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NASA Technical Memorandum 4608

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## Effect of Fiber Surface Modification on Composite Shear Properties

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September 1994

National Aeronautics and
Space Administration

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**Office of Management**

Scientific and Technical
Information Program

1994

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## Summary

Experiments were conducted to establish a correlation between the weight loss of a polyimide (PMR-15) matrix and graphite fibers and the in-plane shear properties of their unidirectional composites subjected to different isothermal aging times up to 1000 hr at 316 °C. The role of fiber surface treatment on the composite degradation during the thermo-oxidative aging was investigated by using A-4 graphite fibers with three surface modifications: untreated (AU-4), surface treated (AS-4), and surface treated and sized with an epoxy-compatible sizing (AS-4G). The weight loss of the matrix, fibers, and composites was determined during the aging. The effect of thermal aging was seen in all the fiber samples in terms of weight loss and reduction in fiber diameter. Calculated values of weight loss fluxes for different surfaces of rectangular unidirectional composite plates showed that the largest weight loss occurred at those cut surfaces where fibers were perpendicular to the surface. Consequently, the largest amount of damage was also noted on these cut surfaces. Optical observation of the neat matrix and composite plates subjected to different aging times revealed that the degradation (such as matrix microcracking and void growth) occurred in a thin surface layer near the specimen edges. The in-plane shear modulus of the composites was unaffected by the fiber surface treatment and the thermal aging. The shear strength of the composites with the untreated fibers was the lowest and it decreased with aging. A fracture surface examination of the composites with untreated fibers suggested that the weak interface allowed the oxidation reaction to proceed along the interface and thus expose the inner material to further oxidation. The results indicated that the fiber-matrix interface affected the composite degradation process during its thermal aging and that the weak interface accelerated the composite degradation.

## Introduction

The commercial availability of composite prepreg material based on a polyimide (PMR-15) has made it possible to design and fabricate fiber-reinforced polymer matrix composites for use in temperatures up to 316 °C, which is nearly twice the use temperature of epoxy-based composites. One of the areas still of vital concern to aerospace industries is the long-term durability and property retention capability of these composites when subjected to extended use at elevated temperatures.

Significant work has been done to quantify the degradation and understand the degradation mechanisms of the polyimide (PMR–15) matrix and its graphite fiber-reinforced composites during various thermal aging conditions (refs. 1 to 8). The matrix and fiber degradation during isothermal aging at elevated temperatures has been quantified by their weight loss (refs. 2 and 6 to 8). The optical observation of neat matrix plates subjected to various isothermal aging times revealed that the polymer degradation occurred in a thin surface layer that developed near the specimen edges and grew inward during thermal aging (ref. 7). The notable features observed in this surface layer were matrix cracks and voids. The surface layer had a different chemical composition compared with that of the bulk matrix. The major mechanisms associated with the matrix weight loss are believed to be the release of cyclopentadiene (a reaction volatile) followed by polymer oxidation resulting in the formation of the surface layer. Because of the compositional difference between the surface layer and the core matrix, there were residual tensile stresses induced during the thermal aging process. The matrix cracks in the surface layer are believed to be the result of these tensile stresses (ref. 7).

A comparison of the weight loss behavior of the resin, fiber, and composites during different aging times at

316 °C revealed that the weight loss of the fibers (Celion 6000) and the composite was very similar whereas the weight loss of the neat matrix resin was about four times higher (ref. 6). Based on the calculation of the surface weight loss fluxes for these composites, it was concluded that the fiber layer containing fibers parallel to the cut surfaces acts as a protective barrier for the resin whereas the fibers that were perpendicular to the cut surface allow cracks to grow inward into the composite and expose more resin and fiber surfaces to degradation. Therefore, in a fiber-reinforced composite plate, only two of the six exposed surfaces are significantly degraded during a prolonged exposure to high temperature (refs. 3 and 6).

The dependence of the thermo-oxidative stability (TOS) of polymer matrix composites on the reinforcing fibers has also been demonstrated (refs. 8 to 12). The earlier polyacetonitrile (PAN)-based fibers that contained a significant alkali content showed poor TOS. The sodium and potassium present on fiber surfaces as contaminants catalyzed the air oxidation of these fibers and thus reduced their TOS (refs. 10 to 12). The more recently produced carbon fibers have much less sodium content and, hence, much improved TOS (ref. 13). More recent studies have shown that the chemically bound nitrogen present in PAN-based carbon fibers also increased the susceptibility of the fibers to thermal oxidation. (ref. 13). Such a finding may suggest that the fiber surface condition will also influence the TOS of these composites.

The purpose of the current investigation was to determine the role of the fiber-matrix interface on the mechanical property degradation of graphite/PMR–15 composites as a result of their aging at elevated temperatures. Because the interface strongly influences the composite shear behavior (ref. 14), experiments were conducted to characterize the in-plane shear behavior of composites having different fiber surface modifications. The shear property data of these composites was correlated with the fracture surface observations made of the failed specimens. The weight loss measurements for the PMR-15, the graphite fibers, and composite plates were also made.

## Materials

The matrix material was PMR–15 and was obtained in the form of imidized molding powder from Dexter Composites. This powder was placed in a tight-fitting compression mold, was then heated at approximately 10 °C/min to 316 °C, and was cured at 316 °C for 2 hr. The cured sheets (approx 100 by 100 by 1.5 mm) were then postcured for 16 hr at 316 °C in an air-convection oven. The matrix material prepared in this manner had a glass transition temperature ($T_g$) of 335 °C.

The reinforcements were Hercules A-4 graphite fibers, classified as an intermediate-modulus PAN fiber. The fibers had three surface conditions: the first, designated AU-4, had no surface modification but came as is from the furnace. The second, designated AS-4, was surface treated with Hercules proprietary treatment. The third fiber, designated AS-4G, was surface treated and then was sized with a water-soluble, epoxy-compatible sizing.

The unidirectional composite prepregs were fabricated from the three batches of graphite fibers (AU-4, AS-4, and AS-4G) by a filament winding technique. The fibers were wound at a pitch of 3.54 turns/cm. The AS-4G fiber was supplied in tows containing 6000 or 12 000 strands/tow so the winding pitch at times was 7.1 tows/cm or 3.53 tows/cm. The AS-4G fiber was "boardy" and contained a greater amount of sizing than is normally used for graphite fibers (0.5 to 1.0 wt %, ref. 15). The boardy nature made winding and impregnation more difficult than with the other two fibers. Impregnation was done using a 50-wt% methanol solution of the monomers. The solution was prepared as it was used. The sheets of prepreg were cut and stacked into bundles containing 12 plies. The stacks were imidized for 1 hr at 204 °C and were then cured for 2 hr at 316 °C. All the composite panels were given a standing air postcure at 316 °C for 16 hr.

The fiber volume fractions of the composite panels were determined from the following procedure. Small composite samples were machined from the cured composite panels and their weight $w_c$ determined. The resin was digested from these samples by placing them in concentrated sulfuric acid in a glass beaker. The beaker was heated until the acid turned black. The mixture cooled. At this point, 30 percent hydrogen peroxide solution was added by drops to the acid until it turned clear again. The process was repeated until all the matrix was dissolved. The fibers were removed by decanting the mixture through a glass filter. The fibers were washed first in distilled water and then in acetone after which the filaments were dried for 15 min at 177 °C in an air-convection oven. The fiber weight $w_f$ was measured. The weight of the resin is given by

$$w_r = w_c - w_f \tag{1}$$

The density of the composite samples was determined by weighing them in air and in isopropyl alcohol. The density $\rho_c$ of the composite was calculated from

$$\rho_c = \frac{w_a}{w_a - w_i} \times \rho_i \tag{2}$$

where

| | |
|---|---|
| $w_a$ | weight of composite in air, g |
| $w_i$ | weight of composite in isopropyl alcohol, g |
| $\rho_i$ | density of isopropyl alcohol, 0.786 g/cm$^3$ |

The fiber volume fraction (in percent) was calculated from

$$V_f = \left(1 - \frac{w_r}{w_c}\right) \frac{\rho_c}{\rho_f} \times 100 \qquad (3)$$

where $\rho_f$ is the density of the fiber (1.76 g/cm$^3$).

The void volume fraction (in percent) was calculated from

$$V_v = 100 - \rho_c \left(\frac{w_r}{\rho_r} + \frac{w_f}{\rho_f}\right) \qquad (4)$$

where

$w_r$ weight content of resin, $\frac{W_r}{W_c} \times 100$

$w_f$ weight content of fiber, $\frac{W_f}{W_c} \times 100$

$\rho_r$ density of resin, 1.32 g/cm$^3$

The average values of the fiber and void volume fractions calculated from this procedure are listed in table I.

The fiber-matrix interface shear strength of the unaged composite materials was assumed to be correlated to the interlaminar shear strength. Such a correlation was shown to exist for graphite-epoxy composite materials (ref. 14). Therefore, the interlaminar shear strengths of these composites were taken as a qualitative measure of their interface shear strength. The interlaminar shear strength values are listed in table II. Based on these data, the AU-4/PMR-15 has the lowest interface shear strength, and the AS-4G/PMR-15 has the highest.

TABLE II.—INTERLAMINAR SHEAR STRENGTHS OF UNAGED COMPOSITES

| Composite | | |
|---|---|---|
| AU-4/PMR-15 | AS-4/PMR-15 | AS-4G/PMR-15 |
| Interlaminar shear strength, MPa | | |
| 55.7 | 89.1 | 96.9 |

## Experiment

The thermal aging of composite specimens can yield different results depending on the specimen surface area-to-volume ratio. For example, individually aged, short test samples (i.e., large surface area-to-volume ratio) exhibit a large reduction in strength values after aging whereas the interior regions of a large square panel exhibit only minor property degradation (ref. 3). Because the mechanical property loss occurring in the interior of a large composite plate is more representative of the behavior of a large structural panel, the thermal aging was conducted on the entire composite plate. After the aging cycle was completed, the test specimens were machined from the interior of the plates.

### Isothermal Aging and Weight Loss

All the thermal aging was done at 316 °C in air-convection ovens with an air change rate of 100 cm$^3$/min. The airflow was horizontal across the width of the oven and across the molded surfaces of the laminates.

For the aging of the neat PMR-15 matrix material, strips approximately 75 by 6.5 by 1.5 mm were cut and baked in an oven at 122 °C for 24 hr. Moisture absorption and desorption studies have shown that this length of time is satisfactory to allow the release of all moisture from the matrix plates (ref. 16). The strips were stored in a desiccator, weighed individually, and then placed in an air-convection oven for aging. The strips were removed from the oven at several time intervals, placed in a desiccator to cool to room temperature, weighed, and then placed again in the oven to continue the aging. The matrix samples were aged for about 2000 hr at 316 °C.

The fiber weight loss during the thermal aging was determined by placing samples from each fiber type in about 2.5-cm-diameter coils and completely enclosing them in small mesh stainless steel screen boxes to prevent the loss of fiber fragments inside the oven. The fibers were first baked in an air-convection oven at 218 °C for 24 hr to remove any entrapped moisture. The fiber samples were weighed and then placed inside the air-convection ovens to age at 316 °C. After each aging time, the screen boxes were placed in a desiccator and allowed to cool, after which the fiber samples were weighed.

TABLE I.—FIBER AND VOID VOLUME FRACTIONS AFTER DIFFERENT AGING TIMES

| Aging time,hr | Composite | | | | | |
|---|---|---|---|---|---|---|
| | AU–4/PMR–15 | | AS–4/PMR–15 | | AS–4G/PMR–15 | |
| | Volume fraction, percent | | | | | |
| | Fiber, $V_f$ | Void, $V_v$ | Fiber, $V_f$ | Void, $V_v$ | Fiber, $V_f$ | Void, $V_v$ |
| 0 | 59.5 | 1.19 | 57.6 | 0.84 | 61.0 | 1.03 |
| 240 | 58.4 | 1.03 | 58.8 | 1.39 | 62.2 | 0 |
| 500 | 57.3 | 0.88 | 56.4 | 1.56 | 55.3 | 0.19 |
| 1000 | 57.3 | 1.09 | 58.9 | 1.65 | 54.8 | 0.68 |

The fibers were placed in the screen box and put back in the oven to continue the aging. Three samples were tested for each fiber type.

Unidirectional composite plates (12 plies), approximately 250 by 80 by 3.6 mm, were baked in an oven at 122 °C for 24 hr to remove any entrapped moisture. The composite plates were placed in a desiccator and allowed to cool to room temperature. The initial weight $w_o$ of the plates was measured and then they were subjected to different thermal aging periods. The plates were positioned in the ovens in special holders. Four aging times were used: 0 (unaged), 240, 500 and 1000 hr. For each aging period, a different composite plate was used. After the aging was completed, the plates were allowed to cool to room temperature in a desiccator before they were weighed again. After the completion of each aging period, the composite plates were also examined with an optical microscope to visually detect any damage.

### In-Plane Shear Tests

The Iosipescu shear tests were performed to characterize the in-plane shear behavior of the unidirectional composites. In comparison with other in-plane shear characterization methods (10° off-axis testing and the $[\pm 45]_S$ tension), the Iosipescu shear test method has yielded more reliable results (refs. 14 and 17). The Iosipescu specimen dimensions and the testing procedure are outlined in reference 12. Cross-ply glass/epoxy end tabs were applied to all the specimens to prevent crushing at the loading ends. All loading was conducted in a displacement-controlled mode on a closed-loop Instron (model 4505) testing machine. The loading rate was 1.0 mm/min. Each specimen was instrumented with a two-element strain gage (Measurement Group No. EA-13-062TV-350) bonded to one face at midregion between the notch roots so that the gages were oriented at +45° or –45° to the horizontal (or vertical) axis of the specimen. In this configuration, one of the gages measured the tensile component of the normal strain and the other, the compressive component.

### Photomicrographs and Fracture Surface Morphology

At the end of each aging period, small samples from the edges of each plate were cut, polished, and examined under an optical microscope to detect microcracking caused by the thermal aging.

In all the Iosipescu shear tests, the failure occurred because the cracks emanating from the roots of the machined notches propagated parallel to the fibers in either direction. To expose the fracture surfaces, a diamond-coated wheel saw was used to cut the specimens in a direction perpendicular to the crack. The cracked surfaces were carefully pulled apart and examined using scanning electron microscopy (SEM).

## Results and Discussion

This section presents results on the degradation during aging at 316 °C of PMR-15, A-4 graphite fibers with three surface modifications, and their composites. The degradation of the polymer and the fibers was monitored by their weight loss and by the physical changes (such as cracking and void growth) that occurred during aging. The composite degradation due to thermal aging was monitored by the weight loss measurements, optical observation of the damage growth induced during the aging, change in the in-plane shear modulus and strength, and fracture surface morphologies.

### Aging of PMR-15 Matrix

For the weight loss measurements of PMR-15 matrix, specimens approximately 75 by 6.5 by 1.5 mm were isothermally aged in an air-convection oven. The weight loss was monitored on 15 matrix samples. The average weight loss and weight loss rates obtained from these specimens are shown in figure 1. Because the matrix weight loss depends on the specimen surface area (ref. 7), the weight loss and weight loss rate data are divided by the average specimen area (fig. 1).

Some of the major observations noted with regard to the matrix degradation during the aging follow: The matrix weight loss occurred rapidly during the first 200 hr. The weight loss rate decreased rapidly with continued aging. Accompanying the weight loss was the formation of a thin surface layer (fig. 2). The exposed sharp edges of the rectangular specimens were easily degraded because of the locally high ratio of surface area to volume at the edges. The surface layer also grew rapidly during the initial 200 hr. With continued aging, void formation occurred and cracks developed in this surface layer. The surface layer is the result of polymer oxidation occurring along the exposed surfaces. That there were higher oxygen-to-carbon ratios in the surface layer compared with those in the core

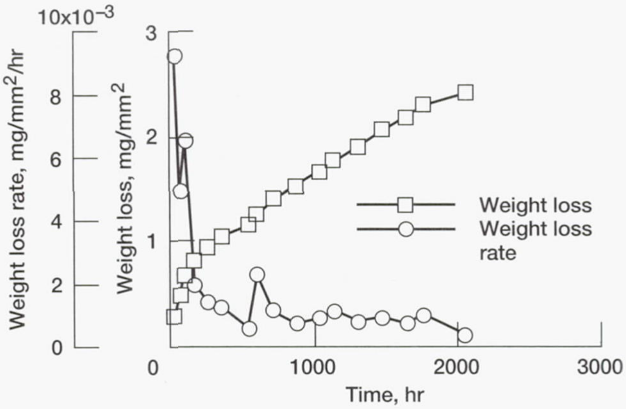

Figure 1.—Weight loss and weight loss rate during aging of PMR-15 matrix specimens at 316 °C. The matrix weight loss occurs rapidly during the first 200 hr.

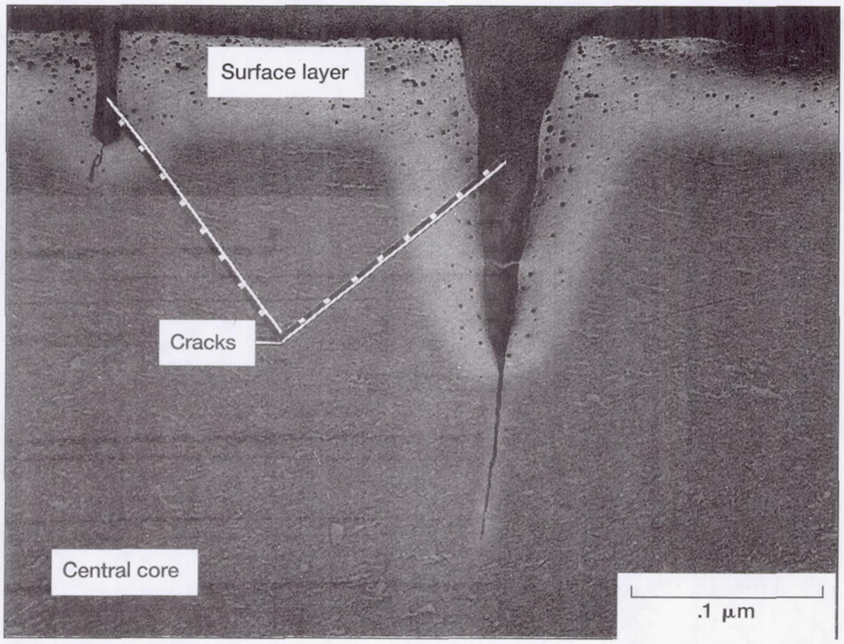

Figure 2.—Surface layer degradation in PMR-15 sample after aging at 316 °C for 362 hr.

material was verified (ref. 7). The oxidized polymer in the surface layer was more brittle than the unoxidized polymer in the interior of the specimen. The cracks in this surface layer were attributed to the interaction between voids that form in the surface layer and the inability of the surface layer to absorb the extensional thermal strains induced by the core polymer (unoxidized). The oxidized surface layer also acted as a protective coating for the interior polymer and thus inhibited the polymer oxidation process with continued aging.

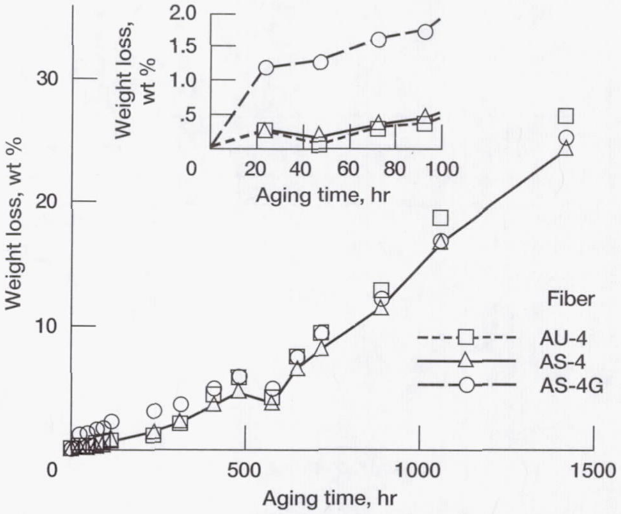

Figure 3.—Percent weight loss of three types of fibers during aging at 316 °C. Figure insert shows details of weight loss for first 100 hr.

## Aging of Graphite Fibers

The percent weight loss during the aging of the three fiber types is plotted in figure 3. Each data point is an average of weight losses from the three specimens. The weight loss data are shown as percentages because the specimen surface-area-to-volume ratios are approximately the same for the three types of fibers. The results showed that the weight loss behavior of AU-4 and AS-4 fibers was similar over the aging time studied. For the first 24 hr of aging, the weight loss rate of the AS-4G fibers was higher than that of the other two fibers (see the insert in fig. 3). Within 300 hr of aging, the weight loss rate of AS-4G fibers approached that of the other two fibers. After 300 hr of aging, all three fiber types exhibited similar weight loss behavior. The initial increased weight loss rate of AS-4G fibers is believed to be caused by the oxidation of the epoxy-compatible sizing present on these fibers. According to the weight loss curves, most of the sizing on the AS-4G fibers was removed within 24 hr of aging. After the removal of this sizing, the AS-4G fiber behavior was similar to the other two fibers. A point to note here is that in comparison with the weight loss in the AU-4 and the AS-4 fibers, the AS-4G fibers lost more than 1.5wt % within the first 100 hr. This result may suggest that the AS-4G fibers used in this study contain more than 1.5wt % of the epoxy-compatible sizing, an unusually high amount of sizing for graphite fibers. Usually the amount is less than 1 percent (ref. 15).

## Aging of Unidirectional Composite Plates

The degradation of unidirectional composites with three fiber-matrix interface conditions was monitored by the weight loss, optical observation of the composite degradation (microcracking), in-plane shear behavior, and shear failure modes at definite time intervals during the aging period at 316 °C.

***Weight loss***.—Weight loss data recorded at three aging times at 316 °C are listed in table III and are plotted in figure 4. These are the total weight losses and include the weight loss occurring from all sides of the composite plate. Earlier studies showed that the composite weight loss behavior depends not only on the specimen size, but also on the specimen geometry (ref. 18).

An analysis of weight loss fluxes was conducted to determine the effective weight loss values for different composite surfaces (see fig. 5). The effective weight loss values were calculated from the TOS data measured with three sizes of composite plates fabricated from the three fiber types. The composite plate sizes were chosen to produce different specimen surface area-to-volume ratios. The weight losses of the three plates can be converted to weight loss per unit area by

$$k_1A_1 + k_2A_2 + k_3A_3 = \Delta w \tag{5}$$

where

$k_i$ weight loss per unit area of composite surface i
$A_i$ surface area of composite surface i
$\Delta w$ weight loss of specimen

TABLE III. —WEIGHT LOSS OF COMPOSITES AFTER AGING AT 316 °C

| Composite | Aging time, hr | | |
|---|---|---|---|
| | 240 | 500 | 1000 |
| | Weight loss, wt % | | |
| AU-4/PMR-15 | 0.60 | 1.27 | 1.70 |
| AS-4/PMR-15 | 0.59 | 1.22 | 1.74 |
| AS-4G/PMR-15 | 1.22 | 2.07 | 6.73 |

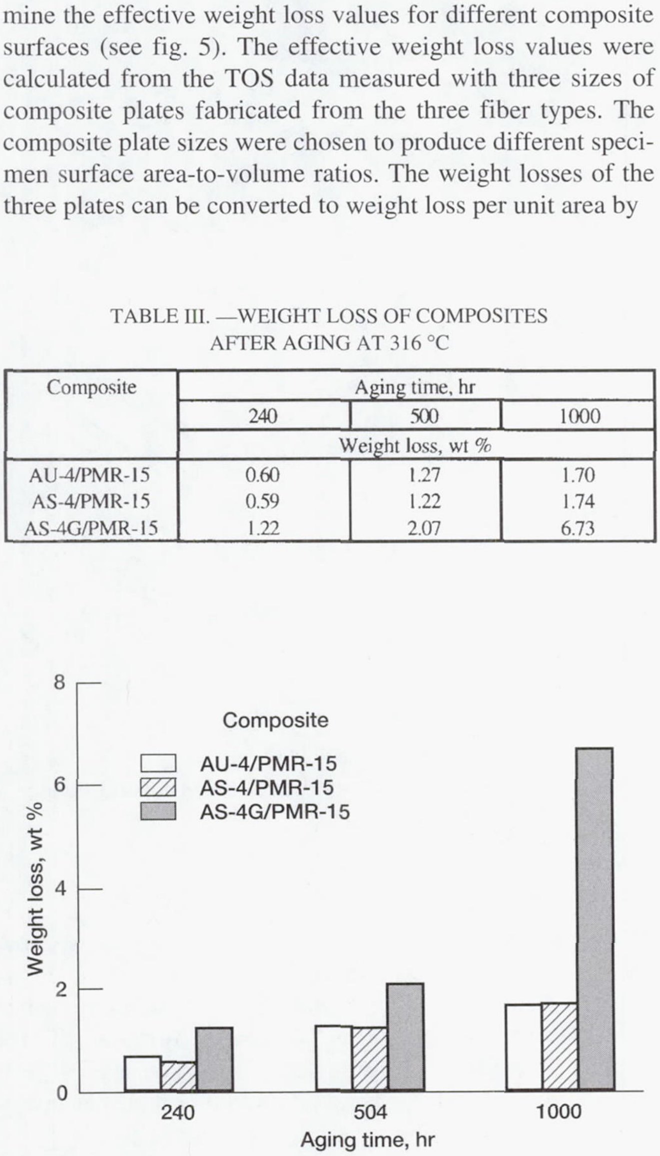

Figure 4.—Percent weight loss of composite panels subjected to three aging times at 316 °C.

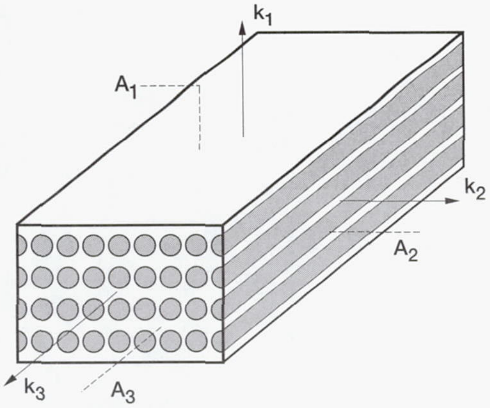

Figure 5.—Different composite surfaces.

For each fiber type, three composite plates with different surface area-to-volume ratios were aged at 316 °C, and the weight loss data were measured at aging times of 0, 240, 500, and 1000 hr. Equation (5) was employed to set up three simultaneous equations for each aging time and for each fiber. These equations were solved to obtain the values of $k_1$, $k_2$, and $k_3$ for each fiber at a particular aging time at 316 °C. These values are listed in table IV and are plotted in figure 6. Based on the results of this analysis, we concluded that the smallest weight loss occurred from the molded surfaces (surface 1 in fig. 5) and the largest weight loss occurred from those cut surfaces where fibers were perpendicular to the surface (surface 3 in fig. 5). This result should be expected because surface 1 is resin rich and acts as a shield for the inner layers by blocking the oxygen penetration from surface 1 to the inner portion of the composite. Therefore, we conclude that most of the weight loss occurring from surface 1 was the result of oxidation of the resin itself. It is possible that for longer aging times, when matrix cracks develop on the surface 1 and provide a path for the oxygen to penetrate into the core, the $k_1$ values may also increase. With regard to the weight loss from surface 3, where the fibers are exposed and are perpendicular to the surface, the thermal degradation could propagate to the inner regions along the fiber-matrix interface, thus producing the largest weight loss flux for surface 3. Consequently, the composite degradation also occurred predominantly on these surfaces.

By comparing the weight loss flux for the different composite systems, the following observation can be made from figure 6. The weight loss $k_1$ occurring from the molded surface

TABLE IV.—WEIGHT LOSS FLUX VALUES CALCULATED

| Composite | Aging time, hrs | Weight loss per unit area of composite surface $k_i$, g/cm $^2$ | | |
|---|---|---|---|---|
| | | $k_1$ | $k_2$ | $k_3$ |
| AU-4/PMR-15 | 240 | $1.59\times10^{-3}$ | $1.16\times10^{-3}$ | $0.277\times10^{-3}$ |
| | 500 | 4.32 | 0.31 | 5.19 |
| | 1000 | 12.0 | 2.02 | 31.0 |
| AS-4/PMR-15 | 240 | $3.10\times10^{-3}$ | $0.70\times10^{-3}$ | $13.7\times10^{-3}$ |
| | 500 | 4.89 | 4.06 | 44.2 |
| | 1000 | 11.2 | 1.56 | 28.7 |
| AS-4G/PMR-15 | 240 | $2.26\times10^{-3}$ | $5.53\times10^{-3}$ | $1.81\times10^{-3}$ |
| | 500 | 4.68 | 0.90 | 6.23 |
| | 1000 | 11.7 | 27.5 | 131 |

(surface 1 in fig. 5) was about the same for the three composite systems (fig. 6(a)). This should be expected because the molded surfaces are resin rich, and the weight losses from them should be primarily caused by the oxidation of resin. With regard to the weight loss flux $k_2$ from surface 2, although the AU-4/PMR-15 and the AS-4/PMR-15 composite plates yielded similar results, the AS-4G/PMR-15 composite plates exhibited a much greater weight loss flux after 500 hr of aging. The oxidation of the excess epoxy-compatible sizing present on the AS-4G fibers was responsible for the increased weight loss flux.

***Microcracking of composites during the thermal aging.***—From each composite panel aged at different times, small specimens were machined from the edges to detect the extent of microcracking caused by the thermal aging. The micrographs of the specimens showing surface 3 (fig. 5) are presented in figures 7 to 9. In all the cases, the composite degradation occurred near the specimen edges. As the aging time increased, a distinct layer of degraded matrix formed at the uncut surfaces and grew inward between the reinforcement fibers. As the degraded matrix layer grew inward, matrix cracks developed perpendicular to the uncut surfaces. The AU-4/PMR-15 specimens had the greatest number of these matrix cracks (fig. 7). At 1000 hr of aging time, the matrix cracks in AU-4/PMR-15 specimens were about 1 to 2 plies deep and about 0.5 to 0.75 mm apart. In comparison, in the AS-4/PMR-15 specimens, the crack depth of the degraded surface layer and the extent of matrix cracking (average crack spacing) were much less (fig. 8). In the AS-4G/PMR-15 specimens, as the aging time increased, void formation occurred near the uncut edges. With aging time, the voids grew in size as well as in concentration. The matrix cracks emanated from these voids and grew inward. Figure 9 shows a dark surface layer produced by the high concentration and coalescence of voids. It is believed that the epoxy-compatible sizing layer present on the AS-4G fibers does not mix with the PMR-15 matrix during the processing of the composites. This layer could have been easily destroyed during the aging (since the $T_g$ of commonly used epoxies is only about 135 °C), thus leaving behind a space between the fiber and the PMR-15 matrix. The thermal degradation proceeded

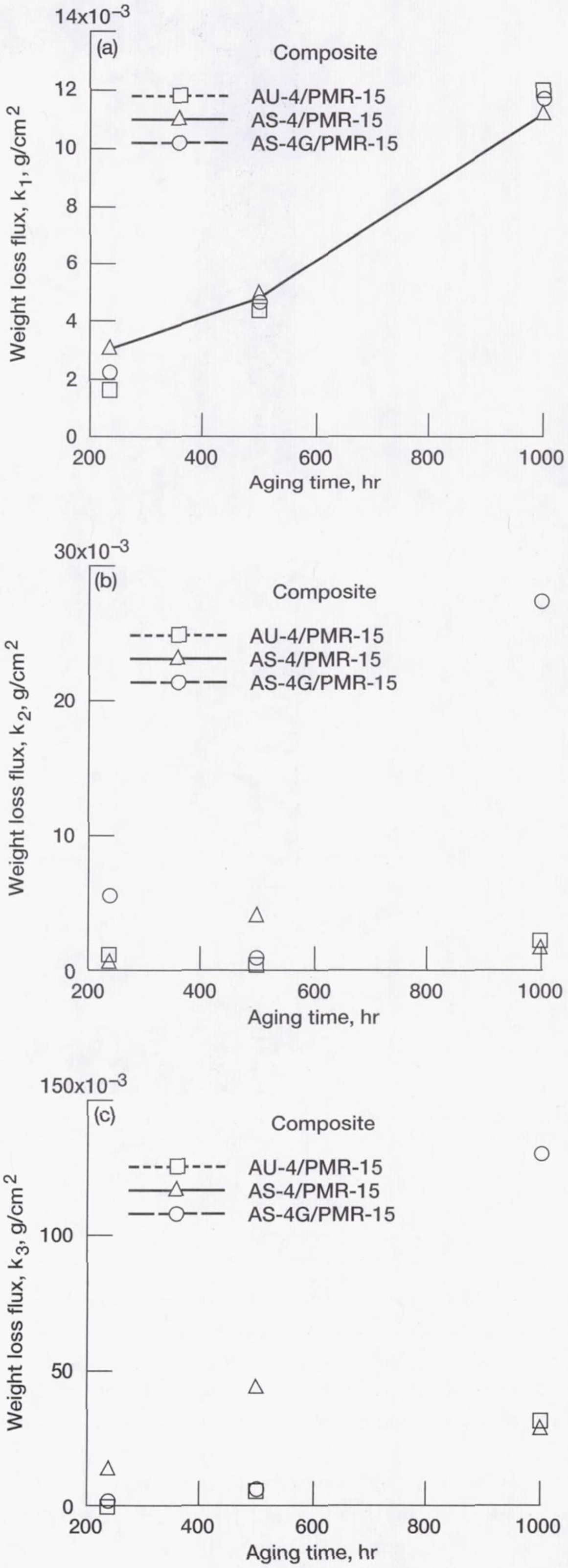

Figure 6.—Composite weight loss fluxes for different composite surfaces (see fig. 5). Aging temperature, 316 °C. (a) Surface 1. (b) Surface 2. (c) Surface 3.

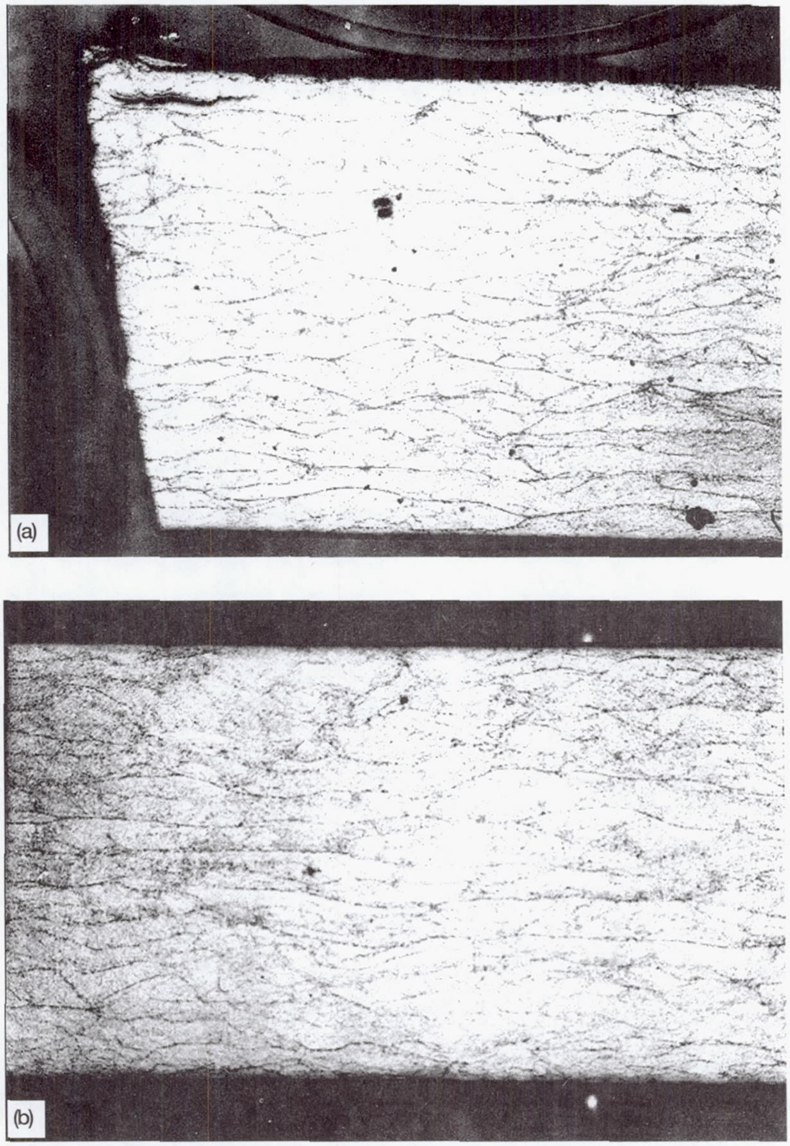

Figure 7.—Damage on cut surface of AU-4/PMR-15 specimens aged for different times at 316 °C. (a) 0 hr, unaged. (b) 240 hr.

along this space and produced void formation in the PMR-15 matrix. A similar growth of voids was also noted in the aging of neat PMR-15 matrix specimens (ref. 7). Thus, the matrix cracks that occurred in the surface layer suggest that matrix oxidation causes the embrittlement of the matrix in the damaged surface layer. This matrix layer is believed to have different mechanical properties (such as higher stiffness and lower failure strain) from the underlying bulk composite material. As a result, tensile stresses may have developed in the damaged layer during the thermal aging process. The brittle matrix layer was not able to sustain these stresses, and therefore, the matrix cracking occurred.

A close examination of the matrix cracks that occurred during the composite aging showed that these cracks propagate along the fiber-matrix interface (fig. 10). The resin rich areas between the fibers showed relatively less damage. The comparison of the damage in the AU-4/PMR-15 and AS-4/PMR-15 composites suggests that the larger amount of interfacial damage observed in the untreated fiber composites (AU-4/PMR-15) is attributed to the weak fiber-matrix interface. In the case of AS-4G/PMR-15 composites, the epoxy-compatible sizing on the fibers, which has a much lower glass transition temperature (compared with the bulk PMR-15 matrix), was easily destroyed during the aging, thus producing large gaps around the fibers.

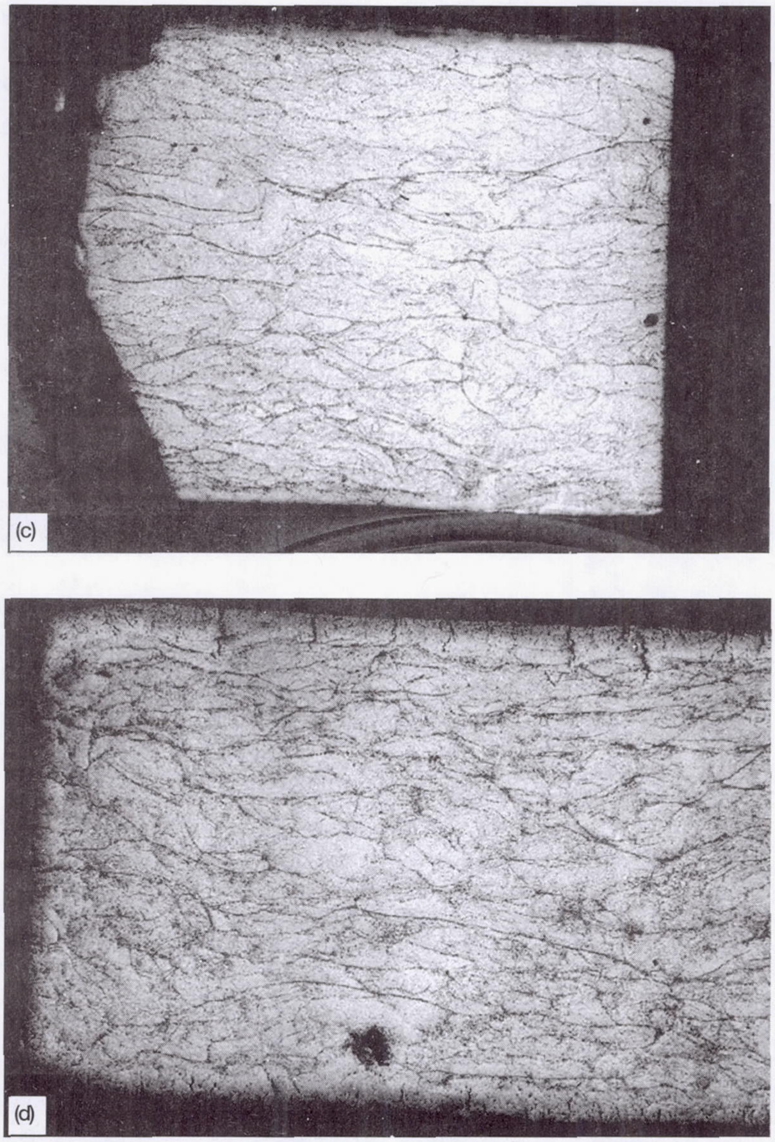

Figure 7.—Concluded. (c) 500 hr. (d) 1000 hr.

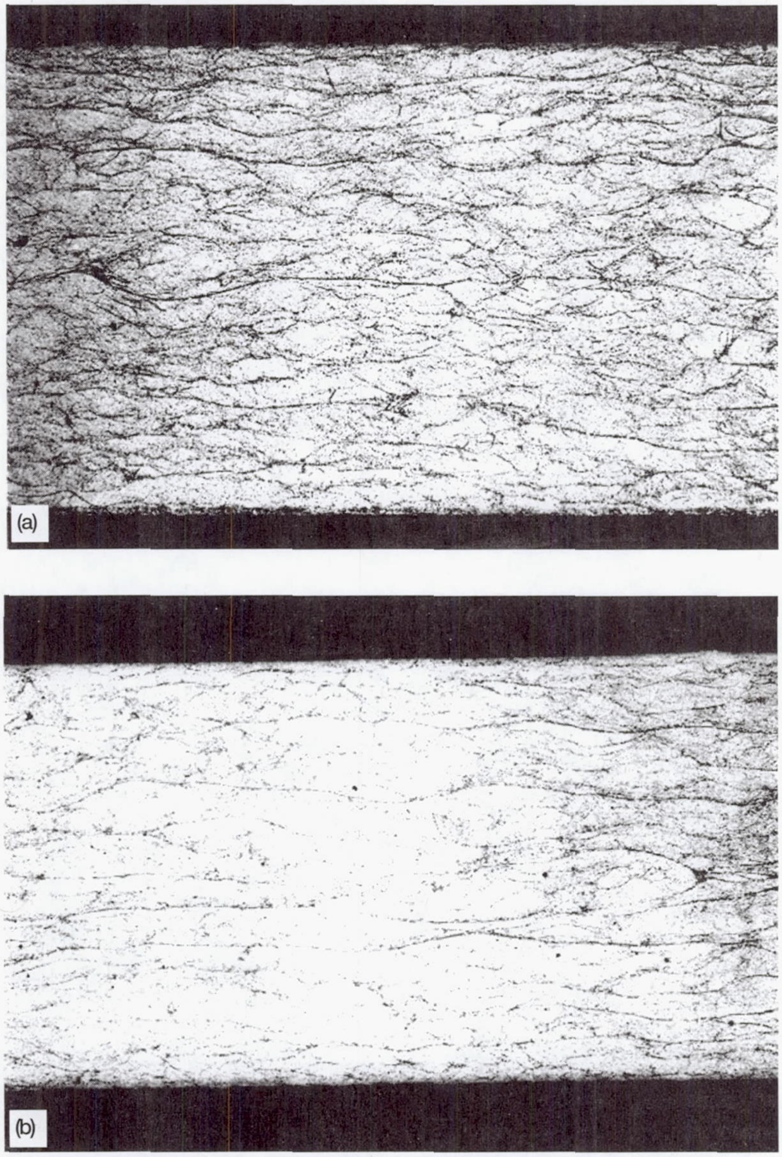

Figure 8.—Damage on cut surface of AS-4/PMR-15 specimens aged for different times at 316 °C. (a) 0 hr, unaged. (b) 240 hr.

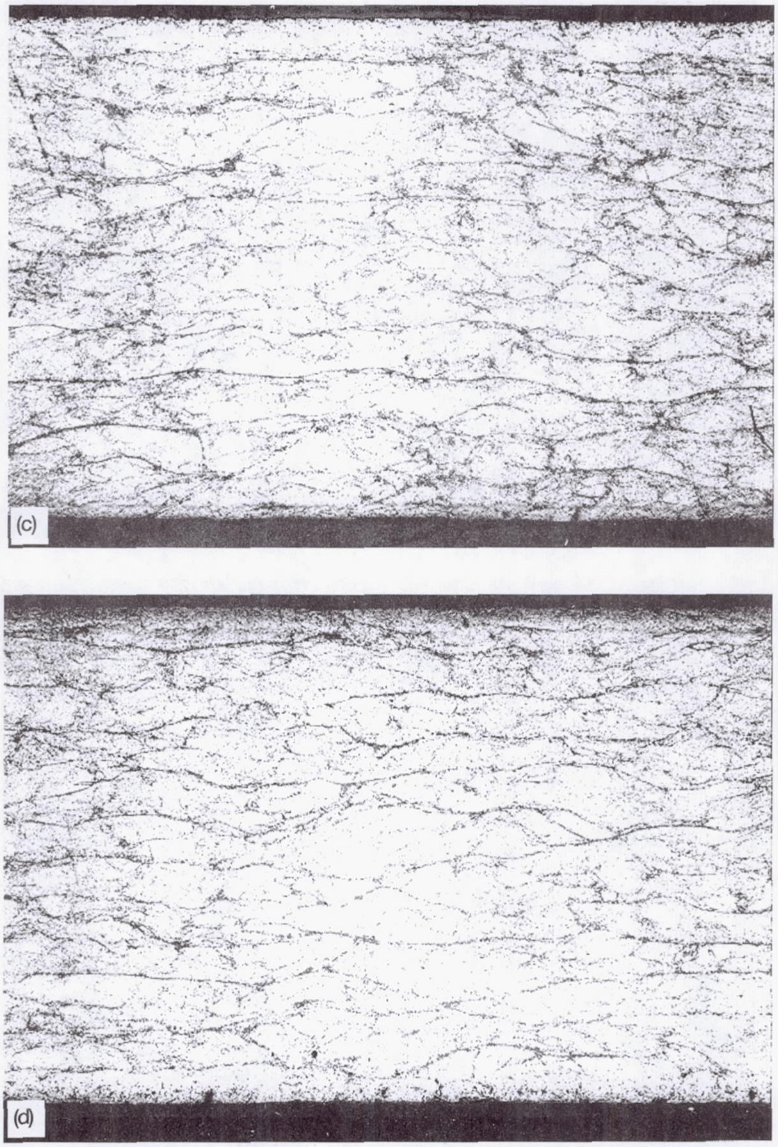

Figure 8.—Concluded. (c) 500 hr. (d) 1000 hr.

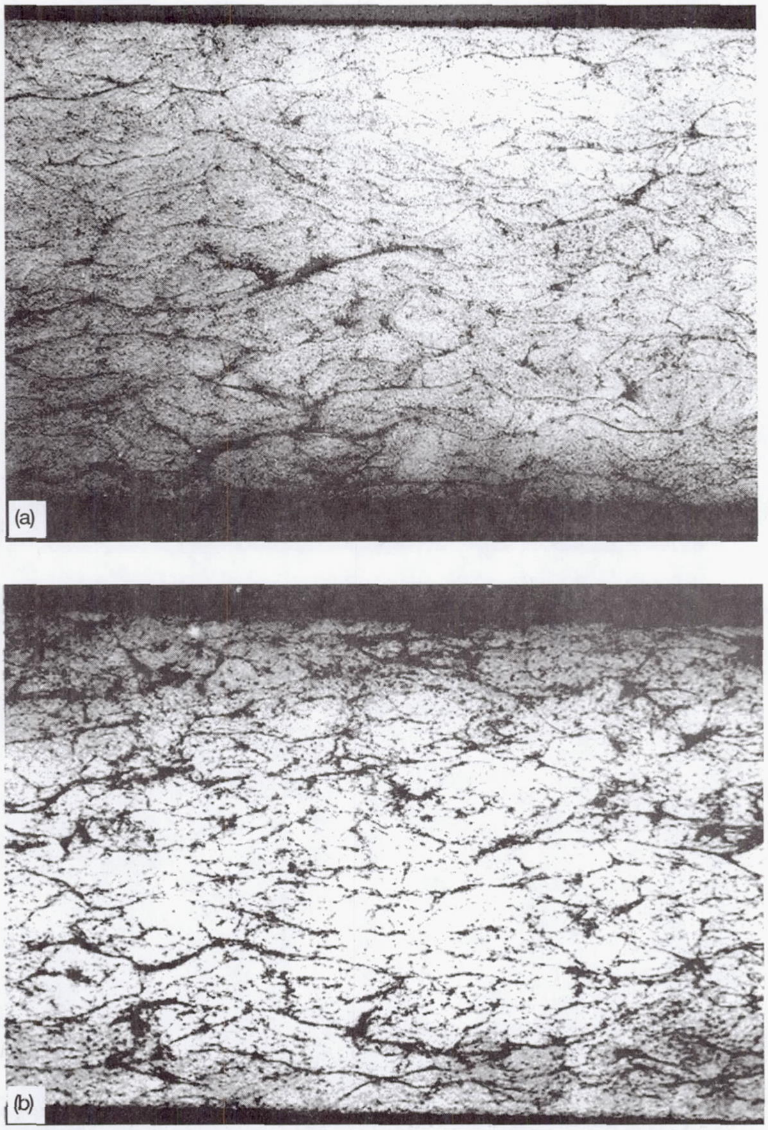

Figure 9.—Damage on cut surface of AS-4G/PMR-15 specimens aged for different times at 316 °C. (a) 0 hr, unaged. (b) 240 hr.

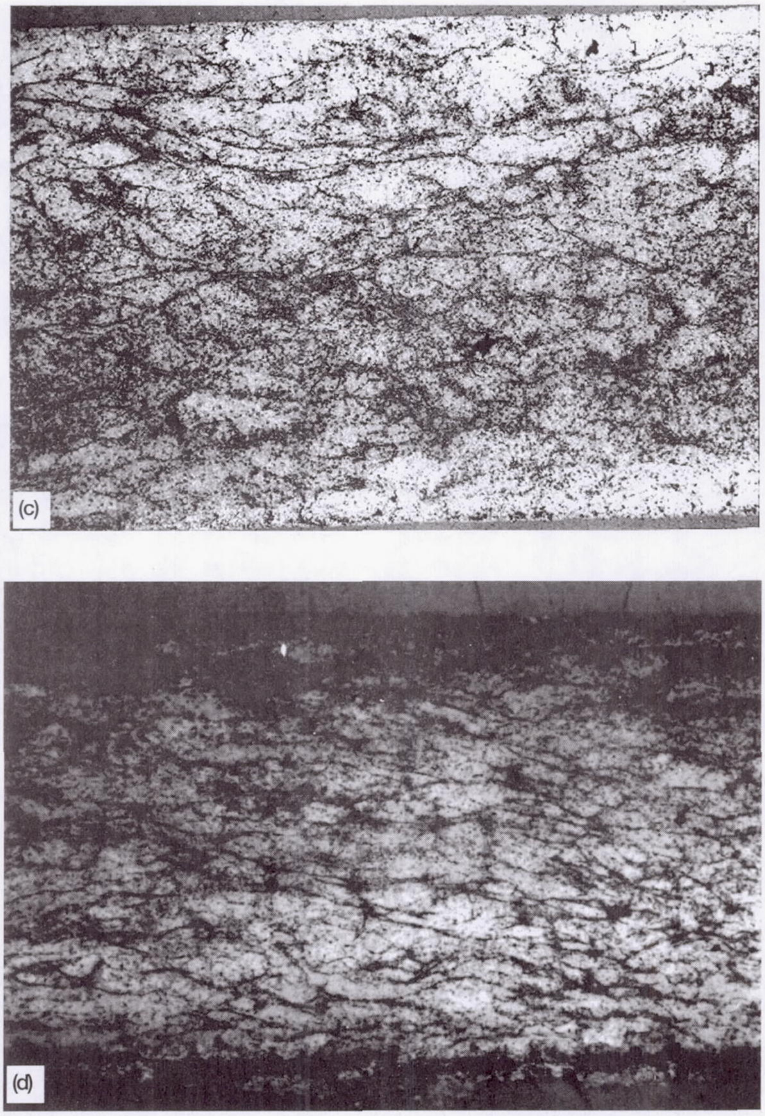

Figure 9.—Concluded. (c) 500 hr. (d) 1000 hr.

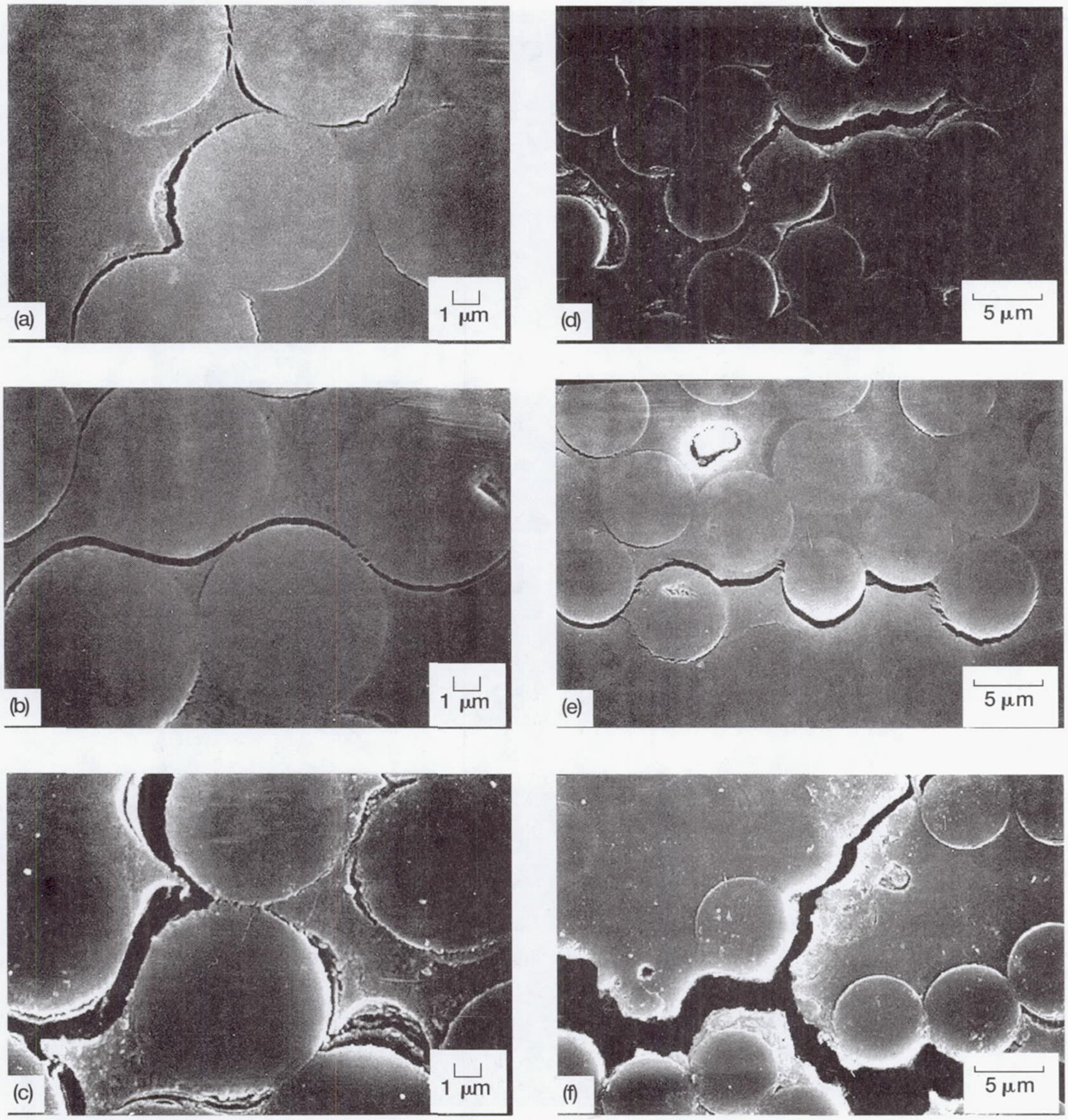

Figure 10.—Matrix cracks in composite specimens after aging for 1000 hr at 316 °C. (a) AU-4/PMR-15, x6000. (b) AS-4/PMR-15, x6000. (c) AS-4G/PMR-15, x6000. (d) AU-4/PMR-15, x2700. (e) AS-4/PMR-15, x3000. (f) AS-4G/PMR-15, x3000.

***In-plane shear properties of composites***.—The in-plane shear modulus and shear strength values obtained from the Iosipescu shear test methods for the three composite materials aged at different times at 316 °C are shown in figures 11 and 12, respectively. Each data point is an average of six specimens. Within the experimental scatter, the difference among the shear moduli of all three composite materials at the four aging times is statistically insignificant. The insensitivity of the fiber surface treatment on the composite elastic properties (e.g., modulus) has been shown for other composite systems (ref. 14). In the earlier part of the loading (from which the modulus is calculated), the interface does not fail and, hence, does not play a significant role. The interface properties become important only at the higher loads when damage is initiated. The modulus also seems to be unaffected by the aging times. The reason is that in all the composite panels subjected to the thermal aging, the damage was confined near the edges of the panels. The shear specimens were machined from the interior regions of these aged panels where the thermal damage was minimal. Therefore, the thermal aging did not produce any significant change in the shear modulus of these composites.

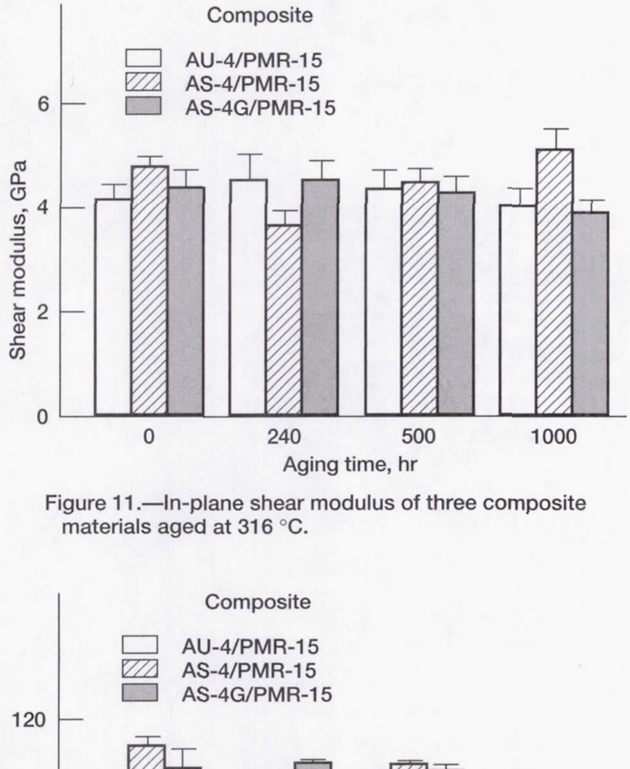

Figure 11.—In-plane shear modulus of three composite materials aged at 316 °C.

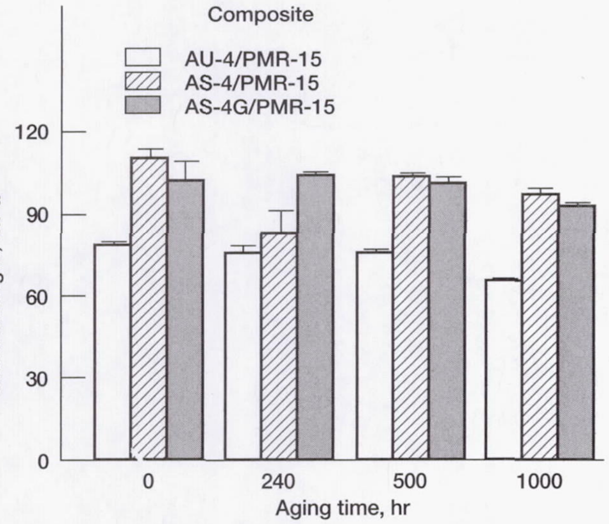

Figure 12.—In-plane shear strength of three composite materials aged at 316 °C.

The in-plane shear strengths for the AS-4/PMR-15 and AS-4G/PMR-15 composites are higher than that of AU-4/PMR-15 at all aging times (fig. 12). Although the shear strengths of the AS-4/PMR-15 and AS-4G/PMR-15 specimens show no trend as a function of aging time, the AU-4/PMR-15 specimens show a decrease in strength with aging. As mentioned earlier in the Experiment section, the shear specimens were machined from the interior regions of the composite panels where no significant thermal degradation was detected; thus, it is not surprising that the thermal aging had an insignificant effect on the shear strength of composites having surface-modified fibers (AS-4 and AS-4G). However, in the case of a relatively thin composite with untreated fibers (AU-4), the weak fiber-matrix interface may have provided a path for the oxidation reactions, thus exposing the interior regions of the composite to degradation. The decrease in the shear strength of the AU-4/PMR-15 composites is attributed to the degradation of the interior regions of the composite. The evidence of this degradation is also noted from the fracture surfaces of the failed specimens (discussed in the following section).

***Fracture surface morphology***.—In all the Iosipescu shear tests, the failure was caused by the cracks that emanated from the roots of the machined notches. These cracks propagated parallel to the fibers in either direction towards the end tabs. A diamond-coated wheel saw was used to cut representative failed specimens from each of the three groups of composites subjected to different aging periods. The specimens were carefully cut in a direction perpendicular to the crack to expose the cracked surfaces. These cracked surfaces were examined using the scanning electron microscopy (SEM). The SEM photographs of these specimens are shown in figures 13 to 15. In the AU-4/PMR-15 specimens, the crack propagated almost entirely along the fiber-matrix interface (fig. 13). The fibers are lying loosely and the fiber surfaces are completely devoid of matrix material. Also, until 500 hr of aging, there was no significant difference in the fracture surface morphologies as a function of aging time. However, after 1000 hr of aging time, some fiber fracture was also noted. We believe that the weak interface in the AU-4/PMR-15 composites may not have provided an effective shield against oxidation and, thus, the untreated AU-4 fibers may have been degraded during the aging. Note that the shear strength of the AU-4/PMR-15 specimens also decreased substantially after 1000 hr of aging (see fig. 12). Significant interfacial failure was also noted in the fracture surfaces of composites with surface modified fibers (AS-4 and AS-4G, figs. 14 and 15). However, in comparison with the AU-4/PMR-15, the extent of the interfacial failure was much less in the AS-4/PMR-15 and AS-4G/PMR-15 specimens. The fibers on the fracture surfaces are still held together by the matrix

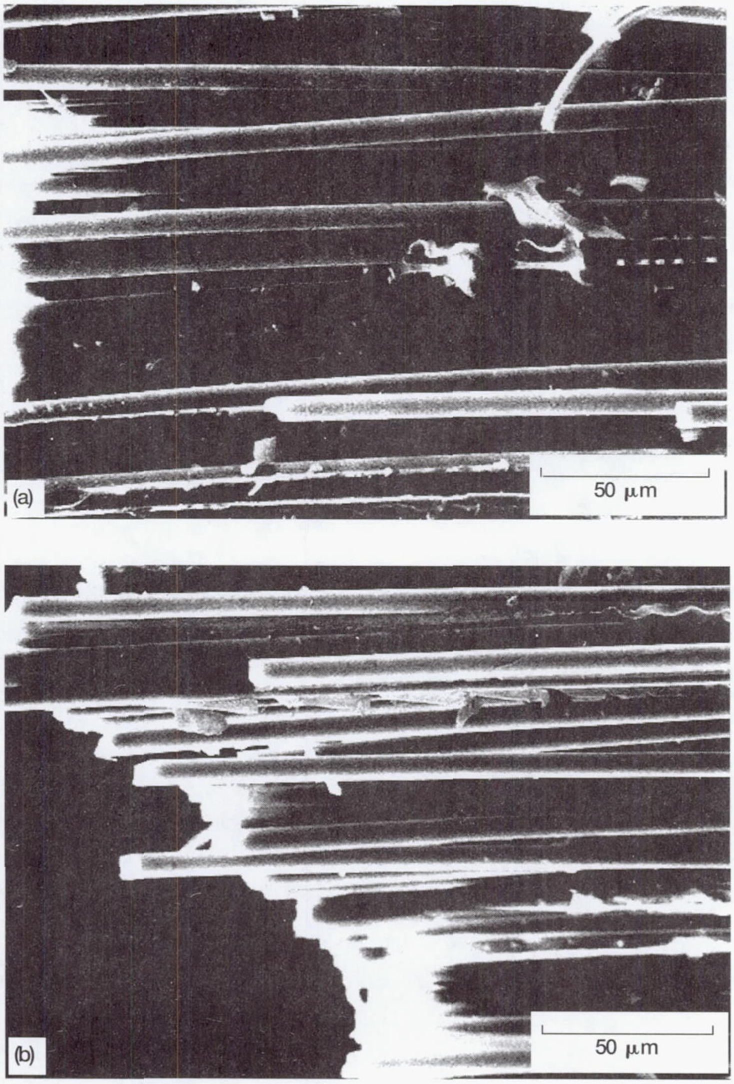

Figure 13.—Effect of aging at 316 °C on fracture surfaces of Iosipescu shear specimens from AU-4/PMR-15 composites. (a) 0 hr, unaged. (b) 240 hr.

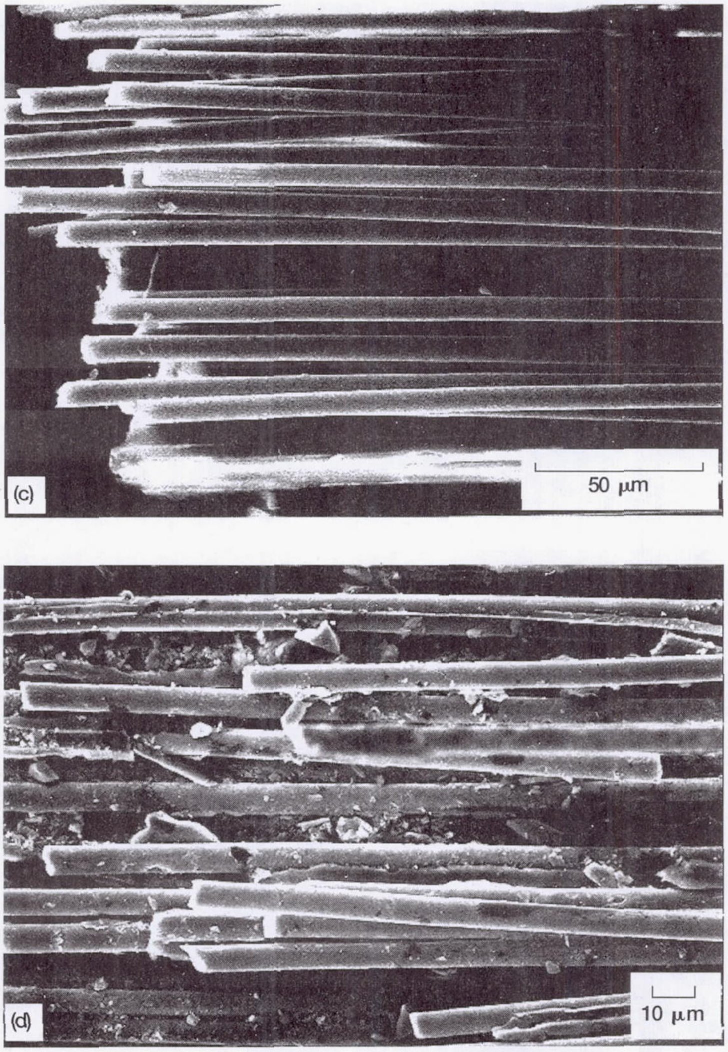

Figure 13.—Concluded. (c) 500 hr. (d) 1000 hr.

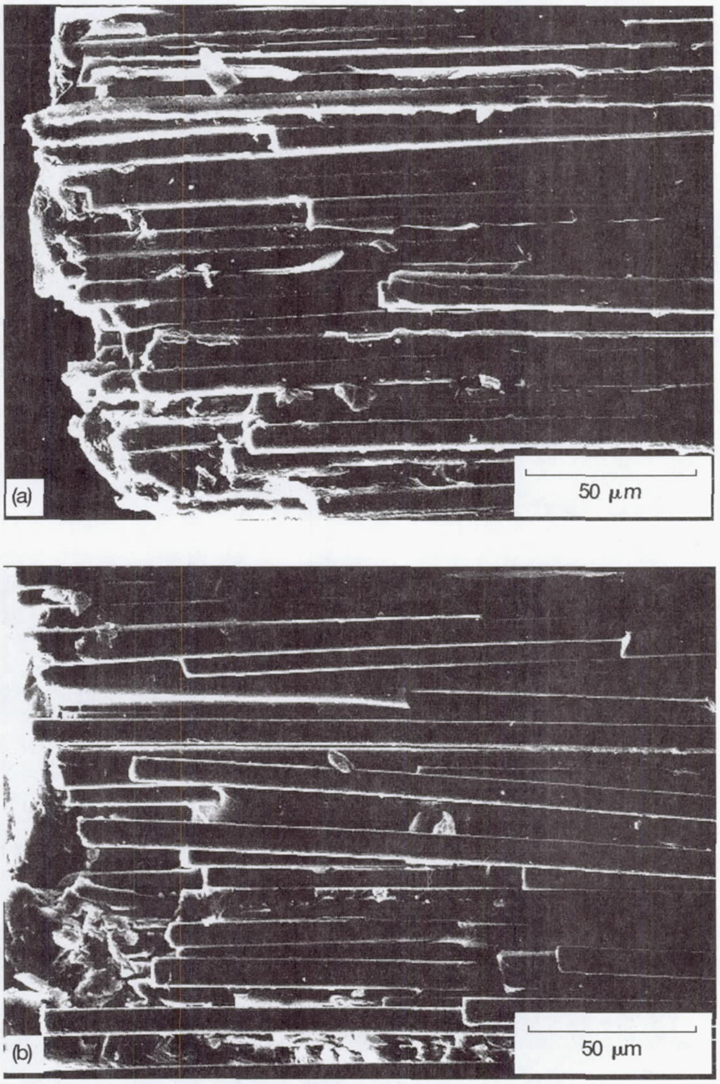

Figure 14.—Effect of aging at 316 °C on fracture surfaces of Iosipescu shear specimens from AS-4/PMR-15 composites. (a) 0 hr, unaged. (b) 240 hr.

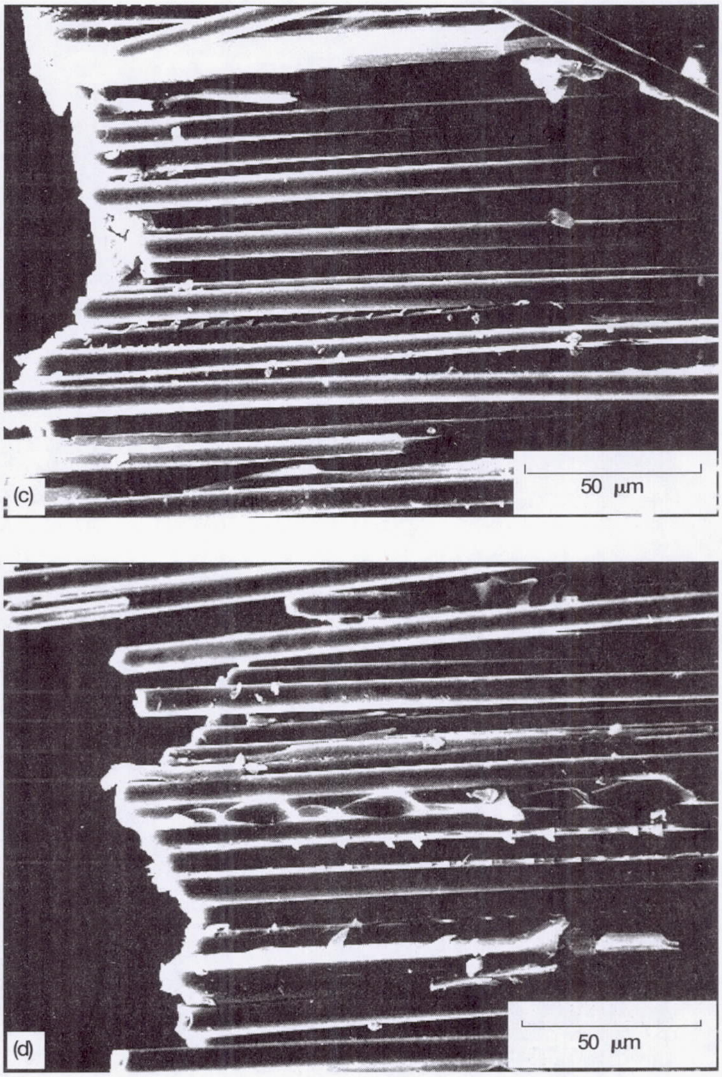

Figure 14.—Concluded. (c) 500 hr. (d) 1000 hr.

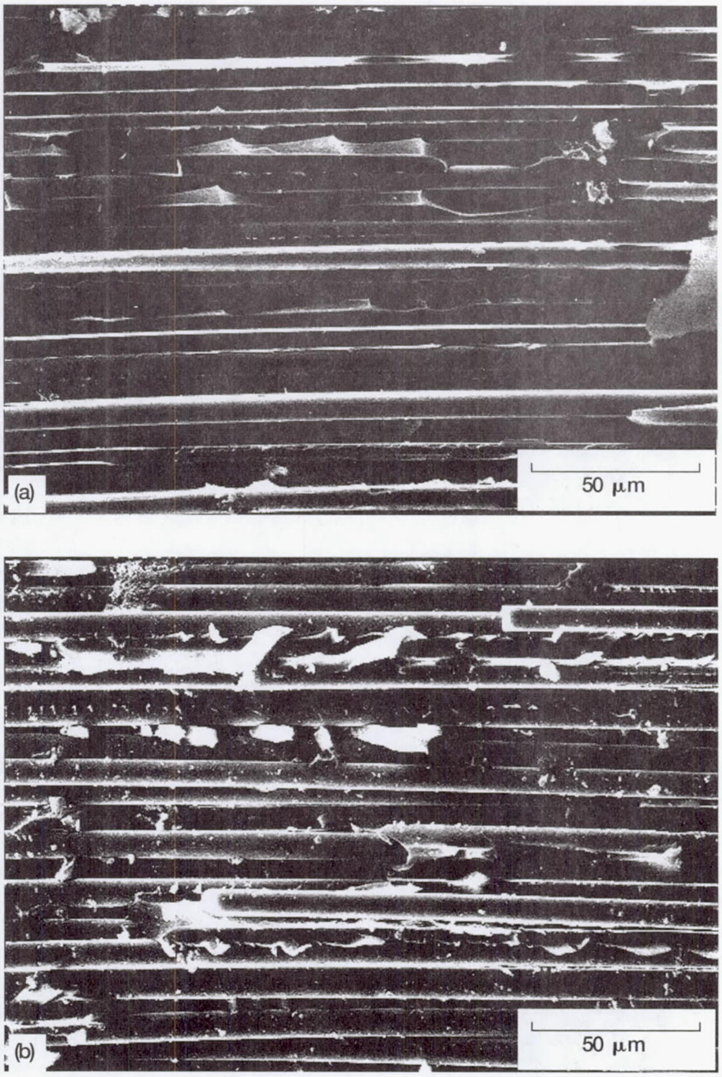

Figure 15.—Effect of aging at 316 °C on fracture surfaces of Iosipescu shear specimens from AS-4G/PMR-15 composites. (a) 0 hr, unaged. (b) 240 hr.

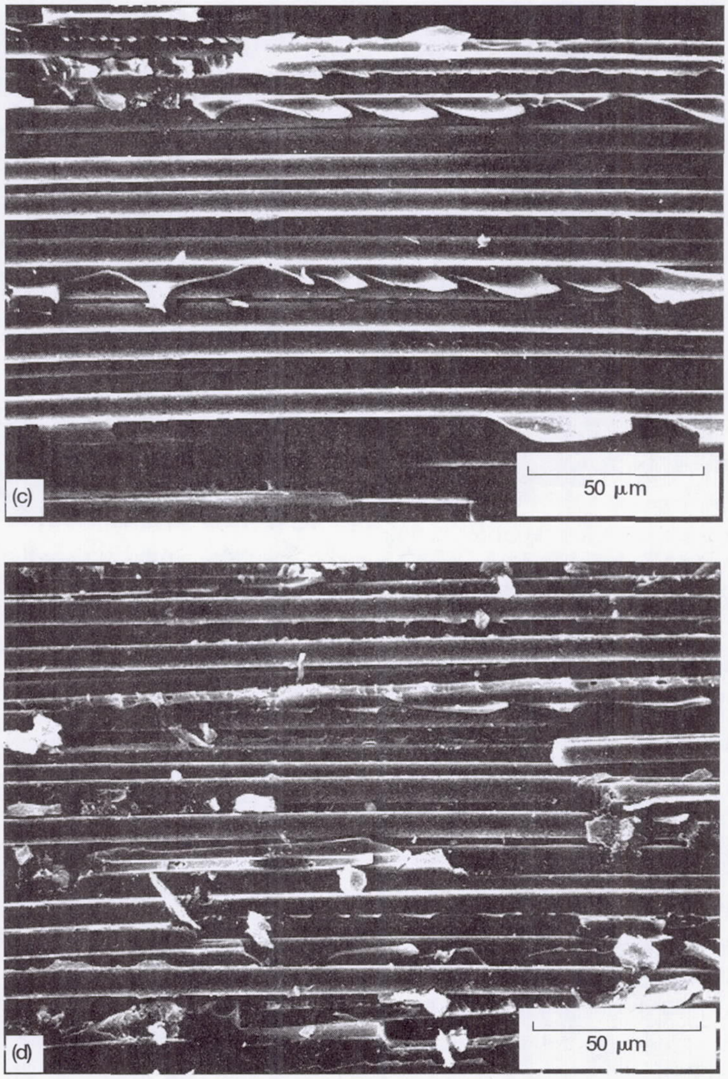

Figure 15.—Concluded. (c) 500 hr. (d) 1000 hr.

material. The fracture surfaces of these composites (AS-4/PMR-15 and AS-4G/PMR-15) had similar features at all the aging times (figs. 14 and 15). These observations are consistent with the variation of shear strength for different aging times (i.e., the shear strengths of AS-4/PMR-15 and AS-4G/PMR-15 were similar and they were not sigificantly affected by the aging times).

## Conclusions

An experimental study was conducted to determine the degradation of PMR-15 matrix, the untreated (AU-4) and surface-modified (AS-4 and AS-4G) graphite fibers, and their composites during their aging for times up to 1000 hr at 316 °C. The degradation was characterized by weight loss, damage growth in the neat resin and composite specimens, in-plane shear properties of composites, and fracture surface morphologies of fractured composite specimens.

The aging of neat PMR-15 specimens produced a rapid weight loss during the first 200 hr. Accompanying the weight loss was the formation of a thin surface layer that grew in thickness with the thermal aging. Significant void formation and matrix cracks also occurred in the surface layer. The cracks in this surface layer are attributed to the interaction among the voids that form in the surface layer and the inability of the surface layer to absorb the extensional thermal strains induced by the core polymer (unoxidized) material.

All three fiber types lost a significant amount of weight during aging at 316 °C. These fibers lost about 25 percent of their weight during the 1400 hr of aging. For the first 300 hr, the AS-4G fibers lost weight more rapidly than the AU-4 and AS-4 fibers. This rapid weight loss was attributed to the oxidation of the lower glass transition temperature $T_g$ sizing present on the AS-4G fibers. After 300 hr, all three fiber types exhibited similar weight loss behavior.

The weight loss flux analysis of composite plates revealed that the smallest weight loss occurred from the molded surfaces and the largest weight loss occurred from those cut surfaces where fibers were perpendicular to the cut surface. Consequently, the composite degradation also occurred predominantly on these cut surfaces. The calculated weight loss fluxes for the cut surfaces were much higher for the AS-4G/PMR-15 composites after 500 hr. The oxidation of the excess resin layer present in the AS-4G fiber was the reason for this behavior.

The damage that occurred during the aging of composite plates was confined to a thin surface layer and was in the form of matrix microcracking. Because the matrix microcracking progressed along the fiber-matrix interface, we concluded that the interface is an important element in determining the extent of surface damage. The composites with the untreated fibers (AU-4) had the largest amount of matrix microcracking in the surface layer. The composites with surface-treated fibers (AS-4) showed the least amount of surface damage. The void formation seen in the composites with surface-treated and coated fibers (AS-4G) was attributed to the oxidation of the excess epoxy-compatible layer present on the AS-4 fibers.

The fiber surface treatment and the aging time had an insignificant effect on the in-plane shear modulus. With regard to the shear strength, the composites with surface-modified fibers yielded a higher shear strength, and in these composites the thermal aging did not cause any measurable degradation in the shear strength. However, the shear strength of composites containing the untreated fibers decreased with thermal aging. The shear strength data correlates with the fracture surface observations of the failed specimens. The fracture surface of AU-4/PMR-15 specimens aged for 1000 hr showed significant fiber damage, which suggested that the weak interface in these composites allowed the oxidation reactions to proceed along the interface, thus causing the fiber degradation.

The results of this study suggested that the interface played a role in determining the thermo-oxidative stability of the composites. The AU-4/PMR-15 composites in which fibers were untreated are expected to perform poorly in an elevated temperature environment. Although the shear properties of the AS-4/PMR-15 and the AS-4G/PMR-15 composites were similar, their weight loss behavior suggests that the AS-4/PMR-15 has the best thermo-oxidative stability.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, July 12, 1994

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## REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*

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| **1. AGENCY USE ONLY** (*Leave blank*) | **2. REPORT DATE**<br>September 1994 | **3. REPORT TYPE AND DATES COVERED**<br>Technical Memorandum |

**4. TITLE AND SUBTITLE**

Thermo-Oxidative Stability of Graphite/PMR-15 Composites: Effect of Fiber Surface Modification on Composite Shear Properties

**5. FUNDING NUMBERS**

WU–510–01–50

**6. AUTHOR(S)**

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**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

**8. PERFORMING ORGANIZATION REPORT NUMBER**

E–8953

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

NASA TM–4608

**11. SUPPLEMENTARY NOTES**

Prepared for the International Conference on Composites Engineering, New Orleans, Louisiana, August 28-31, 1994. Madhu S. Madhukar, University of Tennessee, Knoxville, Tennessee 37996; Kenneth J. Bowles, NASA Lewis Research Center; and Demetrios S. Papadopolous, Case Western Reserve University, Cleveland, Ohio 44106. Responsible person, Kenneth J. Bowles, organization code 5150, (216) 433-3197

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

Unclassified - Unlimited
Subject Category 26

**12b. DISTRIBUTION CODE**

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

Experiments were conducted to establish a correlation between the weight loss of a polyimide (PMR-15) matrix and graphite fibers and the in-plane shear properties of their unidirectional composites subjected to different isothermal aging times up to 1000 hr at 316 °C. The role of fiber surface treatment on the composite degradation during the thermo-oxidative aging was investigated by using A-4 graphite fibers with three surface modifications: untreated (AU-4), surface treated (AS-4), and surface treated and sized with an epoxy-compatible sizing (AS-4G). The weight loss of the matrix, fibers, and composites was determined during the aging. The effect of thermal aging was seen in all the fiber samples in terms of weight loss and reduction in fiber diameter. Calculated values of weight loss fluxes for different surfaces of rectangular unidirectional composite plates showed that the largest weight loss occurred at those cut surfaces where fibers were perpendicular to the surface. Consequently, the largest amount of damage was also noted on these cut surfaces. Optical observation of the neat matrix and composite plates subjected to different aging times revealed that the degradation (such as matrix microcracking and void growth) occurred in a thin surface layer near the specimen edges. The in-plane shear modulus of the composites was unaffected by the fiber surface treatment and the thermal aging. The shear strength of the composites with the untreated fibers was the lowest and it decreased with aging. A fracture surface examination of the composites with untreated fibers suggested that the weak interface allowed the oxidation reaction to proceed along the interface and thus expose the inner material to further oxidation. The results indicated that the fiber-matrix interface affected the composite degradation process during its thermal aging and that the weak interface accelerated the composite degradation.

**14. SUBJECT TERMS**

Composites; Fibers; Carbon; Shear properties; Thermo-oxidative stability; Surfaces; Interfaces; Iosipescu test

**15. NUMBER OF PAGES**

29

**16. PRICE CODE**

A03

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|---|---|---|---|
| **17. SECURITY CLASSIFICATION OF REPORT**<br>Unclassified | **18. SECURITY CLASSIFICATION OF THIS PAGE**<br>Unclassified | **19. SECURITY CLASSIFICATION OF ABSTRACT**<br>Unclassified | **20. LIMITATION OF ABSTRACT** |