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LONG-TERM THERMAL AGING OF CELION/V378A COMPOSITE MATERIALS

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SUMMARY

Celion®6000/V378A* graphite/bismaleimide composite materials were aged in air at temperatures of 177, 204, 232 and 260°C for various times up to 15,000 hours. Three unidirectional specimen types were aged: short beam shear (SBS), flexure, and 153 mm square panels. Aged specimens of V378A laminates exhibited excellent thermal stability. Extensive cracking was observed during aging on the 0° edges of the unidirectional laminates. These cracks penetrated as deep as 12 mm from the edge. The cracking appeared to have little or no effect on the observed properties of the laminates. The study indicates that the useful life of unrestrained unidirectional graphite/V378A laminates is 10,000 hours or greater at 177°C to 232°C and 2,000 to 5,000 hour at 260°C.

®Celion is a registered trademark of Celanese Corp.

*V378A is the trade designation of a modified bismaleimide resin manufactured by U. S. Polymeric Company of Santa Ana, CA.

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INTRODUCTION

Graphite-reinforced composites have been studied and used extensively in aircraft structures for over a decade. Graphite/epoxy composites have generally proved adequate for these applications and are considered to be the most easily processed class of composite materials. Efforts have been made, more recently, to identify matrix resins for graphite composites that have improved environmental performance at high temperatures and under hot-wet conditions. Addition type polyimide resins are available that fill these requirements but require cure conditions significantly more severe than the epoxy systems (refs. 1 and 2). A number of addition bismaleimide resins are currently being examined as epoxy replacements. U. S. Polymeric has introduced a modified bismaleimide matrix resin (V378A) that has fostered a great deal of interest for aerospace applications (refs. 3 and 4). Laminates of V378A can be autoclave cured at similar conditions to epoxy laminates (ref. 5). The hot-wet properties of V378A laminates have been found to be superior to epoxy laminates and have similar dry mechanical properties (refs. 3 and 6).

Most of the interest has naturally been concerned with epoxy replacement applications at operational temperatures of 130°C or less. However, bismaleimide resins as a class should have useful properties up to 300°C. This study endeavored to define the high temperature aging limits of unstressed unidirectional Celion 6000/V378A laminates. Specimens of this material were aged in air at temperatures of 177°C up to 260°C for periods up to 15,000 hours.

EXPERIMENTAL

Materials and Fabrication

The tested composite laminates were fabricated from a unidirectional prepreg of U. S. Polymeric V378A modified bismaleimide and Celion 6000 carbon fiber (epoxy compatable sizing). This prepreg was a net resin type (no bleeding of excess resin necessary). A conventional autoclave process based on the prepreg vendor's recommendations was used (ref. 3). Unidirectional layups were vacuum bagged between steel caul plates as shown in figure 1. The autoclave curing and postcuring cycles are detailed in figure 2. The laminate layup was heated under full vacuum and 0.7 MPa (100 psi) applied pressure to 177°C in 2 hours. The temperature was held at 177°C for 4 hours and the laminate cooled to room temperature, maintaining vacuum and pressure, in approximately 1 hour. The laminate was debagged and given a free standing postcure in an air oven. This postcure consisted of: heat to 246°C and hold for 4 hours, followed by a temperature increase to 288°C and hold for 1 hour, then cool to room temperature.

After fabrication, the laminates were subjected to ultrasonic c-scan inspection. The acceptable laminates were cut into square panels, short beam shear (SBS) specimens, and flexure specimens. Dimensions are shown in figure 3. The initial properties were determined and are listed in Table I. The laminates had low voids and a fiber volume of 62-63%. The glass transition temperatures (Tg) indicated that the laminates were adequately cured. The Tg of the thicker laminates were about 14°C lower than the thinner laminates. The measured SBS and flexural strengths were normal for a material of this type.

EQUIPMENT AND PROCEDURES

Isothermal Aging

Forced-convection horizontal airflow was used for the isothermal-aging environment at 177°C, 204°C, 232°C, and 260°C. The average air velocity was approximately 0.75 m/sec. The 153-mm square panels were supported on their edges, 12 mm apart with air flowing between each panel. The flexure and SBS specimens were placed in stainless-steel mesh baskets located to insure even exposure to the oven air flow. The specimens and panels were given various exposure times up to 15,000 hours. At predetermined intervals, specmens were removed for weight loss determinations and mechanical testing. The precut SBS specimens were tested at room temperature (RT), 177°C, 204°C, 232°C, and 260°C, and the precut flexure specimens were tested at RT, 177°C, and 232°C. The square panels were weighed and then cut into SBS specimens, as shown in figure 1, and tested at room temperature.

Weight Loss Measurement

Specimen weight changes were determined by weighing each specimen set rather than each specimen individually. This technique shortened the time necessary to weigh the specimens and thus minimized measurement inaccuracies due to moisture pickup during weighing.

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. 7). A nominal 4:1 ratio of span to thickness was used. The elevated-temperature tests were performed in a quartz lamp clamshell oven. Thermocouples located in close proximity to the test specimen were used to control and monitor temperature. Each specimen was maintained at the test temperature for 5 minutes before applying the load. Eight replicates of the precut SBS specimens were tested at each condition.

The flexure tests conformed to ASTM Standard Test Methods for Flexural Properties of Plastics and Electrical Insulating Materials (D790-71) (ref. 8). A three-point loading fixture and a nominal 32:1 ratio of span to thickness were used. The elevated-temperature flexure tests were run in the same quartz lamp oven used for the SBS tests. Three replicate specimens were tested at each condition.

RESULTS AND DISCUSSION

The effect of long-term isothermal aging on the SBS strength, flexural strength and weight-loss of Celion/V378A unidirectional laminates is illustrated in figures 4 to 16. Room temperature strength retention of the precut SBS specimens as a function of thermal aging is summarized in figure 4. Specimens aged at each temperature showed an initial increase in shear strength: to almost 120% of initial for the 260°C aged specimens and to nearly 130% of initial for the other aging temperatures. After this initial strength increase, the specimens aged at all temperatures exhibited a gradual decrease in shear strength. The strength of the 260°C aged specimens began to drop off as early as 500 hours whereas the others did not show any significant decrease until about 2000 hours. The relative thermal stability exhibited by these specimens shows the normal decrease in stability with increasing aging temperature. However, the thermal aging curves for 177°C-232°C differ only slightly, whereas aging at 260°C has a significantly greater effect on the room temperature shear strength.

In figure 5 is shown the variation in shear strength of SBS specimens cut from 153 mm square panels thermally aged for various times at temperatures from 177°C to 260°C. Like the aged precut SBS specimens these panels shown an initial strength increase before declining. However, the square panels evidenced a much greater stability than the precut specimens. The strength of the 260°C aged panels peaked at about 120% of as-fabricated strength, similar to the precut specimens, then the shear strengths dropped to 107% of as-fabricated after 5,000 hours, whereas the strengths of the precut specimens declined to 75% of as-fabricated after 5,000 hours. The strengths of the panels aged below 260°C peaked at about 10,000 hours and after 15,000 hours had declined only to the as-fabricated value.

In figures 6 to 9 are shown both room temperature and elevated temperature SBS strength variations for the precut specimens thermally aged at 177°C, 204, 232 and 260°C. Each of these figures shows the same general pattern of strength variation at the different temperatures. The RT and elevated temperature strength curves are arranged in descending order of strength with increasing test temperature for each of the aging temperatures. At aging temperatures from 177°C to 232°C the variation in elevated shear strength was only slight with RT and elevated strengths converging after 10,000 to 15,000 hours. Figure 9 shows the less explicable behavior at the 260°C aging temperature. The variation in strength with aging time is greater and more irregular. In fact, at 5,000 hours, the curves are diverging.

The weight-losses of the aged precut specimens and aged square panels are shown in figures 10 and 11. The weight-loss curves of the precut specimens are very similar to those of the square panels: both sets of curves are very smooth and show a regular increase in weight-loss with time and temperature. They correlate with their respective strength curves only in the most general sense. While there is a steady loss of weight from the beginning of aging with no breaks or changes in the weight-loss pattern, the strength curves are much more irregular. The precut specimens show a consistently higher specific weight-loss rate than the aged panels. This difference in weight-loss behavior and the difference in shear strength variation indicate that there is geometry effect in aging of laminates of V378A. Similar behavior has been previously reported for several graphite/polyimide composite materials (refs. 9, 10 and 11).

The variation of RT and elevated temperature flexural strengths for Celion/V378A thermally aged at 177°C, 204°C, 232°C and 260°C are indicated in figures 12 to 15. Figure 12 demonstrates that the room temperature flexural strength of V378A laminates hardly varies on aging for 15,000 hours at 177°C. The elevated temperature flexural strength values show a steady increase during aging until they nearly converge with the room temperature value at 15,000 hours. This behavior is repeated for aging at 204°C and 232°C (figures 13 and 14). The variation in flexural strength on aging at 260°C is seen in figure 15. At this aging temperature, there is a small but significant decrease in room temperature flexural strength after 5,000 hours aging. The elevated temperature flexural strengths show a pronounced increase with aging time until about 2,000 hours where they begin to decline. There was no significant change in flexural modulus during aging at any of these temperatures.

Weight-loss histories of the flexure specimens aged at the various temperatures are shown in figure 16. These curves show the same regular pattern exhibited by the precut SBS specimens and square panels. In fact, the weight-loss curves of the flexure specimens are practically identical to those of the precut SBS specimens. Again there does not appear to be any definite correlation of weight-loss with changes in flexural strength.

In previous studies of thermal aging behavior of graphite/polyimides a strong correlation was found between SBS strength changes and both weight-loss and the depth of cracks found in the 0° edge of the specimens (refs. 9, 10 and 11).

Similar cracks were observed to occur and grow with aging in the 0° edges of all of the specimens in this study. This is illustrated by the photomicrograph of the 0° edge of a specimen aged at 232°C for 15,000 hours (fig. 17). The depth of the cracks was measured by using a dye penetrant x-ray technique (refs. 10 and 11). The measured crack-depth versus aging time at each aging temperature for specimens cut from the corners of the aged 153 mm square panel, is shown in figure 18. Microscopic examination of the specimens indicated that these edge cracks are formed early in the aging process; generally in the first 100 to 200 hours. The crack-depth curves show that the crack growth is very slow until about 2,000 hours for the panels aged at 260°C, then the crack-depth increases dramatically to about 11 mm. This crack-depth is approximately 2/3 the length of a SBS specimen. Aging at lower temperatures produces similar but slower crack growth.

To check for correlations of property changes to crack growth, shear strength and weight-loss were plotted versus crack-depth. The weight-loss/crack-depth curves are shown in figure 19. The individual curves are smooth and regular but do not show any direct causative relationship between weight-loss and crack-depth. The lack of correlation between shear strength and crack-depth was even more pronounced. Considering the magnitude of the cracking it is surprising that there is not some correlation between shear strength and cracking.

To further examine this phenomena, the shear strength data taken from different areas of the square panels was analyzed. Figures 20 to 23 show the shear strength averages at the edges and overall panel averages as a function of aging time and temperature. Generally, there does not appear to be any significant difference in shear strength of specimens taken from the 0° edge, where the cracks occur, and anywhere else in the panel.

None of the specimens in this study exhibited extensive surface damage after aging. There was a barely perceptable fuzziness of the surfaces after 5,000 hours at 260°C and 10,000 hours at 232°C. This is a result of resin loss in the surface layers. However, the degree of apparent surface damage is quite small for the overall weight loss observed. The graphite/ polyimides (PMR-15 and LARC-160) reported in reference 11 exhibited significantly greater apparent surface damage at comparable weight-losses.

These tests indicate that large unstressed laminate panels of graphite/ V378A should have a lifetime at temperatures up to 232°C of greater than 10,000 hours. At 260°C the lifetime of an unstressed panel would be greater than 2,000 hours. However, the severe cracking that occurs at the 0° edge of aged panels would be expected to limit service time in most applications due to applied stresses. It seems probable that the edge-crack-growth rate would be significantly accelerated under cyclic stress, leading to early fatigue failures.

CONCLUSIONS

Graphite fiber laminates of V378A exhibit excellent thermal stability when aged in air at temperatures from 177°C to 260°C. Severe cracking was observed during aging on the 0° edges of unidirectional laminates. These cracks penetrated as deep as 12 mm from the edge. The cracking had little or no effect on the observed properties of the laminates. The study indicates that the useful life of unrestrained unidirectional graphite/V378A laminates is 10,000 hours or greater at 177°C to 232°C and 2,000 to 5,000 hours at 260°C.

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TABLE I. PROPERTIES OF UNAGED UNIDIRECTIONAL CELION/V378A LAMINATES

*Fiber volume, percent	62
Density, g/cc	1.60
Glass transition temp., Tg, °C	305
SBS strength, MPa	
RT	69.5
177°C	56.1
204°C	50.8
232°C	43.3
260°C	37.0
Flexural strength, MPa	
RT	1742
177°C	1152
232°C	1041

*Based on vendors certification that V378A resin density = 1.272 g/cc and fiber areal weight = 148 g/m^2.

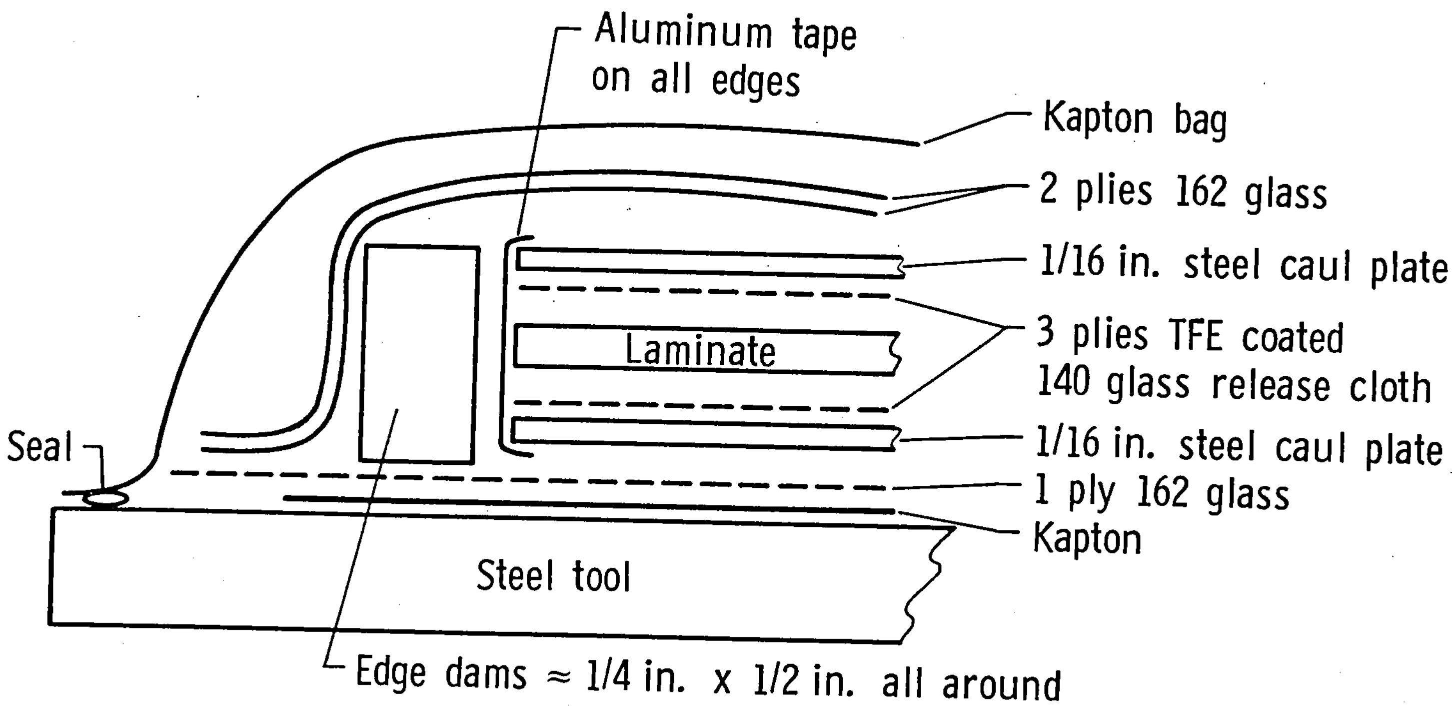

Figure 1.- Autoclave processing layup for Celion/V378A laminates.

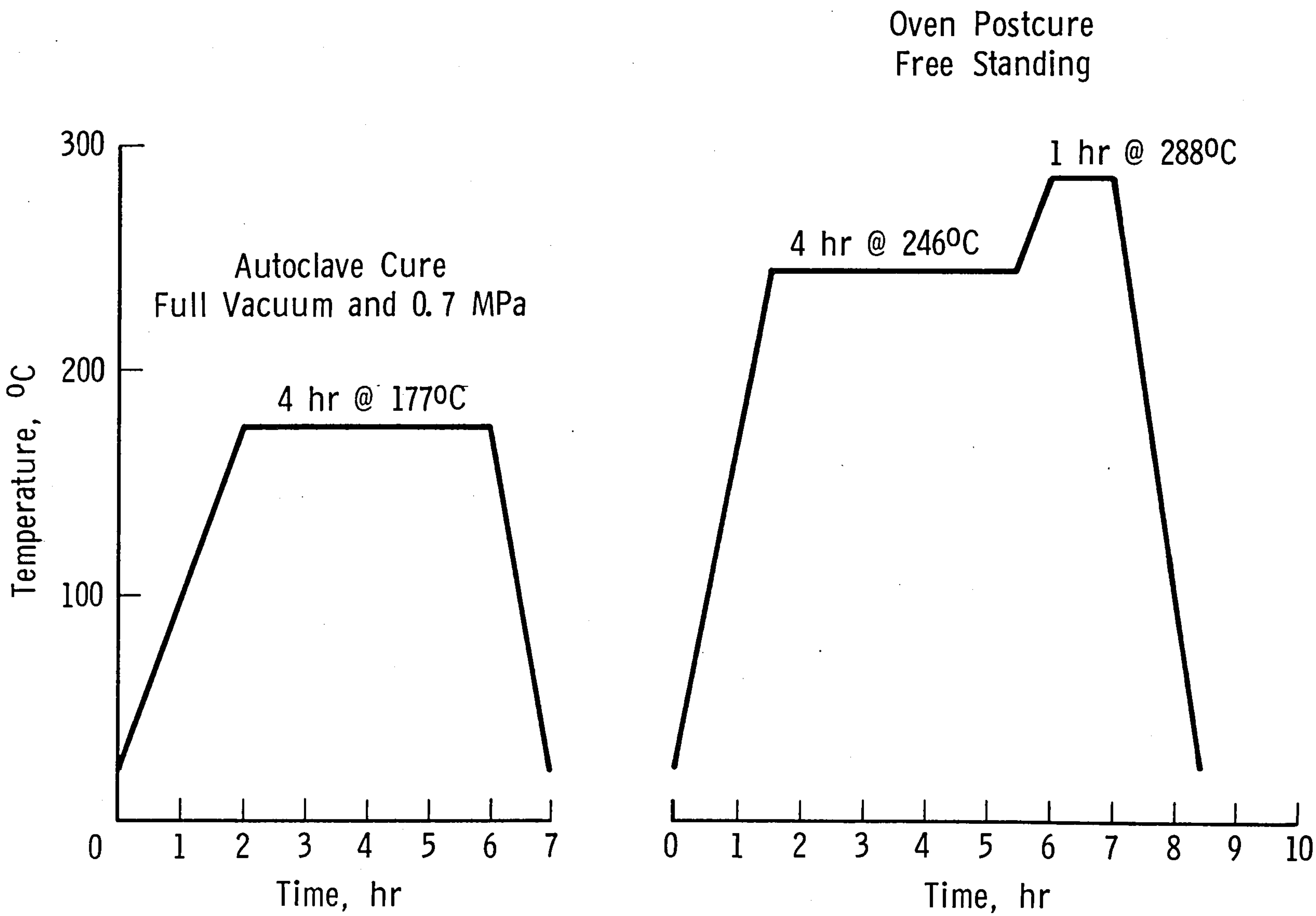

Figure 2.- Cure cycle for the Celion/V378A laminates.

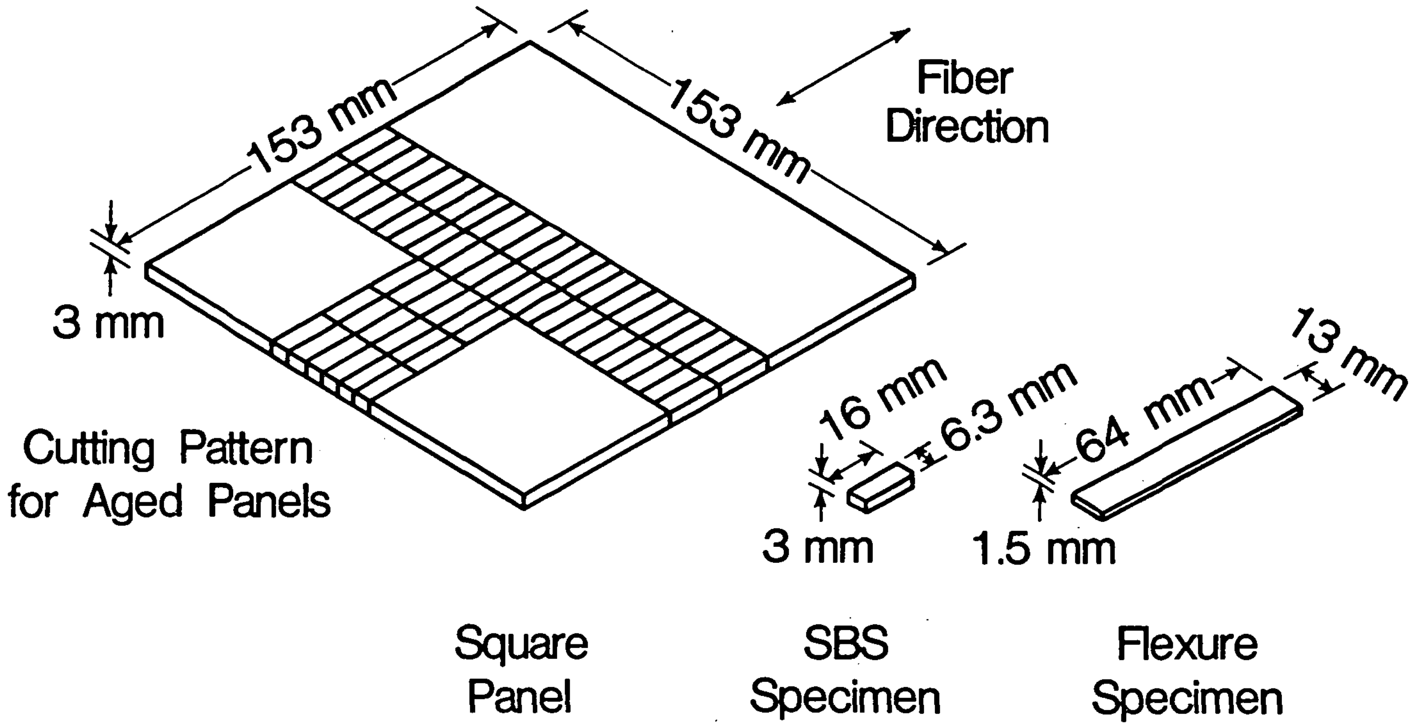

Figure 3.- Test specimen geometry.

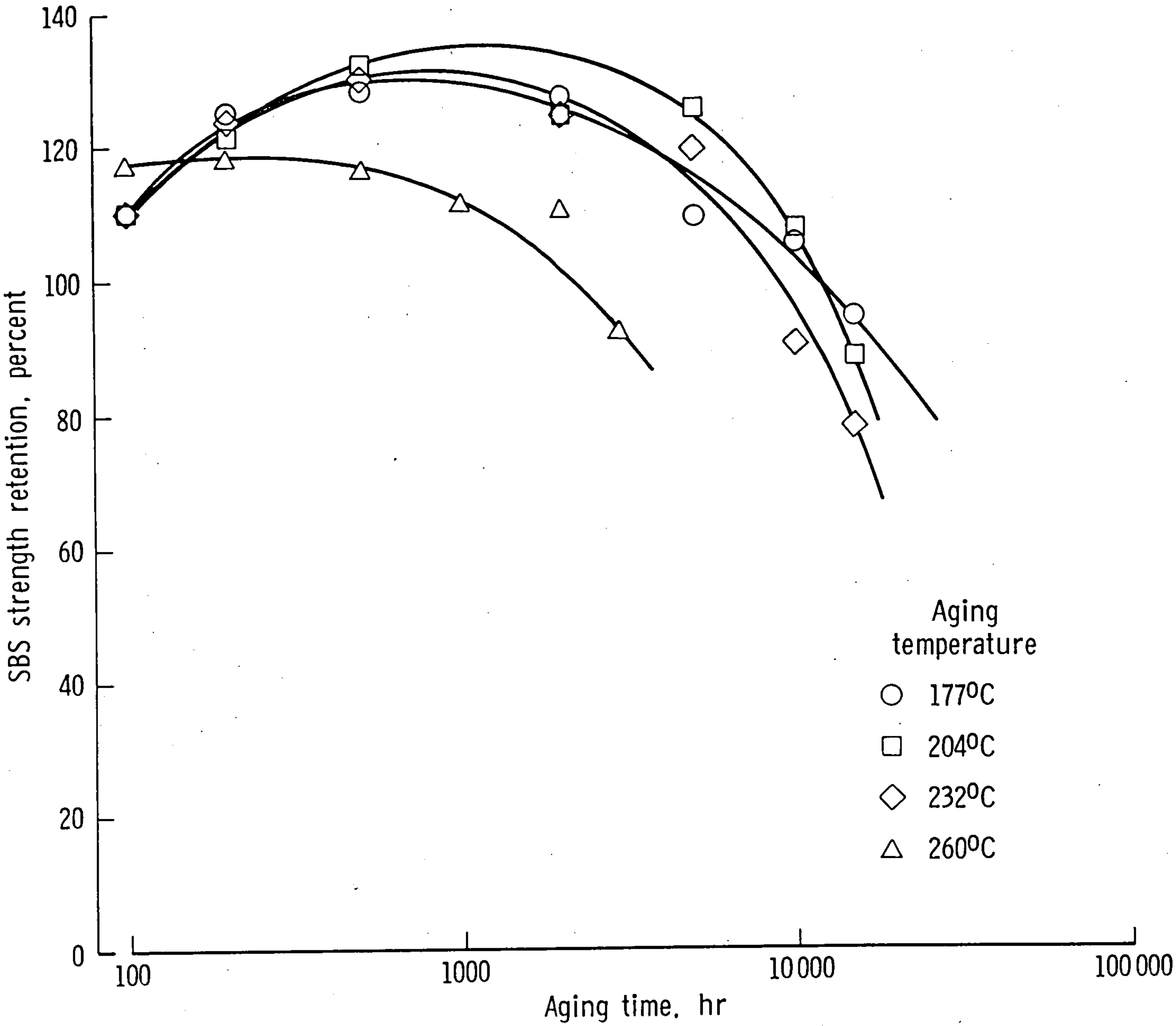

Figure 4.- SBS strength retention of Celion/V378A precut specimens aged at 177°C, 204°C, 232°C and 260°C. Tested at room temperature.

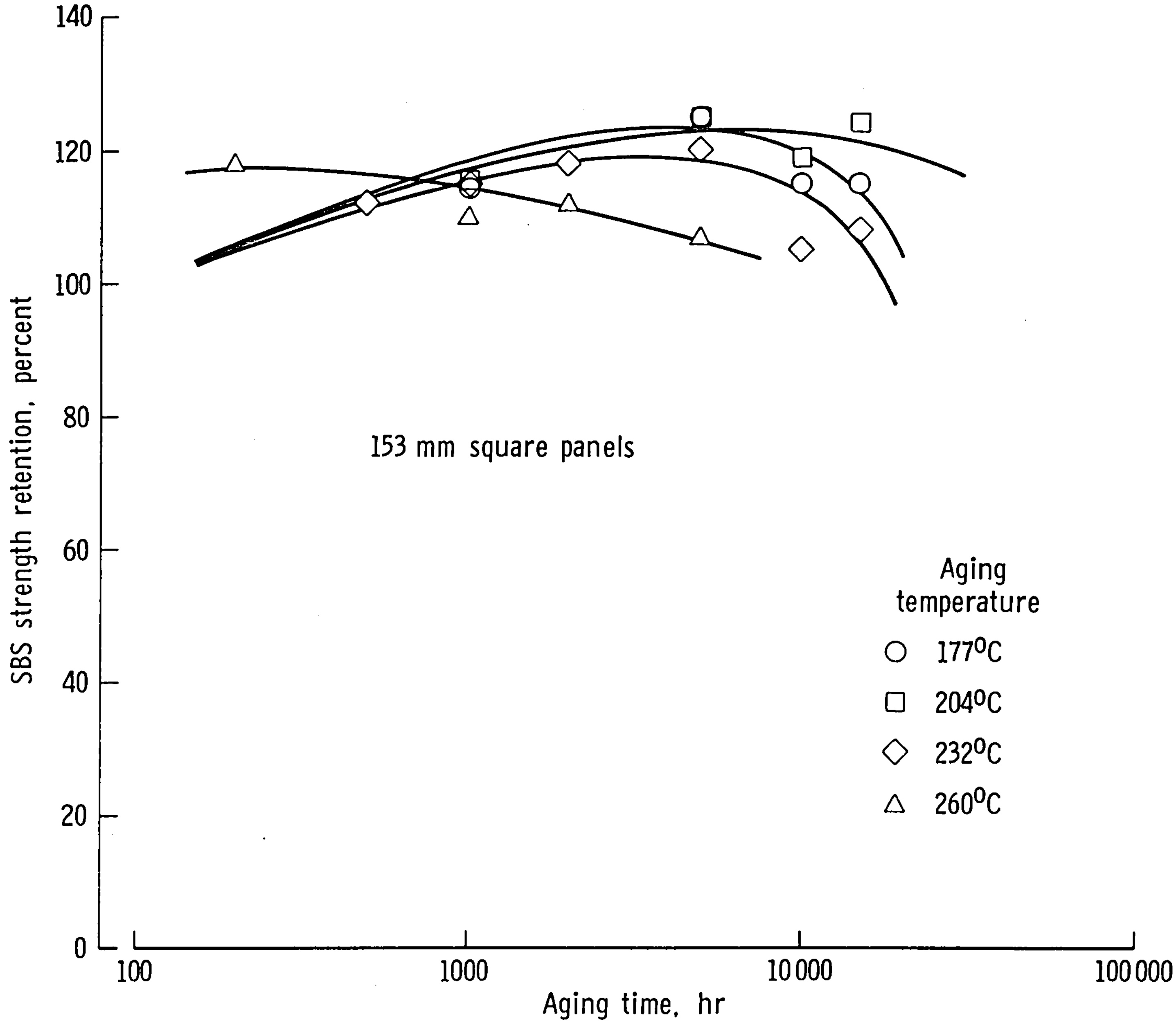

Figure 5.- SBS strength retention of Celion/V378A panels aged at 177°C, 204°C, 232°C and 260°C. Tested at room temperature.

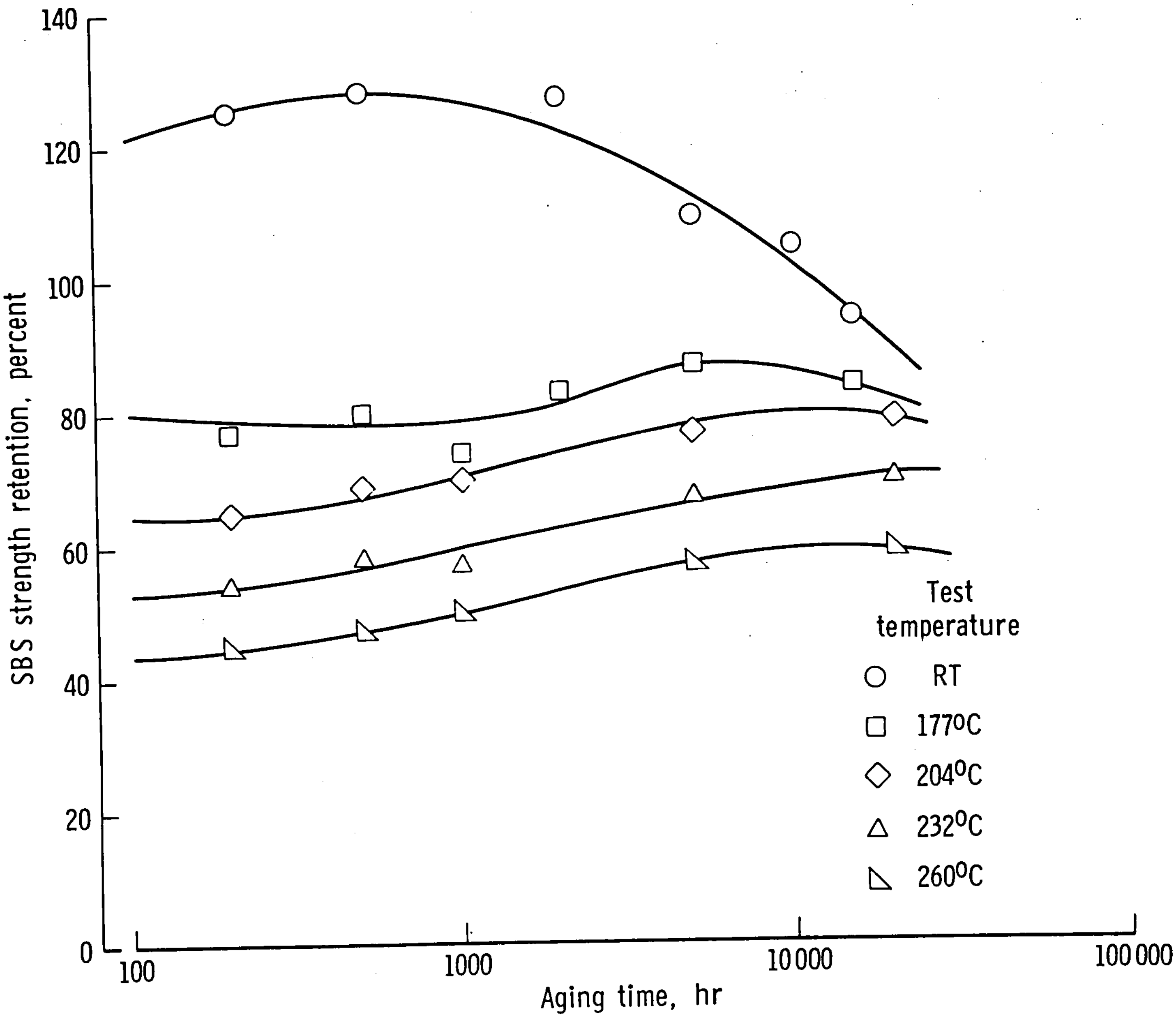

Figure 6.- SBS strength retention of precut specimens of Celion/V378A aged at 204°C.

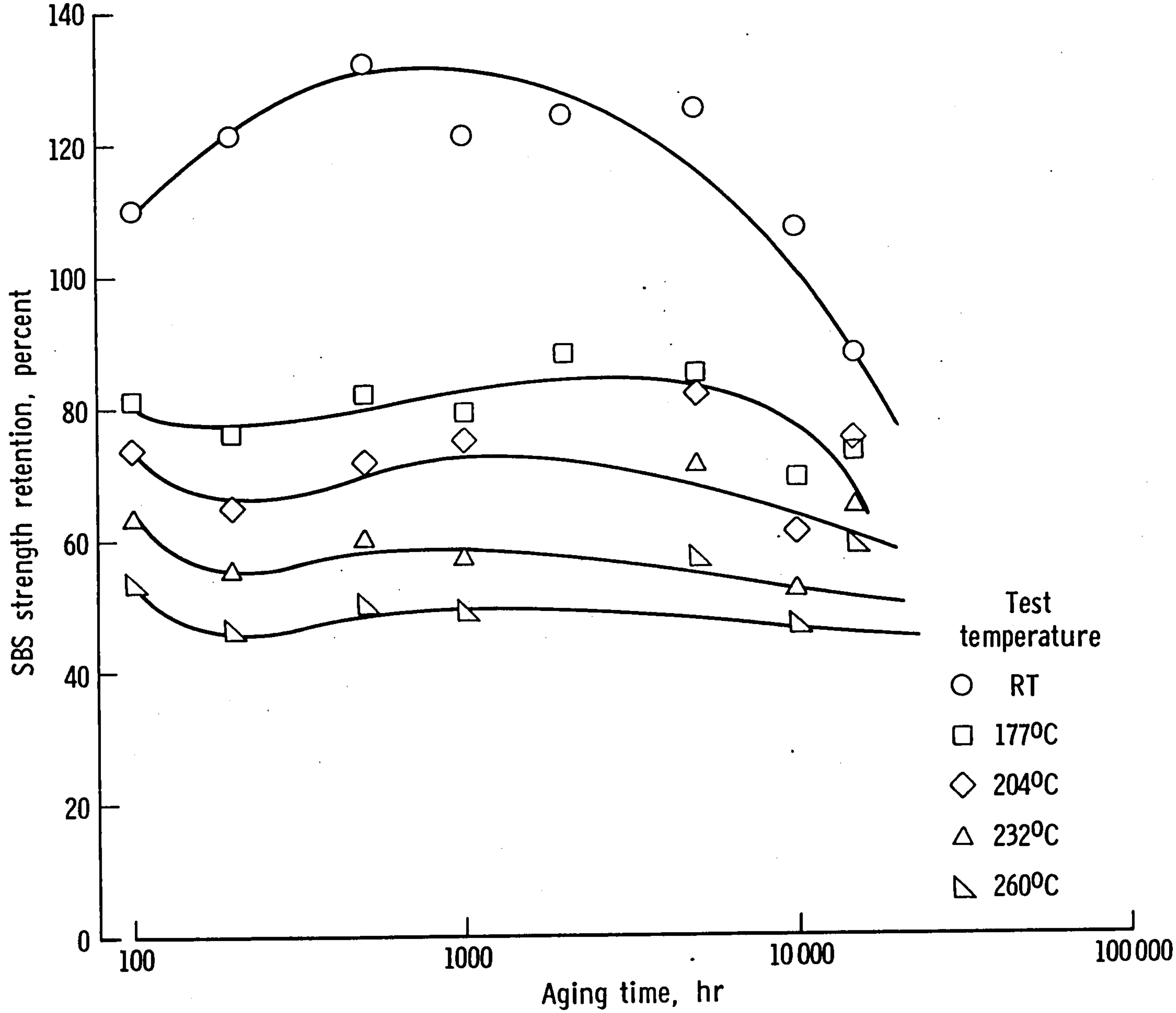

Figure 7.- SBS strength retention of precut specimens of Celion/V378A aged at 204°C.

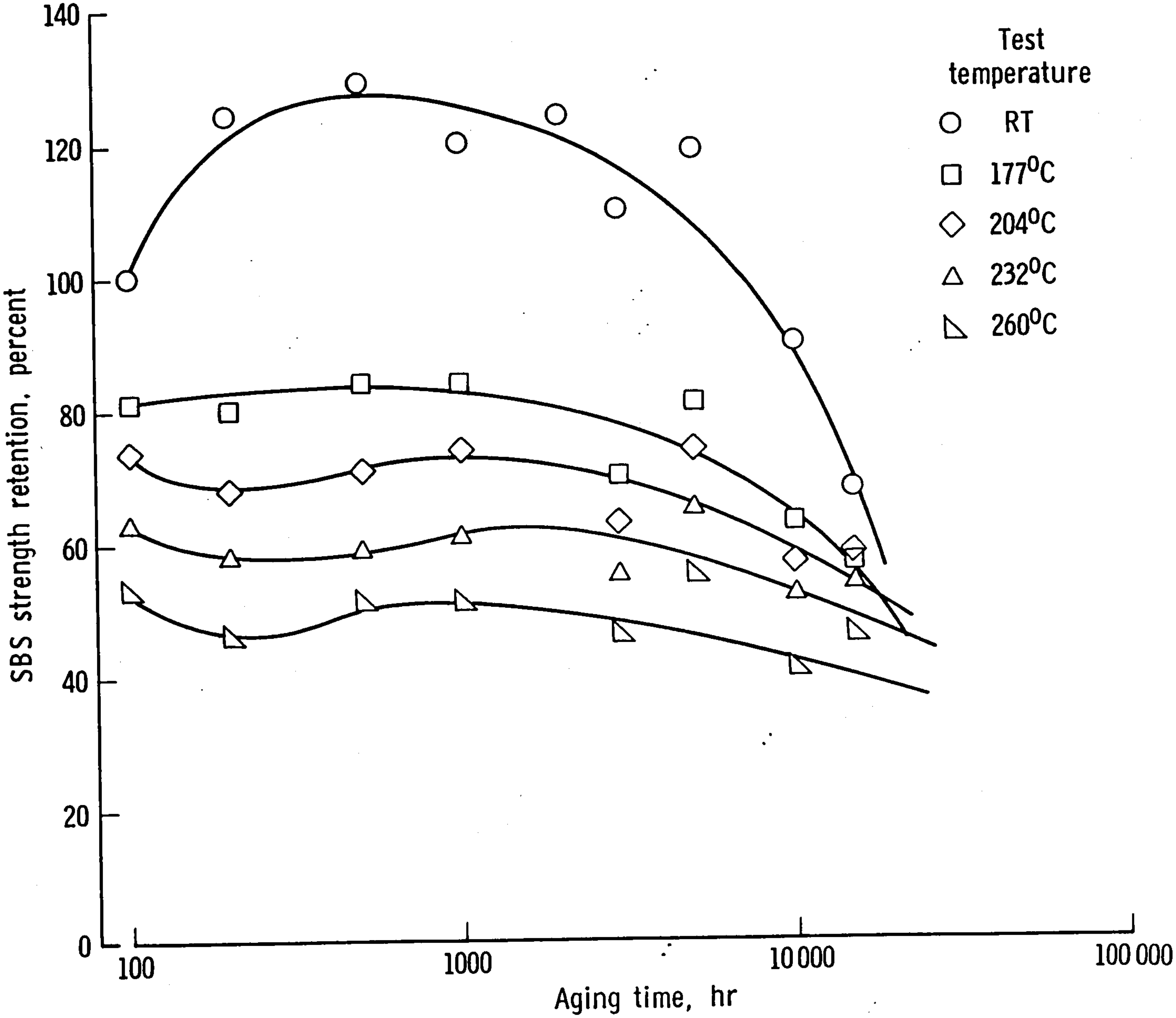

Figure 8.- SBS strength retention of precut specimens of Celion/V378A aged at 232°C.

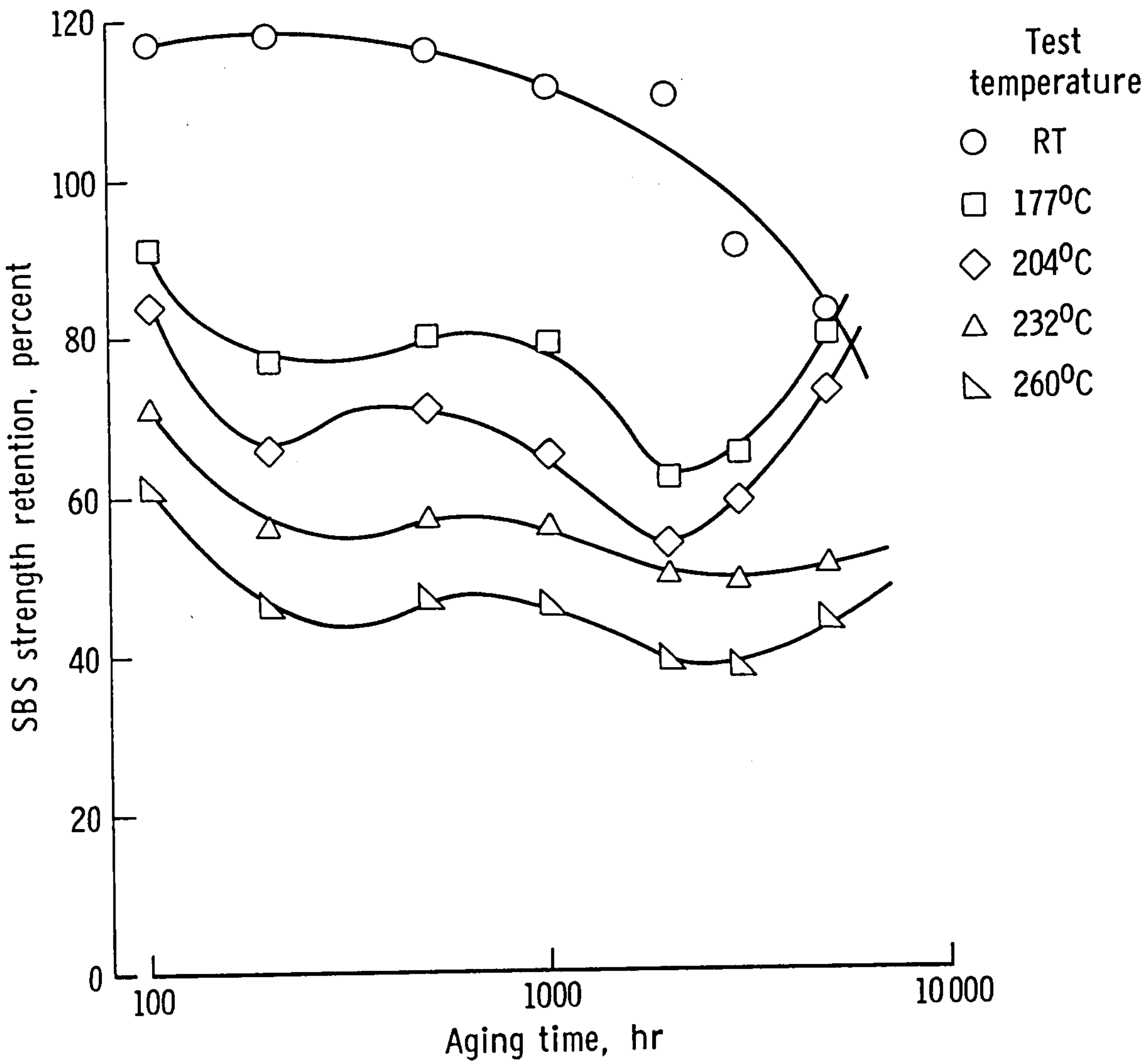

Figure 9.- SBS strength retention of precut specimens of Celion/V378A aged at 260°C.

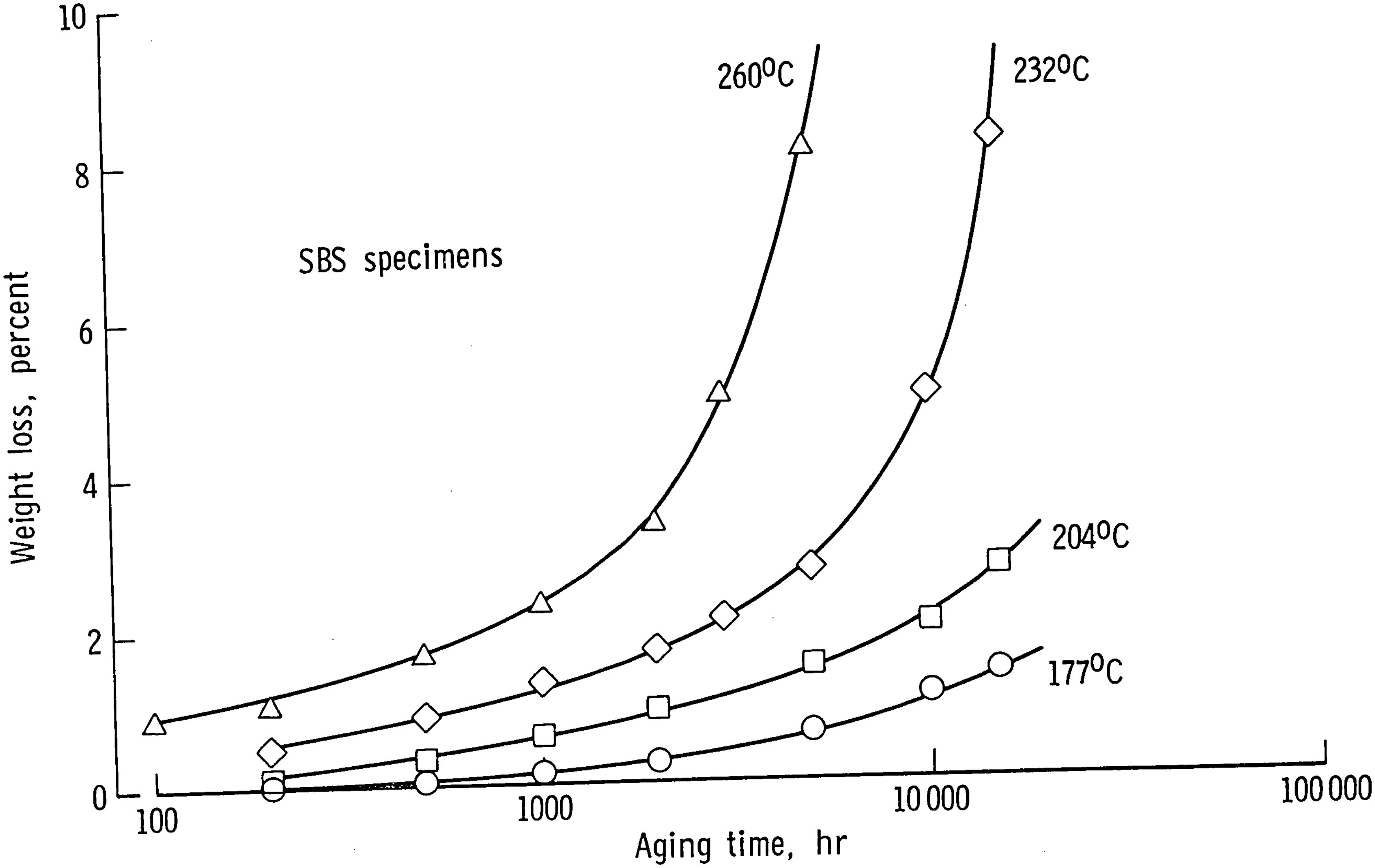

Figure 10.- Weight losses of precut specimens of Celion/V378A aged at 177°C to 260°C.

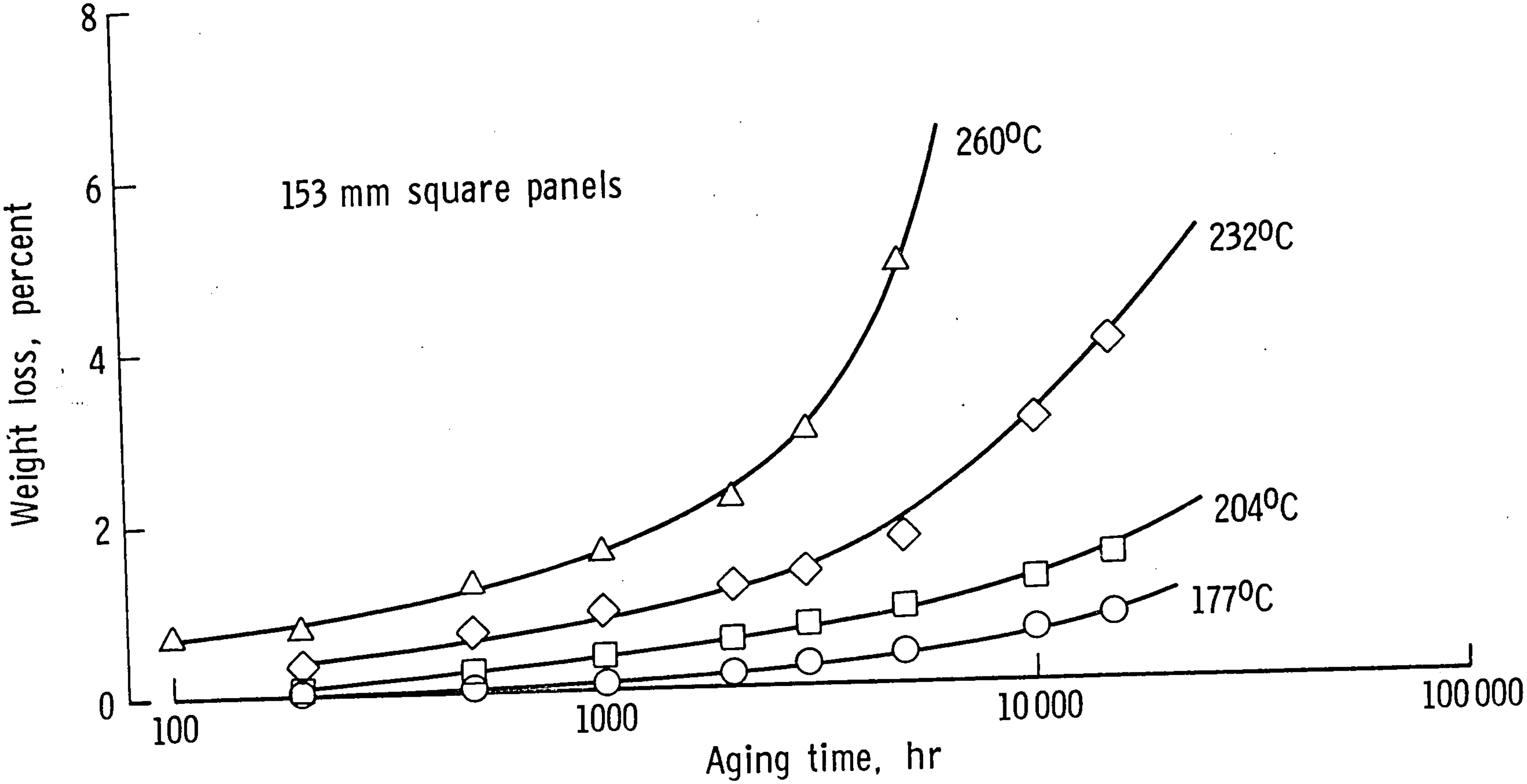

Figure 11.- Weight losses of square panels of Celion/V378A aged at 177°C to 260°C.

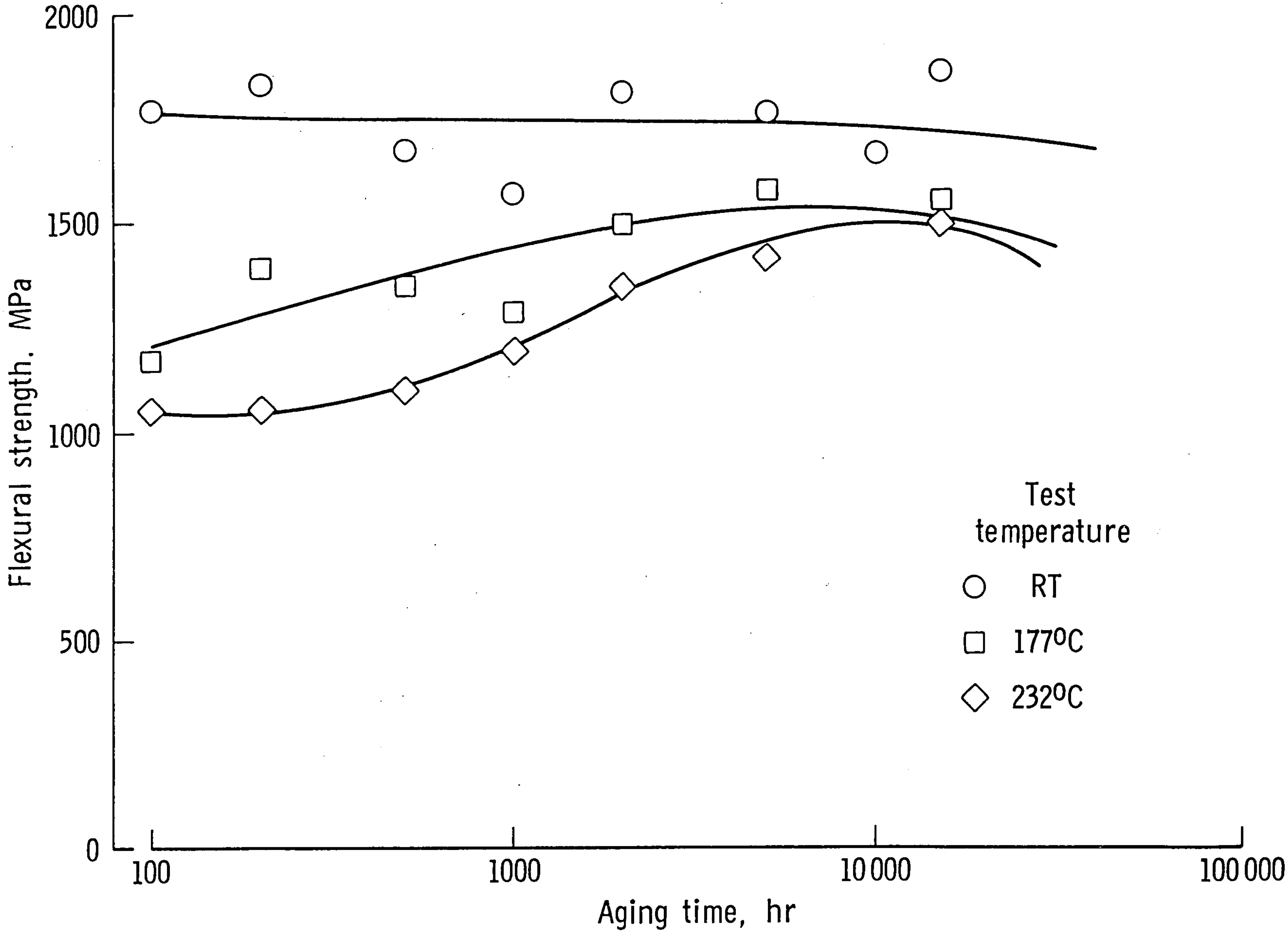

Figure 12.- Flexural strengths of precut specimens of Celion/V378A aged at 177°C.

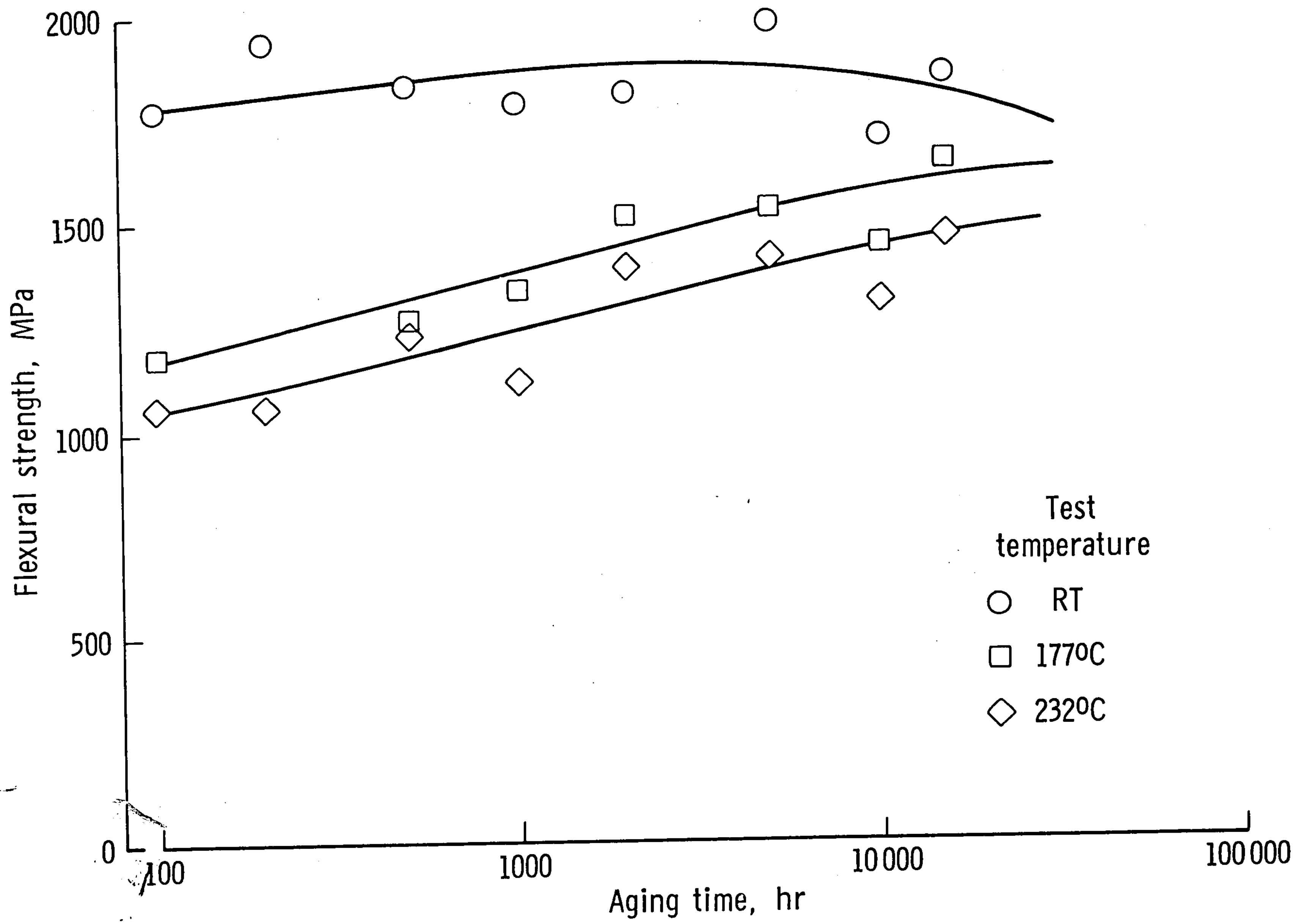

Figure 13.- Flexural strengths of precut specimens of Celion/V378A aged at 204°C.

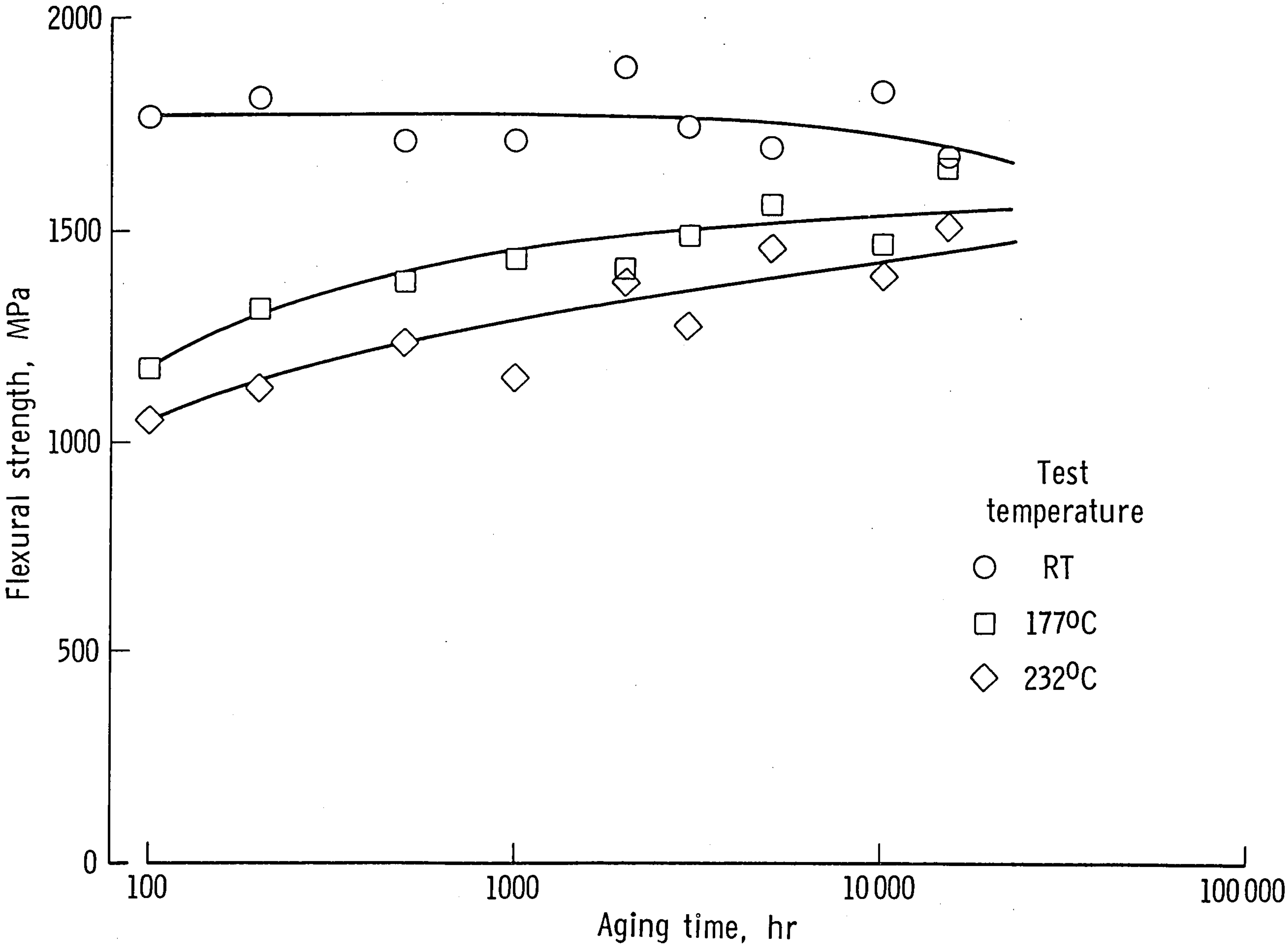

Figure 14.- Flexural strengths of precut specimens of Celion/V378A aged at 232°C.

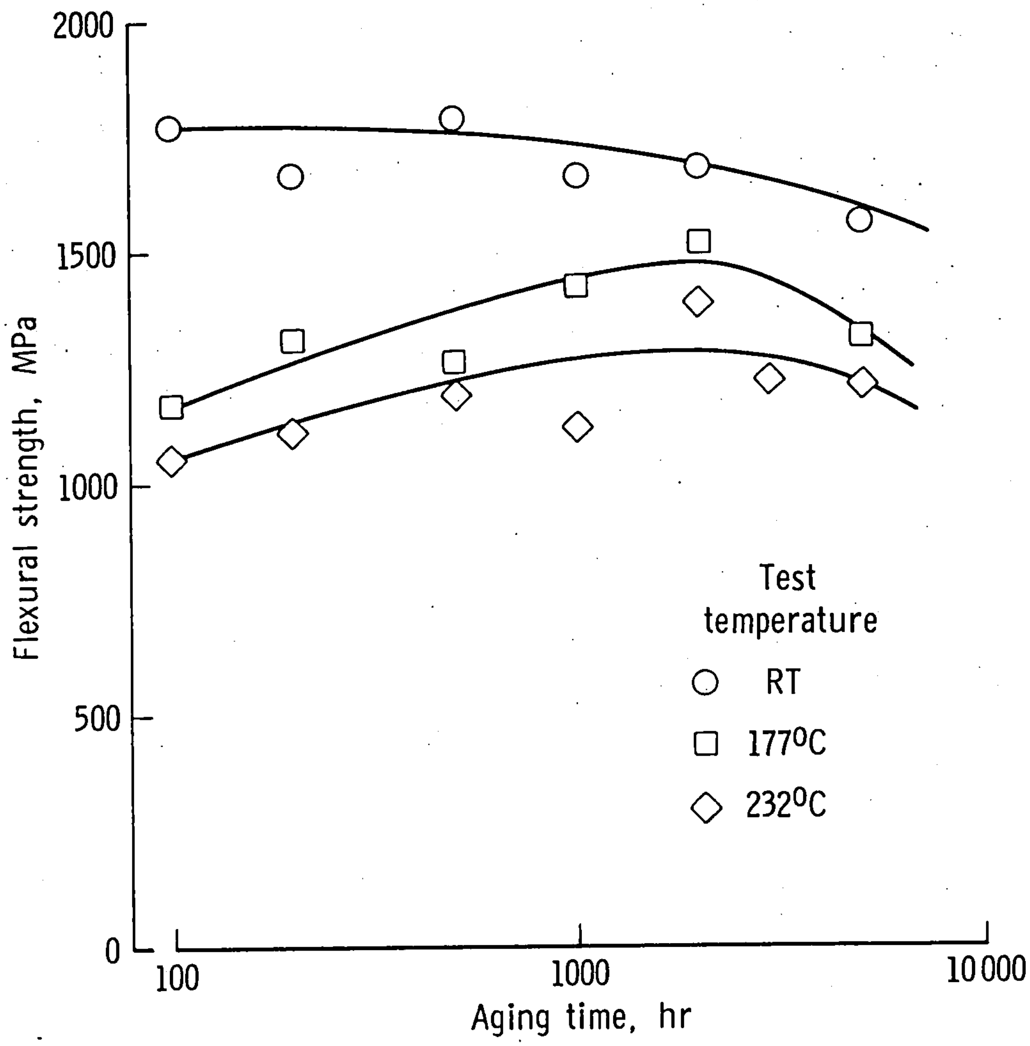

Figure 15.- Flexural strengths of precut specimens of Celion/V378A aged at 260°C.

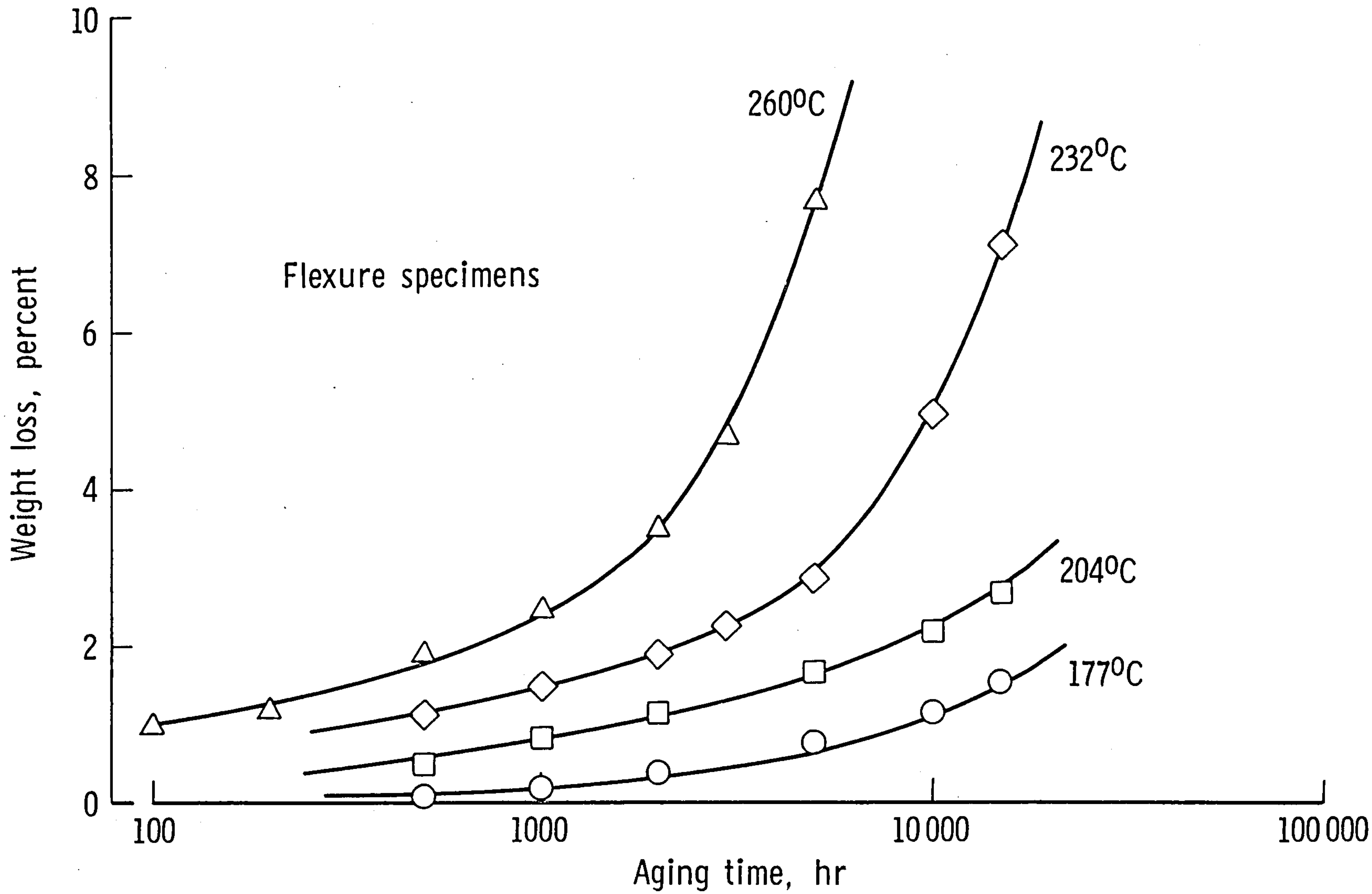

Figure 16.- Weight losses of precut flexural specimens of Celion/V378A after aging.

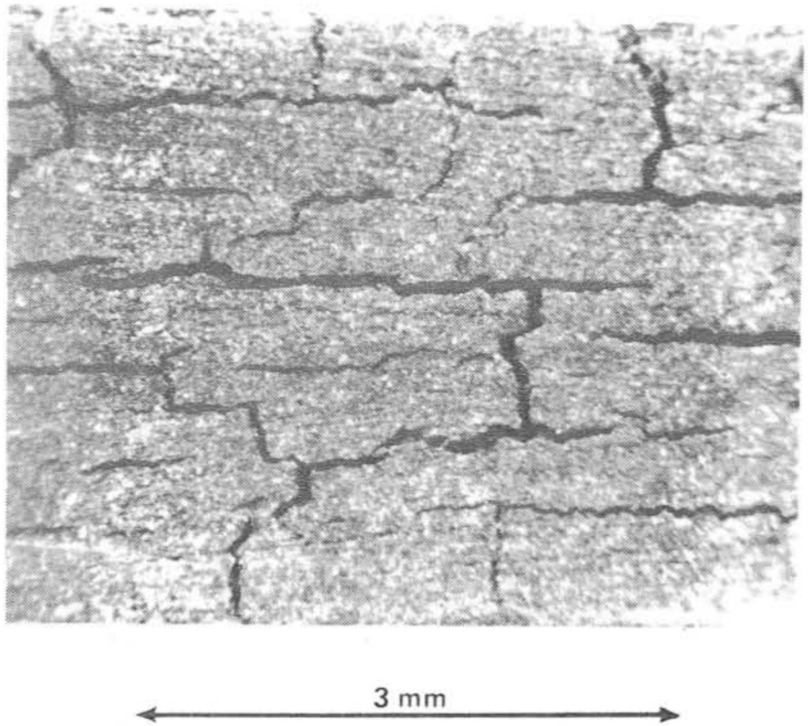

Figure 17.- Photomicrograph of 0° edge of Celion/V378A specimen aged at 232°C for 15000 hours.

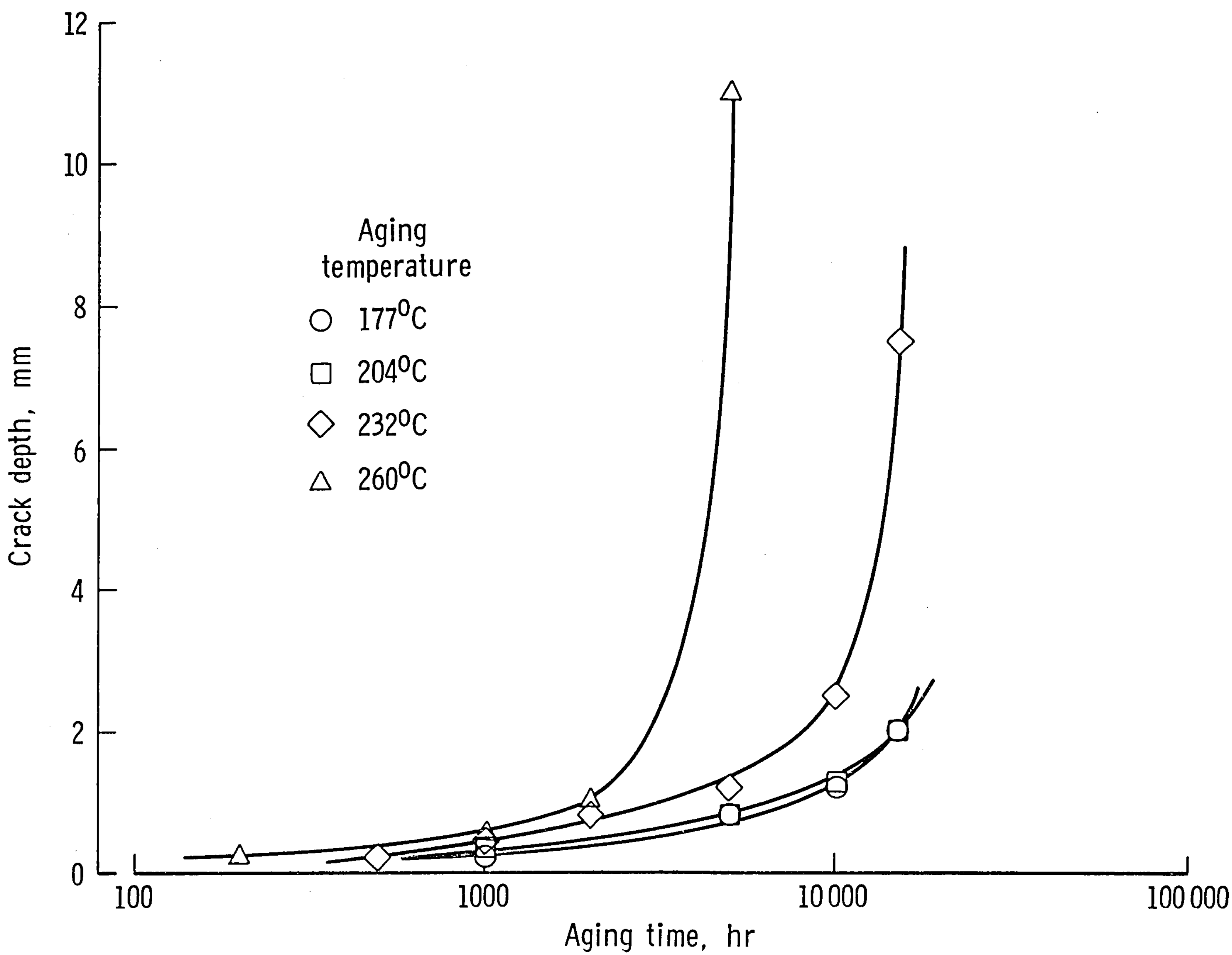

Figure 18.- Edge crack growth in aged Celion/V378A laminates.

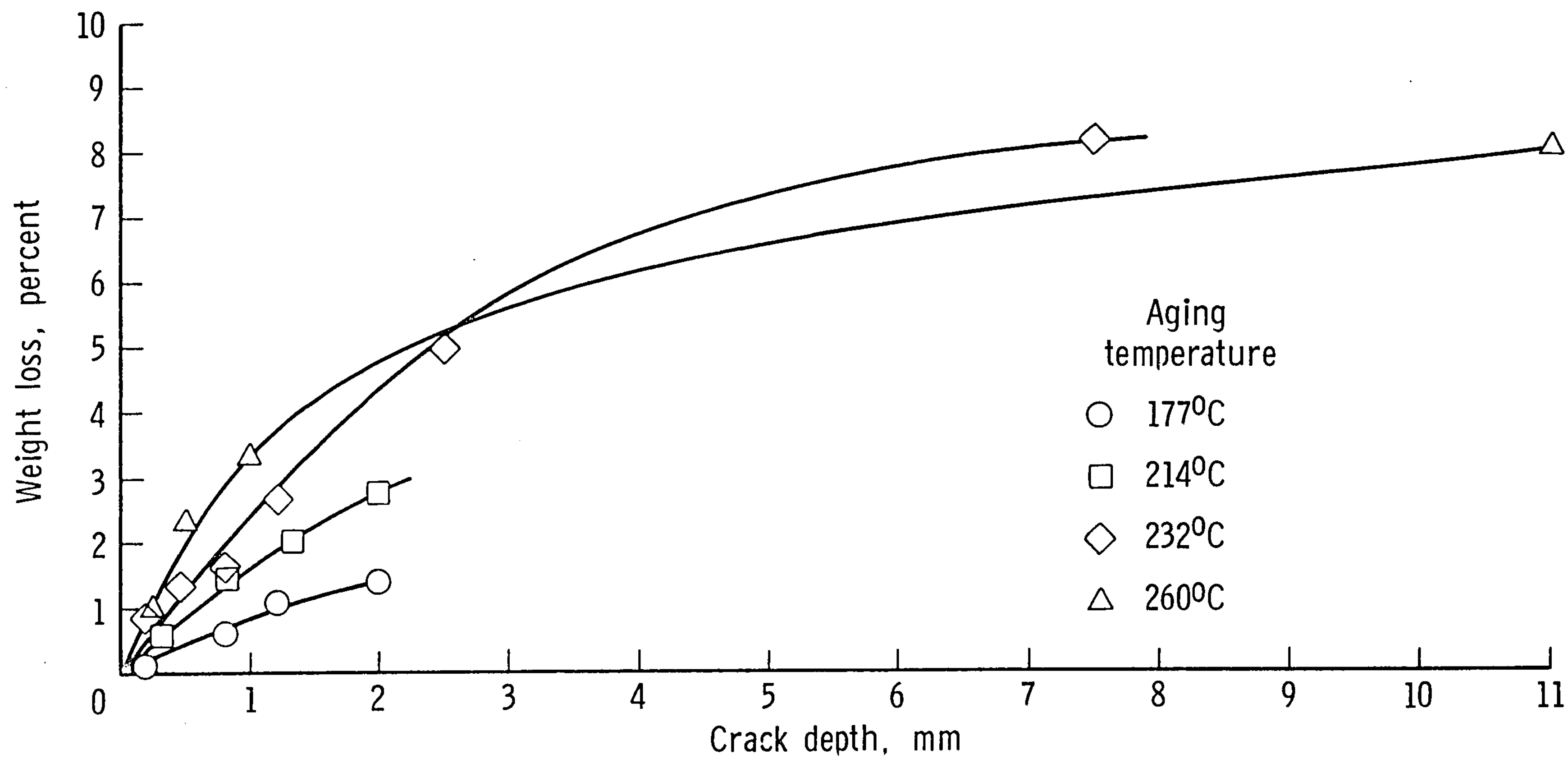

Figure 19.- Correlation of weight-loss and crack-depth in aged Celion/V378A specimens.

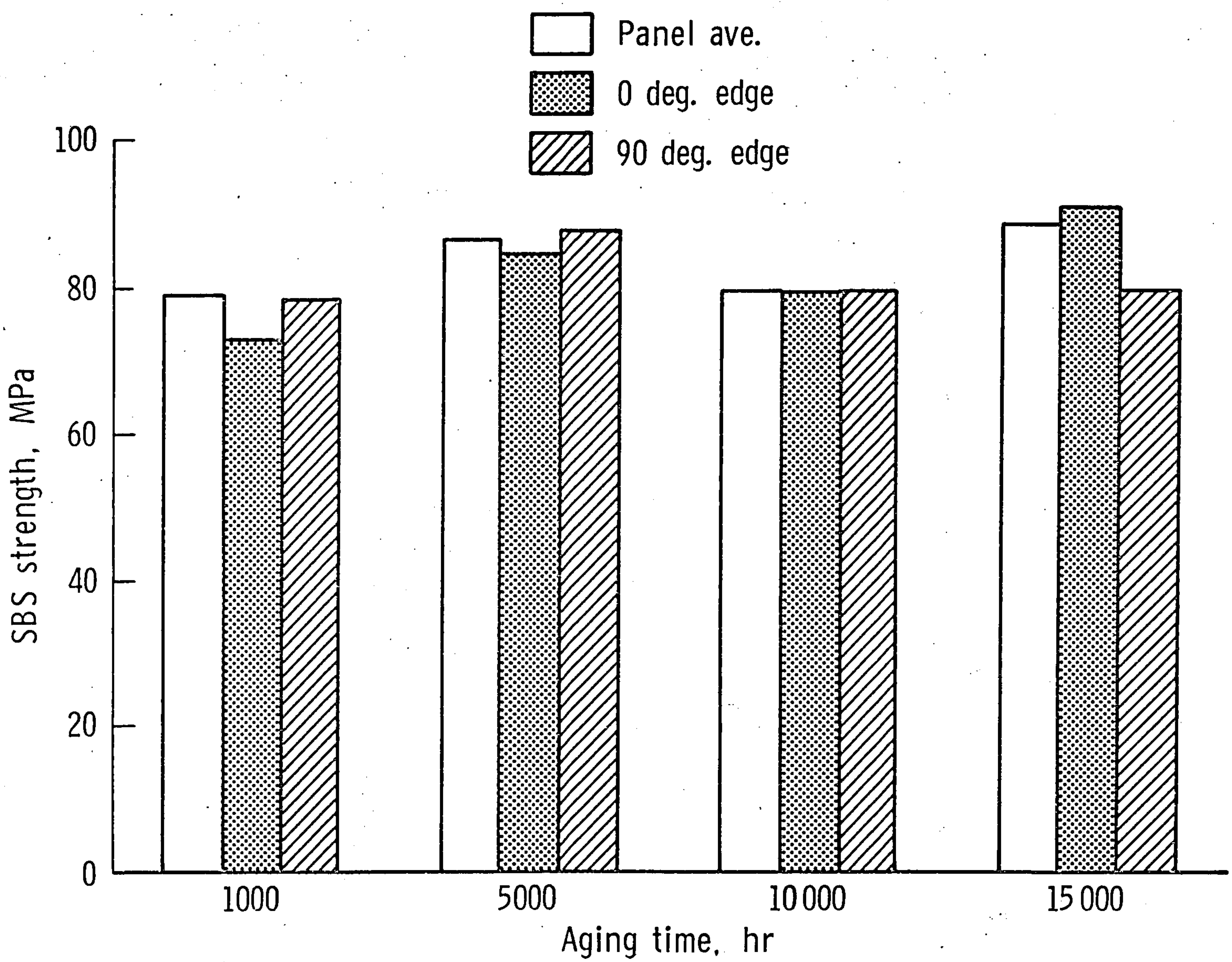

Figure 20.- Comparison of shear strengths of specimens taken from several areas of square Celion/V378A panels aged at 177°C.

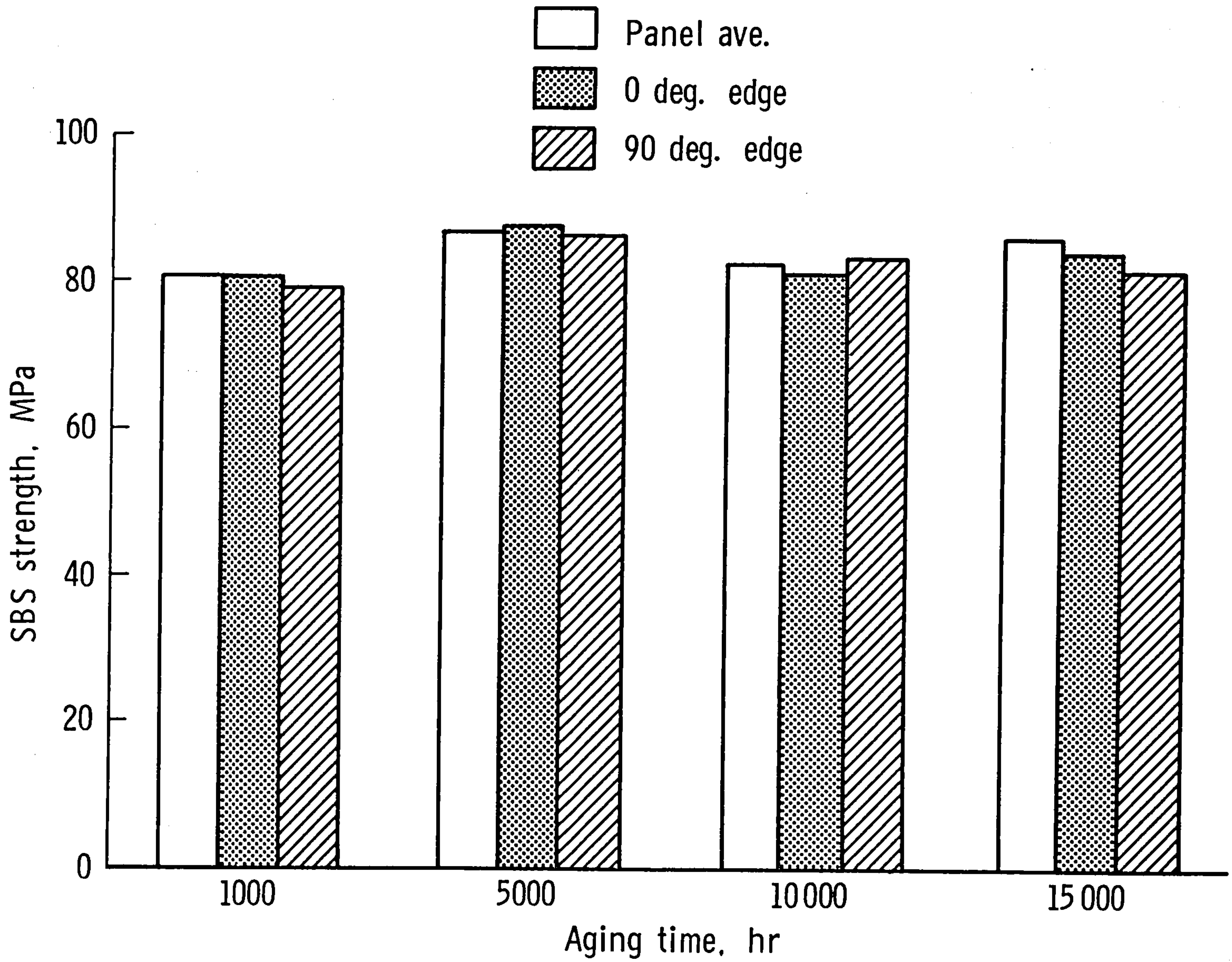

Figure 21.- Comparison of shear strengths of specimens taken from several areas of square Celion/V378A panels aged at 204°C.

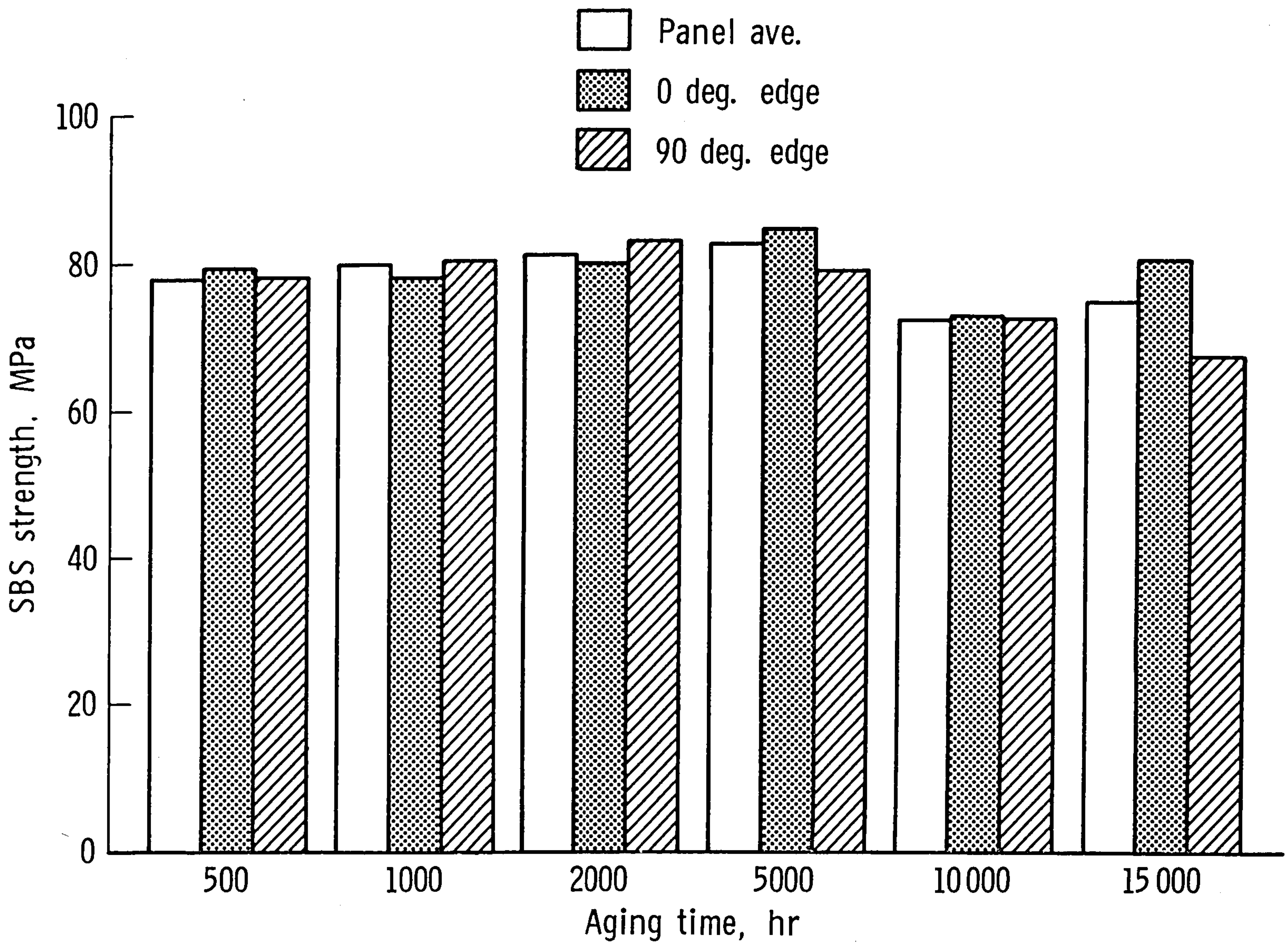

Figure 22.- Comparison of shear strengths of specimens taken from several areas of square Celion/V378A panels aged at 232°C.

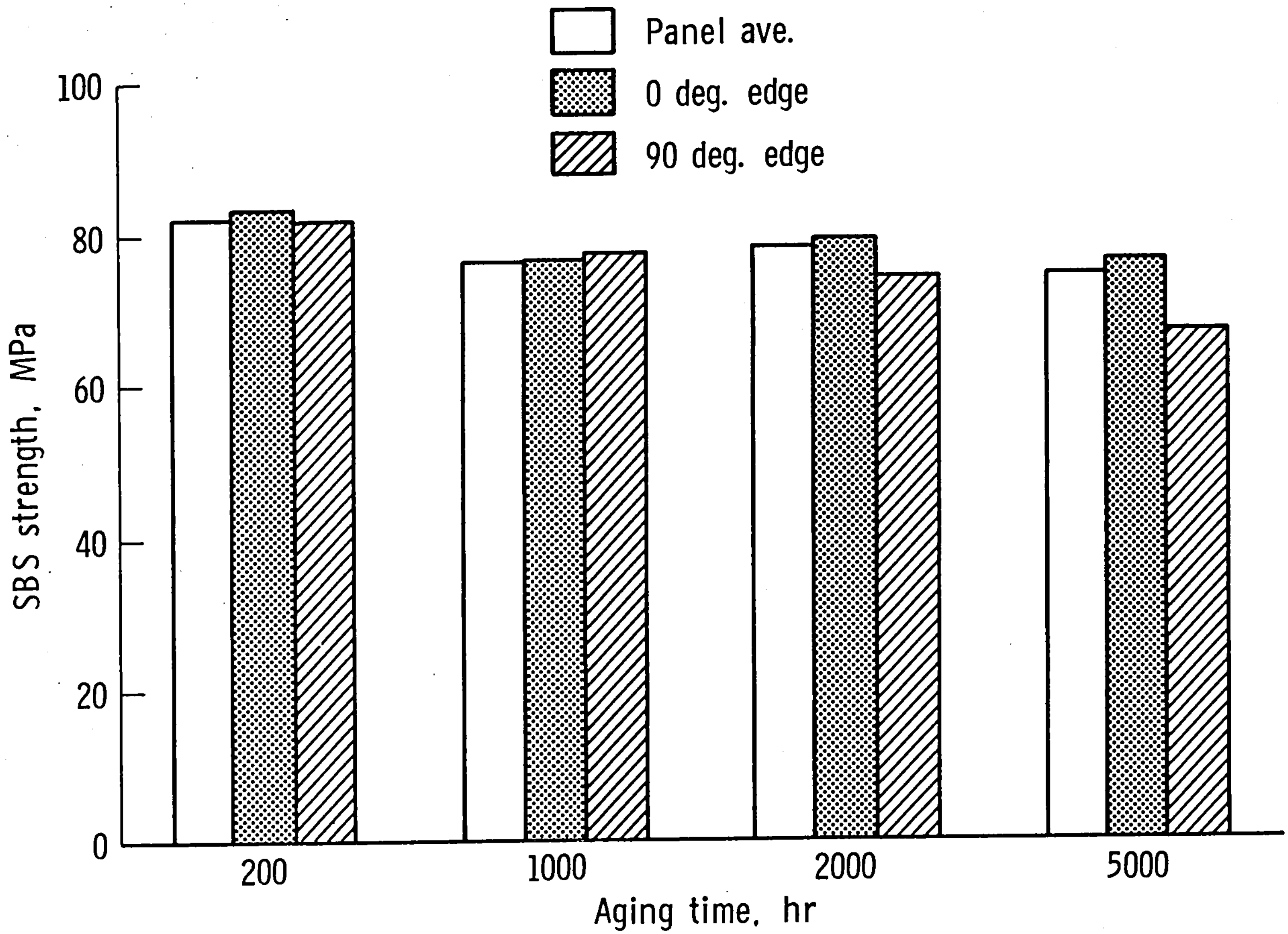

Figure 23.- Comparison of shear strengths of specimens taken from several areas of square Celion/V378A panels aged at 260°C.

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15. Supplementary Notes

16. Abstract

Celion 6000/V378A graphite/bismaleimide composite materials were aged in air at temperatures of 177, 204, 232 and 260°C for various times up to 15,000 hours. Three unidirectional specimen types were aged: short beam shear (SBS), flexure, and 153 mm square panels. Aged specimens of V378A laminates exhibited excellent thermal stability. Extensive cracking was observed during aging on the 0° edges of the unidirectional laminates. These cracks penetrated as deep as 12 mm from the edge. The cracking appeared to have little or no effect on the observed properties of the laminates. The study indicates that the useful life of unrestrained unidirectional graphite/V378A laminates is 10,000 hours or greater at 177°C to 232°C and 2,000 to 2,000 hour at 260°C.

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