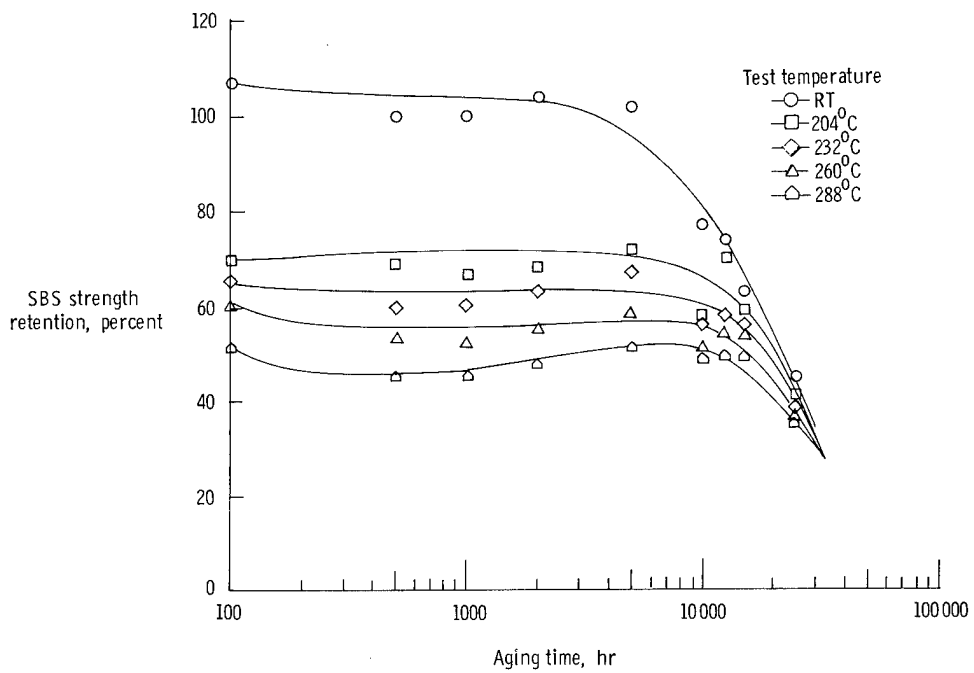


Figure A6. Shear strength retention of Celion/PMR-15 specimens aged at 232°C.

# APPENDIX A

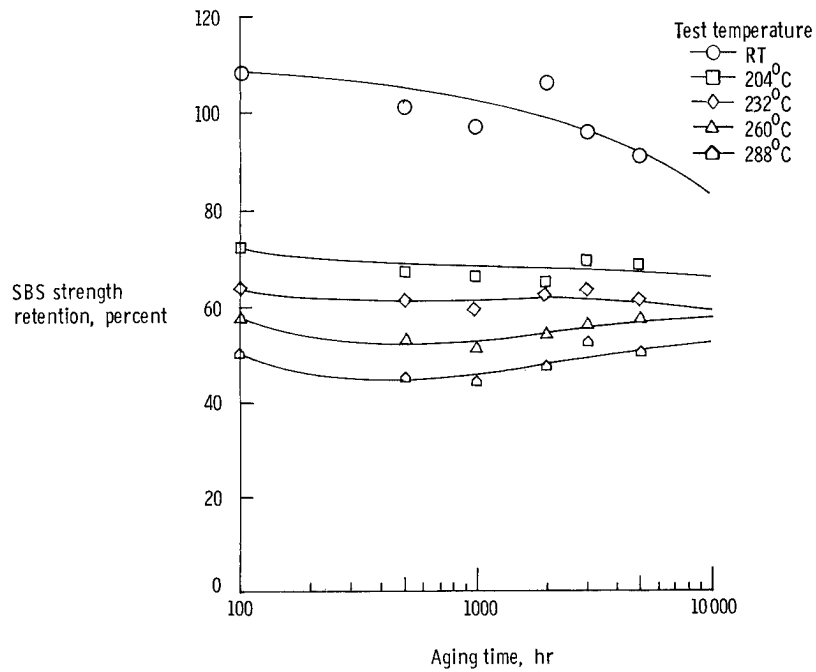


Figure A7. Shear strength retention of Celion/PMR-15 specimens aged at 260°C.

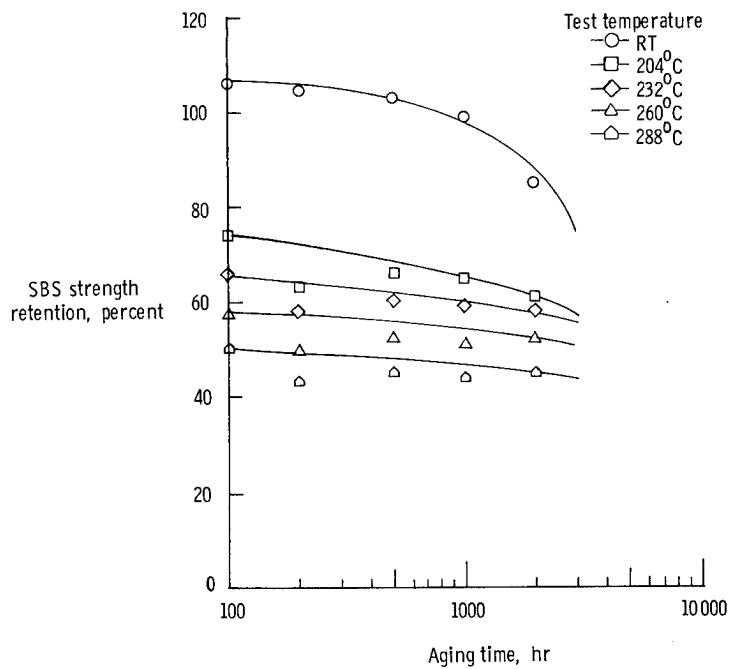


Figure A8. Shear strength retention of Celion/PMR-15 specimens aged at 288°C.

## Appendix B

### Analysis of Aged Square Panels

The unidirectional 153-mm square panels aged for various times at temperatures of 204°C, 232°C, 260°C, and 288°C were machined so that SBS specimens were taken across the panels in both directions. Overall average shear strength values were determined for each panel and for specimens taken at the 0° edges and the 90° edges. These strengths are compared with those of aged precut SBS specimens for the four aging temperatures in figures B1 to B8. Figure B1 shows the SBS comparison for Celion/LARC-160 aged up to 25 000 hours at 204°C. There do not appear to be any significant differences until 25 000 hours, when the specimen strengths as a percent of initial strength are 90 percent for the overall panel average, 85 percent for the specimens taken from the 90° edge, 70 percent for the specimens from the 0° edge, and 50 percent for the aged precut specimens.

The LARC-160 materials aged at 232°C show similar but better defined behavior (fig. B2). After 5 000 hours of aging, there is a definite ordering of the SBS strengths according to location in the panel. The overall panel average and the specimens taken from the 90° edge were relatively unaffected, but the specimens taken from the 0° edge exhibited some degradation, and the precut SBS specimens degraded the most. Af-

ter 25 000 hours at 232°C, the overall average panel strength was about 70 percent of the initial strength, and the 90° edge retained about 65 percent; however, the 0° edge retained only about 30 percent, and the precut specimens, 25 percent. This general pattern was also maintained for the LARC-160 aging at 260°C and 288°C (figs. B3 and B4). Although the top and bottom surfaces showed evidence of degradation during aging at each temperature, the overall average shear strength was not significantly affected nor were the almost identical values for specimens taken from the 90° edge. Specimens taken from the 0° edges of the aged panels had measured strength losses almost as great as those of the aged precut SBS specimens.

The SBS strength retention of the aged square panels of Celion/PMR-15 can be seen in figures B5 to B8. The aging behavior of these laminates was similar to that observed for the LARC-160 panels. There was little strength degradation in the PMR-15 panels aged to 25 000 hours at 204°C. Although the panels aged at 232°C exhibited steady degradation at the 0° edge, there was little significant change in the overall average shear strength of the panels until 25 000 hours, when the average shear strength had decreased 20 percent. Aging at 260°C and 288°C had less effect on the PMR-15 panels than on the LARC-160 panels. The 260°C and 288°C aging times were not sufficient to observe any significant PMR-15 degradation.

APPENDIX B

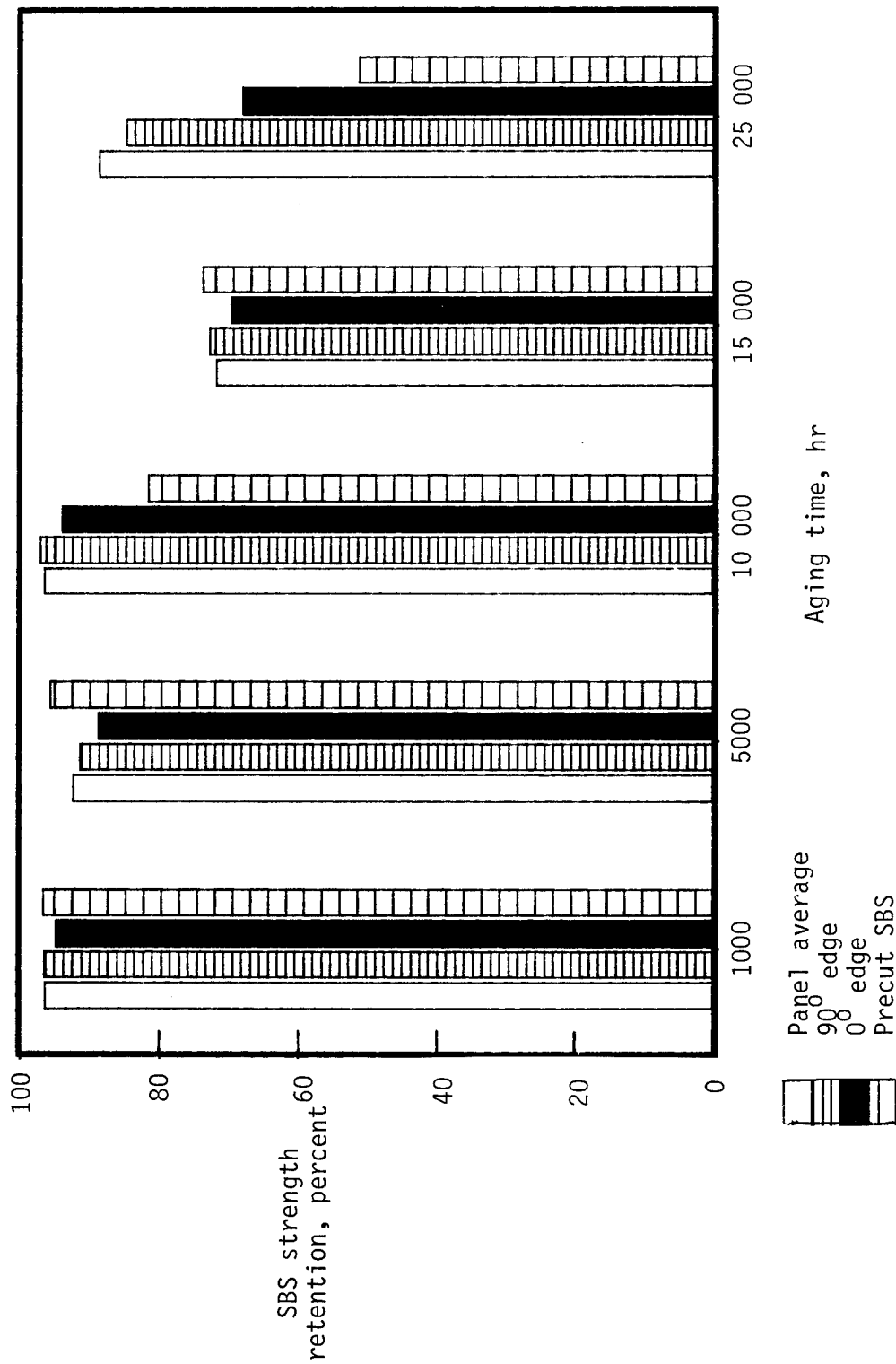


Figure B1. Comparison of shear strengths of specimens taken from several areas of square Celion/LARC-160 laminates aged at 204°C.

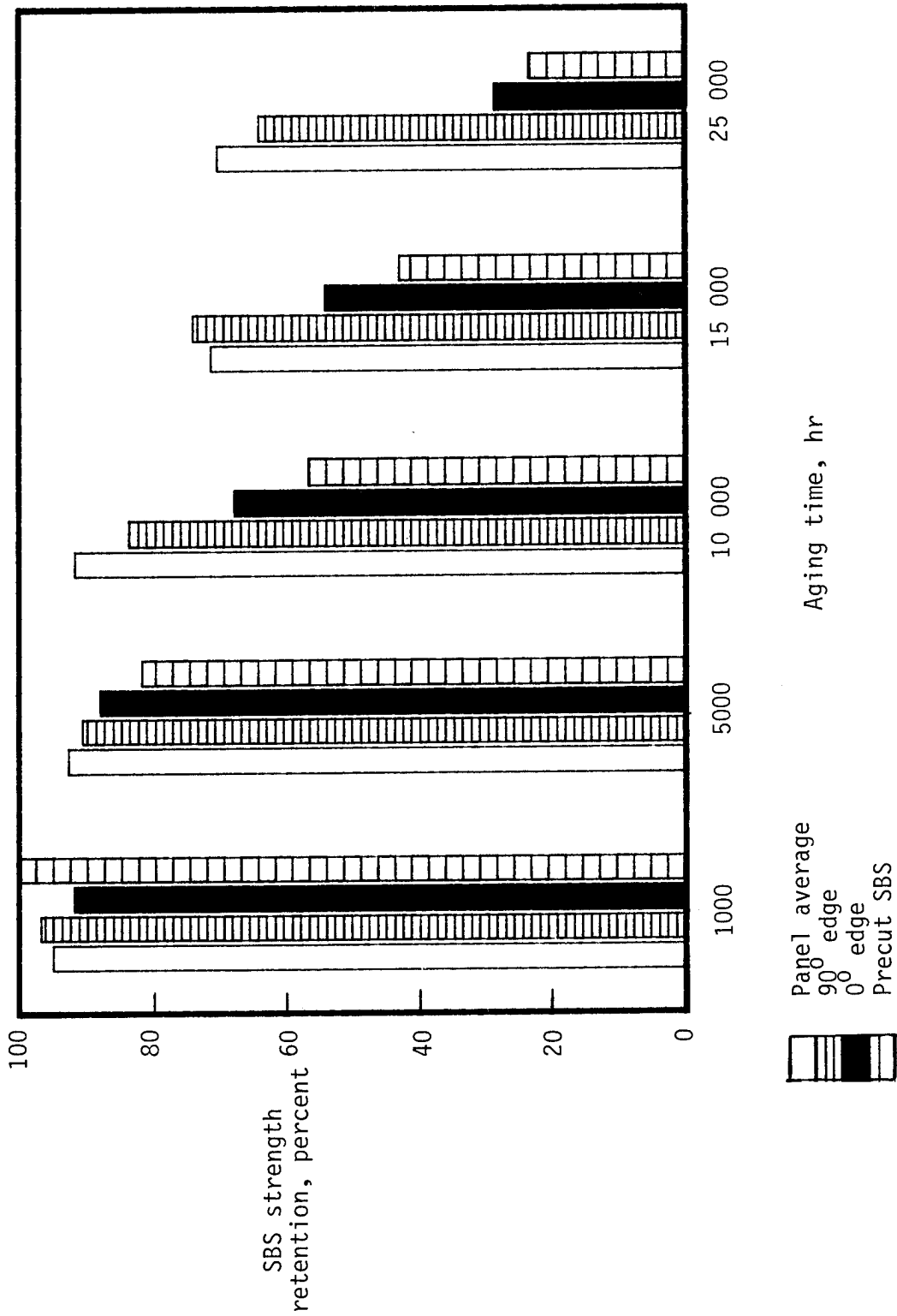


Figure B2. Comparison of shear strengths of specimens taken from several areas of square Celion/LARC-160 laminates aged at 232°C.

APPENDIX B

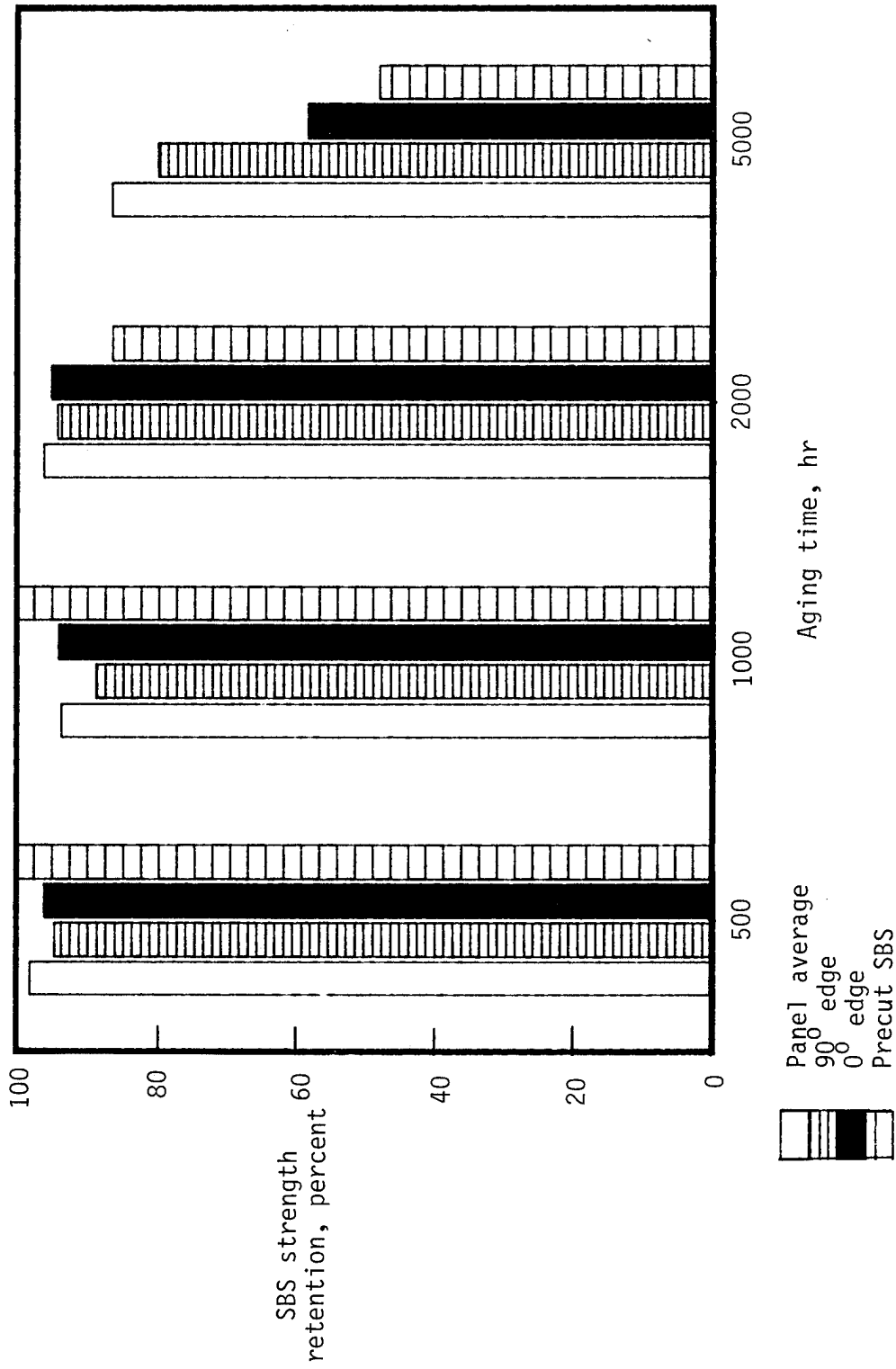


Figure B3. Comparison of shear strengths of specimens taken from several areas of square Celion/LARC-160 laminates aged at 260°C.

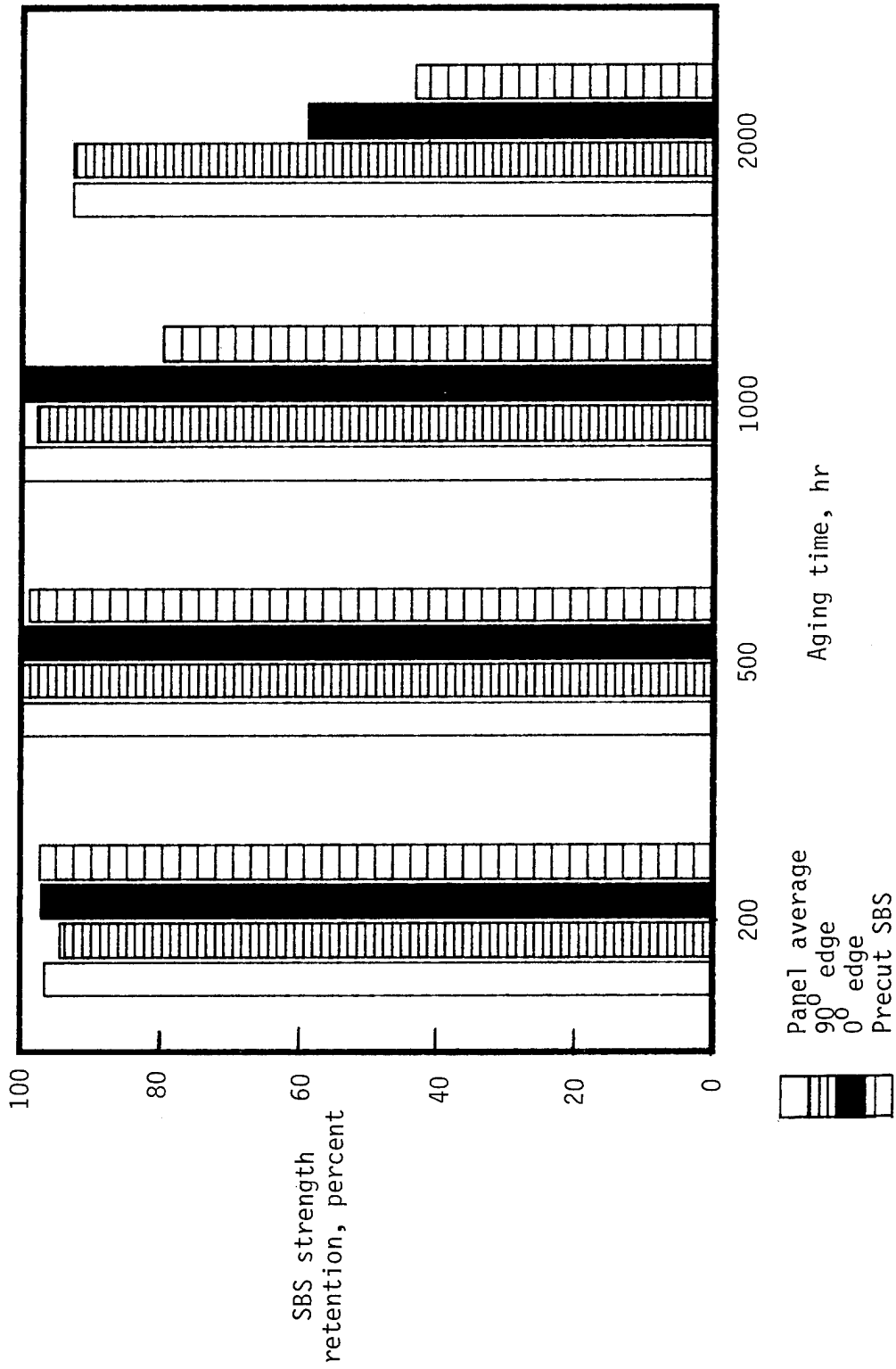


Figure B4. Comparison of shear strengths of specimens taken from several areas of square Celion/LARC-160 laminates aged at 288°C.

APPENDIX B

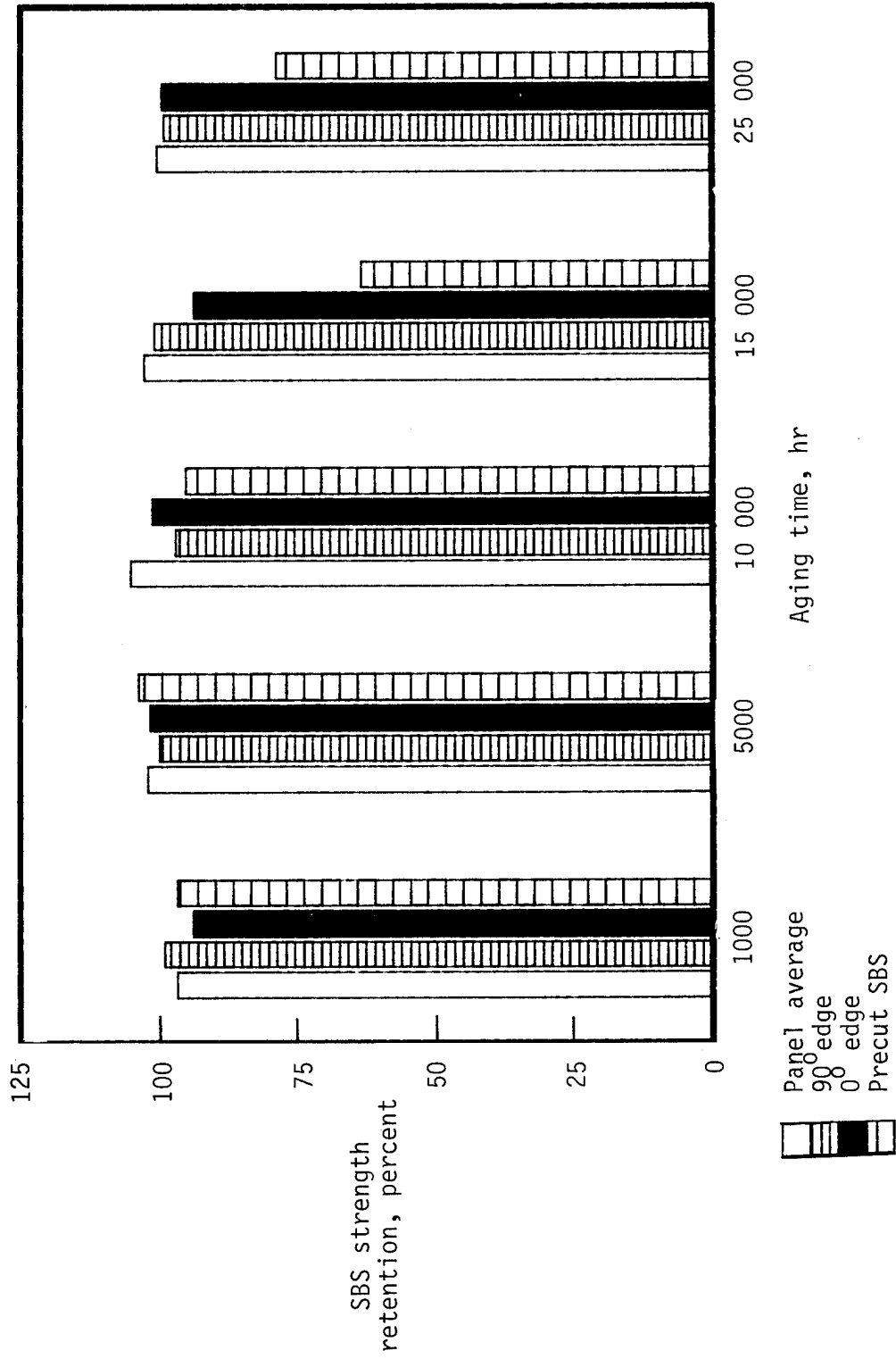


Figure B5. Comparison of shear strengths of specimens taken from several areas of square Celion/PMR-15 laminates aged at 204°C.

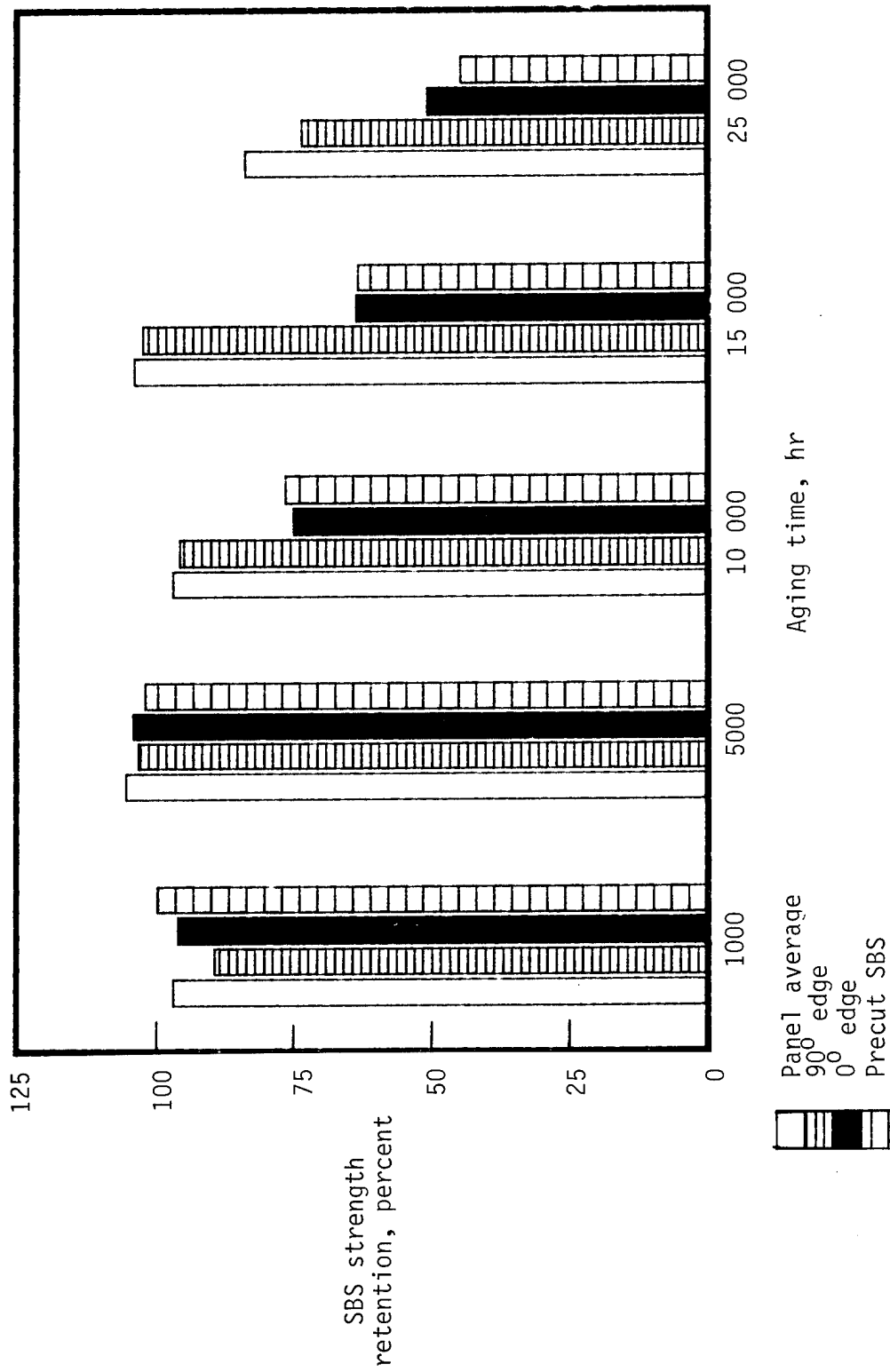


Figure B6. Comparison of shear strengths of specimens taken from several areas of square Celion/PMR-15 laminates aged at 232°C.

APPENDIX B

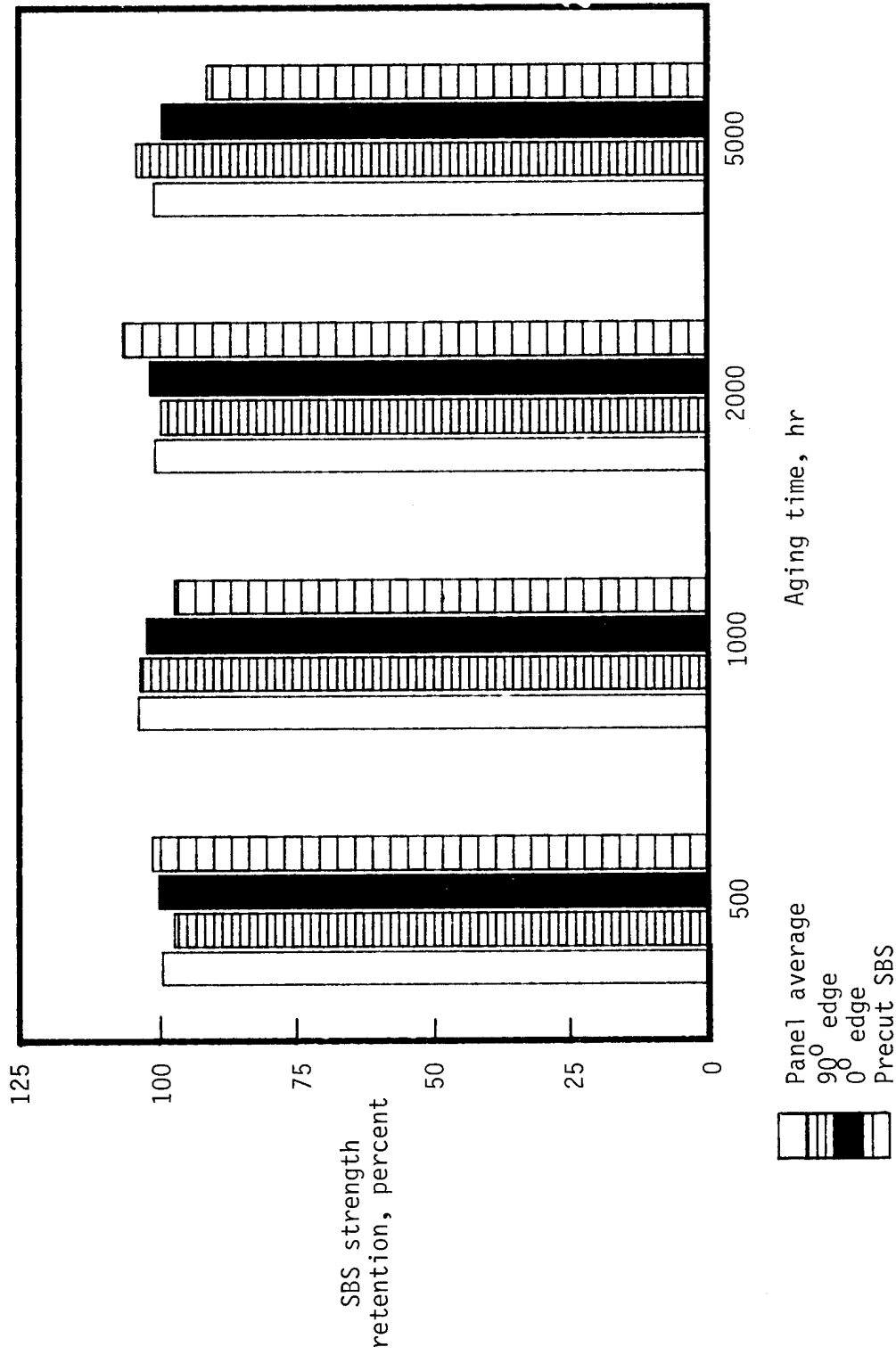


Figure B7. Comparison of shear strengths of specimens taken from several areas of square Celion/PMR-15 laminates aged at 260°C.

APPENDIX B

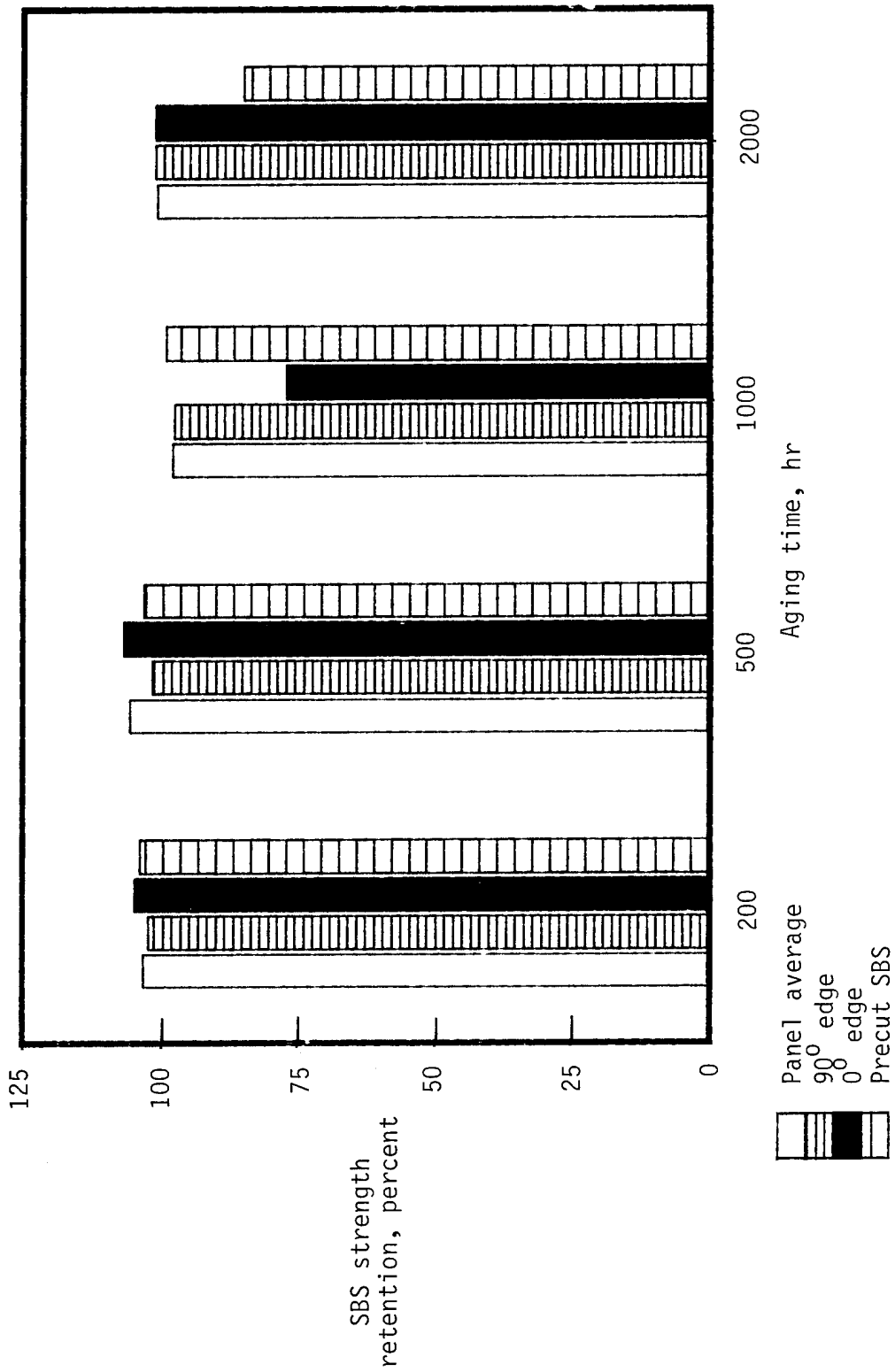


Figure B8. Comparison of shear strengths of specimens taken from several areas of square Celion/PMR-15 laminates aged at 288°C.

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16. Abstract Two graphite/polyimide composite materials were aged in circulating air ovens at temperatures of 204°C, 232°C, 260°C, and 288°C for various times up to 25 000 hours. The composites were (1) Celanese Celion 6000 graphite fiber and PMR-15 polyimide resin (Celion/PMR-15) and (2) Celion 6000 graphite fiber and LARC-160 polyimide resin (Celion/LARC-160). Three unidirectional specimen geometries were studied: short beam shear (SBS) specimens, flexure specimens, and 153-mm square panels. The interior regions of the square panels exhibited only minor property degradation. The individually aged SBS and flexure specimens exhibited large reductions in strengths after aging. Both laminate materials cracked and degraded preferentially at the specimen edge perpendicular to the fibers.			
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