MECHANICAL PROPERTIES OF POLYMIDE-RESIN/GLASS-FIBER LAMINATES FOR VARIOUS TIME, TEMPERATURE AND PRESSURE EXPOSURES

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ABSTRACT

An experimental investigation has been conducted to study the behavior of a polyimide-resin/glass-fiber laminate over a range of temperatures from -320° F to 1050° F. In addition, the behavior was studied before and after various exposures to temperatures from 450° F to 800° F and pressures of 760, 35 and 10^{-6} torr. Mechanical properties in flexure and shear were determined by 3-point bending tests on more than 1100 small laminated beam specimens. A general trend of decreasing strength with increasing temperature, exposure time and pressure is observed; however, results indicate that good bonding was developed in the polyimide-resin/glass-fiber system in spite of a 24 percent void content of the laminate. Exposure times of 10,000 hours have been completed. Low pressure exposures support the postulation of a degradation mechanism based on oxidation of the polyimide resin. The effect of exposure on certain properties of laminated beams shows good correlation with the effect of similar exposures on selected properties of honeycomb sandwiches.

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INTRODUCTION

The use of laminated glass fiber and resin materials has increased manyfold for control surfaces and secondary structural applications in subsonic commercial and military aircraft. Nonmetallic honeycomb sandwich construction in many of these applications produced lightweight structures with adequate strength and stiffness and increased sonic fatigue resistance as compared to conventional metallic skin-stringer construction.

Laminated glass fiber and resin panels also are candidates for use in supersonic aircraft. To date, the most significant drawback for this application has been the lack of a suitable resin which will retain adequate mechanical properties to support the glass fibers after long-time exposures in the elevated temperature operating environment of a supersonic transport. A recently developed group of aromatic polymers known as polyimides has shown promise of stability at elevated temperatures and of having the capability of use as a matrix material in glass-fiber laminates. However, little is known about limiting conditions of time, temperature and stress.

The investigation reported herein was initiated to study the effects of various exposure conditions on the mechanical properties of laminated beams and small honeycomb core sandwiches fabricated by vacuum bagging polyimide-resin/glass-fiber material. Exposure conditions included continuous exposures at temperatures from 450° to 600° F and at pressures of 760, 35 and 10^{-6} torr in air. The exposure temperature of 450° F was selected as representing the approximate operating temperature of large surface areas of a Mach No. 2.7 supersonic transport. The exposure pressure of 35 torr is equivalent to that at 60,000-foot cruising altitude. Exposures at 600° F were selected to produce accelerated exposure effects inasmuch as the design requirement for service life of the supersonic transport has been placed at 50,000 hours. After exposure, standard beam bending tests were conducted at room temperature and at the exposure temperatures.

The initial investigation has been extended to study the behavior of the polyimide-resin/glass-fiber material over a larger range of temperatures from -320° to 1000° F in order to better define the material's capability for applications in space and other high performance vehicles. Secondary purposes of this investigation are to determine the mechanism of mechanical property degradation and to correlate exposure effects on material properties of the laminated beams with effects on structural behavior of the honeycomb sandwiches.

SPECIMENS AND TEST PROCEDURES

Specimens

Two types of laminated beam test specimens were used in this investigation, 1.00 × 3.00-inch flexure test beams and 0.25 × 0.62-inch interlaminar shear test beams (fig. 1). All specimens were produced from a polyimide resin and glass fabric by the Defense Products Division of the Brunswick Corporation. The materials used were E-glass fabric

(181 style) with the A-1100 finish pre-impregnated with an E. I. duPont deNemours and Co., Inc., polyimide resin designated PI-2501. Laminated material was prepared in 1-ft^2 sections from 13 plies of the polyimide/glass fabric. The material was alined with the warp direction of all plies parallel. Vacuum bagging procedures were utilized and no significant processing difficulties were noted.

Elevated temperature curing was done with a partial vacuum maintained at pressures between 35 and 250 torr during cure. The oven cure cycle included heating to 350° F, with intermediate holds, over a period of 2.75 hours and holding at 350° F for 1.5 hours. Postcures at 760 torr in air included 2 hours each at 400°, 450°, 500°, and 550° F and 8 hours at 600° F. Laminate thicknesses averaged approximately 1/8 inch. Diamond cutoff wheels were used to cut the beam specimens from the laminated material after postcure. Results of several resin burnout determinations indicated that the laminated material consisted of the following partial volumes: glass, 48-51 percent; polyimide resin, 26-28 percent; and voids, 23-24 percent.

Exposure Conditions

Eight exposure conditions are included in the investigation reported in this study. The first five include continuous exposures for times ranging from 2 hours to 10,000 hours, at temperatures of 450°, 525°, 600°, 700° and 800° F in circulating air laboratory ovens at a pressure of 760 torr with the moisture content of the air maintained at a level corresponding to a dewpoint of 60° F (50 percent relative humidity at 80° F).

Two additional exposure conditions were selected to simulate high-altitude operating conditions of pressure and humidity at temperatures of 450° and 600° F. The specimens were heated in ovens mounted in vacuum chambers and maintained at a pressure of 35 torr by continuous vacuum pumping against a controlled leakage of air with a dewpoint lower than −50° F which corresponds to less than 50 parts per million of water vapor.

The eighth exposure condition was chosen to study a proposed oxidation-degradation mechanism in the polyimide resin. Specimens were exposed at 600° F in an oven mounted in a vacuum chamber which was pumped with no deliberate leakage initially to pressures in the 10^{-6} torr range, and after several hundred hours stabilized at 1 to 2×10^{-7} torr.

Tests

All mechanical tests were performed in universal hydraulic testing machines. Generally three or more specimens were tested for a specific exposure condition and type of test. Flexure tests and interlaminar shear tests were run in general accordance with the procedures suggested by the American Society for Testing and Materials in Standards D-790 and D-2344, references 1 and 2, respectively. Three-point loading was applied to all specimens at a crosshead speed of 0.05 inches/minute (see fig. 1). The longer beams were proportioned to fail by flexure with a 2-inch span and the shorter beams to fail by shear with a 0.5-inch span. A dial gage was used with the longer beam tests to provide center deflection data for flexural modulus determinations.

After exposure, tests were conducted at room temperature and at elevated temperature. The elevated temperature tests were conducted at nominally the same conditions of temperature, pressure and moisture to which the specimens were subjected during exposure. Generally, a one-half hour holding period was used to stabilize temperatures prior to loading.

RESULTS AND DISCUSSION

Results presented in the following sections are based on tests of over 1100 laminated beam specimens. Average room temperature properties of the polyimide-resin/glass-fiber laminates as-fabricated are based on tests of 17 flexural and 20 interlaminar shear specimens randomly selected from the entire group. Strength and modulus values presented in this paper were determined from elementary beam bending and shear analysis. Flexural test results gave an average flexural modulus of 3,220,000 psi and an average flexural strength of 74,700 psi with failure occurring in the glass fibers on the tension side of the beam. Interlaminar shear test strength averaged 6,280 psi with failures occurring in about equal numbers along the beam midplane and along planes at one-fourth to one-third of the beam thickness.

In a study of shear test methods (ref. 3) a more rigorous elasticity solution for the shear stresses in a rectangular beam showed that the theoretical maximum shear stress occurred near the point of loading along a plane at one-fourth the beam thickness, and was about 11 percent higher than the maximum shear stress along the midplane obtained from elementary theory. The 11-percent difference represents the local effect near the point of load application. The experimental portion of reference 3 also showed that some failures occurred at the plane at one-fourth of the beam thickness and some occurred at the midplane.

The strength and modulus values and the failure modes presented in this paper indicate that even with a 23-24 percent void content good bonding existed between the glass fabric and the polyimide resin in the specimens as-fabricated.

Effects of Temperature

The effects of temperature on the modulus and strengths of polyimide-resin/glass-fiber laminated beams are presented in figures 2-4. The data symbols represent averages of four or more tests at temperatures up to 700° F, and single tests above 700° F. The variability in the test data as indicated by the vertical lines and hash-marks above and below the data symbol is considerable for some of the test temperatures, but the trends of the data are clearly indicated by the curves drawn through the data symbols. Subzero tests were conducted with the specimen and test fixtures immersed in either liquid nitrogen or a mixture of liquid acetone and dry ice. All other tests (at temperatures greater than zero) were conducted in air at ambient laboratory pressure and moisture conditions. At temperatures up to and including 700° F specimens were held at the test temperature for 30 minutes prior to loading. Above 700° F the hold time was reduced to only 10 minutes to minimize the effects of more rapid deterioration of the polyimide resin at the higher temperatures.

The variation of flexural modulus with temperature is shown in figure 2. Only a slight decrease in modulus was observed with increasing temperature up to 600° F. From 600° to 800° F the modulus decreased rapidly to about one-fourth of the room temperature value. At temperatures greater than 800° F an unexplained stiffening effect was observed with the modulus at 900° F nearly doubling its minimum observed value. Even at the maximum test temperature of 1050° F, the modulus was higher than at 800° F. Strengthening effects similar to this high temperature stiffening were also observed and are shown in figures 3 and 4.

Flexural strength variations with test temperature are shown in figure 3. A gradual decrease from the room temperature strength was observed with increasing temperatures, with a marked strength decrease at temperatures greater than 600° F. At subzero temperatures the increase in flexural strength from the room temperature value was substantial. Mode of failure was tensile fracture of the glass fibers from room temperature to 600° F. At 600° F a combination of tensile and compressive failures occurred and at 700° F and above all failures were compressive or combined compressive and shear. Also a mixture of tensile and compressive failures occurred at subzero test temperatures. Compressive failures generally occur when the resin matrix has insufficient strength or stiffness to stabilize the glass fibers at stress levels up to their tensile strength at the particular temperature.

Interlaminar shear strength variations with test temperature are shown in figure 4. Again a gradual decrease in strength was observed with increasing temperature, with a rapid strength decrease beginning at 450° F. At subzero temperatures the percentage increase in shear strength from the room temperature value was not as great as was the flexural strength.

Effects of Exposure

Room temperature properties.- The effects of exposure to various elevated temperatures on the residual room temperature modulus and strengths are shown in figures 5-7. The data symbols represent averages generally of three tests in which about the same variability occurred as shown previously for the effects at temperature. All the exposures were conducted at ambient laboratory pressure (designated as 760 torr). The flexural modulus data (fig. 5) indicate little effect from exposure until a critical time is reached after which the residual modulus decreases rapidly. At 600° F this critical time appears to be about 1,000 hours; at 700° F about 100 hours; and at 800° F something less than 10 hours. No significant change in modulus has occurred in the maximum exposure times achieved to date at either 525° or 450° F (6,500 and 10,000 hours).

The flexural strength data (fig. 6) generally show a decreasing trend with increasing exposure time at any particular temperature. However, the strength decrease begins at a shorter exposure time than did the modulus data, and at the previously indicated critical times for modulus, the residual flexural strength is down to less than 20 ksi. Also even the 450° F exposure data showed a significant strength decrease at 10,000 hours.

The residual room temperature interlaminar shear strength data (fig. 7) indicates a similar decreasing trend with increasing exposure time and increasing exposure temperatures. Shear strengths appear to start decreasing even earlier than flexural strengths at each of the exposure temperatures considered from 450° F to 800° F. Thus the smaller specimen and the easier-to-conduct test seems to give the more critical assessment of the material behavior.

Correlation of strength after high and low temperature exposures.— A time-temperature parameter plot of residual room temperature flexural and shear strength is shown in figure 8 after various exposure times and temperatures from 450° to 700° F at ambient laboratory pressure (760 torr). The strengths are plotted as a function of the Larson-Miller parameter (ref. 4), T_R $(C + \log t)$ in which T_R is the exposure temperature in degrees Rankine, C is a constant which is empirically adjusted to make the data for the various exposure temperatures fall on or near to the same curve, and t is the exposure time in hours. The fact that the beam strength data aline quite well by this approach even though a different value of the constant C is used for flexure than for shear permits preliminary estimates to be made of lifetime after exposure to various lower temperatures. If a 50-percent degradation of strength is arbitrarily selected as the criterion for service life for polyimide-resin/glass-fiber components, then a service life of 20,000 to 24,000 hours at 450° F is predicted on the basis of these data. The solid lines are faired through the existing 450° F data for exposure times to 10,000 hours. The dashed curves are extended through the shorter-time, higher-temperature data and appear to be reasonable extensions of the 450° F solid curves.

Elevated temperature properties.- The effects of exposure on the residual elevated temperature flexural strength is shown in figure 9 and a comparison is made with the corresponding room temperature flexural strengths. Only two of the five exposure temperatures, 450° and 600° F, are shown to indicate the trend. The differences that exist between room temperature strength and 600° F strength after short exposures to 600° F air tend to diminish as the exposure times become longer, and after 200 hours at 600° F there is essentially no difference between residual flexural strength at room temperature and 600° F. A similar trend can be seen for the 450° F exposures, although the convergence of the room temperature and 450° F strength curves occurs at a slower rate, which is not unexpected as the strength degradation for 450° F exposures also occurs at a slower rate than for 600° F exposures. It is evident that the effects of exposure are less detrimental to the elevated temperature flexural strength than to the room temperature flexural strength.

Effects of Pressure

The influence of pressure during exposure on the residual room temperature flexural strength is shown in figure 10 for 600° F exposures and figure 11 for 450° F exposures. The 600° F exposures were conducted at three pressure levels; ambient laboratory atmospheric pressure designated 760 torr, 35 torr and a hard vacuum of at least 10^{-6} torr. As shown in figure 10, reducing the 600° F exposure pressure has a beneficial effect by increasing flexural strength. Or for a given flexural strength, reducing the exposure pressure increases the exposure lifetime. Thus for elevated temperature applications, if the temperatures were 600° F, the lifetime would be increased by a factor of ten at 35 torr pressure as compared with 760 torr. An even more dramatic effect is shown for 600° F exposures in a hard vacuum. No degradation has occurred in residual room temperature strength for exposures as long as 4,000 hours.

This increase in lifetime at reduced pressure also is observed for 450° F exposures in figure 11. Because of the generally lower rates of degradation associated with 450° F exposures, the effects of reducing pressure from 760 torr to 35 torr are not as obvious. However, essentially no degradation has occurred at 35 torr in 6,500 hours of 450° F exposure. A sufficient number of specimens are continuing to be exposed to this 450° F – 35 torr environment to obtain data up to 50,000 hours.

Degradation Mechanism

The degradation of mechanical properties that has been discussed in preceding sections has been accompanied by mass losses from the specimens. These mass losses also tend to increase with increasing temperature and exposure time and decrease with decreasing exposure pressure. Physical evidence indicates that the mass losses occur by formation of a volatile product. Thus a degradation mechanism based on an oxidation process is postulated. The 600° F exposures in a hard vacuum provide almost no oxygen to combine with the polyimide-resin specimens, hence no oxidation and no mechanical degradation which is in agreement with the flexural strength data shown in figure 10. Mass losses measured in 4-ply laminates of a parallel investigation (ref. 5) were observed to be similar to the mass losses of the 13-ply laminates which indicates that thickness has no effect and thus the oxidation is more a function of the surface area of the internal voids which are rather uniformly distributed throughout the specimen than it is of the exterior surface area.

Figure 12 provides observations indicating that such an oxidation process is actually occurring. Photomicrographs of cross sections of four laminated beam specimens are shown. The black areas are voids in the specimen. The dotted areas are cross sections of glass fibers running perpendicular to the plane of the figure; the wavy areas are glass fibers running parallel to the plane of the figure. The white areas are polyimide resin. The horizontal dimension is the 13-ply thickness of the specimen. The first specimen (upper left) has had no exposure and is typical of high strength polyimide/glass laminates. In this as-fabricated condition, polyimide-resin/glass-fiber laminates produced by the vacuum bagging process have rather high void contents, approximately 23-24 percent in the specimens tested. After 1,000 hours exposure at 450° F and 760 torr (upper right of figure 12), the void areas have become slightly enlarged. After 1,000 hours exposure at 600° F and 35 torr (lower left), the void areas appear more numerous than in the as-fabricated specimen. After 1,000 hours exposure at 600° F and 760 torr (lower right), the resin has been so depleted by the oxidation of the internal void surfaces that very little matrix is left to support the glass fibers, resulting in very little residual strength.

Comparison of Honeycomb Sandwich Data with Laminated Beam Data

In the present experimental investigation data have been presented for the mechanical properties of polyimide-resin/glass-fiber laminated beams. In a parallel study (ref. 5) honeycomb-core sandwich specimens have been subjected to many of the same exposure conditions as the laminated beams. The sandwich specimens were produced by vacuum bagging and curing two 4-ply face sheets with 0.50-inch thick sections of honeycomb core in a manner similar to the laminated beam specimens. Both face sheets and core were polyimide resin impregnated E-glass fabric. After exposure, sandwich specimens have been strength tested in edge compression, flatwise tension and core shear.

Because data were generated for both structural sandwich specimens and material specimens, comparisons can be made of the effect of exposure on certain properties of the laminated beams with the exposure effect on sandwich properties. Such a comparison is made in figure 13 where exposure effects on the shear strength ratio of honeycomb sandwiches are correlated with exposure effects on the interlaminar shear strength ratio of laminated beams. The shear strength ratio is the ratio of the strength after exposure to the corresponding strength before exposure for either the honeycomb-core sandwich or the laminated interlaminar shear beam. Figure 13 presents the strength comparison after 760 torr exposures at 600° F and 450° F. It appears that the interlaminar shear strength ratio for beams is a reasonable predictor of the shear strength ratio for sandwiches.

A similar comparison was made in reference 5 which indicated that the flexure strength ratio of laminated beams correlates with the flatwise tensile strength ratio of sandwiches. Thus it appears that data from relatively simple tests on inexpensive laminated beams can be used to provide predictions of the exposure effects on more complex and expensive structural specimens.

CONCLUDING REMARKS

More than 1100 laminated beam specimens fabricated from a polyimide resin and E-glass fabric have been subjected to various environmental exposures and then strength tested to study the high temperature capabilities of this material. Room temperature mechanical property tests of as-fabricated beam specimens indicate that good bonding can be developed in the polyimide-resin/glass-fiber system even with a 24 percent void content. For short exposures of 10-30 minutes, tests at exposure temperature indicate usable strength exists over a temperature range from -320° to 1050° F. For long exposures at elevated temperatures, a gradual decrease in strength occurs with increasing exposure time, temperature and pressure. Two thousand hours of exposure at 600° F and 760 torr resulted in complete degradation of mechanical properties. Ten thousand hours at 450° F and 760 torr resulted in a reduced strength of about 70 percent of initial values. Reducing the exposure pressure from 760 to 35 torr increased the lifetime of specimens by a factor of ten. Reducing the exposure pressure still further to a hard vacuum (10^{-6} torr) resulted in no strength degradation for 600° F exposures as long as 4,000 hours. The mechanical property degradation mechanism appears to be an oxidation process involving the polyimide-resin matrix with a volatile oxide formation from the surface areas of the internal voids. Degradation of specific room temperature mechanical properties of honeycomb-core sandwiches due to environmental exposure can be fairly accurately predicted by the degradation of selected properties of laminated beams, when all properties are ratioed to the corresponding as-fabricated value.

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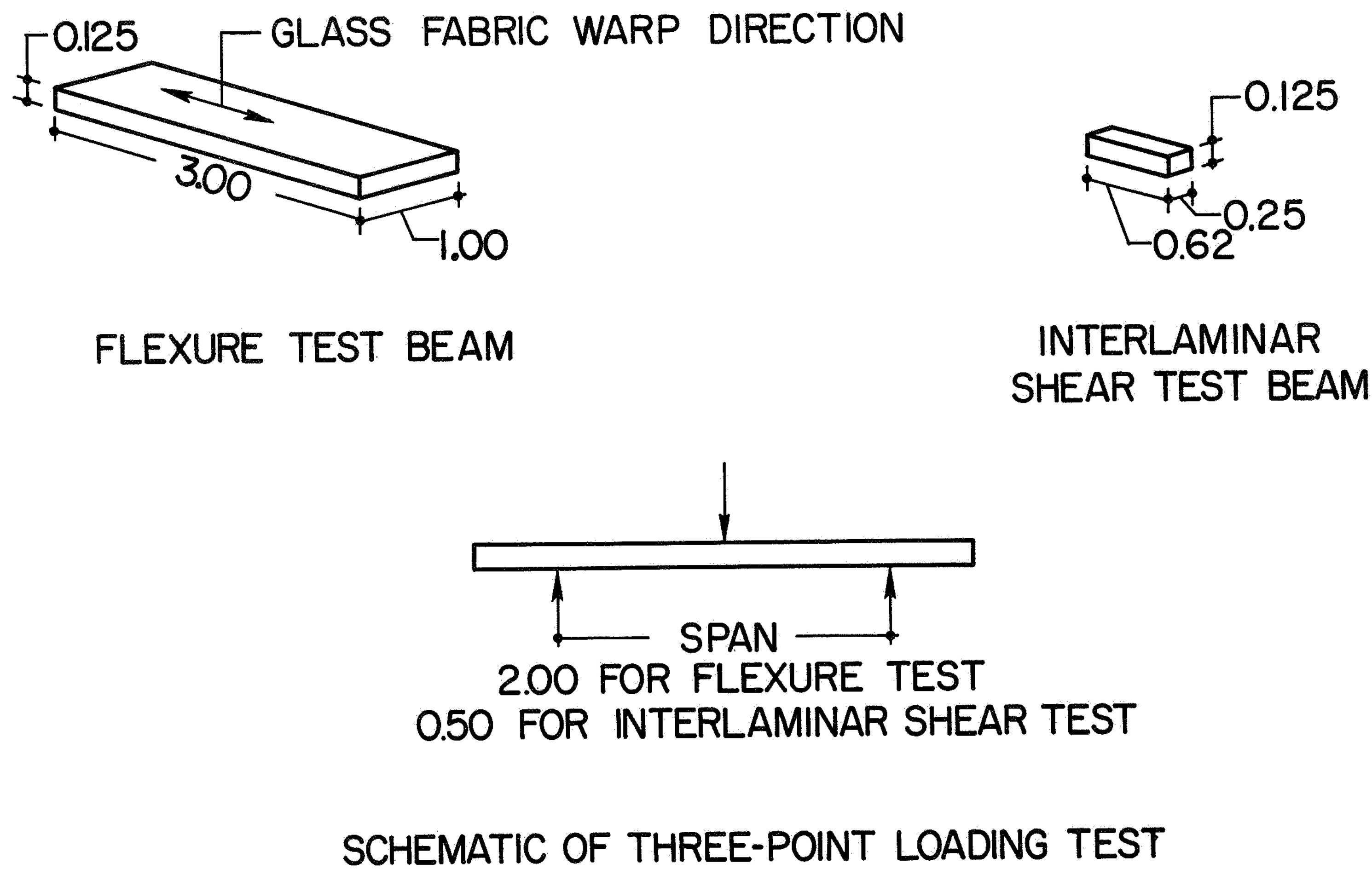

Figure 1.- Laminated beam test specimens and loading.

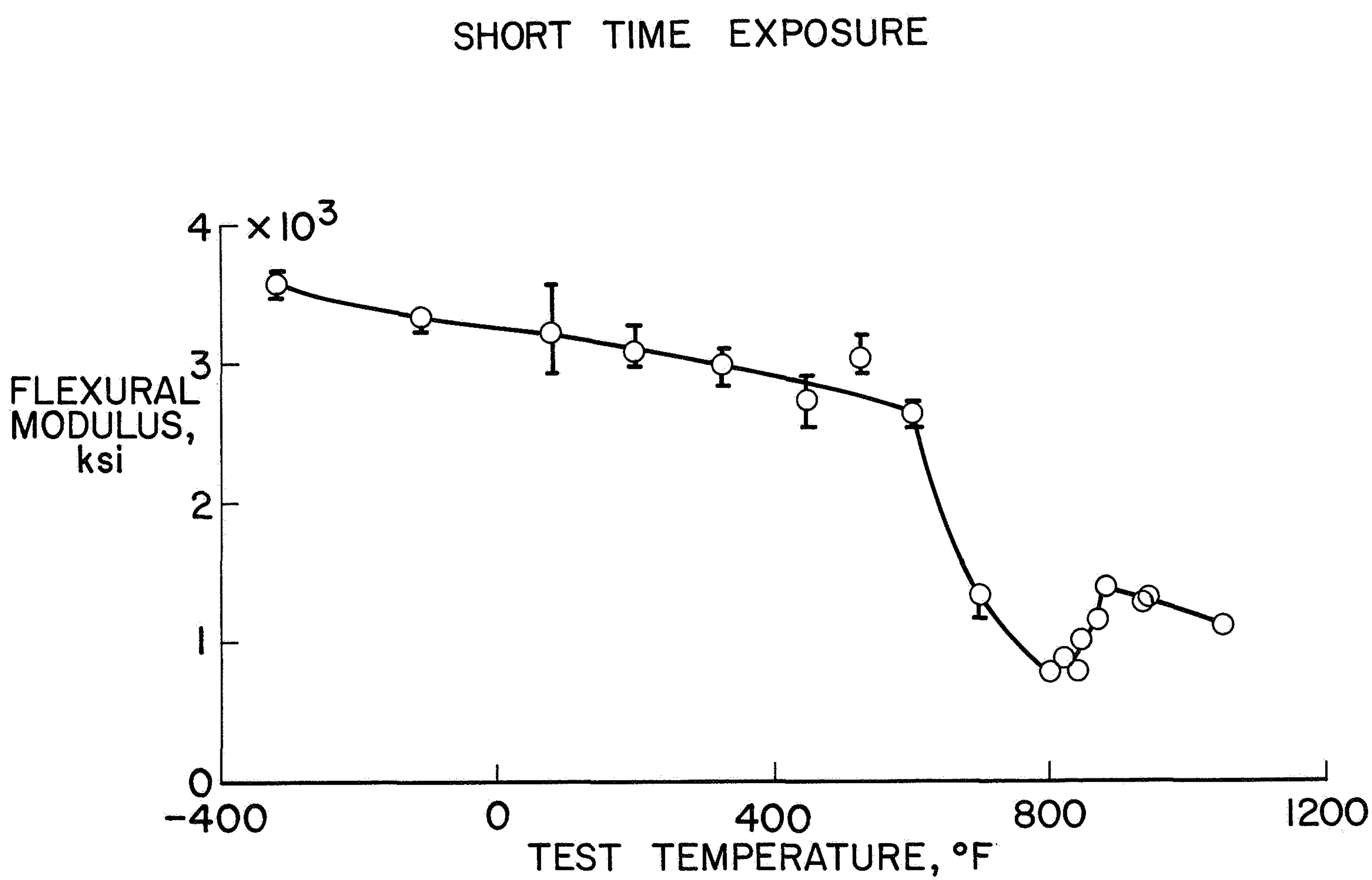

Figure 2.- Flexural modulus variation with temperature.

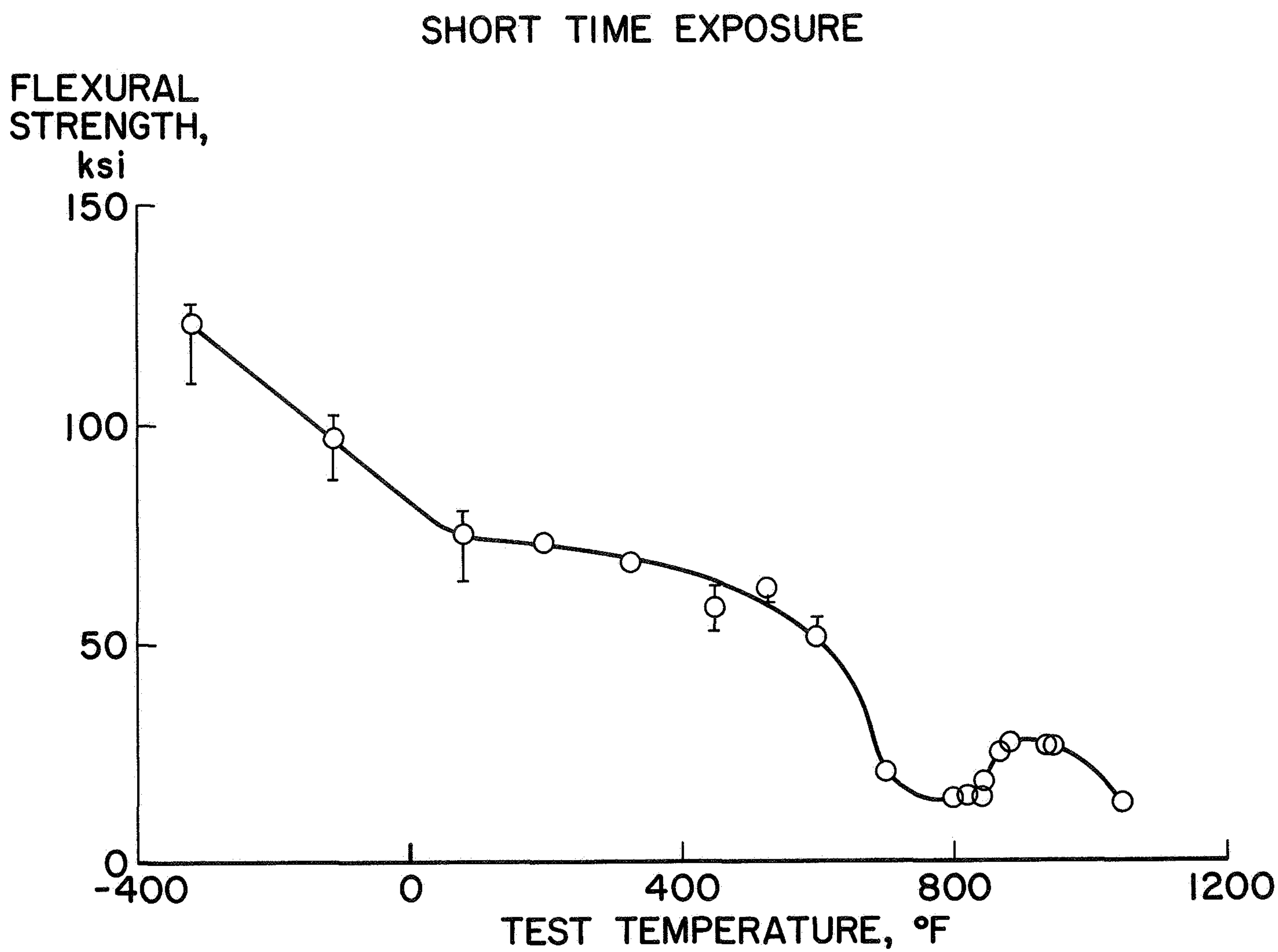

Figure 3.- Flexural strength variation with temperature.

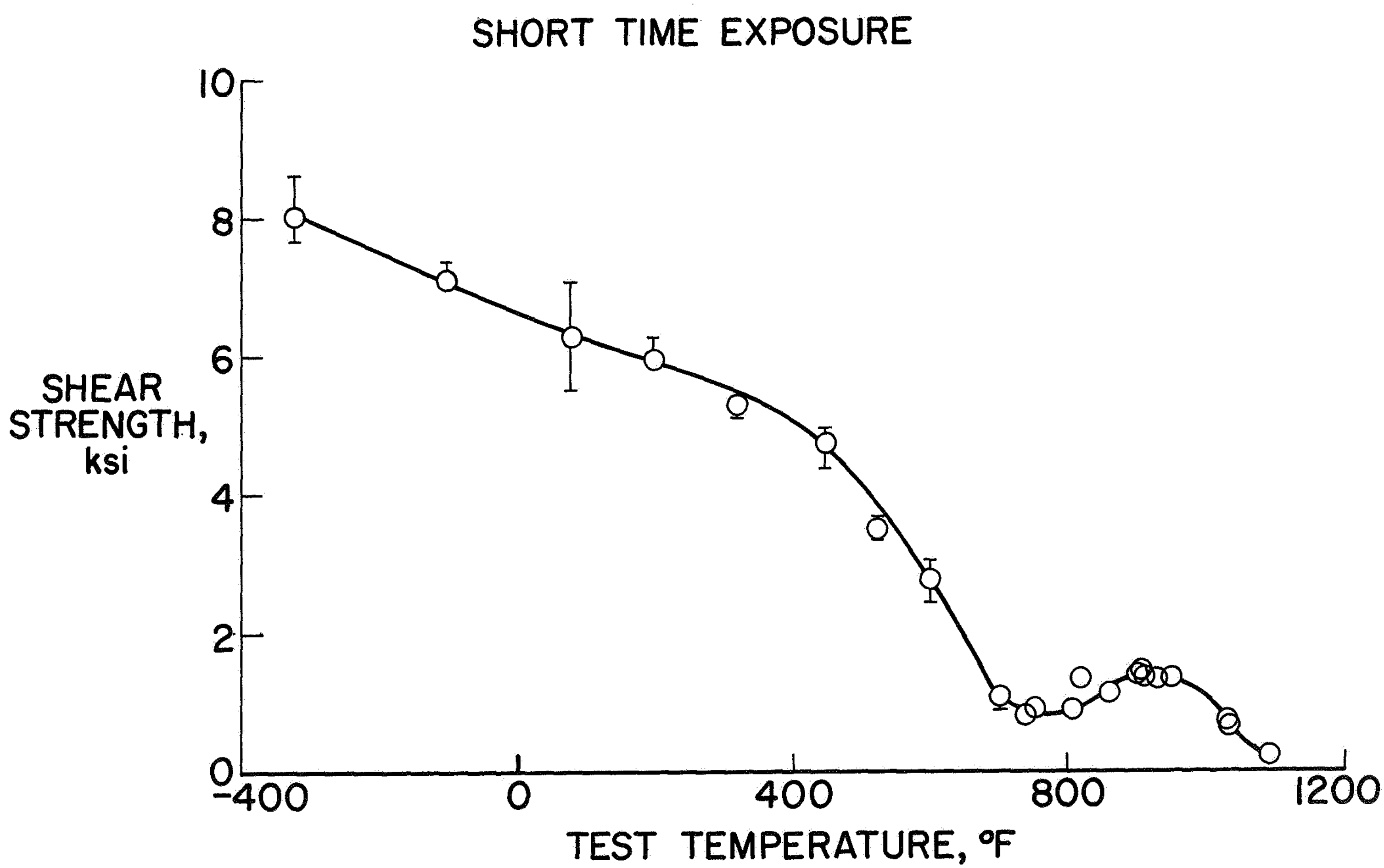

Figure 4.- Interlaminar shear strength variation with temperature.

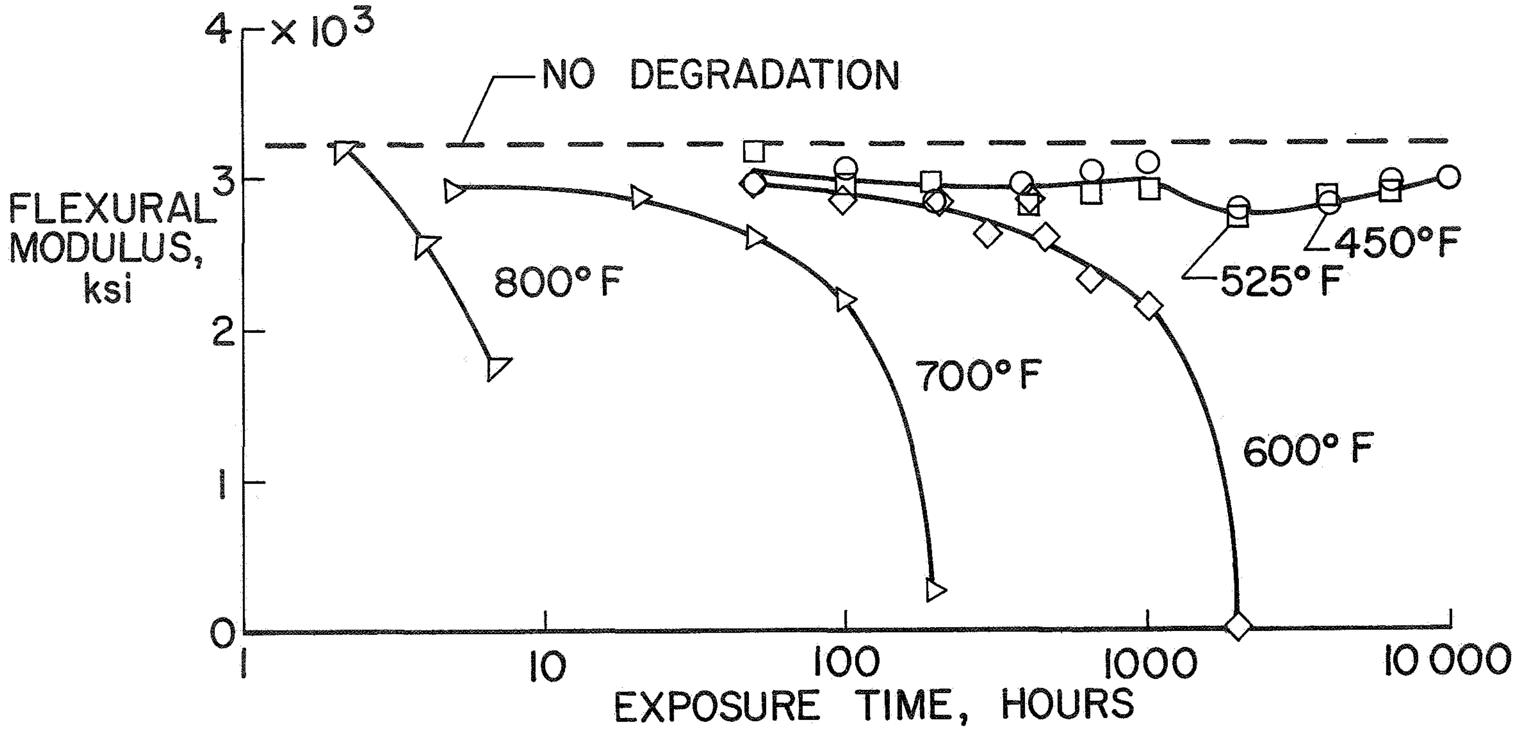

Figure 5.- Variation of room-temperature flexural modulus with exposure time at elevated temperatures.

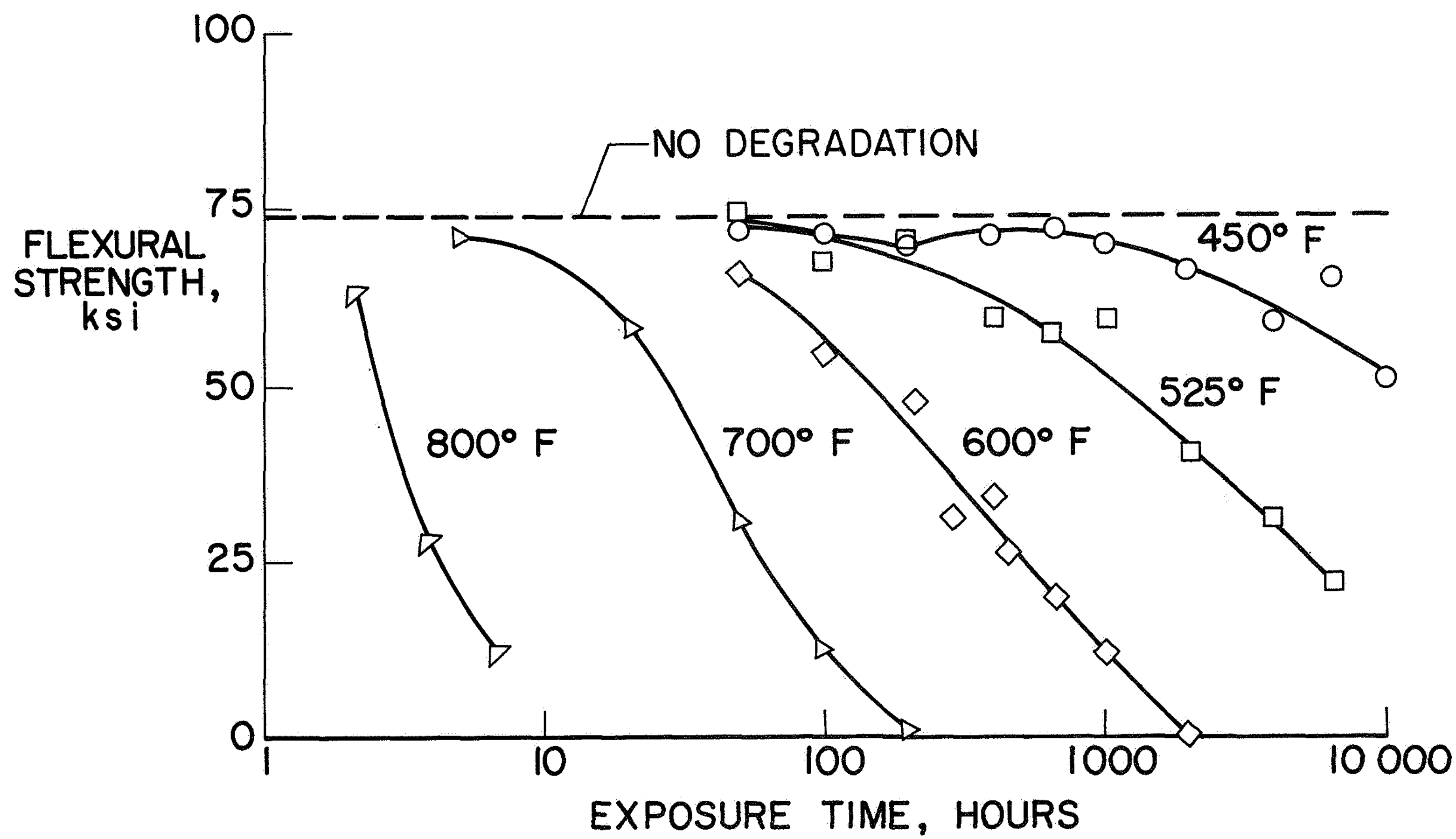

Figure 6.- Variation of room-temperature flexural strength with exposure time at elevated temperatures.

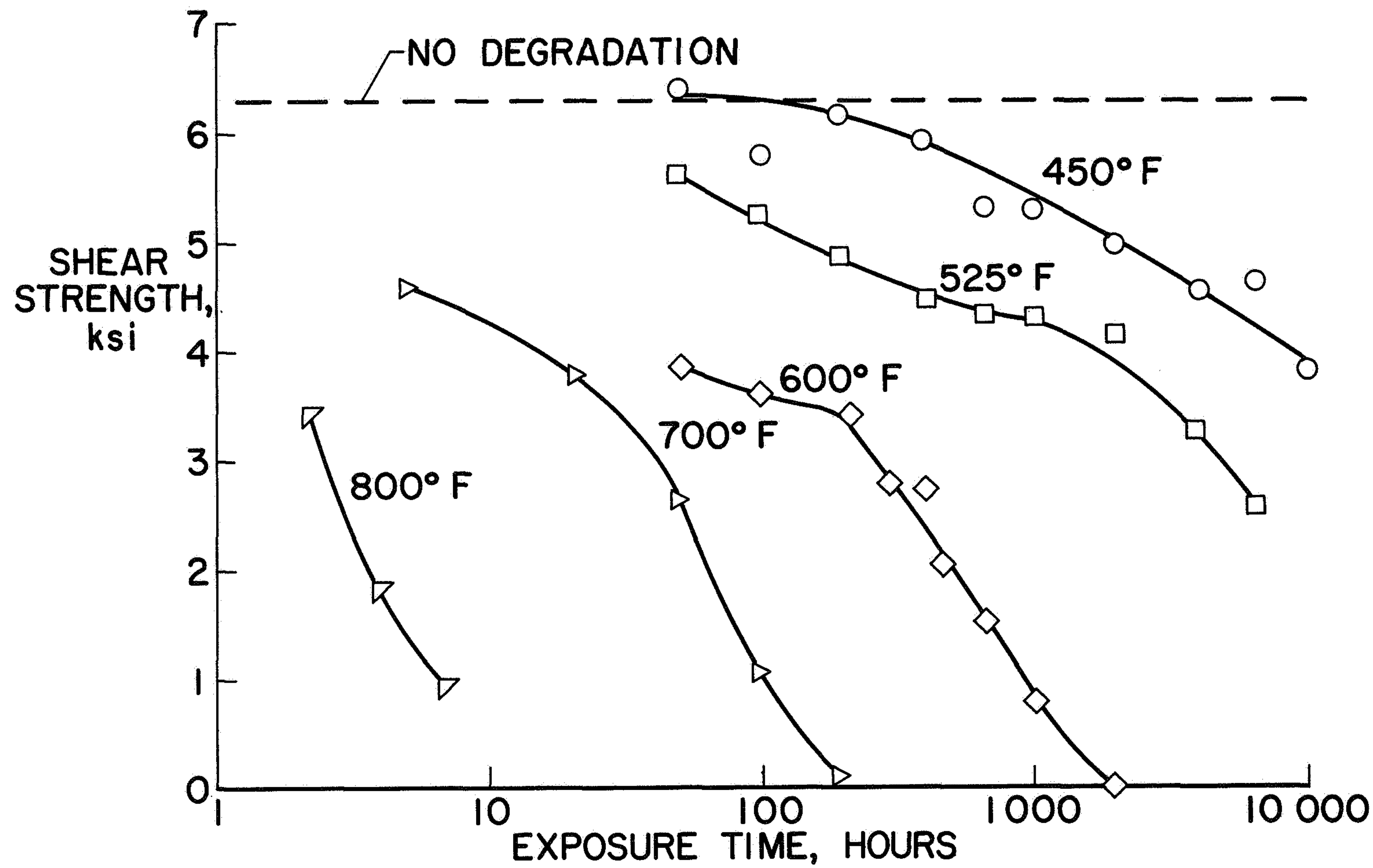

Figure 7.- Variation of room-temperature interlaminar shear strength with exposure time at elevated temperatures.

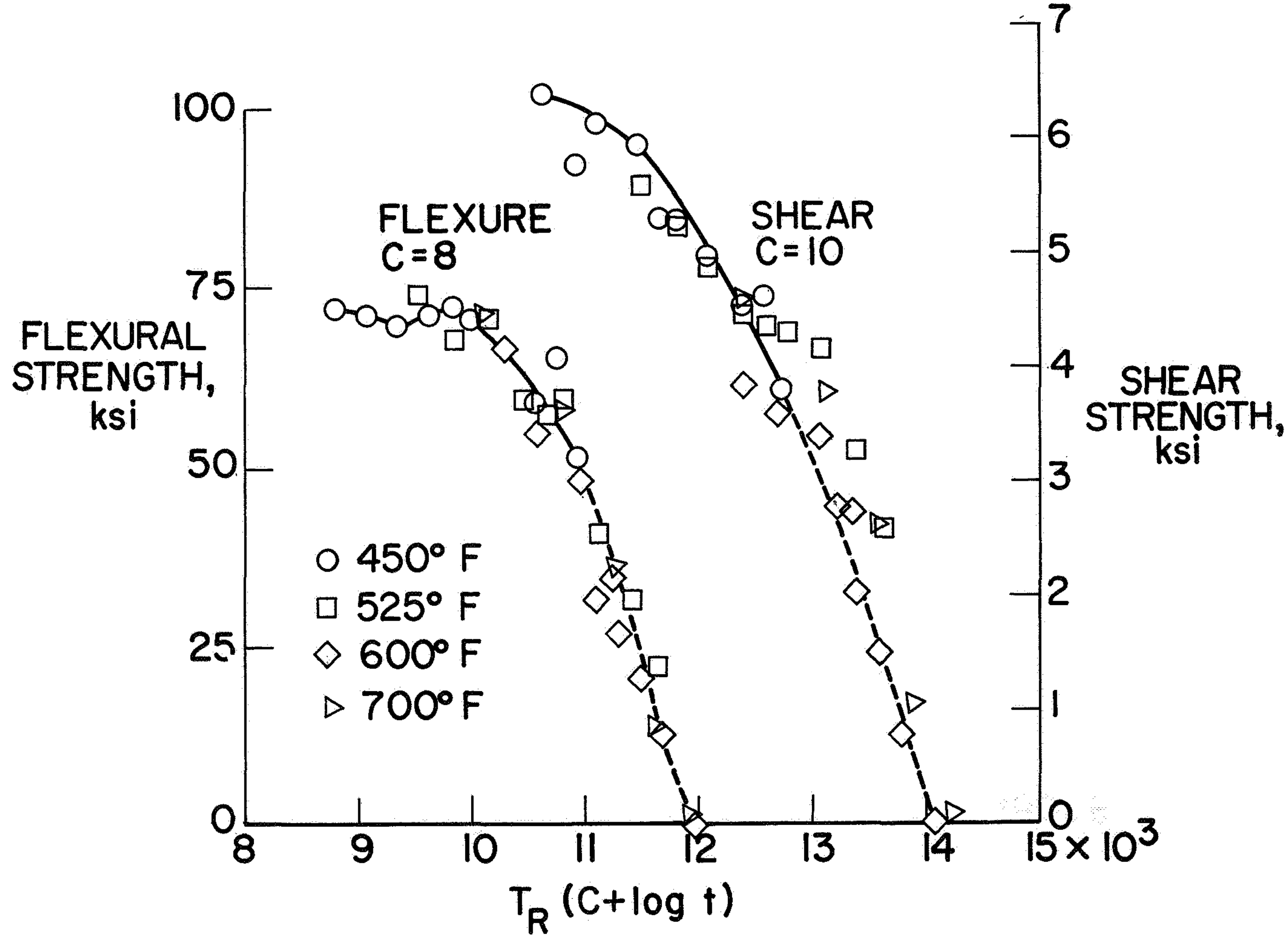

Figure 8.- Correlation of room-temperature strength after various exposure times and temperatures at 760 torrs.

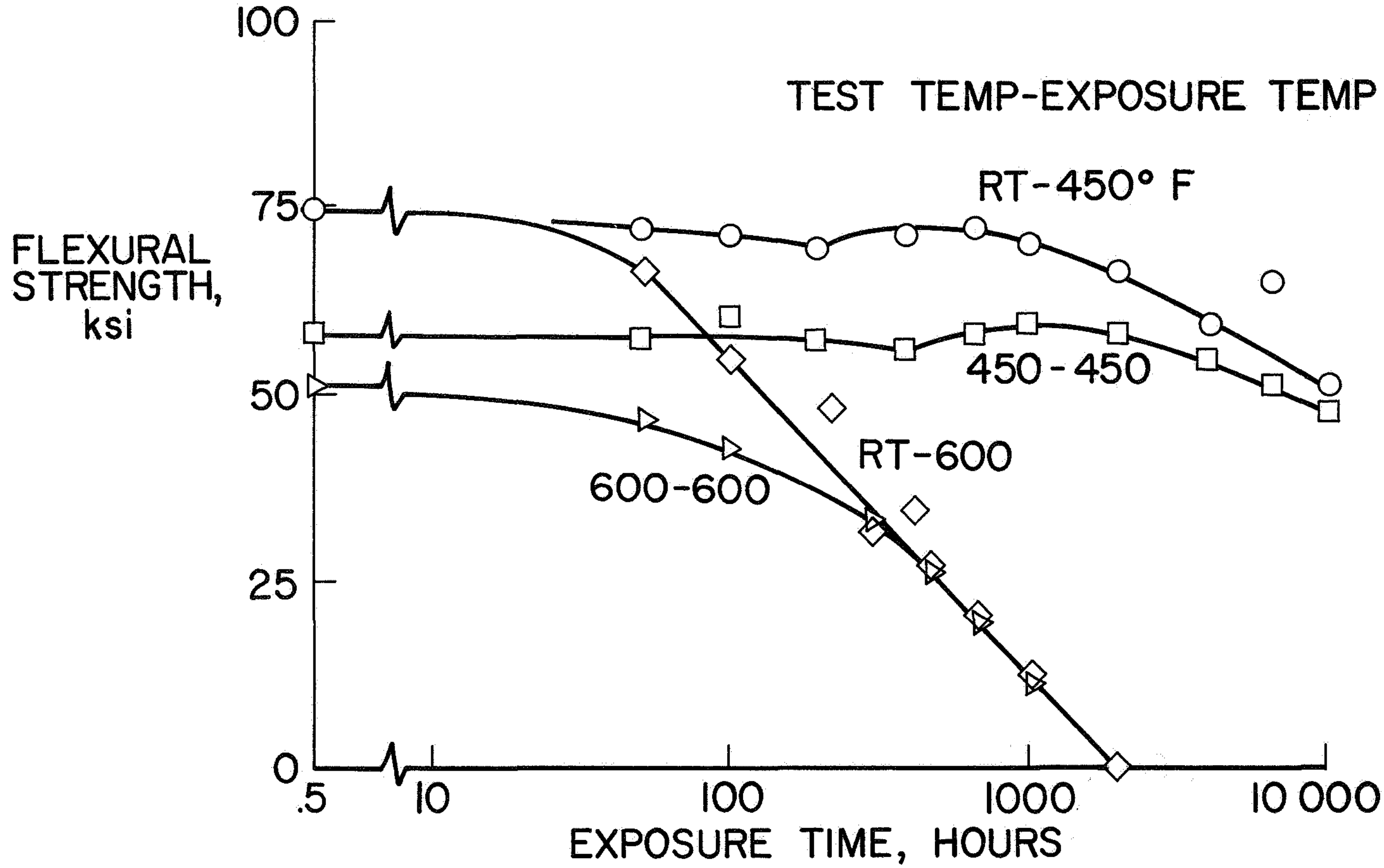

Figure 9.- Comparison of flexural strengths tested at room temperature and at exposure temperature after various exposure times.

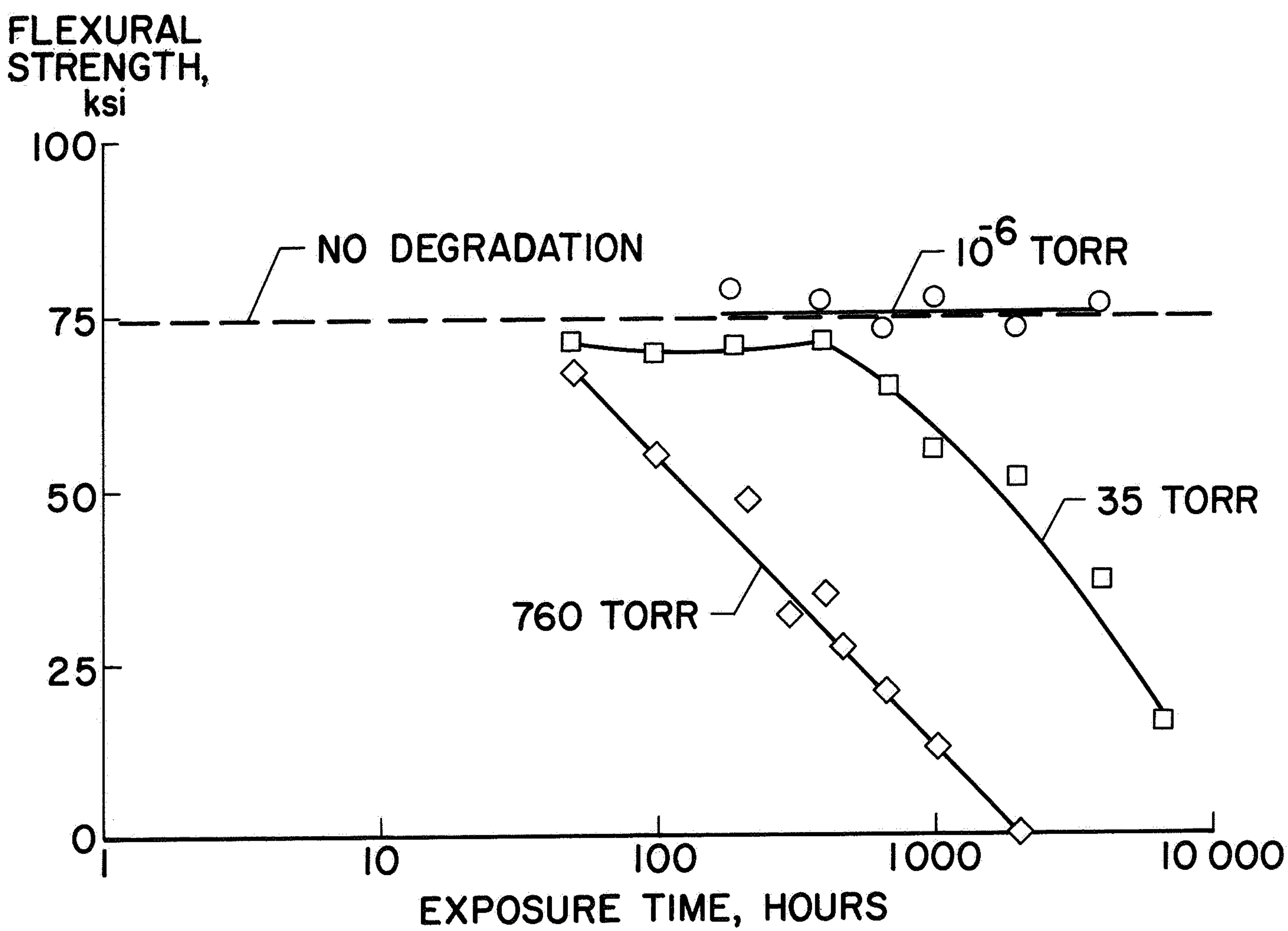

Figure 10.- Influence of pressure during exposure at 600° F on room-temperature flexural strength.

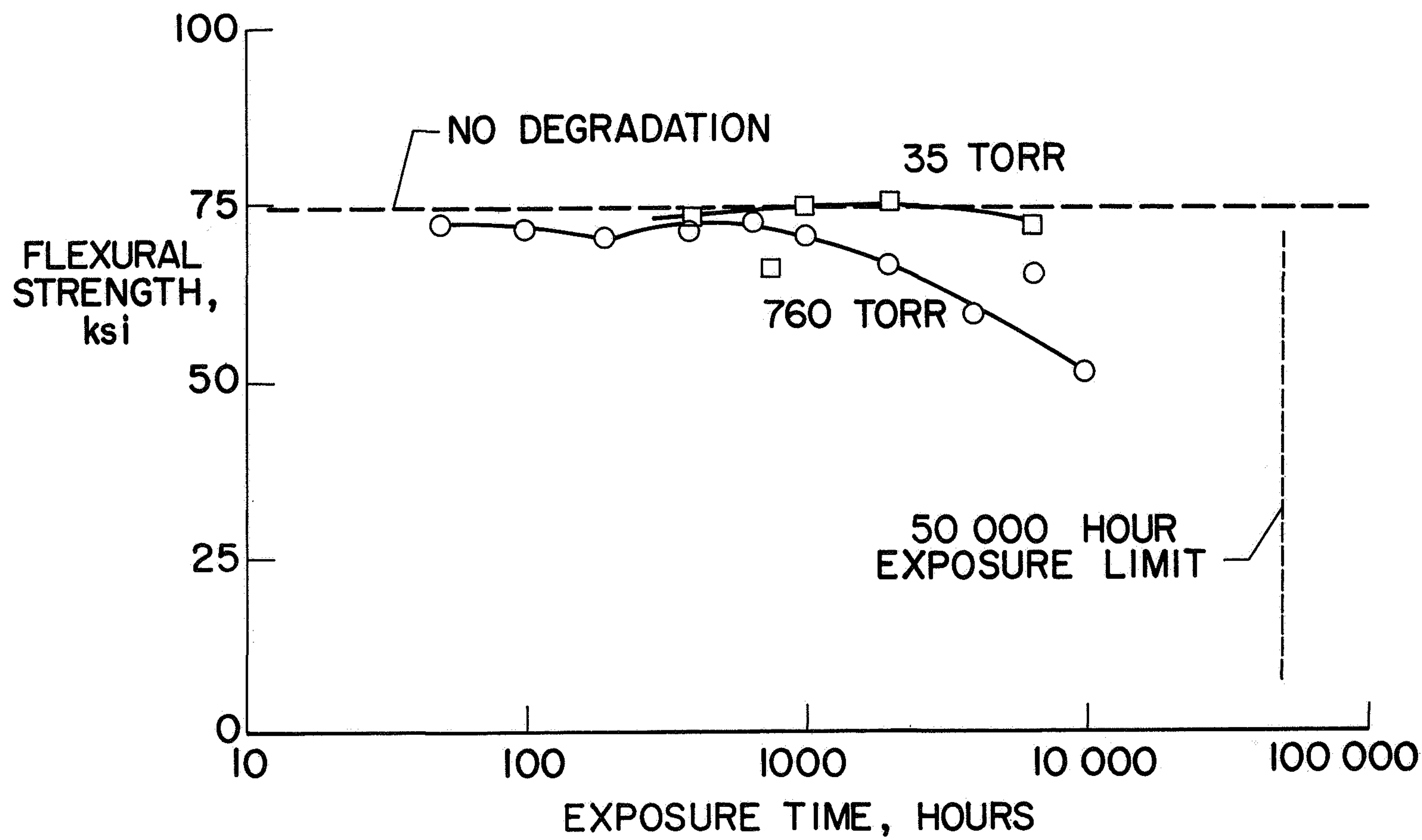

Figure 11.- Influence of pressure during exposure at 450° F on room-temperature flexural strength.

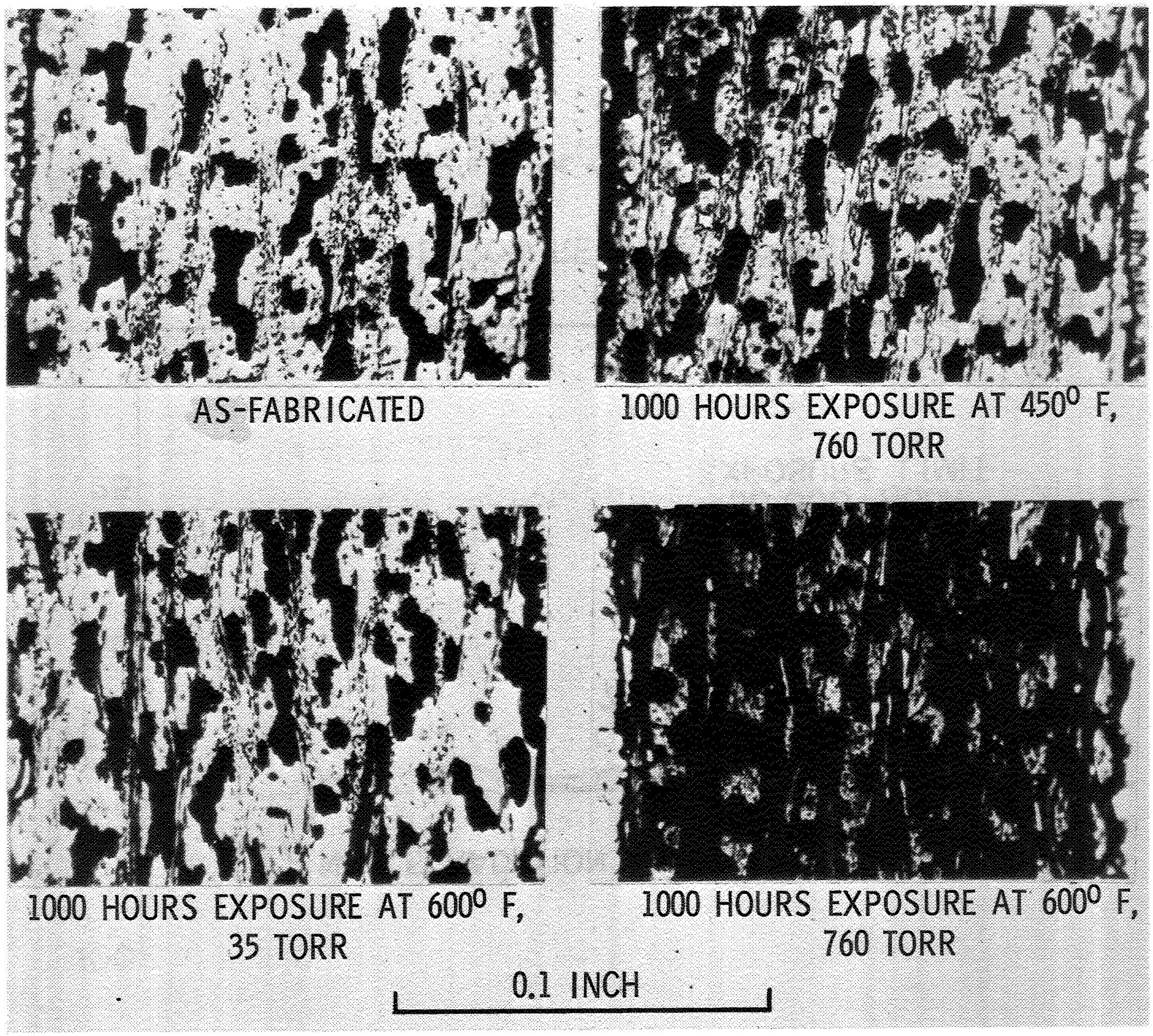

Figure 12.- Photomicrograph of cross sections of polyimide-resin/glass-fiber laminated beams for various exposure conditions.

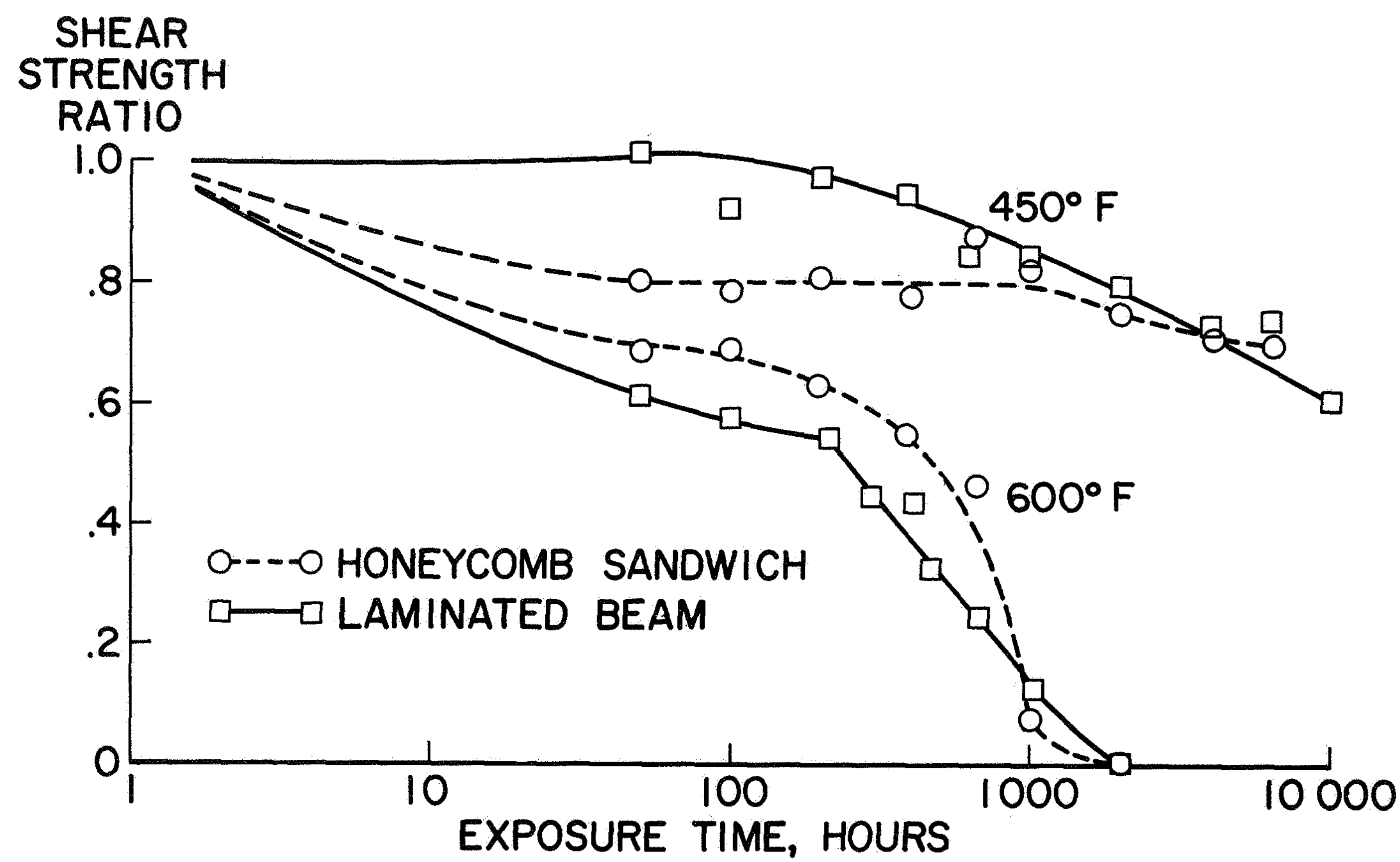

Figure 13.- Comparisons of the effect of 760-torr exposure on shear strength ratios of honeycomb sandwiches and laminated beams.

NASA-Langley, 1968