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# EFFECT OF LONG-TERM THERMAL AGING ON COATED CELION/LARC-160 COMPOSITES

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EFFECT OF LONG-TERM THERMAL AGING ON COATED CELION/LARC-160 COMPOSITES

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## SUMMARY

Coated and uncoated unidirectional laminates of Celion®/LARC-160 graphite/polyimide were thermally aged in air at temperatures of 204, 260 and 316°C for various times up to 15,000 hours. Selected panels were coated with a high temperature coating resin (polyphenylquinoxaline--PPQ): (1) edges only, (2) top and bottom only, (3) completely, or (4) not at all. Periodically during aging, panels were removed from the ovens, weighed and short beam shear (SBS) specimens cut from selected locations in the panels. The protective coating did not influence the retention of SBS strength during thermal aging but did lessen the amount of weight-loss incurred. The integrity of the PPQ coating was completely destroyed during aging at 316°C.

®Celion is a registered trademark of BASF Structural Materials, Inc.

## INTRODUCTION

Langley Research Center has been engaged in advancing composites and composite structure technology for over two decades. Langley has been especially active in developing composite materials such as graphite/polyimides for aerospace applications at temperatures higher than the conventional graphite/epoxies. One major concern is the long-term durability of these materials at elevated temperatures. There have been numerous studies of short-term thermal aging behavior of graphite/polyimide composites (refs. 1 to 5). In ref. 6-8, this author, reported the results of thermally aging graphite/polyimides for extended periods of time up to 25,000 hours. It was noted that for long-term aging at temperatures up to 288°C (550°F) the primary damage mechanisms were edge cracking and surface degradation rather than bulk deterioration of the laminates. Since this was thought to be, at least partially, a surface phenomena, protecting the surface with a high temperature coating might help extend the service life of these laminates.

Results of a thermal aging study of graphite/polyimide (Celion 6000/LARC-160) laminates coated with a high temperature film-forming resin are reported herein.

## EXPERIMENTAL

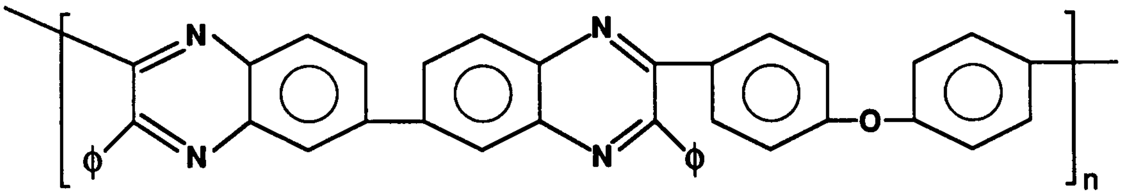
### Laminate Fabrication

The tested composite laminates were fabricated from unidirectional prepreg tape of Celion 6000 carbon fibers (NR-150B2 polyimide finish) in a LARC-160 polyimide resin matrix. The prepreg was supplied by Fiberite. Unidirectional layups of 24 plies, approximately 45 cm by 76 cm, were precompacted in a vacuum bag as shown in figure 1(a). The staging conditions are given in figure 1(b). A similar vacuum bag arrangement was used for the subsequent autoclave cure process (figure 2). The cure temperature profile is given in figure 3. Full vacuum and 738 kPa (200 psi) pressure were held throughout the cure cycle.

After fabrication, the laminates were subjected to ultrasonic C-scan inspection. The acceptable laminates were cut into 7.62 cm (3 inch) square panels, some of which were subsequently coated.

Laminate Coating

Selected panels of the LARC-160 laminates were coated with a polyphenylquinoxaline (PPQ) resin, chosen for its high temperature resistance. This PPQ resin is an experimental material having the following structure:




Preparation of this material is described in ref. 9. As prepared, the PPQ had an inherent viscosity ($\eta$) of 1.51 dl/g and glass transition temperature (Tg) of 295°C. The coating solution was prepared as a 10% solids solution in a 1:1 mixture of m-cresol and xylene.

The laminate panels selected for coating were prepared by lightly sanding with 200 grit sand paper and washing clean with ethanol and then dried at 100°C for 1 hour in a circulating air oven. Selected parts of the panels (figure 4) were then coated with the PPQ resin using a small paint brush. The coated panels were then air dried at:

100°C - 1 hour

200°C - 1 hour

316°C - 16 hours

The dried coatings were examined microscopically for integrity and with the exception of a few small bubbles were found to be well formed. A few samples of the coating were peeled to measure an average coating thickness of 25.4 μm (0.001 in).

## Isothermal Aging

Forced-convection horizontal airflow ovens were used for the isothermal-aging environment at 204°C (400°F), 260°C (500°F) and 315°C (600°F). The average air velocity was approximately 0.75 m/sec. The 3-inch square panels were supported vertically on their edges, 12 mm apart with air flowing between each panel. The panels were given various exposure times up to 15,000 hours. At predetermined intervals, selected panels were removed for testing. These panels were weighed to determine weight loss, examined under a microscope and then short beam shear specimens were machined from the panels as shown in Figure 5.

## Mechanical Testing

SBS tests were performed in conformance with ASTM Standard Test Method for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short Beam Method (D2344-76) (ref. 10). A nominal 4:1 ratio of span-to-thickness was used. The measured SBS strength values were averaged in the following manner:

0° edge SBS - Average of rows A and C

90° edge SBS - Average of the two edge specimens in row B

Panel ave - weighed ave of rows A, B and C

# RESULTS AND DISCUSSION

The effect of long-term isothermal aging on SBS strength and weight-loss of LARC-160/Celion unidirectional laminates (coated and uncoated) is illustrated in figures 6 to 11. Room temperature SBS strengths of uncoated and the 3 coated configurations after 15,000 hours aging at 204°C are summarized in figure 6. There is little difference between the uncoated panels and any of the coated panels. In each case the SBS strengths of specimens taken from the 0° edge of the panels seemed to be significantly less than the strengths elsewhere in the panel. This same edge dependent behavior was reported in ref. 6, where it was attributed to severe transverse and interlaminar cracking progressing deeper into the panel with increasing aging time and temperature. Indeed, as can be seen in the photographs of figure 12, there is severe cracking in the 0° edge of both the coated and uncoated panels. Although the coating remains intact over most of the surface, the cracking pattern and crack sizes are approximately the same as the uncoated. There has been some local cracking of the coating over the largest cracks. The coating has not prevented the cracking but has probably limited oxidation of the internal surface of the cracks. This is supported by the weight-loss data of the panels aged at 204°C shown in figure 9. The panels without coating on the edges had significantly greater weight-loss throughout aging than those with edge coating. In addition, the photomicrographs in figure 13 show several cracks penetrating the 90° edge of the uncoated panel but no observable cracks in the 90° edge of the coated specimens. There was some damage to the coating itself on the 90° edges. Figure 14 shows a microphotograph of the 90° edges of a totally coated specimen where an area of the coating 1.5 mm long has come completely off.

The effect of coating and geometry on SBS strength after aging at 260°C and 316°C is shown in figures 7 and 8. As can be seen in these figures, there was no consistent effect on shear strength due to either coating or geometry.

The panels aged at 260°C and 316°C had severe cracking on the 0° and 90° edges similar to the panels aged at 204°C. This is illustrated by the photomicrographs of the edges of the edge coated panel aged at 316°C for 1000 hours shown in figure 15. Perhaps more significant than the cracking shown in these photographs is the indication of almost complete destruction of the coating. As can best be seen in the 0° edge photo, the coating is severely cracked and peeled, affording little or no protection from oxidation.

The weight-loss data shown in figures 10 and 11 for the 260°C and 316°C aging show behavior similar to that at 204°C. There is slightly less weight-loss for the two edge coated configurations aged at 260°C but the effect is less than was seen at 204°C. When aged at 316°C, these panels initially show reduced weight-loss with coated edges but after aging 1000 hours the weight-loss for all four configurations is practically the same, reflecting the fact that the edge coating is functionally gone.

It is apparent from the preceding that coating Celion/LARC-160 panels with a 25 μm coating of PPQ has little or no effect on their cracking behavior or shear strength when thermally aged. It does appear that the coating retards oxidative weight-loss at temperatures up to 260°C. At temperatures above 260°C the coating provides some protection for about 500 hours after which the coating is sufficiently damaged to be useless.

It is possible that a thicker coating would have afforded more protection, however, the thermal aging results reported in ref. 6 and this effort indicate that the oxidative degradation of panels occurs primarily at the edges and does not affect the overall panel properties severely. Large panels will mainly deteriorate by strictly thermal degradation only rather than surface oxidation. A protective coating will have little or no effect on this degradation.

## CONCLUSIONS

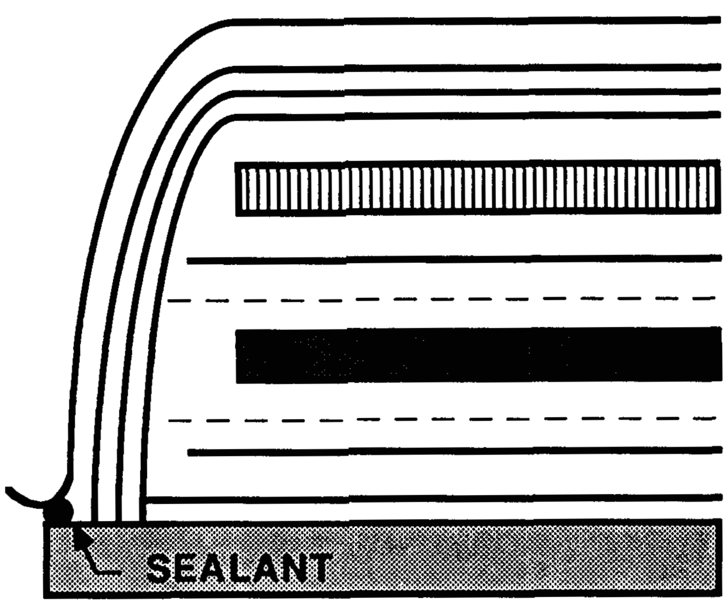
The use of a protective PPQ coating on Celion®/LARC-160 laminates afforded some surface damage protection when these laminates were thermally aged at temperatures of 204°C to 316°C. The protective coating did not help retain mechanical properties during thermal aging. The PPQ coating did not survive intact after 1000 hours of aging at 316°C. Coating of graphite/ polyimides composites such as Celion 6000/LARC-160 will probably not significantly increase their service life at elevated temperatures.

# REFERENCES


1. Dexter, H. Benson; Davis, John G., Jr., eds.: Graphite/Polyimide Composites. NASA CP-2079, 1979.
2. Maximovich, M. G.; Bergren, O.; and Lockerby, S.: Development of LARC-160/NR 150B2 Polyimide Graphite Hybrid Composites. NASA CR-159196, 1980.
3. 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, Apr. 1972, pp. 905-915.
4. St. Clair, Terry L.; and Jewell, Robert A.: Solventless LARC-160 Polyimide Matrix Resin. Selective Application of Materials for Products and Energy, Volume 23 of National SAMPE Symposium and Exhibition, Soc. Advance. Mater. and Process Eng., c. 1978, pp. 520-527.
5. Kray, R. J.: Development of New Addition-Type Composite Resins. NASA CR-3276, 1981.
6. Nelson, James B.: Long-Term Thermal Aging of Two Graphite/Polyimide Composite Materials. NASA TP-2369, 1984.
7. Nelson, James B.: Thermal Aging of Graphite/Polyimide Composites. Long-Term Behavior of Composites. ASTM STP 813, T. Kevin O'Brien, Ed., ASTM, 1983, pp. 206-221.
8. Nelson, James B.: Edge Crack Growth in Thermally Aged Graphite/Polyimide Composites. NASA TM-85763, 1984.

9. Hergenrother, P. M.: Polyphenylquinoxalines: Synthesis, Characterization and Mechanical Properties. J. Appl. Polym. Sci., vol. 18, 1974, pp. 1779-1791.

10. Standard Test Method for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short-Beam Method. ASTM D 2344-76. Part 36 of 1982 Annual Book of ASTM Standards, 1982, pp. 381-384.




**(a) Vacuum bag layup.**

1. APPLY 12.7cm (5in) Hg VACUUM AND HOLD FOR FULL CYCLE.
2. HEAT TO 218°C (425°F).
3. HOLD AT 218°C (425°F) FOR 30 MINUTES.
4. COOL TO LESS THAN 65°C (150°F) BEFORE RELEASING VACUUM.

**(b) Staging conditions.**

Figure 1. Typical (a) vacuum bag layup and (b) staging conditions for Celion/LARC-160 composite precompaction.

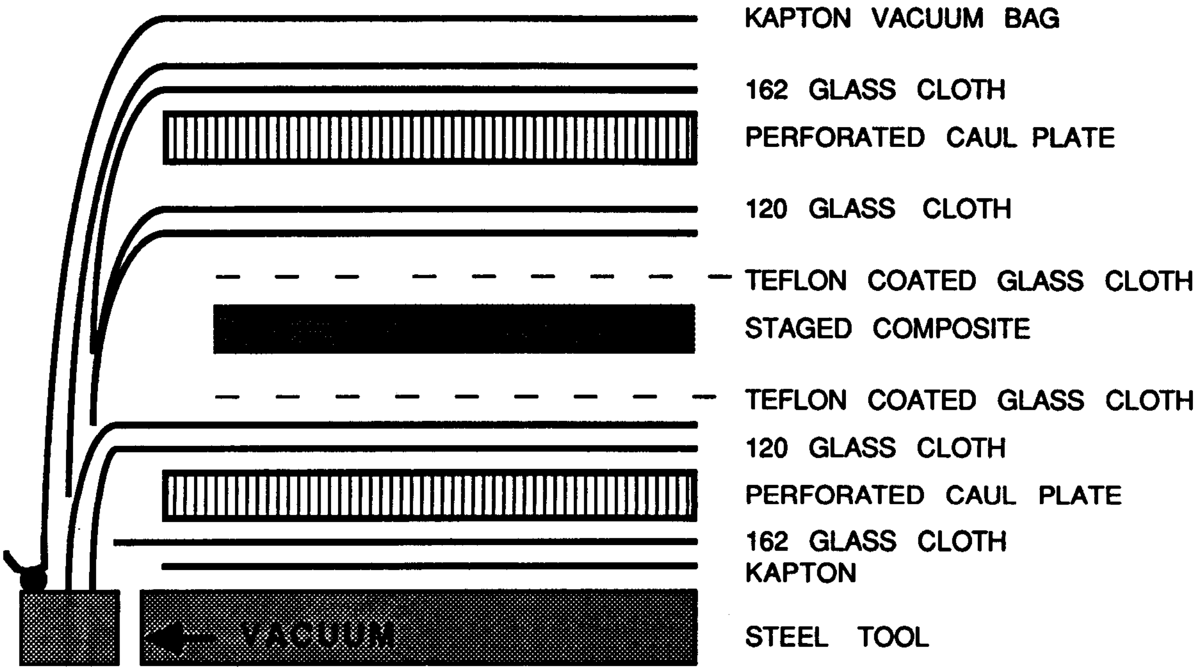



Figure 2. Vacuum bag layup for autoclave cure processing of Celion/LARC-160 composite panels.

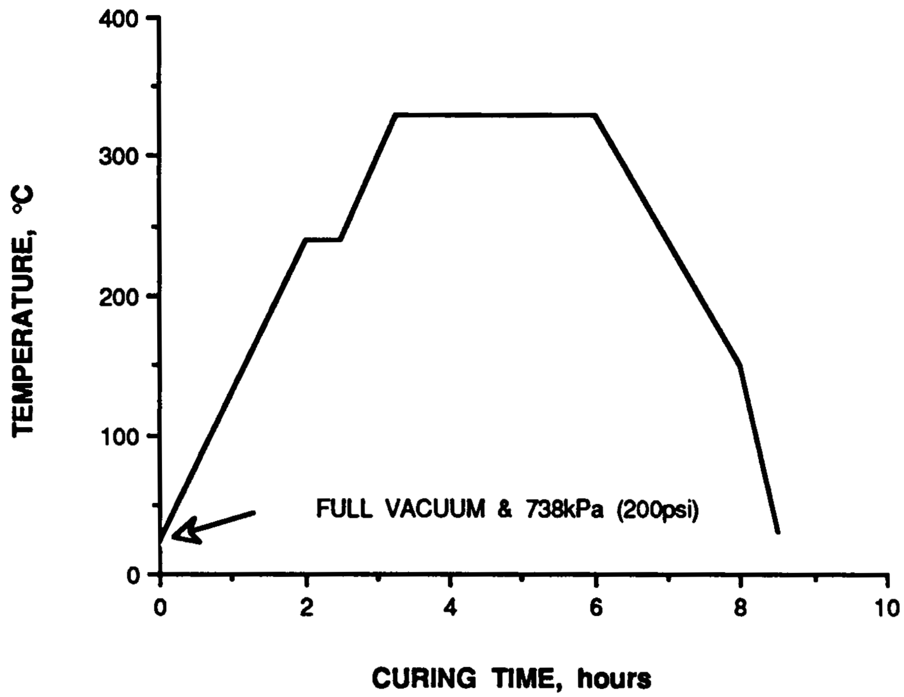
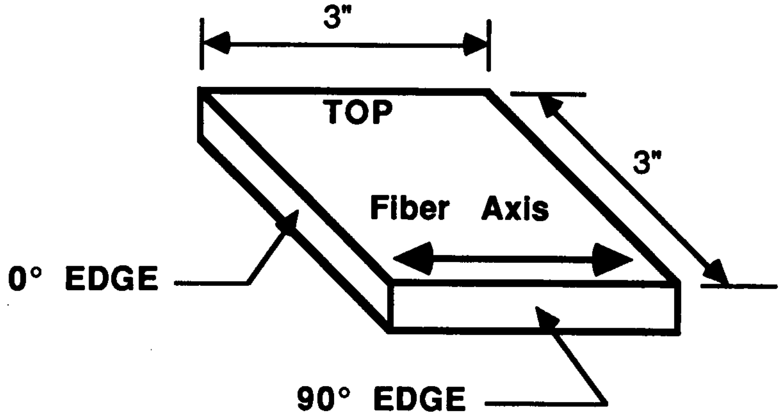



Figure 3. Cure cycle for Celion 6000/LARC-160 composite panels




**PANEL COATING**

(1) Total (top, bottom & all edges)

(2) Top & bottom

(3) Edge (both 0° & 90°)

Figure 4. Test panel configuration showing areas coated with PPQ resin.

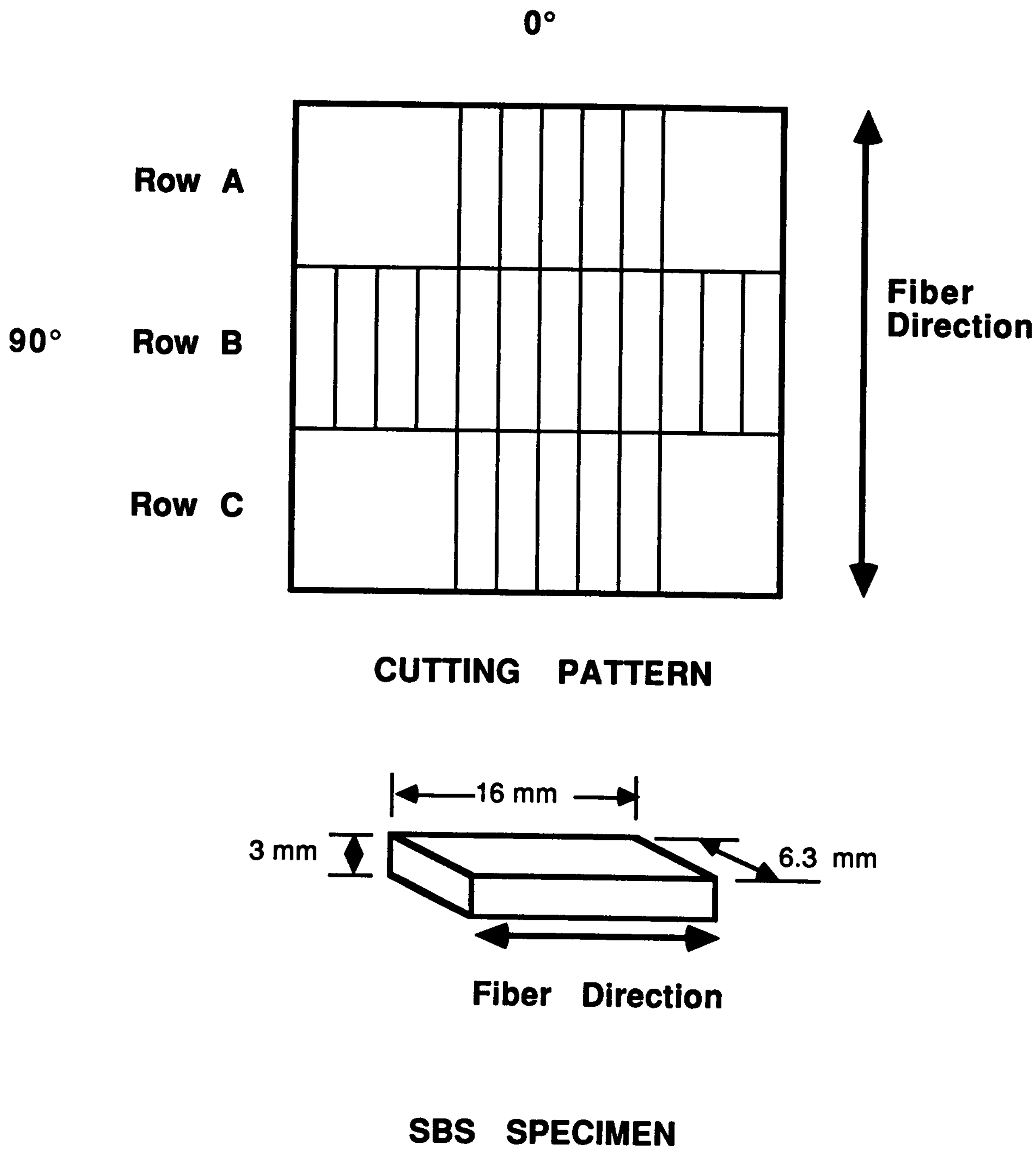



Figure 5. Aged panel cutting pattern and SBS specimen geometry.

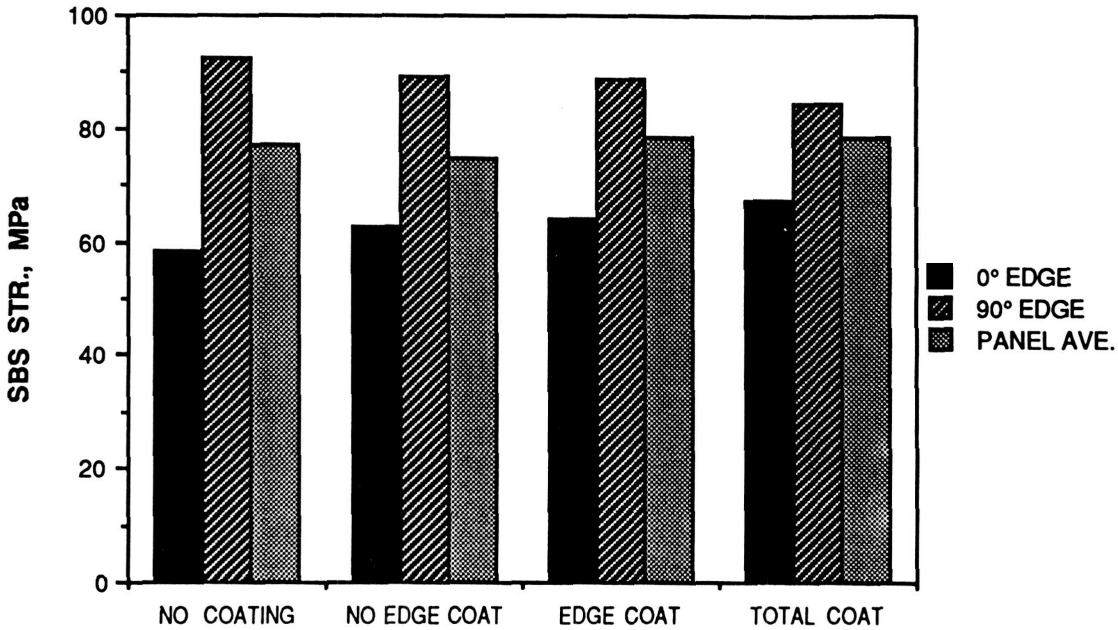



Figure 6. Room temperature SBS strength retention of specimens machined from coated and uncoated panels of Celion/LARC-160 aged 15,000 hours at 204°C.

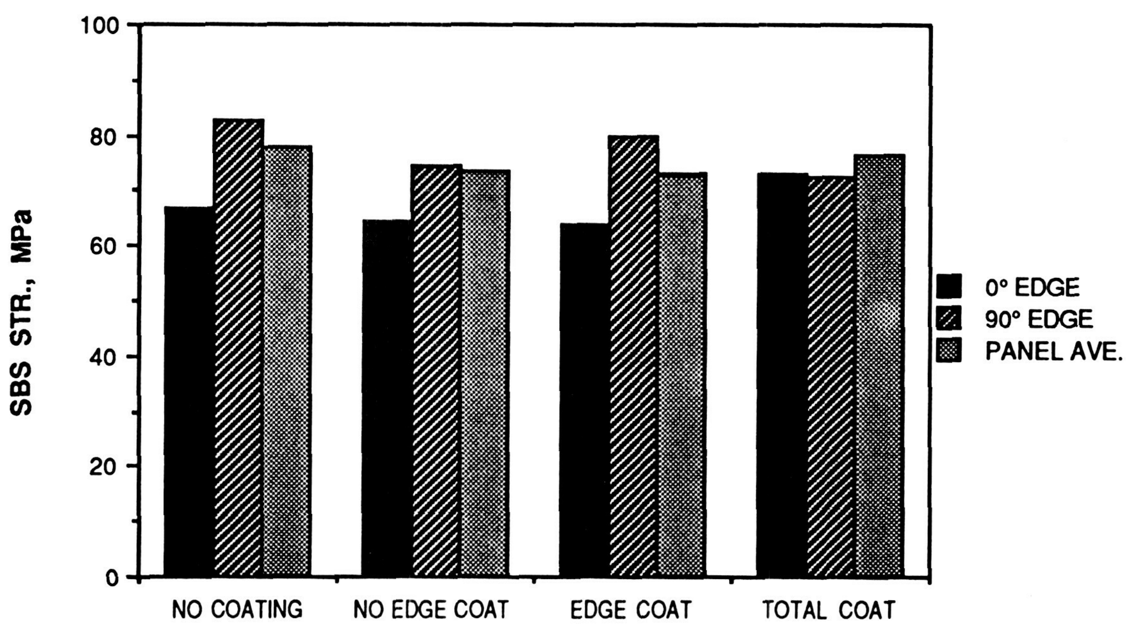



Figure 7. Room temperature SBS strength retention of specimens machined from coated and uncoated panels of Celion/LARC-160 aged 5000 hours at 260°C.

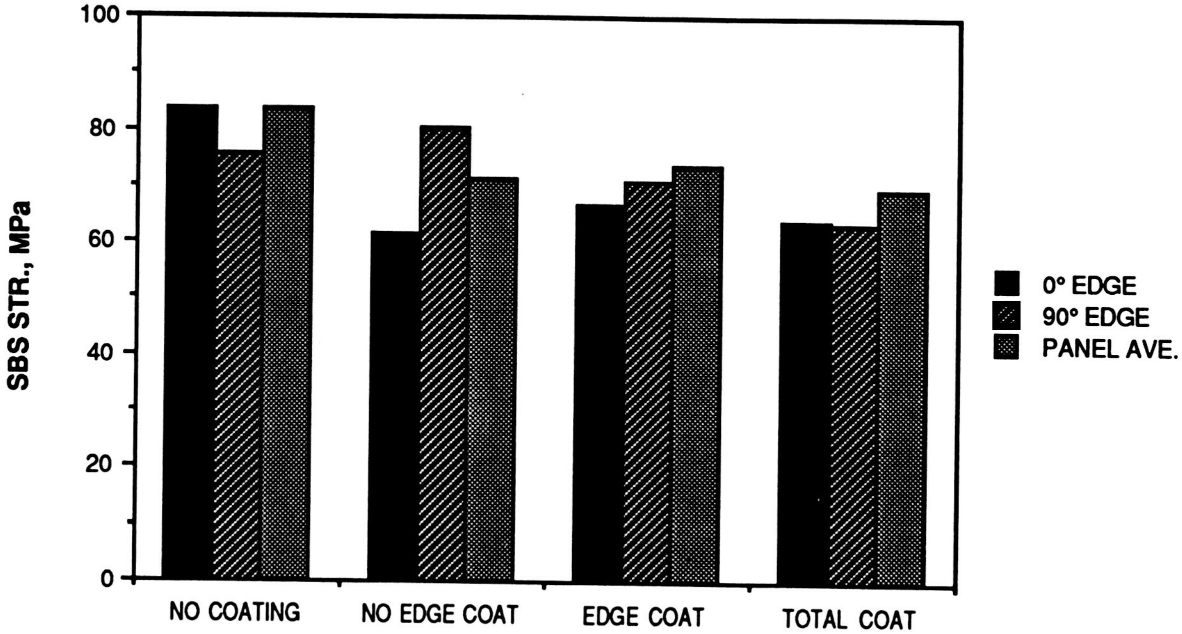



Figure 8. Room temperature SBS strength retention of specimens machined from coated and uncoated panels of Celion/LARC-160 aged 1000 hours at 316°C.

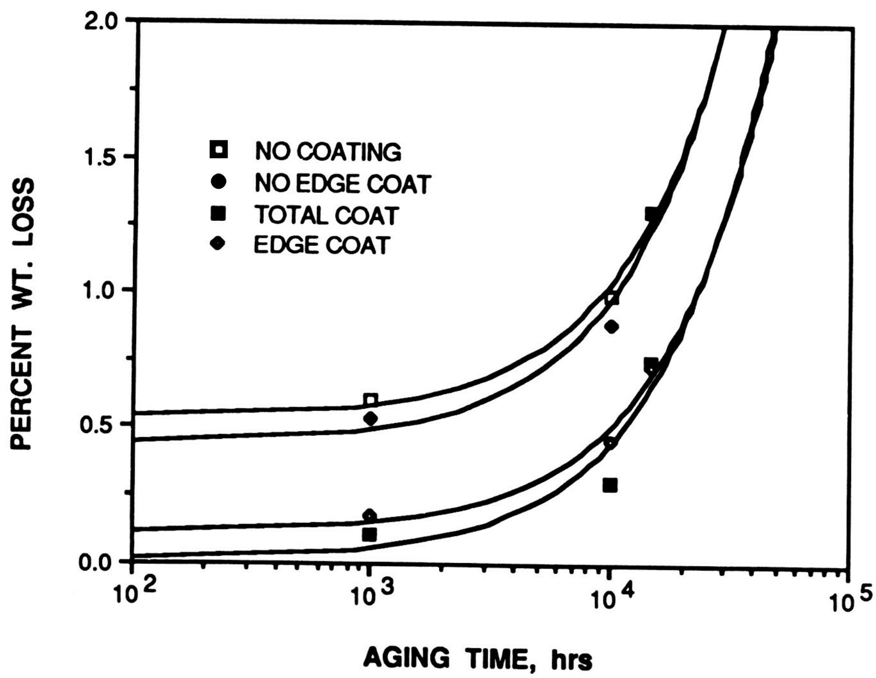



Figure 9. Weight loss of coated and uncoated panels of Celion/LARC-160 aged at 204°C.

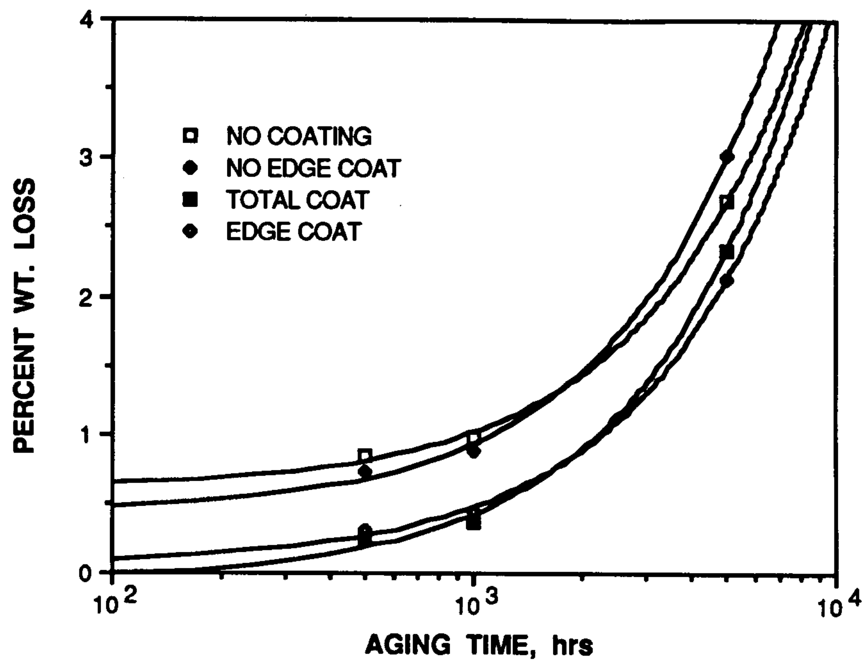



Figure 10. Weight loss of coated and uncoated panels of Celion/LARC-160 aged at 260°C.

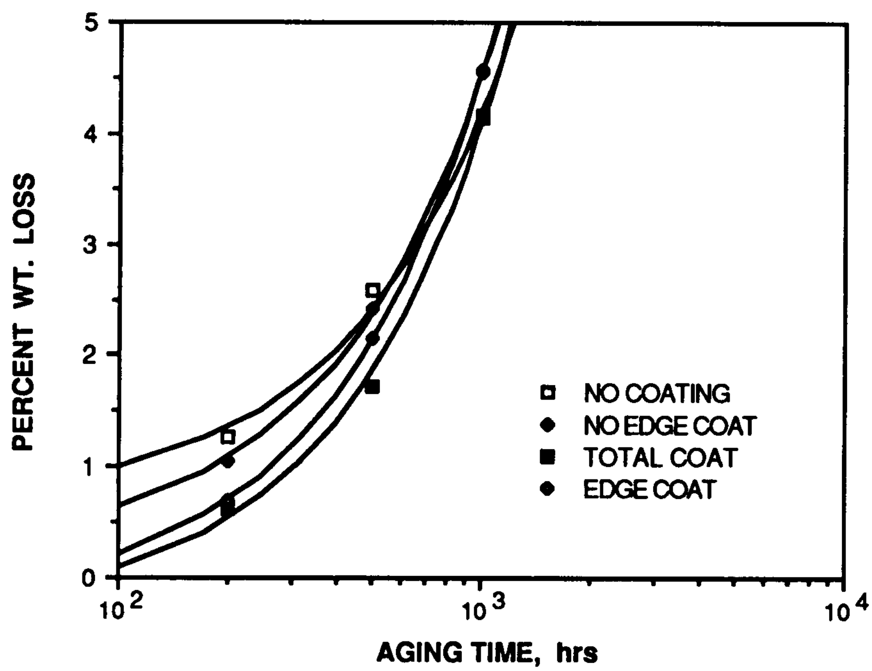



Figure 11. Weight loss of coated and uncoated panels of Celion/LARC-160 aged at 316°C.

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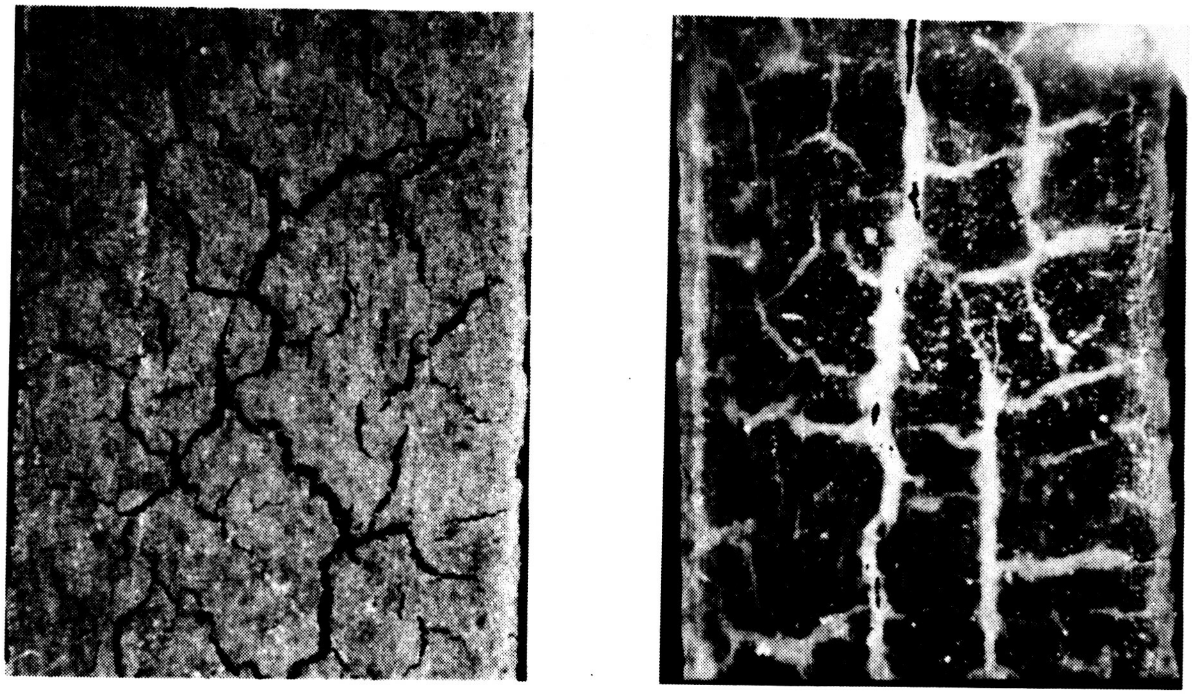
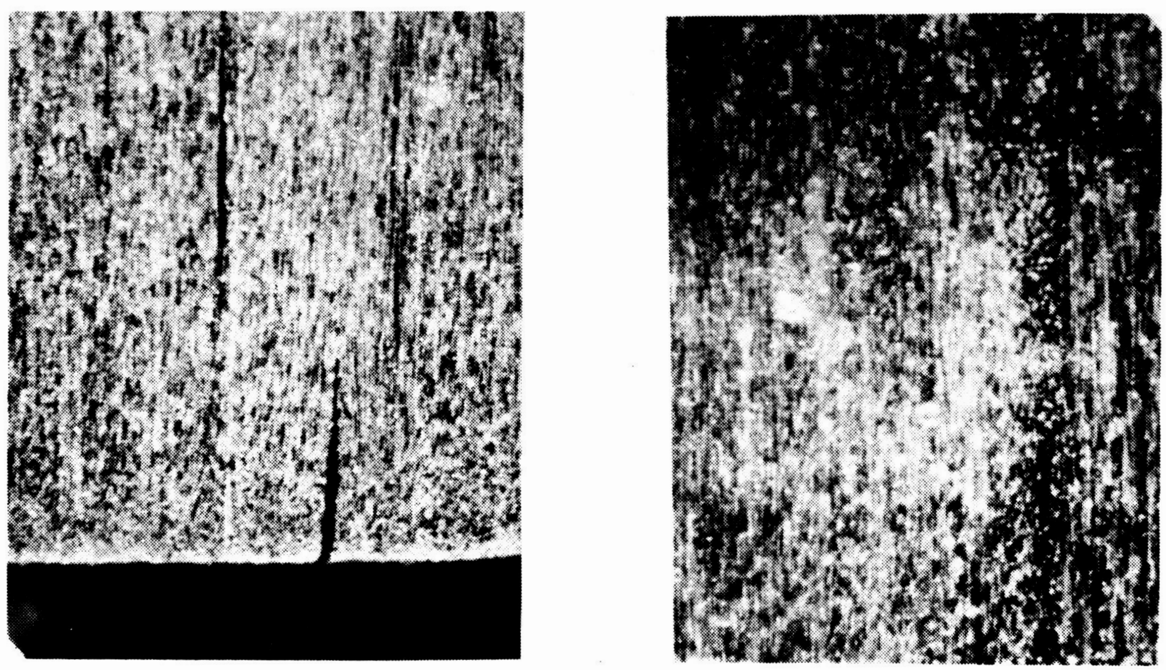


**UNCOATED**
**20X**

**COATED**
**20X**

Figure 12. Photomicrographs of the 0° edge of coated and uncoated panels of Celion/LARC-160 aged for 15,000 hours at 204°C.



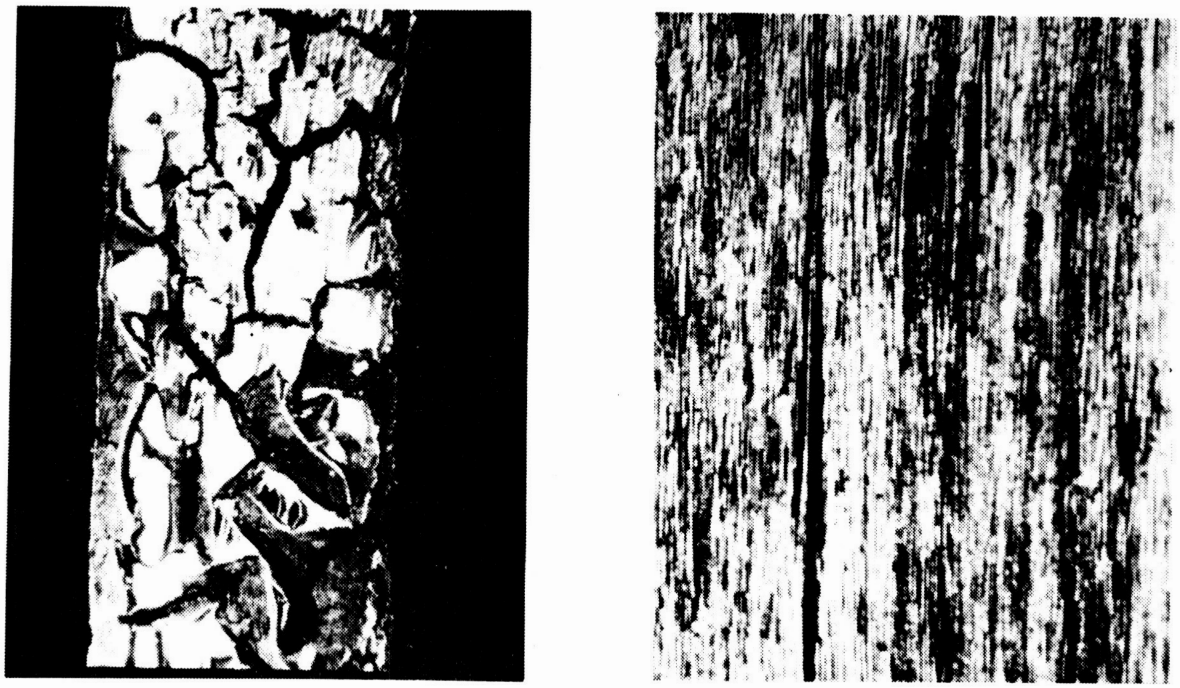
UNCOATED
39X

COATED
39X

Figure 13. Photomicrographs of the 90° edge of coated and uncoated panels of Celion/LARC-160 aged for 15,000 hours at 204°C.

**COATED**
**20X**

Figure 14. Photomicrograph of the damaged coating on the 90° edge of a Celion/LARC-160 panel aged for 15,000 hours at 204°C.



**COATED**
**0° EDGE**
**13X**

**COATED**
**90° EDGE**
**39X**

Figure 15. Photomicrographs of the coated edges of a Celion/LARC-160 panel aged for 1000 hours at 316°C.

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16. Abstract

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