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Transverse Flexural Tests as a Tool for Assessing Damage to PMR–15 Composites From Isothermal Aging in Air at Elevated Temperatures

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TRANSVERSE FLEXURAL TESTS AS A TOOL FOR ASSESSING DAMAGE TO PMR-15 COMPOSITES FROM ISOTHERMAL AGING IN AIR AT ELEVATED TEMPERATURES

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ABSTRACT

To date, the effect of thermo-oxidative aging on unidirectional composite mechanical properties has been monitored by the measurement of interlaminar shear strength (ILSS) and either three or four point longitudinal flexural strength (LFS) of the composites being tested. Both test results are affected by the fiber-to-matrix bonding, the former being dependent on the shear resistance of the interface and the latter on the degree of load sharing by the fibers through the fiber/matrix interface.

Recently, fiber/matrix interfacial bond strengths have been monitored using a transverse flexural strength (TFS) test method. This test method was used to evaluate the effect of fiber surface treatment on the fiber/matrix bond. The interface bonding was varied in these tests using Hercules A-fibers with three types of surfaces that produce bonds of poor, better, and good quality. The TFS was found not only to be sensitive to the bonding, but also to the aging time of unidirectional A-fiber/PMR-15 composites. This relationship reflects the mechanism by which the PMR-15 degrades during thermal aging.

Key Words:
Composites
Polymers
Graphite fibers
Thermo-oxidative stability
Flexural strength
Interlaminar shear strength

INTRODUCTION

Transverse flexural strength (TFS) tests on unidirectional graphite-fiber-reinforced composites were studied to assess the effects of fiber/matrix bonding on composite mechanical properties.[1-4] A number of interesting conclusions have been proposed as a result of these works. Some of them are

- Transverse flexural strength measurements produce less scatter than transverse tensile strength data because of the differences in the test gage length. The test gage length for the flexural test approaches the width of a line.
- Since the gage length is very small, the flexural strength is usually larger than the tensile strength because the probability that flaws are present in the test specimen gage length is greatly reduced.
- The flexural strength is very sensitive to the interfacial bonding between the composite reinforcement and the polymer matrix.
- The transverse flexural strength is independent of the test span used. This allows small specimens to be used for strength measurements.

Previous work directed toward understanding the thermo-oxidative stability of PMR-15 resin[5] shows that the oxidative degradation takes place in a thin surface layer, whereas the central portion of the test specimen remains relatively unchanged chemically. The effect of thermo-oxidative aging on composite mechanical properties is monitored by short-beam shear tests which measure the interlaminar shear strength (ILSS), ASTM D-2344, and by longitudinal flexural strength (LFS) tests, ASTM D-790, either three- or four-point loading, which indicate the load sharing ability of the fiber/matrix interfaces along the outer surfaces of the composites. Since this property (0° flexural strength) is fiber dominated, it may not indicate the true extent

of thermal aging damage. Attempts to correlate polymer matrix thermo-oxidative stability with composite stability must include the effects of matrix degradation on composite mechanical properties degradation. Thus, composite surface degradation must be monitored by using test methods sensitive to changes in the surface conditions as were seen to develop in PMR-15 neat resin during aging tests.[5]

The purpose of this work was twofold: (1) to determine the effect of graphite fiber surface treatment on the thermo-oxidative stability and strength retention of PMR-15 composites, and (2) to develop and evaluate test methods which can be used to assess the effects of isothermal elevated temperature aging on composite structural properties. Information presented herein should be useful for developing models to predict lifetimes for composite structures at elevated temperatures for the required periods of service demanded by the aircraft industries.

MATERIALS

The materials used in this study were the polyamide matrix polymer PMR-15 and three Hercules A-fibers, AU-4, AS-4, and AS-4G. The AU-4 fiber has an untreated surface. The AS-4 fiber was treated to introduce active sites on the fiber surface, and the third fiber, AS-4G, was surface treated and then the surfaces were sized with a water-soluble, epoxy-compatible sizing referred to here as the G-sizing. The three different types of fiber surfaces were expected to produce three different types of interfacial bonding.

The prepreg material was made by filament winding the fiber at 9 turns per inch for the AU-4 and AS-4 fibers and 18 turns per inch for the AS-4G fiber. The prepreg was then cut into 7.62- by 25.4-cm panels containing 12 or 9 plies to make unidirectional composites which were cured at 316 °C in a matched metal die mold in a heated press. The details of the processing

procedure are given in Reference 6. The 50 percent by weight of monomeric solution in methanol that was used to impregnate the wound fibers was made at Lewis as it was used. Also included herein are some data from other research work with different reinforcement fibers and PMR-15 matrix.

The composite specimens used in this study measured 76.2 by 25.4 by 3.6 cm or 76.2 by 25.4 by 2.3 mm. They were cut to these dimensions with a water-cooled diamond wheel. The specimens were aged in an air circulating oven with an air flow rate of 100 cm^3/min. The specimens were removed from the oven at regular intervals, and placed in a desiccator where they cooled to room temperature. The specimens were then weighed and their dimensions were measured. The composite coupons were then cut into appropriately sized specimens for ILSS, transverse flexure, and longitudinal flexure tests. The sizes were as follows:

ILSS = 19.7 by 5.08 by 3.3 mm

TFS = 25.4 by 5.08 by 3.3 mm

LFS = 76.2 by 5.08 by 3.3 mm

All flexure and ILSS tests were run in a Model 1125 Instron tensile test machine at a crosshead displacement rate of 0.127 cm/min. The tests were run as specified in ASTM D-790 and D-2344 with a flexural span-to-length ratio of 20 and an ILSS span-to-length ratio of 5. The failed specimens were examined using optical and scanning electron microscopy (SEM) to determine failure modes and indications of fiber/matrix bonding efficiencies. Flexural tests were also run on aged neat resin specimens measuring 76.2 by 5.1 by 3.1 mm or 76.2 by 5.1 by 6.2 mm.

RESULTS

Initial tests were run to corroborate the findings described in Reference 1 concerning the independence of the measured transverse flexural strength in respect to the test span. Test spans of 19, 38, and 63.5 mm were used in measuring the transverse flexural strengths of composites reinforced with the various graphite fibers. The results are presented in Table 1. The data in the table indicate that there were no differences in the TFS's when the test span was changed from 19 to 38 mm. When the test span was increased to 63.5 mm, a thickness-to-span ratio of 22.5 and 28.4 for the AS-4 and AU-4 reinforced composites, respectively, the measured TSF's decreased to about 71 and 76 percent for the same two materials. Also, the standard deviations of the measurements from the 19- and 38-mm span AS-4 composites were much larger than those of the other tests. The locations of the failures were very close to the center of the spans of the beams, and all failures appeared to be tensile failures.

Figure 1 shows the neat resin oxidative weight loss rates at 288 °C as a function of time. The rate decreases sharply during the first 100 hr of aging, and then decreases gradually until about 700 hr when it appears to stabilize at a constant rate of 0.03 mg/hr. It has been observed that a surface layer of degraded polymer grows during the aging of the PMR-15 resin.[5] Figure 2, taken from Reference 5, shows a plot of the measured layer as a function of aging time at 316 °C. Again, the growth of the layer is accelerated during the first 700 hr and then it appears to approach a constant value after this time.

Figure 3 contains data from room-temperature ILSS and transverse flexural tests of AU-4, AS-4, and AS-4G graphite-fiber-reinforced composites aged in air at 316 °C for different times. A comparison of the AU-4 and the AS-4 fiber-reinforced composite data indicates that the surface treatment improved the ILSS and the transverse flexure strength significantly. In

contrast, the G-sizing only improved the transverse flexural strength while the ILSS remained about the same. The ILSS values for all three composites remained approximately constant during the aging time that was studied.

The transverse flexural strengths for the AS-4G and AS-4 fiber-reinforced composites degraded at about the same rate, and appear to approach a constant value after about 800 hr of aging. The strength of the AU-4 reinforced composite decreased slightly to the same constant value as the other two composites. The transverse flexural moduli of some of the composites are shown in Figure 4 as a function of aging time at 288 and 316 °C. It is apparent that the surface degradation caused a significant loss in flexural moduli as the aging time increased. Increasing the aging temperature from 288 to 316 °C almost doubled the rate of decrease of the moduli.

Figure 5 shows data from three-point flexural tests of neat resin PMR-15 specimens that were aged for various times at 288 °C and then tested to failure at room temperature. The flexural strength of the neat resin increased initially because of additional crosslinking through oxygen atoms, and retained a significant percentage of its flexural strength during the 1000 hr of aging time. At this temperature, the observed surface layers of degraded polymer did not contain surface cracks to act as stress risers.

Composite specimens were examined after thermal exposure using optical microscopy. Figures 6 to 9 show the surfaces perpendicular to the unidirectional graphite reinforcement fibers in PMR-15 composites that were aged in air at 288 °C. There are surface cracks in the top and bottom surfaces that were resin rich as fabricated. No cracks were observed on the side surfaces because they were freshly cut after the aging was completed. The cracks are about 1/2 to 1 ply deep, which correspnds to a maximum of about approximately 0.17 mm. The relation between crack depth and aging time at 288 °C for Celion 6000/PMR-15 composites is shown in Figure 10.

DISCUSSION

The results from this study and the observations from Reference 5 can be interpreted to explain the microcracking phenomenon due to thermal cycling and also to composite mechanical properties degradation caused by aging at elevated temperatures. The degradation of the TFS with increased aging time appears to follow the growth of the surface layer of PMR-15 as described in Reference 5. Even though no surface cracks were observed in neat resin PMR-15 specimens aged at 288 or 316 °C, the layer thicknesses stabilized at about the same dimension as the surface layer in the 288 °C PMR-15 aging tests (Figs. 6 to 9). Possibly the presence of the reinforcement fibers enhanced the surface cracking, which was oriented parallel to the surface reinforcement, because of the residual stresses that developed from the matrix cure. The stresses are due to the coefficient of thermal expansion differences between the fiber and the matrix during cooldown, and the dimensional changes taking place in the expanding surface layer during aging.[5]

The presence of these cracks strongly suggests that fracture toughness theory may be used to model the degradation of the transverse flexural strength with aging time. The regression analysis relating crack depth to aging time, calculated from the data shown in Figure 10, yields an exponent of 1.5 for the resulting power equation. The degradation of the transverse flexural modulus appears to be similar to that of the TFS and is probably due to the effective decrease in specimen thickness as the cracks penetrate the specimen. These cracks are also sites for additional penetration of the composite by oxygen to cause further thermo-oxidative damage. This type of attack is shown for the neat resin in Figure 11.

Using just the ILSS and LFS test data to assess thermo-oxidative damage in polymer matrix composites can be misleading. ILSS tests measure the composite strength in the neutral

plane, with failure expected at the ends of the specimens. Results from Reference 5 indicate that no oxidative degradation occurs in this area of the composite unless the specimen cut surfaces have been oxidized. This is substantiated by the ILSS measurements presented herein. Also, the LFS does not change significantly during the first 800 hr, as shown in Table 1, because this property is dependent on the fiber strength, which does not change during aging. The LFS can decrease after longer times when the specimen thickness decreases; however, when the actual thickness is used in calculating the LFS, little change is observed. The TFS has been shown to be comparable to but significantly higher than the composite transverse strength.[1] In turn, the transverse tensile strength, being a matrix-dominated property, is related to shear and compressive strengths of composites which are also matrix dominated. These are properties which limit the use of these materials in structural applications.

CONCLUDING REMARKS

Except for the observed effect of the span dimension on the TFS, the results of this study are in agreement with those of Reference 1. In addition, this study shows that TFS measurements can be a valuable tool in studying the role of interfacial bonding and the effects of elevated temperature aging on the mechanical behavior of polymer matrix composite materials. The results also indicate the importance of understanding the mechanisms involved in polymer composite oxidation and the effects of these mechanisms on the mechanical properties retention of the material being tested. The main concern is with those properties that are sensitive to surface changes. Holes, machined surfaces, delaminations, and large cracks must be protected from exposure to the environment at elevated temperatures.

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TABLE 1.—TRANSVERSE FLEXURAL STRENGTH OF COMPOSITES WITH DIFFERENT SPANS

	AS-4/PMR-15			AU-4/PMR-15		
	Span, mm					
	19	38	76	19	38	76
Strength, MPa	110.3	106.7	75.7	49.9	34.4	37.7
Standard deviation	16.8	1.22	1.82	2.15	1.33	1.9
Fiber, vol%	56.9	56.9	56.9	60.4	60.4	60.4
Voids, vol%[a]	1.3	1.3	1.3	1.6	1.6	1.6

[a]Calculated.

TABLE 2.—MECHANICAL PROPERTIES OF AS-4 REINFORCED PMR-15 UNIDIRECTIONAL COMPOSITES AFTER AGING IN AIR AT 316 °C FOR 1200 HR

	D Composite			E Composite			G Composite		
	LFS, MPa	TFS, MPa	ILSS, MPa	LFS, MPa	FLS, MPa	ILSS, MPa	LPS, MPa	TFS, MPa	ILSS, MPa
Average	1235	24	70	1290	22	72	932	16	65
Standard deviation	84.0	3.0	9.3	66.0	1.1	6.2	125.0	3.2	5.96
Fiber, vol%	61.2	------	------	56.9	------	------	60.2	------	------
Voids, vol%	1.4	------	------	2.6	------	------	1.1	------	------

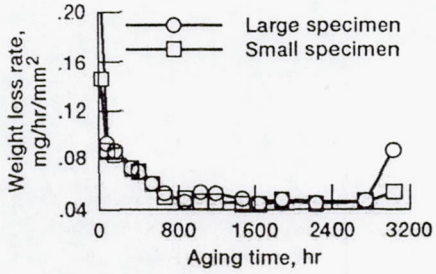

Figure 1.—Weight loss rate of PMR-15 aged in air at 288 °C.

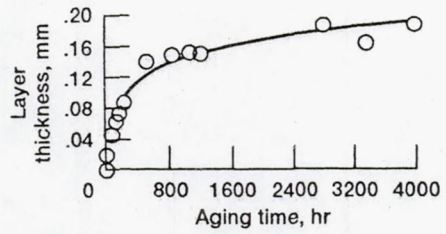

Figure 2.—PMR-15 surface layer thickness at 316 °C as a function of aging time.

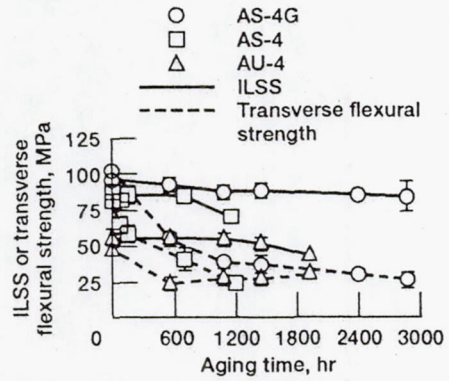

Figure 3.—Strengths of A-fiber composites with PMR-15 matrices as a function of surface treatment and aging time at 316 °C.

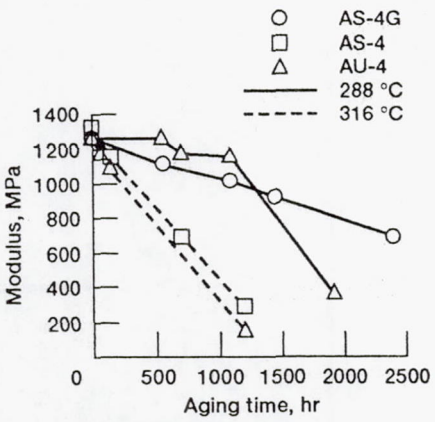

Figure 4.—Composite transverse flexural modulus as a function of aging time in air at 288 and 316 °C.

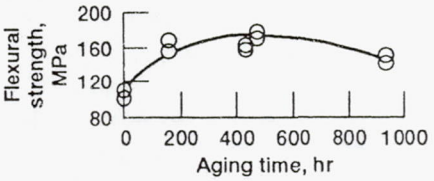

Figure 5.—Flexural strength of PMR-15 resin as a function of aging time at 288 °C.

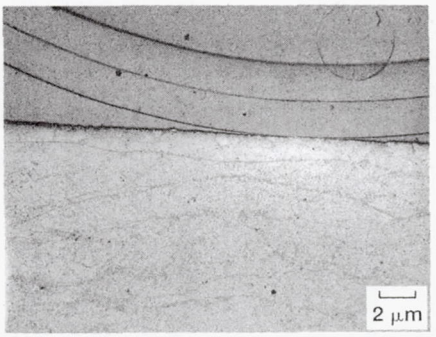

Figure 6.—AS4/PMR-15 composite aged for 1005 hrs in air at 288 °C.

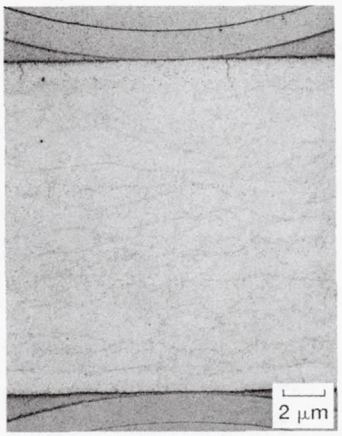

Figure 7.—AS4/PMR-15 composite aged for 1508 hrs in air at 288 °C.

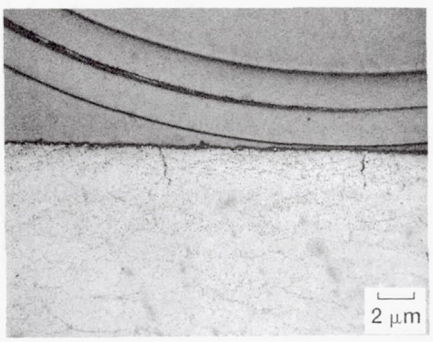

Figure 8.—AS4/PMR-15 composite aged for 2012 hrs in air at 288 °C.

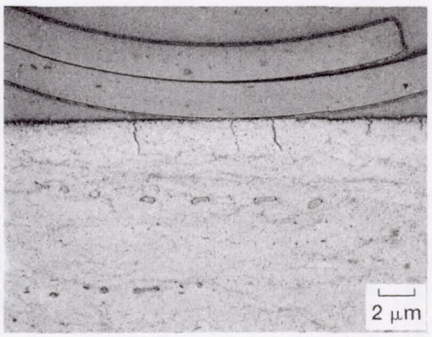

Figure 9.—AS4/PMR-15 composite aged for 2514 hrs in air at 288 °C.

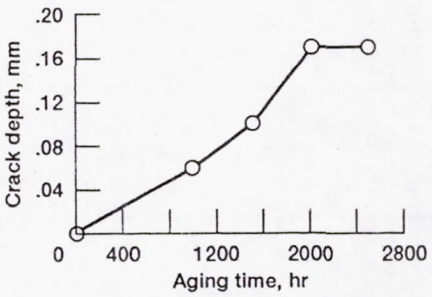

Figure 10.—Relation between crack depth and aging time for celion 6000/PMR-15 composites and aging time in air at 288 °C.

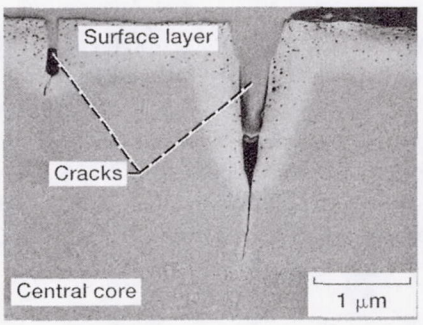

Figure 11.—PMR-15 resin aged in air at 343 °C.

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13. ABSTRACT ***(Maximum 200 words)***

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