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Aging Effects on the Interlaminar Shear Strength of High-Performance Composites

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The effect of isothermal aging on interlaminar shear strengths of quasi-isotropic composites laminates were evaluated by using ASTM D 3846-94, Standard Test Method for In-Plane Shear Strength of Reinforced Plastics. Thermoset bismaleimide (IM7/5260) and thermoplastic polyimide (IM7/K3B) were investigated to determine the aging degradation in different matrix materials. The laminates were 24 plies and had a lay up of [−45/90/45/0]3S. Aging temperatures were 300, 350, and 400°F and aging time varied from a few hours to 28 months. Nonaged specimens were also tested for baseline values. Significant differences were noted between these two different matrices. Isothermal aging for IM7/5260 initially caused postcuring effects prior to an overall decrease in interlaminar shear strength. Strength degradation was directly dependent on both aging temperatures and times. In addition, accelerated aging effects at 400°F were observed. For the IM7/K3B specimens no postcure effects were observed. The interlaminar shear strength decreased for longer aging times, but showed little variation for different temperatures. Aging at 400°F did not show any accelerated aging effects. The interlaminar shear strength results were compared with previously obtained compression after impact data. Similar trends in strength degradation were observed.

Introduction

Background

THE aerospace industry realizes that future aircraft designs must be safe, efficient, quiet, and cost effective. Some current designs do not consider composites as a weight-savings option, but as a requirement in order to meet mission objectives for range and payload. A supersonic transport would further subject its composite structure to new environmental conditions. Flying at Mach 2.4 exposes the structure to temperatures in the 300–350°F range during cruise. For an aircraft with a proposed service life of 60,000 h, this type of sustained exposure is expected to affect the matrix's material properties and consequently the laminate's strength.

Aging Degradation

Creating a successful design implementing advanced composites with prolonged exposure to elevated temperatures requires not only a detailed knowledge of the stresses and strains that are induced by the applied loads, but also the effect this operating environment has on the material properties. It is, therefore, necessary to evaluate and understand the behavior of composite materials subjected to such exposure.

Graphite fibers, individually, are not affected by isothermal exposure. However, the polymer matrix surrounding the composite plies is susceptible to chemical and physical changes. These reactions can permanently change the material properties of the laminate, by forming new chemical bonds, breaking established bonds, or both. Consequently, these nonreversible reactions will then affect the matrix's resistance to delamination. Once delamination occurs, the laminate will experience losses in strength and stiffness.

The matrix material used in advanced composites interconnects the fiber reinforcements. Presently, epoxy resin is the primary thermoset composite matrix for aircraft applications. In all thermoset materials the matrix is cured by means of time, temperature, and pressure into a dense, low-void-content structure in which the fibers are aligned in a specific orientation related to the direction of anticipated loads.

The composition of the matrix is an important element in determining the material behavior that binds the fibers together. The matrix formulation determines the cure cycle and influences such properties as compression and shear strengths, creep, thermal resistance, moisture sensitivity, and ultraviolet sensitivity, all of which affect the laminate's long-term durability.

Epoxy resins are widely used because of their good structural characteristics and ease of processing. However, they have a maximum operating temperature of about 200°F. Bismaleimide resins can be used in environments up to 350°F and are also fairly easy to process. Polyimide resins can be used in environments up to 500–600°F and have increased toughness, but can be expensive to process.[1]

If a polymer can be melted, it is categorized as a thermoplastic. Otherwise, it is a thermoset. The long molecular chains in thermosets are connected during the cure cycle by "cross-links" of covalent bonded atoms, which make the entire specimen a single macromolecule. Epoxy and bismaleimide resins are both thermoset matrices; polyimide is a thermoplastic matrix.

A postcure reaction can occur when unreacted, polymeric components continue to react after the cure cycle is complete. These reactions are generally hastened with increasing aging temperatures, although they typically occur only during the initial stages of long-term aging. Nonetheless, the polymerization or cross-linking that transpires will create a denser polymer network, thereby resulting in a stiffer and stronger material. However, a material with too many cross-links or a very high molecular weight can be brittle and have low fracture resistance. Even at low temperatures additional cross-linking and chain growth can occur. Although only a limited amount of postcure reaction will take place before a saturation point is reached, this postcure reaction to elevated temperatures can cause a change in the properties of the materials.

There has been a considerable amount of research completed concerning the detrimental effects of aging on composite properties, some of which involved compression after impact (CAI) strength, transverse flexure strength, and glass transition studies. However, very little work has been completed concerning the aging effects on

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the interlaminar shear strength of advanced laminated composites. The interlaminar shear strength is solely a function of the matrix properties. Therefore, by examining the laminates shear strength one can directly hypothesize the relative strength of the matrix.

Objective

The specific objective of this research was to determine and compare the effects of isothermal aging on the interlaminar shear strength of a thermoset bismaleimide laminate (IM7/5260) and a thermoplastic aromatic polyimide laminate (IM7/K3B). The specimens were aged at 300, 350, and 400°F for up to 28 months. The duration of aging times was chosen according to the expected strength of the composites; high temperatures had a shorter duration than low temperatures. The data provided information on failure mechanisms and degradation characteristics and were compared to a previous CAI study.

Experimental Procedures

Test Matrix

A total of 72 IM7/5260 specimens were tested: 9 with zero aging, 17 aged at 300°F for 0.4 to 28 months, 25 aged at 350°F for 0.14 to 14 months, and 21 aged at 400°F for 0.007 to 1.9 months. A total of 79 IM7/K3B specimens were tested: 3 with zero aging, 27 aged at 300°F for 3 to 24 months, 27 aged at 350°F for 1 to 24 months, and 30 aged at 400°F for 1 to 24 months.

Aging temperatures of 300 and 350°F were chosen because of their correlation to in-flight temperatures experienced by potential composite structure at Mach 2.4. Aging at 400°F was evaluated to study the relationship of accelerated aging. All specimens were aged at sea level, which creates a more aggressive aging environment than the estimated service environment of 65,000 ft. The higher atmospheric pressure at sea level accelerates the oxidation degradation.[2]

The maximum aging time for IM7/5260 was 28 months. Although this is less than the expected cruise life of a commercial aircraft, it was considered sufficient to draw meaningful conclusions about the long-term aging characteristics of the polymeric material. The times for IM7/5260 were chosen based on the change in glass transition temperature as a function of time and temperature for the composite material studied. When a polymer is heated, it transforms gradually from a glass, wherein the material is rigid, to a rubber, in which the molecules have small-scale mobility and the modulus is gradually reduced. This transition does not occur suddenly, as in phase transitions, and therefore, attempting to assign a single value as the glass transition temperature T_g to the range of temperatures is somewhat arbitrary. Nonetheless, this ΔT_g information,[3] derived from a curve fit of T_g tests, was used to determine the appropriate aging times. The times were selected such that the change in T_g would be equivalent between data points, in hope that this would then create an equivalent change in strength properties. Final aging times at each temperature were chosen according to the expected amount of degradation. That is, shorter aging times were used with higher aging temperatures. Longer aging times would not have provided useful data because strength of the specimen dropped below acceptable levels for engineering applications.

The maximum aging time for IM7/K3B was 24 months. Because the correlation between ΔT_g and CAI strength degradation proved poor in IM7/5260, a more uniform test matrix was selected for IM7/K3B. Each aging temperature had the same aging times. Eight aging times were chosen, with a several month interval between successive aging times. Smaller intervals were used initially to capture short-term behavior. Longer time intervals were used at the end of the study because aging behavior became constant.

Specimen Preparation

The IM7/5260 graphite bismaleimide and IM7/K3B materials studied in this research were received as 24 × 22 in. panels with an average thickness of 0.141 in. and a quasi-isotropic lay up. The panels were cut into 4 × 6 in. samples and were then isothermally aged in three precision laboratory ovens.

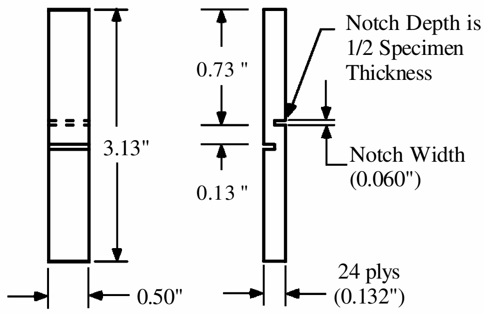

Fig. 1 Specimen details for interlaminar shear test.

The ovens were operated in a recirculating airflow mode, which limited fresh air exchange to only oven cooldown events, that typically occured about once a month and kept the chamber pressure lower than if the oven were operated in a forced air mode. Once the specimens were sealed inside, the ovens were programmed to reach aging temperature at a controlled rate of 3°F/min. The ovens were then set to continuously maintain the desired aging temperature. Temperature was maintained to within ±1°F of the set temperature at all points inside the oven. After aging for a set of specimens was completed, the ovens were allowed to cool, and the specimens were removed. Cooling rates could not be electronically controlled, but were maintained at less than 3°F/min by controlling the amount of room-temperature air flowing into the ovens. Times spent during the removal process were not counted toward the total aging time of the specimens. Time tracking and age scheduling were recorded manually at the ovens and in a computer spreadsheet.[4]

The interlaminar shear test specimens were cut per American Society for Testing and Materials (ASTM) standard D 3846-94, Standard Test Method for In-Plane Shear Strength of Reinforced Plastics, from these samples. The specimens were trimmed to 0.5 × 3.13 in. with two centrally opposed 0.060 in. notches 0.25 in. apart. The laminate lay up is [−45/90/45/0]3S with the 0-deg direction parallel to the 3.13-in. dimension.

A fully dimensioned, as-machined test specimen, including tolerances, is shown in Fig. 1. After machining, all specimens were measured, and data were recorded.

Interlaminar Shear Tests

The interlaminar shear test consisted of applying a compressive load uniformly along the 0-deg direction until failure occurred. These tests followed the protocol described in ASTM D3846-94, which covers the determination of the in-plane shear strength of reinforced thermosetting plastics in flat sheet form in thickness ranges of 0.100–0.206 in. Although various kinds of shear tests are widely used to assess composite bond strength, this test method uniquely addresses shear strength of composites having randomly dispersed fiber orientation.

During testing, the specimen is supported in a steel jig designed to hold the specimen with zero out-of-plane displacement, while permitting in-plane sliding, simulating simply supported conditions on both outside faces. The specimen was mounted into the support jig, such that it was flush with the base and centered. A half-spherical plate was set on top of the specimen to ensure a uniformly applied load.

Once the testing apparatus was assembled, it was centered on the table of a variable load cell. A 2400-lb load cell was used for these tests, resulting in a minimum load indicator increment of 2 lb. The lower arm was moved down at a constant rate of 0.050 in./min until failure occurred. The maximum load carried by the specimen and length of failed area with respect to either half of the ruptured surface was recorded along with the room's temperature and humidity.

Experimental Results

Failure Mechanisms

Failure as a result of interlaminar shear is represented as fracture in the plane of the plies, along the longitudinal axis of the specimen,

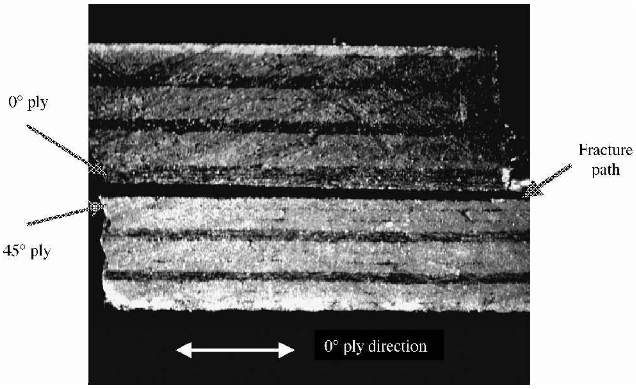

Fig. 2 Micrograph of fracture path for IM7/K3B aged at 400°F (24 months).

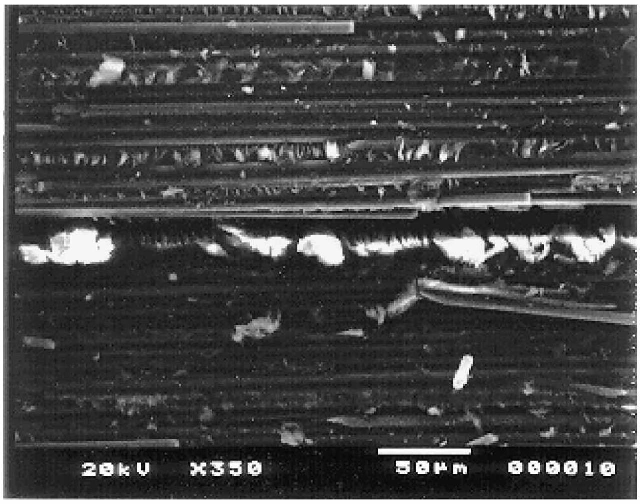

Fig. 3 Fracture surface (SEM 350x) IM7/5260, nonaged.

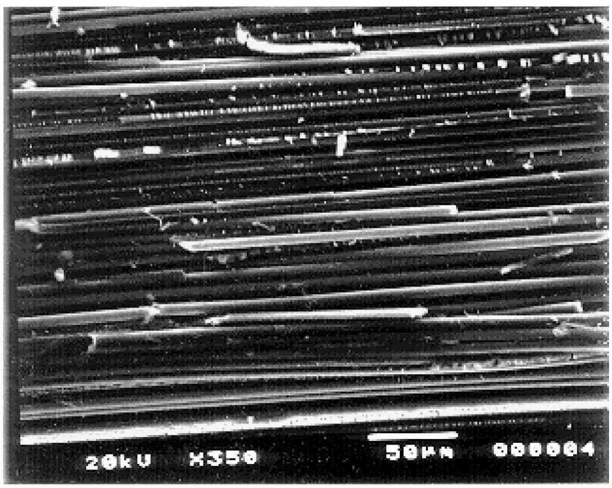

Fig. 4 Fracture surface (SEM 350x) IM7/5260, aged at 400°F (two months).

between two centrally located notches. The failure consistently occurred within the center zero plies near the forty-fives. Micrographs of a side view of the specimens show the typical fracture line. The specimen shown in Fig. 2 is typical of all of the specimens, which failed as a result of interlaminar shear.

The fracture surface was examined by the use of a scanning electron microscope. Photos of IM7/5260 (Figs. 3 and 4) show a significant difference between the aged and nonaged specimens. The matrix appears to break down and leech away during the aging

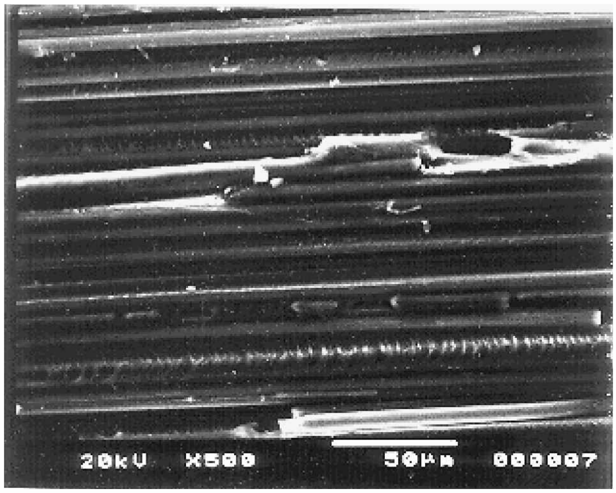

Fig. 5 Fracture surface (SEM 350x) IM7/K3B, nonaged.

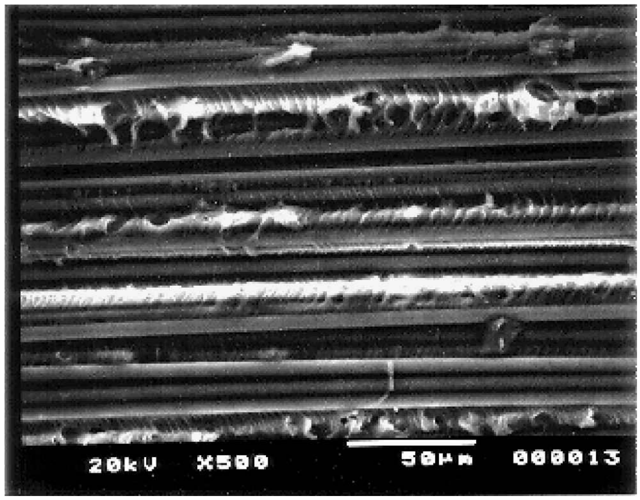

Fig. 6 Fracture surface (SEM 350x) IM7/K3B, aged at 400°F (24 months).

process. Whereas the nonaged specimen shows matrix bridging, the aged specimen shows bare fibers. Photos of IM7/K3B (Figs. 5 and 6) show very little difference between aged and nonaged specimens. The matrix surrounds the fibers in both specimens.

Effects of Aging on Interlaminar Shear Strength

The maximum shear load carried by the specimen during the test is recorded, and the interlaminar shear strength is calculated by

$$\sigma_{\mathrm{ILS}} = P_{\max}/wl$$

where $P_{\max}$ is the maximum load carried by the specimen, most often occurring simultaneously to failure and w and l are the width and length of the fracture surface, respectively.

Even though every effort was made to standardize the testing process, some scatter did exist within the material systems. However, much more significant are the differences between the material systems, IM7/5260 and IM7/K3B.

The two material systems responded markedly different to elevated thermal aging. IM7/5260 degrades primarily as a result of oxidation, with degradation growing in from the exposed surfaces.[5] The degradation rates are driven by exposure to elevated temperature and oxygen. For IM7/K3B, however, these data suggest that exposure to elevated temperature and oxygen has only a minor effect on degradation.[6]

For nonaged IM7/5260 specimens the average interlaminar shear strength is 6959 psi with a standard deviation of 612 psi compared with 12,018 psi with a standard deviation of 605 psi for IM7/K3B.

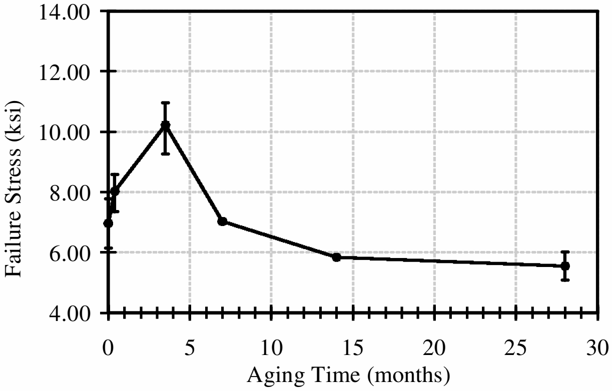

Fig. 7 Interlaminar shear strength for IM7/5260 aged at 300°F.

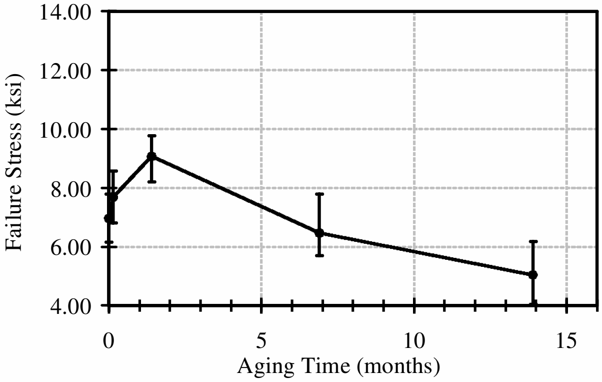

Fig. 8 Interlaminar shear strength for IM7/5260 aged at 350°F.

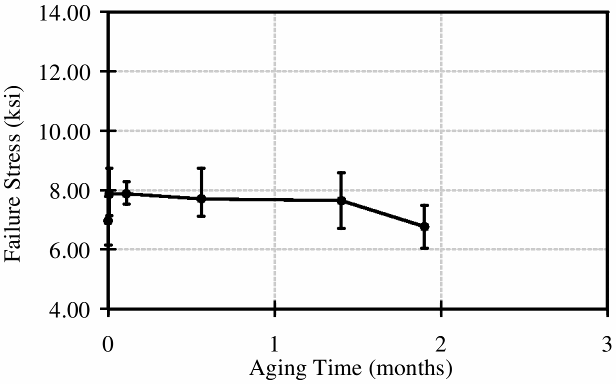

Fig. 9 Interlaminar shear strength for IM7/5260 aged at 400°F.

The average interlaminar shear strength at each testing point for IM7/5260 and IM7/K3B is shown in Figs. 7–13 and 14–20, respectively.

Clearly IM7/5260 shows not only a lower interlaminar shear strength, but also a more rapid degradation. The results of the interlaminar shear tests are discussed here in further detail, independently, for the two material systems.

Figures 7–9 show the failure stress of IM7/5260 at 300, 350, and 400°F, respectively. Figure 13 combines the three temperature ranges for an overall comparison. Postcure effects are common across all three temperature ranges. The polymer chains of the matrix material continue to link together, forming a stronger network, which drives failure strength higher. However, postcure does proceed more slowly at lower temperatures. At 400°F the postcure effect lasts only for about one-tenth of a month of continuous aging, whereas at 300 and 350°F postcure is sustained for 10 and 9 months, respectively. With respect to the actual service life of an aircraft, IM7/5260 exposed to 400°F temperatures would complete a cure after a few months, whereas a complete cure would require several years of aging at 300 and 350°F.

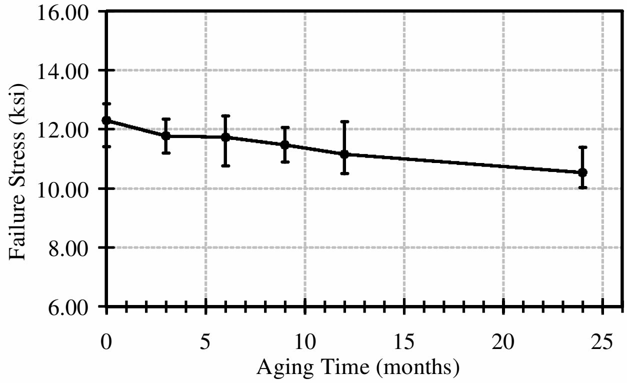

Fig. 10 Interlaminar shear strength for IM7/K3B aged at 300°F.

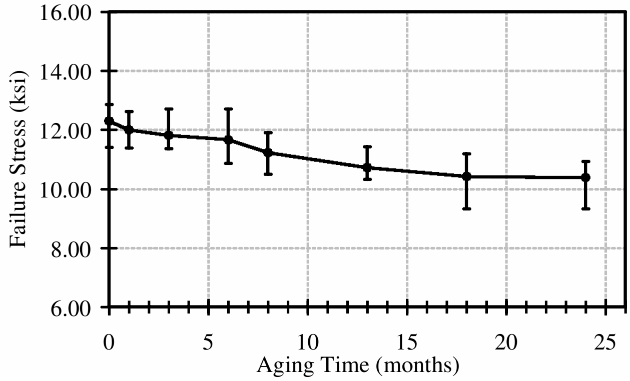

Fig. 11 Interlaminar shear strength for IM7/K3B aged at 350°F.

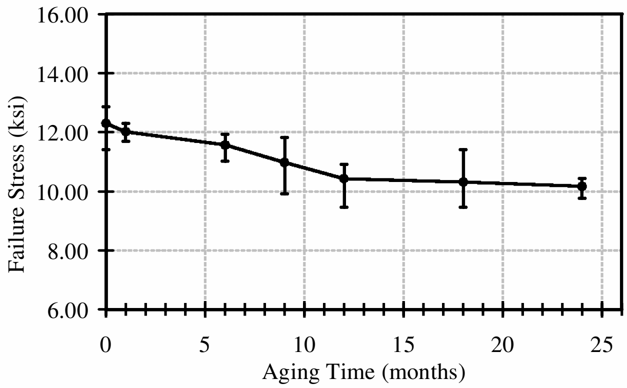

Fig. 12 Interlaminar shear strength for IM7/K3B aged at 400°F.

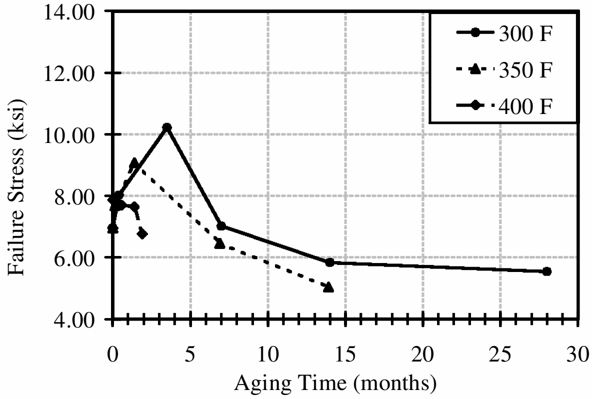

Fig. 13 Interlaminar shear strength for IM7/5260.

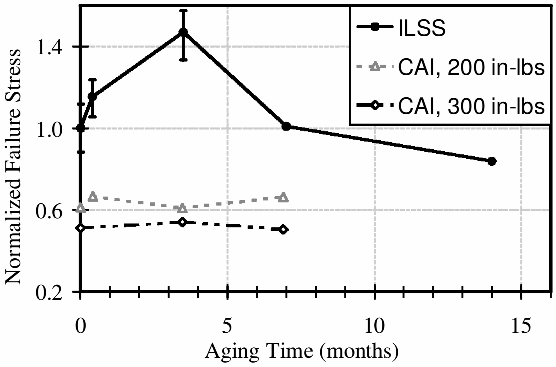

Fig. 14 Normalized failure stress for IM7/5260 aged at 300°F.

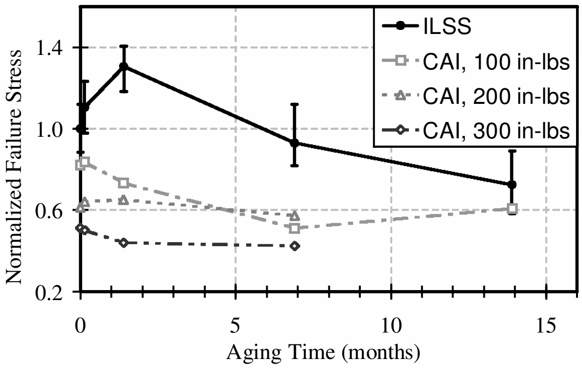

Fig. 15 Normalized failure stress for IM7/5260 aged at 350°F.

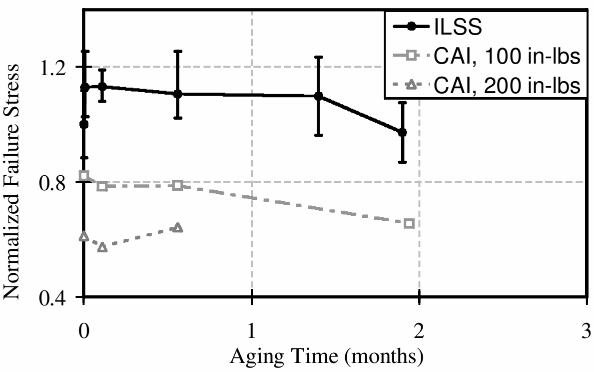

Fig. 16 Normalized strength for IM7/5260 aged at 400°F.

The degradation effects of interlaminar shear strength also follow a similar trend. Aging at 300°F shows strength degradation after postcure that is initially rapid, then levels off. There is a 20.4% decrease in overall strength during a 28-month cure period. However from its maximum postcure value, the strength decreases 45% in the last 24-month period. At 350°F the strength degradation after postcure is almost linear, continuous, and steady. The overall decrease is 27.6% during a 14-month cure period and a 45% decrease from the maximum postcure strength during the last $12\frac{1}{2}$ months. At 400°F the degradation is accelerated and pronounced. In just over one month it decreases 14% from the maximum postcure value. It can be estimated, by extrapolation, that 45% degradation in strength would be reached in less than four months.

These results compared favorably with previous research investigating CAI strength degradation of the same material.[3,7] Figures 14–16 show the interlaminar shear strength and CAI strength together. The interlaminar shear strength is normalized to the Interlaminar Shear strength at room temperature. The CAI

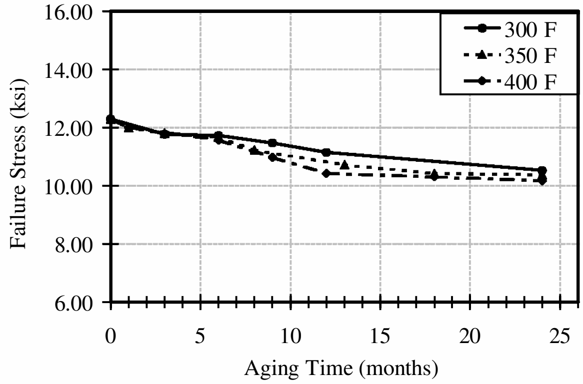

Fig. 17 Interlaminar shear strength for IM7/K3B.

strength is normalized to the CAI strength at room temperature with zero impact. It is the trend and not the actual values that are significant. Both tests show initial postcure effects, followed by strength degradation. Although for the CAI specimens the postcure is sometimes overshadowed by impact damage. This is especially true for the 400°F aged specimens. Because the postcure caused the material to become brittle, the impact after aging produced very large damage areas, thereby exacerbating the weakened state of the entire specimen. The CAI strength decreased 25% after 14 months of aging at 350°F, and it was predicted that a similar decrease would occur at 400°F after three months of continuous aging. This compares well with the four-month prediction for a matched decrease in interlaminar shear strength at 350 and 400°F.

The interlaminar shear strengths of IM7/K3B at 300, 350, and 400°F are shown in Figs. 10–12. Figure 17 combines the three temperature ranges for an overall comparison. As is obvious from the plots, there are no noticeable postcure effects for any of the aging conditions.

All IM7/K3B specimens, however, do have a common trend of a small decrease in interlaminar shear strength over the 24-month cure period. For the specimens aged at 300°F, the decrease was fairly constant for the entire range. An overall 14.3% decrease in strength was observed. However, for those aged at 350 and 400°F, most of the degradation occurred in the first 13 months.

For specimens aged at 350°F, the interlaminar shear strength decreased 15.6% during the 24-month aging period; it decreased 12.8% during the first 13 months. Therefore, 83% of the degradation occurred in the first 54% of aging time. The specimens aged at 400°F experienced an overall decrease of 17.3% in strength for those aged 24 months; a decrease of 15.2% occurred for those aged 12 months. Therefore, 88% of the degradation occurred in the first 50% of aging time at 400°F. After 13 months of aging, the decrease in strength continued at a much slower rate for both the 350 and 400°F specimens. Further aging is expected to cause even less change in strength. A very significant observation is the lack of difference in aging degradation among the various temperatures. Clearly, the specimens aged at 400°F do not show any signs of accelerated aging. For the specimens aged 24 months, there is only a 1.5% difference in strength between the 300 and 350°F specimens, a 2% difference in strength between the 350 and 400°F specimens, and a 3.5% difference between 300 and 400°F specimens.

These results also compared favorably with previous research investigating CAI strength degradation of IM7/K3B.[2,7] Figures 18–20 show the interlaminar shear strength and CAI strength together. The interlaminar shear strength is again normalized to the ILS strength at room temperature, and the CAI strength is normalized to the CAI strength at room temperature with zero impact. Again, it is the trend and not the actual values that are significant. Both tests show the lack of postcure effects, the steady degradation at 300°F, the faster degradation in the earlier stages of the 350 and 400°F specimens, and a leveling off or saturation strength at 350 and 400°F.

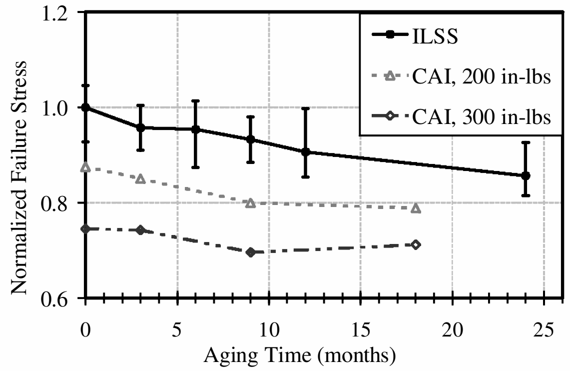

Fig. 18 Normalized failure stress for IM7/K3B aged at 300°F.

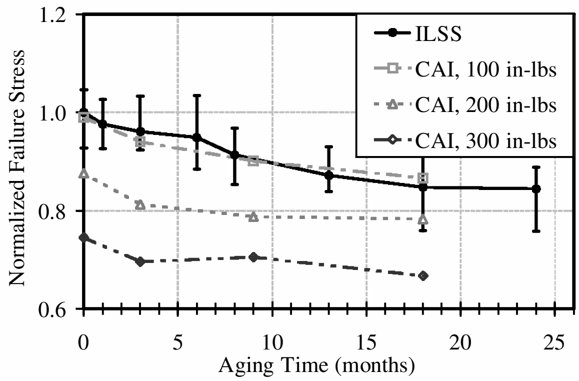

Fig. 19 Normalized failure stress for IM7/K3B aged at 350°F.

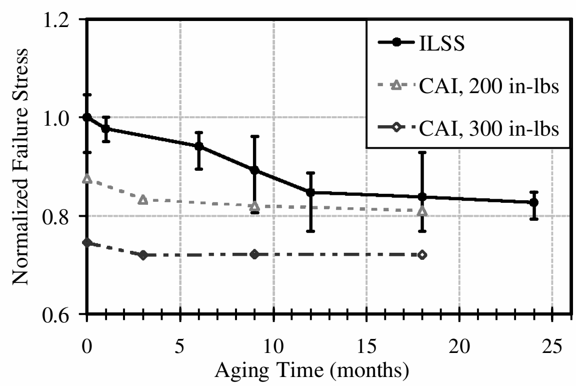

Fig. 20 Normalized failure stress for IM7/K3B aged at 400°F.

Conclusions

A testing program was developed to investigate the isothermal aging effects on a thermoset bismaleimide laminate (IM7/5260) and a thermoplastic aromatic polyimide laminate (IM7/K3B). The specimens were aged at 300, 350, and 400°F for up to 28 months.

For the thermoset bismaleimide laminate (IM7/5260) aging effects are highly significant. Postcuring effects are strongly evident as the interlaminar shear strength initially increases. After the initial increase the interlaminar shear strength steadily decreases as a result of degradation of the matrix properties. Strength degradation occurs, not only as aging temperatures increase, but also as aging times increase. Aging at 400°F induces an accelerated process, approximately 600% faster than at 300°F, and 312% faster than 350°F. At 300°F the strength decreases 45% after postcure in 24 months. At 350°F the strength decreases 45% after postcure in 12 months. And at 400°F the strength decreases 14% after postcure in just over one month.

For the thermoplastic aromatic polymide laminate (IM7/K3B) there is no noticeable postcure effect. The specimens do exhibit small, but nonetheless, measurable decreases in interlaminar strength. The ones aged at 300°F lost 14.3% of their strength in a 24-month period. Aging at 350 and 400°F caused a 15.6 and 17.3% strength loss respectively in the same time period. A significant difference from IM7/5260 is that strength degradation in IM7/K3B was responsive to aging times, but not as much to aging temperatures.

Comparison to CAI data was favorable for both material systems. With IM7/5260 similar trends were noted for both postcure effects and strength degradation. Likewise, for IM7/K3B both the CAI tests and interlaminar shear tests found no postcure effects, little change in strength as a result of aging time, and negligible degradation as a result of temperature increases.

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