Effects of 450° and 600°F Exposures on the Mechanical Properties of Polyimide/Glass-Fiber Honeycomb Sandwiches and Laminated Beams

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Sandwich panels constructed from a composite material of glass fiber and polyimide resin are candidates for use in large skin areas on Mach 2.7 supersonic transports. Results of a study to determine the effects of various exposures on the mechanical properties of about 740 specimens are presented. These composite material specimens were fabricated by vacuum bagging from polyimide resin, impregnated glass fabric. Some exposures simulate parameters of the supersonic transport operating environment. Honeycomb-core sandwiches were tested before and after exposure to determine edge compression strength and modulus, shear strength and modulus, and flatwise tensile strength. Laminated beams were tested to determine flexure strength and modulus, and interlaminar shear strength. Results indicate that good bonding can be developed in the polyimide-resin/glass-fiber system. Results of tests after exposure indicate that this material is promising for supersonic transport applications at 450°F, but that severe degradation of mechanical properties will occur after 1000 hr of exposure at 600°F. The effect of exposure on certain properties of laminated beams shows good correlation with the effect of similar exposures on selected properties of sandwiches, and supports the postulation of a degradation mechanism based on internal oxidation and volatile oxide formation.

Nomenclature

C = constant in Larson-Miller parameter
E_c = compressive modulus of sandwich, based on average face sheet thickness, ksi
E_f = flexure modulus of laminated beam, ksi
G = effective shear modulus of sandwiches in double shear, ksi
S_H = interlaminar shear strength of laminated short beam, ksi
S_S = shear strength of sandwiches in double shear, ksi
T_K = temperature, °K
t = time, hr
σ_c = edge compressive strength of sandwiches, based on average face sheet thickness, ksi
σ_f = flexure strength of laminated beams, ksi
σ_t = flatwise tensile strength of sandwiches, ksi

Subscripts

o = average value for as-fabricated specimens

Introduction

During the past decade the use of laminated glass fiber and resin honeycomb-core sandwich construction for control surfaces and secondary structural applications in subsonic commercial and military aircraft and on helicopters has increased manyfold. Nonmetallic honeycomb sandwich construction in these applications produces lightweight structures with adequate strength and stiffness, and the further advantages of transparency to radar signals and increased sonic fatigue resistance as compared to conventional metallic skin-stringer construction.

Thus, laminated glass fiber and resin sandwich panels appear to be strong candidates for large skin areas of Mach 2.7 supersonic transports. To date, the most significant drawback for this application has been the lack of a suitable resin matrix material that will retain adequate mechanical properties to support the glass fibers after long-time exposures in the elevated temperature operating environment of the supersonic transport. A recently developed group of aromatic polymers known as polyimides has shown promise for meeting the requirements of long-time elevated temperature stability and the capability of use as a matrix material in glass-fiber laminates (see, for instance, Refs. 1 and 2).

The primary purposes of the investigation reported herein are to determine the effects of various exposure conditions on the mechanical properties of small honeycomb-core sandwiches and laminated beams of polyimide-resin/glass-fiber material; and to attempt to predict long-time behavior at 450°F from short-time exposures at 600°F. Sandwich properties were determined in edge compression, flatwise tension, and double shear tests. Laminated beam properties were determined in bending tests. Exposure conditions included continuous exposures at both 600°F and 450°F at 760 torr in air with a dew point of 60°F (sea-level pressure environment); and continuous and 2-hr cyclic exposures at 600°F at 35 torr in air with a dew point below −50°F (high-altitude environment). The approximate operating temperature of large surface areas of a Mach 2.7 supersonic transport will be 450°F. Exposures at 600°F were selected to produce accelerated exposure effects. Secondary purposes of this investigation are to correlate exposure effects on structural properties with effects on material properties; and to determine the mechanism of mechanical property degradation.

Specimens and Test Procedures

Specimens

The 740 specimens tested to date in this evaluation consisted of about 320 small honeycomb-core sandwiches, which represented typical structural specimens; and about 420 laminated beams, which provided material properties. Nominal dimensions are shown in Fig. 1. The specimens were produced from a polyimide-resin and glass fabric. The polyimide resin used was a commercially available (E. I. duPont de Nemours and Co. Inc.) polyimide designated PI-2501, formed from the polycondensation reaction between an aromatic tetra-basic acid and an aromatic diamine. E-glass fabric (181 style) with the A-1100 finish was impregnated with the resin and "B-staged."[3] Honeycomb core used in this

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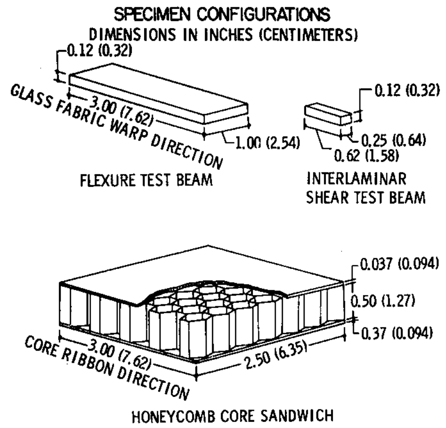

Fig. 1 Configurations and nominal dimensions of test specimens. Dimensions are shown in inches and parenthetically in centimeters.

investigation was obtained from Hexcell Products Inc. This core, designated HRH 324, is made from the PI-2501 impregnated E-glass fabric. The HRH 324 core used had $\frac{3}{16}$-in. cells and a nominal weight of 4.5 lb/ft^3. However, the specific sections of core utilized in the specimens of this study were considerably lighter, approximately 2.8 lb/ft^3. This was traced to variability of resin content within a fabricated block of honeycomb core. The manufacturer reports that the variability has been considerably reduced in current core production.

All specimens were fabricated in accordance with NASA specifications by the Defense Products Division of the Brunswick Corporation under contract NASl-5864. Vacuum bagging procedures were utilized, and no significant processing difficulties were reported. Laminated beam specimen material was prepared in 1-ft^2 sections from 13 plies of the polyimide/glass fabric, which were stacked, with the warp direction of each ply parallel, on a vacuum plate that utilized a perimeter bleeder spring arrangement for removal of volatiles. Silicone release agents were used. Dry glass cloth provided a reservoir for excess resin. A polyvinyl alcohol film was used as the vacuum bag and the vacuum was 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 hr and holding at 350°F for 1.5 hr. Postcures at 760 torr in air included 2 hr each at 400°, 450°, 500°, and 550°F and 8 hr at 600°F. Beam thicknesses averaged approximately $\frac{1}{8}$ in. Results of several resin burnout determinations indicated that the laminated material consisted of the following partial volumes: glass, 48–51%; polyimide resin, 26–28%; and voids, 23–24%.

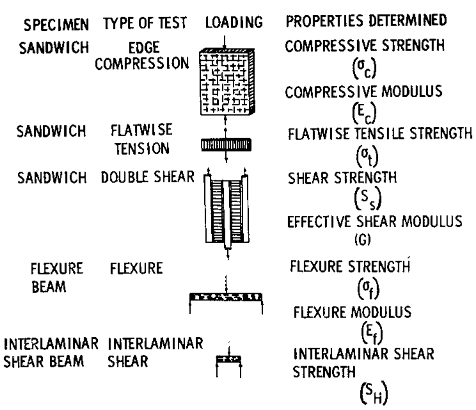

Fig. 2 Types of mechanical property tests, schematics of loading, and properties determined for polyimide-resin/glass-fiber specimens.

Sandwiches were also produced by the vacuum bagging technique. Face sheets were formed of 4 plies each of 2501 polyimide/glass fabric and 0.50-in.-thick sections of honeycomb core. The core was roller-coated on both sides with a polyimide binder solution to provide strong bonds with the face sheets. The face sheets were laminated and bonded to the core in one operation, with the core ribbon direction and the face sheet warp parallel to the long dimension of the sandwiches, using the same cure and postcure procedures previously described for the laminated beams. Large sandwich panels, approximately 16 by 26 in., were produced. Face sheet thicknesses averaged approximately 0.037 in.

Laminated beam specimens and sandwich specimens were cut from the large panels. Diamond cutoff wheels were used. This process produced edges that were flat, square, parallel, and clean enough to eliminate the need for further finishing.

Exposure Conditions

Four exposure conditions have been investigated thus far in this study. The first two include continuous exposures for times ranging from 50 to 2000 hr at 600°F in laboratory ovens at a pressure of 760 torr with the moisture content of the air maintained at a dew point of 60°F, and exposures up to 4000 hr at 450°F at the same pressure and moisture conditions. The 450°F exposures are planned to be continued to 20,000 hr.

The third exposure condition was chosen to simulate ambient supersonic transport operating conditions of pressure and humidity at the higher exposure temperature of 600°F. The specimens were heated in an oven mounted in a vacuum chamber and maintained at a pressure of 35 torr by continuous vacuum pumping against a controlled leakage of air that had been dried in a commercial dessicant unit to a dew point lower than −50°F (which corresponds to less than 50 ppm of water vapor). At the 60,000-ft operating altitude of the supersonic transport, the air is extremely dry, containing only 1 to 10 ppm (by weight) of water vapor.[4] Specimens were exposed continuously for approximately 50, 100, 200, 400, 650, and 1000 hr.

The fourth exposure condition was quite similar to the third, described previously, except that the specimens were

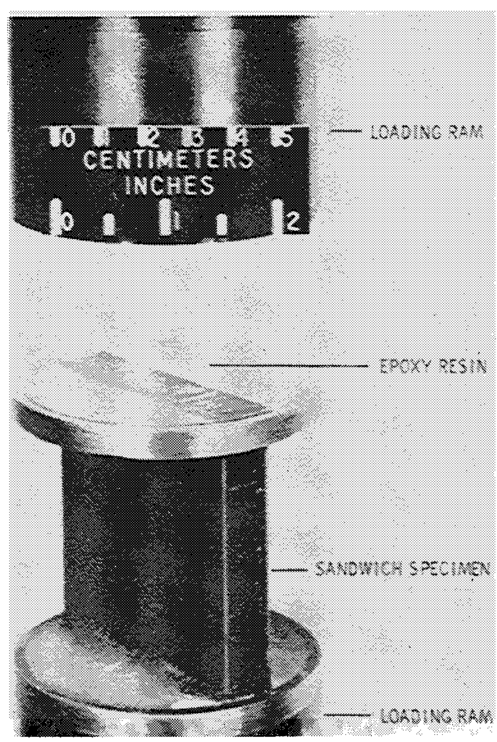

Fig. 3 Edge compression test setup for polyimide-resin/glass-fiber, honeycomb-core sandwich specimens. Specimen ends are encapsulated in epoxy resin.

heated in 2-hr cycles at 600°F in air at 35 torr and a dew point below −50°F. Between each heating cycle, laboratory air was passed over the specimens for at least ½ hr after a 20-min cooldown to room temperature.

Test Procedures

All mechanical tests were performed in universal hydraulic testing machines. At least two and generally three or more specimens were tested for a specific exposure condition and type of test. These tests are illustrated schematically in Fig. 2.

Three types of tests were run on the honeycomb-core sandwich specimens: edge compression, flatwise tension, and double shear. All sandwich tests were conducted at room temperature. For the edge compression tests, the ends of the sandwich were encapsulated in epoxy resin to provide support against end failures. The encapsulated ends were placed directly against the loading ram and cross heads of the testing machine (Fig. 3). A dial gage provided specimen shortening data for compressive modulus determinations. Corrections to the over-all compressive shortening were made on the basis of strain readings obtained from resistance-type wire strain gages bonded to the center of each face on two typical sandwiches. In order to perform flatwise tension tests, which provide a measure of bond strength between sandwich face sheets and core, the sandwich face sheets were bonded to steel blocks with an epoxy film adhesive. The steel blocks were pulled apart in a tensile test (Fig. 4). A double shear test, using two sandwiches for each data point, provided the symmetry of loading which is lost in single lap, shear tests. The sandwich faces were bonded to steel grips with the epoxy film adhesive; and the assembly was pulled apart, as shown in Fig. 5. Over-all shear deflections of both sandwiches for shear modulus determinations were measured with differential transformers mounted on the steel grips.

Flexure tests and interlaminar shear tests, used to provide material properties, were run in general accordance with the procedures suggested by the American Society for Testing and Materials in Standards D-790 and D-2344, Ref. 5 and 6, respectively. Test fixtures are shown in Figs. 6 and 7. Three-point loading was applied to all specimens; the longer beams were proportioned to fail by flexure and the shorter beams by shear. A dial gage provided center deflection data for flexural modulus determinations. These material property tests were run both at room temperature and elevated temperatures. The elevated temperature tests were conducted at nominally the same conditions of temperature, pressure, and moisture to which the specimens were subjected during exposure.

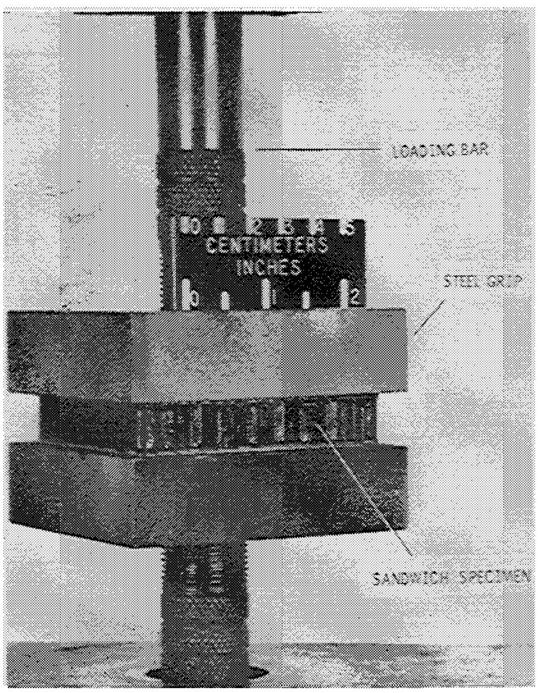

Fig. 4 Flatwise tension test setup for polyimide-resin/glass-fiber, honeycomb-core sandwich specimens.

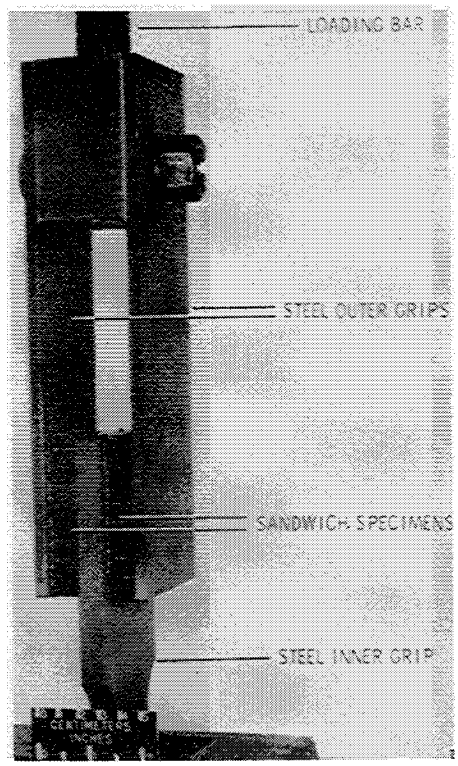

Fig. 5 Double shear test setup for polyimide-resin/glass-fiber, honeycomb-core sandwich specimens.

Results and Discussion

The reader can readily see that the test data from this evaluation become quite voluminous. Because of space limitations, only a few properties will be discussed and the trends of others will be briefly indicated in this report.

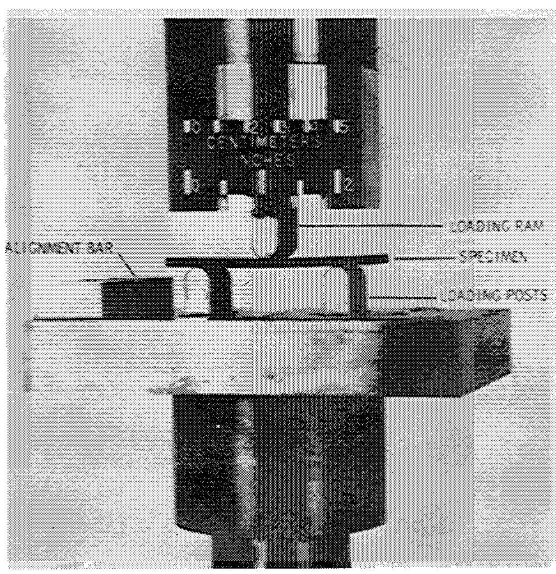

Fig. 6 Flexure test setup for polyimide-resin/glass-fiber laminated beam specimens.

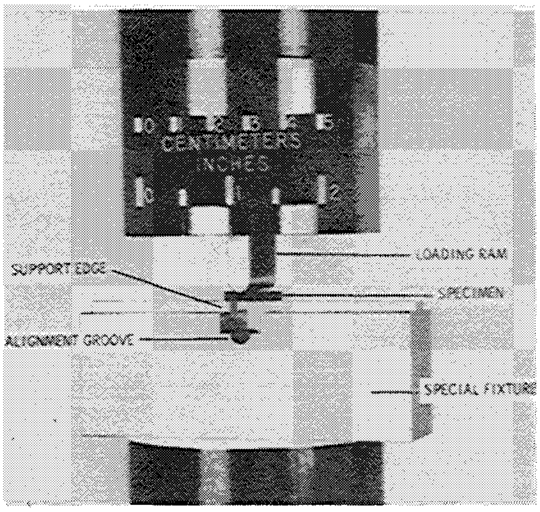

Fig. 7 Short beam interlaminar shear test setup for polyimide-resin/glass-fiber laminated beam specimens.

Table 1 Average room-temperature properties and failure modes of as-fabricated polyimide-resin/glass-fiber specimens

Property	Value, psi	Failure mode
	Sandwich properties	
Edge compression strength[a]	50×10^3	General shear in face sheets
Compressive modulus[a]	4×10^6	
Flatwise tensile strength[b]	660	Partially face sheet to core bond, partially core material
Shear strength[b]	270	
Effective shear modulus[c]	12×10^3	Core material
	Beam properties	
Flexure strength[d]	74×10^3	Tensile outer surface
Flexure modulus[d]	3.2×10^6	
Interlaminar shear strength[d]	6.2×10^3	Neutral axis shear

[a] Average of 7 tests.
[b] Average of 5 tests.
[c] Average of 4 tests.
[d] Average of 9 tests.

As-Fabricated Specimens

The first significant result of this program was revealed by tests of as-fabricated specimens. Average room-temperature properties and failure modes of sandwiches are shown in Table 1. These room-temperature properties are comparable to those for good quality epoxy-resin/glass-fiber composites and indicate that even with the 23–24% void content the polyimide resin provides good support for the glass fibers. The failure mode in the edge compression test was that of general shear in the face sheets, not debonding between the face sheet and honeycomb core. Failures in flatwise tensile tests occurred partially in the bond and partially in the core material for each specimen. Shear test failures occured in the core material. These strength and modulus values and failure modes indicate very good bonding in face sheets, and between honeycomb-core and face sheets of sandwiches.

Average room-temperature properties and failure modes for laminated beam specimens are also given in Table 1. These strength and modulus values and failure modes indicate good bonding between layers of laminated beams.

Effects of Temperature and Exposure on Laminated Beam Properties

The effects of temperature and exposure on the flexure strength of laminated beams are presented in Fig. 8. The ordinate is the ratio of flexure strength after given conditions of test temperature and/or exposure to the average as-fabricated flexure strength, 74 ksi (from Table 1). The variability in the test data, as indicated by the hash-marks (range of data) above and below the data symbol (average value), was considerable for many exposure conditions; but the trends of the data are clearly indicated by the lines drawn through the data symbols. It may be noted that an increase in test temperature from room temperature to 600°F reduced flexure strength of as-fabricated specimens by about 30%. Exposures to 450°F and 760 torr for 386 hr resulted in small reductions of flexure strength, both at 80° and 450°F. Cyclic exposures to 600°F and 35 torr for 400 cumulative hr reduced room-temperature strength somewhat but had essentially no effect on 600°F strength. Exposures to 600°F and 760 torr for 471 hr severely degraded room-temperature strength, reducing it by about 65%. However, specimens that had undergone the same exposure conditions had approximately the same strength at 600°F as at room temperature. The general trend of Fig. 8 indicated that high-temperature exposures have a more severe effect percentage-wise on room-temperature strength, than on high-temperature strength; and that exposures at higher pressures are more severe than those at lower pressures for similar times.

Figure 9 shows the effects of temperature and exposure on the flexural modulus of beams in a plot similar to that of Fig. 8. An increase in test temperature from room temperature to 600°F reduced modulus by about 20%. A comparison of Figs. 8 and 9 also indicates that exposure effects on modulus are much less severe than on strength. Modulus degradation was again more severe percentage-wise on modulus at room temperature than on modulus at elevated temperature.

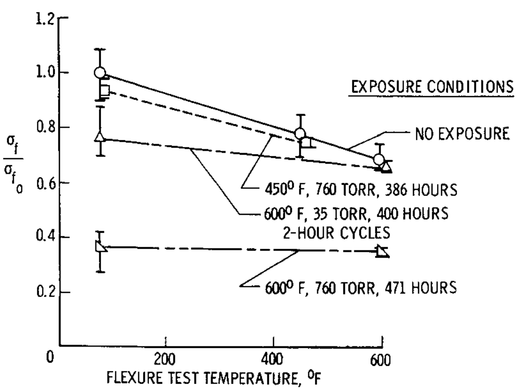

Fig. 8 Effects of test temperature and several exposure conditions on flexure strength of polyimide-resin/glass-fiber laminated beams.

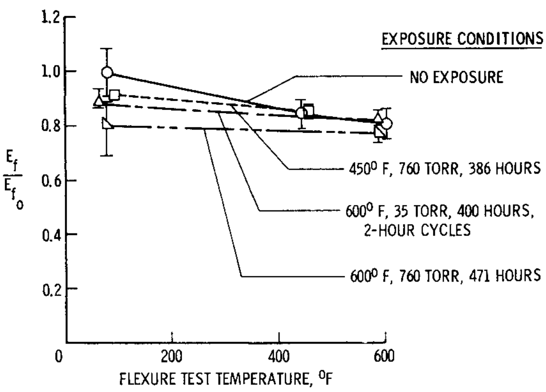

Fig. 9 Effects of test temperature and several exposure conditions on flexure modulus of polyimide-resin/glass-fiber laminated beams.

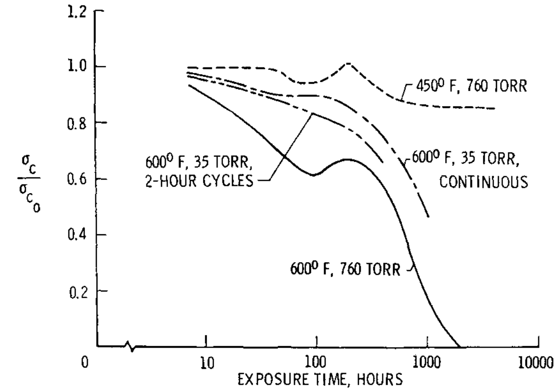

Fig. 10 Variation of average room-temperature, edge compression strength with exposure time for polyimide-resin/glass-fiber, honeycomb-core sandwich specimens.

Effects of Exposure on Sandwich Properties

The effect of exposures in several environments on the room-temperature compressive strength of sandwiches is shown in Fig. 10. The ratio of compressive strength after exposure to the average compressive strength of as-fabricated specimens is plotted as a function of exposure time, which is on a logarithmic scale. The 600°F exposure at 760 torr had the most severe effect on compressive strength, reducing it to zero after 2000 hr exposure. The continuous exposures at 600°F and 35 torr degraded compressive strength roughly one-half as much as the higher pressure and moisture content for similar exposure times. The cyclic exposures seem to have had an intermediate effect on compressive strength, at least for exposure times up to 400 hr. Since the supersonic transport will operate at about 450°F, the considerable strength deterioration after 1000 hr exposure at 600°F does not preclude the use of polyimide-resin/glass-fiber sandwich construction in these vehicles. The 450°F curve indicates that little degradation in compressive strength is noted for exposures up to 4000 hr in the pressure and moisture environment which was most severe at 600°F. Similar exposure effects were noted for flatwise tensile strength ratio, shear strength ratio, and shear modulus ratio.

Figure 11 shows the effect of exposure on compressive modulus ratio of sandwiches. The plot is quite similar to that of Fig. 10. No significant modulus degradation was noted in any exposure environment investigated for exposures up to 1000 hr. Only after exposures that caused gross strength deterioration (2000 hr at 600°F, 760 torr) was there a severe drop in compressive modulus ratio.

A time-temperature parameter plot of sandwich specimen strength properties is shown in Fig. 12 for 450° and 600°F

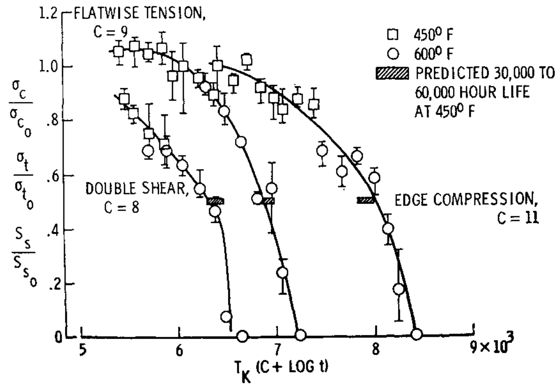

Fig. 12 Correlation of room-temperature polyimide-resin/glass-fiber sandwich strength after various exposure times at 450° and 600° F and at 760 torr.

exposures at 760 torr. The compressive strength ratio, flatwise tensile strength ratio, and shear strength ratio are plotted as a function of the Larson-Miller parameter,[7] in which T_K is exposure temperature in °K, C is a constant that is empirically adjusted to make the data for both temperatures fall on the same curve, and t is time in hours. The fact that the sandwich data align quite well by using this approach permits preliminary estimates to be made of lifetime after exposure to various temperatures. If a 50% degradation of strength is arbitrarily selected as the criterion for service life of a supersonic transport, then a service life of from 30,000 to 60,000 hr at the 450° F operating temperature is predicted on the basis of these data. This service life is shown in Fig. 12 by the short horizontal bars that cover a calculated range of the abscissa parameter from 30,000 to 60,000 hr at 450° F for each type of loading. Polyimide-resin/glass-fiber sandwich construction thus shows considerable promise for supersonic transport applications, but data for longer exposures at 450°F must be available to fulfill this promise.

Comparison of Sandwich Data with Laminated Beam Data

Because data were generated for both structural specimens and material specimens, it is possible to correlate the effect of exposure on certain properties of the beams with the exposure effect on sandwich properties. If such correlations can be made, data from relatively simple tests on inexpensive laminated beams can be used to provide predictions of the exposure effect on more complex and expensive structural specimens. Such a correlation is made in Fig. 13, where exposure effects on flatwise tensile strength ratio of sandwiches are compared with exposure effects on flexure strength ratio of laminated beams on a plot similar to those

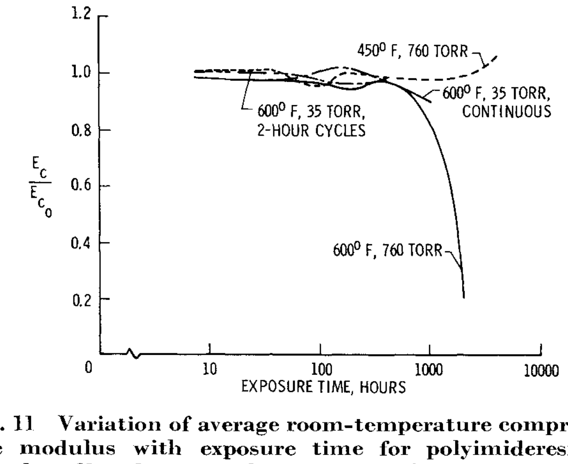

Fig. 11 Variation of average room-temperature compressive modulus with exposure time for polyimideresin/glass-fiber, honeycomb-core sandwich specimens.

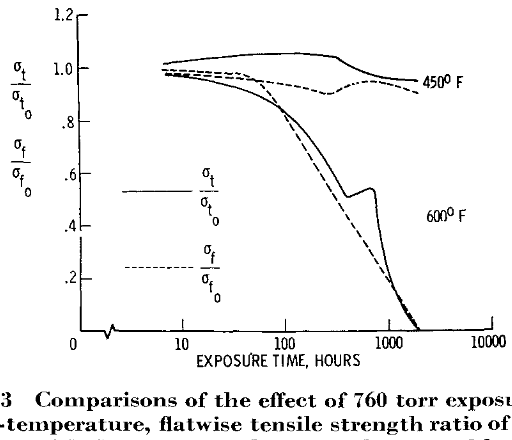

Fig. 13 Comparisons of the effect of 760 torr exposure on room-temperature, flatwise tensile strength ratio of sandwiches with flexure strength ratio of laminated beams.

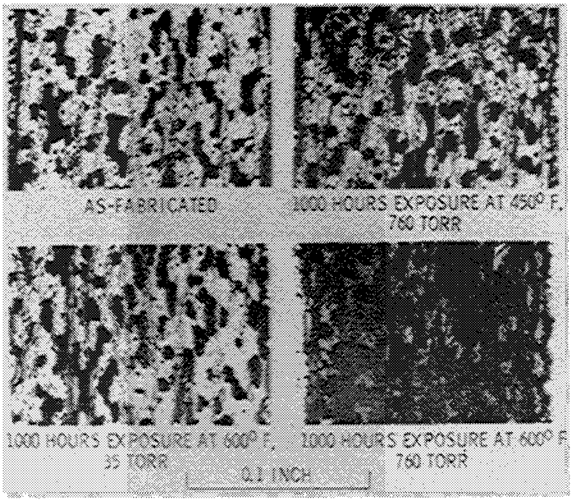

Fig. 14 Photomicrographs of cross sections of polyimide-resin/glass-fiber laminated beams.

shown previously. It appears that the flexure strength ratio of beams is an accurate predictor of the flatwise tensile strength ratio of sandwiches at both 600° and 450°F in the 760 torr exposures.

Similar plots (not shown) indicate that interlaminar shear strength ratio of beams appears to be a good predictor of both edge compressive strength ratio and shear strength ratio of sandwiches; and flexural modulus ratio of beams appears to be a good predictor of compressive modulus ratio of sandwiches.

Mechanical Property Degradation Mechanism

Because similar degradation effects occur in 13-ply laminated beams and 4-ply sandwich face sheets, it is believed that degradation is more a consequence of internal rather than external oxidation. A degradation mechanism based on a predominately internal oxidation process involving a volatile oxide is therefore postulated. Figure 14 suggests that such a process is actually taking place. Photomicrographs of cross sections of four laminated beam specimens are shown. The first specimen (upper left) has had no exposure. In the as-fabricated condition, polyimide-resin/glass-fiber laminates produced by the vacuum bagging process have rather high void contents, approximately 25% in the specimens tested in this evaluation. This cross section is not indicative of a poor specimen, it is typical of polyimide/glass laminates; recall that this specimen has high strength. The black areas are voids in the specimens. The dotted areas are cross sections of glass fibers running perpendicular to the plane of the slide; the wavy areas are glass fibers running parallel to the plane of the slide. The white areas are polyimide resin. The horizontal dimension is the 13-ply thickness of the specimen. After 1000-hr exposure at 450°F and 760 torr (upper right of Fig. 14), the void areas have become slightly enlarged. After 1000-hr exposure at 600°F and 35 torr (lower left), the void areas appear more numerous than in the as-fabricated specimen. After 1000-hr exposure at 600°F and 760 torr (lower right), the resin has been so depleted by the internal oxidation process that very little matrix is left to support the glass fibers, resulting in very little residual strength in both sandwiches and laminated beams.

Concluding Remarks

From the preliminary results of a study of the effects of several exposure environments on the properties of polyimide-resin/glass fiber laminates, the following conclusions may be drawn.

1) PI-2501 polyimide-resin/E-glass fabric laminated honeycomb-core sandwich construction shows considerable promise as a lightweight material for secondary structural applications in a Mach 2.7 supersonic transport; but data for longer exposures at 450°F (505°K) must be available to fulfill this promise.

2) Room-temperature mechanical property tests on sandwich and beam specimens indicate that good bonding can be developed in the polyimide-resin/glass-fiber system.

3) High-temperature exposures appear to have a more severe effect percentage-wise on room-temperature properties than on high-temperature properties.

4) Two thousand hours of exposure at 600°F and 760 torr resulted in complete degradation of mechanical properties; 600°F exposures at 35 torr had a less severe effect. No significant mechanical property degradation has been noted after 4000-hr exposure at 450°F.

5) Degradation of specific room-temperature mechanical properties of sandwiches due to 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.

6) The mechanical property degradation mechanism appears to be a predominately internal oxidation process involving the polyimide-resin matrix, with volatile oxide formation.

References

[1] Milek, J. T., "Polyimide plastics: A state of the art report," Electronic Properties Information Center Rept. S8, Air Force Materials Lab. (October 1965).

[2] Todd, N. W. and Wolff, F. A., "Polyimide plastics withstand high temperatures," Mater. Design Eng. **60**, 86–91 (August 1964).

[3] "PI-2501 'B-Staged' Fiberglass Prepreg," Technical Information Sheet, E. I. du Pont de Nemours Co. Inc., Philadelphia, Pa. (July 1965).

[4] Murcray, D. G., Murcray, F. H., and Williams, W. J., "Distribution of water vapor in the stratosphere as determined from infrared adsorption measurements," J. Geophys. Res. **67**, 759–766 (February 1962).

[5] *1965 Book of ASTM Standards. Part 27* (American Society for Testing and Materials, Philadelphia, Pa., 1965), pp. 293–299.

[6] *1966 Book of ASTM Standards. Part 26* (American Society for Testing and Materials, Philadelphia, Pa., 1966), pp. 497–501.

[7] Larson, F. R. and Miller, J., "A time-temperature relationship for rupture and creep stresses," Trans. Am. Soc. Mech. Engrs. **74**, (July 1952).