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INTRODUCTION

Previous work[1-5] has shown a definite geometric dependence of the thermo-oxidative stability (TOS) of polyimide composites reinforced with graphite fibers. This dependence is attributed to the cut edges, which enhance the oxidative attack over these surfaces. The normally exposed resin-coated surfaces generally oxidize at a slower rate than the cut edges. In the search for new, high-temperature matrix resins for use above the temperature limits currently established for the widely used PMR–15 polyimide matrix resin, the research materials that are produced are usually only available in small quantities. Therefore, small test specimens must be used to measure the mechanical properties and to determine the thermal stabilities of these new materials. As the specimen size decreases, the ratio of edge surface to total surface can increase so that the aging weight loss data reflect the TOS of the edges rather than that of the surface designed to be exposed to the environment. Instead of using the thermal aging tests of small specimens as only a ranking or screening test, as is commonly done now, it would be highly desirable to be able to correlate either the data from these specimens or preferably the data from neat-resin TOS tests with the actual long-term aging behavior of structural components made from these materials. Current development plans for subsonic commercial aircraft engines include establishing accelerated test methods and modeling long-term environmental effects.

As a part of this planning an effort is being made to understand the mechanisms involved in the thermal aging of both polymers and fiber-reinforced composites. A number of material specimens have been processed for testing at the Lewis Research Center specifically for this effort. These specimens vary not only in size but also in ply layup design. These materials were isothermally aged at various temperatures. The data from these TOS testing efforts have been assembled and are presented herein. The materials that were studied included unidirectional and crossplied composites, fibers with three different surface treatments, and PMR–15 neat resin. Specimen sizes varied from 2.54 by 0.51 by 0.20 cm thick to 10.2 by 10.2 by 0.66 cm thick. Successful efforts were made to correlate composite stability with neat-resin thermal behavior.

MATERIALS

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

The prepreg material was made by filament winding the fiber at a pitch of 3.54 turns per centimeter (9 turns per inch). The AS–4G fiber was supplied in tows containing 6000 or 12 000 strands per tow, so that the winding pitch at times was 7.1 tows per centimeter (18 tows per inch) or 3.55 tows per centimeter (9 tows per inch). The AS–4G fiber was "boardy" and appeared to contain a greater amount of sizing than is normally used for graphite fibers (0.5 to 1.0 percent by weight). The boardy nature made winding and impregnation more difficult than was experienced with the other two fibers. Monomer impregnation was done by using a 50-percent-by-weight methanol solution of the monomers. The solution was prepared as it was used. The sheets of prepreg were cut into 7.62- by 25.4-cm panels, and the panels were stacked into bundles containing 9 or 12 plies. The stacks were imidized for 1 hr at

204 °C and then cured for 2 hr at 316 °C. All of the panels were given an air postcure at 316 °C for 16 hr. Details of the PMR–15 neat-resin preparation are presented in Reference 6.

EXPERIMENTAL PROCEDURE

Weight Loss

All thermal aging was done in air-convection ovens with an air change rate of 100 cm^3/min. The airflow was horizontal across the width of the oven. The resin or composite specimens were positioned within the ovens on their long side edges in special holders. Fiber specimens were contained in flat boxes made from stainless steel screen. All specimens were allowed to cool to room temperature in a desiccator before they were weighed. After the weighing was completed, the specimens were returned to the ovens.

X-radiography

X-radiographs of composite specimens were obtained by using the following procedure:

- An application of 1,4 diiodobutane was brushed on the cut-edge surfaces of the composite specimens.
- The liquid was allowed to remain on the surfaces for 30 to 60 sec, and then it was wiped off of the surfaces.
- The dried specimens were then radiographed and the images were saved on Polaroid 55 film. The x-ray exposure time and voltage were varied to produce the best resolution and contrast.

The 1,4 diiodobutane is a liquid that is opaque to x rays. Exposing the specimen to the liquid results in the liquid penetrating cracks or delaminations. The presence of the diiodobutane in these flaws allows them to be observed as dark areas in the resulting Polaroid x-radiographs.

Interlaminar Shear Strength

Interlaminar shear strength measurements were made at room temperature in accordance with American Society of Testing and Materials (ASTM) specification D–2344. The span-to-depth ratio was 5:1.

RESULTS

Neat Resin

The weight loss data for the PMR–15 neat resin at 288, 316, and 343 °C are presented in Figure 1. The data points were calculated as weight loss rates per unit area at each weighing time by dividing the weight loss by the specimen areas and the aging time in hours. The degradation mechanism and other details of aging changes are described in Reference 6.

Fiber

The thermo-oxidative stabilities of the three graphite fibers at three different temperatures are compared in Figure 2. The weight loss data are shown as percentages because the specimen surface-to-volume ratios are approximately the same for all three fibers. The surface areas of the AS and AU fibers were measured by a Brunauer-Emmett-Teller (BET) nitrogen/krypton adsorption method. The surface area of the AS fibers was found to be less than that of the AU fiber. The values were 0.35 and 0.43 m^2/g, respectively. Three observations are worthy of mentioning. The first is that the epoxy sizing on the AS–4G fiber completely disappeared within the first 24 hr of exposure at all three temperatures. The second point is that the fiber aging data at 288 °C indicate that the AS–4 and AU–4 fibers lost weight at about the same rate over the aging time that was studied. Also, the AS–4G fiber appeared to lose weight at the same rate as the other two fibers after the initial loss of sizing (1.5 percent) at this temperature (288 °C). This amount of sizing is unusually high for graphite fibers. Usually, the fiber sizing amount is less than 1 percent. The third point is that at the higher temperatures of 316 and 343 °C, the initial 1.5-percent weight loss, attributed to the sizing degradation, was no longer observed after the first 600 and 200 hr of aging, respectively.

The weight loss curve for the AS–4G fiber in Figure 2(c) falls below the other two. The reason could be that the fiber was protected by the sizing as the sizing oxidized off the fiber surface. In effect this would delay the initiation of fiber oxidation for 200 or 600 hr and until a weight loss of 1.5 percent was realized. This delay can be visualized by moving these points (200 hr, 1.5 percent) in Figure 2(c) to

the origin of the graph. One interesting observation from this work that is not apparent in the data is the rapid weight gain observed for the fibers when they were removed from the ovens and allowed to cool to room temperature. Even after being stored in a desiccator, the fibers gained weight after they were placed on the scale. The AU–4 fiber appeared to gain weight at a faster rate than the other two fibers. This behavior may have influenced the recorded weight values.

Large-magnification scanning electron micrographs (SEM) in Figure 3 show no topological differences between the AU–4 fibers and the other two, nor do they show any differences between unaged and aged AU–4 fibers except for diameter differences.

X-ray photoelectron spectroscopy (XPS) was used to examine the unaged and aged fiber surfaces. The results are presented in Table 1. A comparison of the three different fiber surfaces indicates little differences for carbon and oxygen contents on the surfaces of the three different fibers. One significant difference is apparent in surface nitrogen content. Nitrogen was not detected on the surface of the AU–4 fiber, but the AS–4 and AS–4G fibers contained measurable amounts of the element. It had been concluded[7,8] that nitrogen on the surface of graphite fibers can produce better fiber/matrix bonding. In order to understand how the nature of the active sites on graphite surfaces influence the strength of the fiber/matrix bond, a much more detailed study must be undertaken. The data in Table 2 indicate that the AU–4-fiber-reinforced composite exhibited the smallest interlaminar shear strength (ILSS), suggesting weaker fiber/matrix bonding. Also it is interesting to note that after the AU–4 fiber was aged at 316 °C, the carbon content dropped slightly and the oxygen and nitrogen surface concentrations increased. The oxygen content increased significantly after a 7.8-percent weight loss.

Unidirectional Composites

Weight loss data for the 7.6- by 2.54-cm unidirectional and 45° crossplied composites are presented in Figure 4, which compares the thermal stabilities of the two types of composites. The weight loss data are presented as percentages in this figure because the specimens have the same surface-to-volume ratio.

It is apparent that there was a great difference between the weight loss data for the small unididirectional and the crossplied specimens. The crossplied composites exhibited more rapid weight loss. Theie three different fiber-reinforced, unidirectional composites all appeared to exhibit the same level of TOOS. The curves plotted by using the weight loss data of the composites with different reinforcement surfrface treatments do not mirror the plots of the data from the bare-fiber TOS tests shown in Figure 2. Theie epoxy sizing on the AS–4G fibers was apparently protected from oxidation and degradation by the polylyimide matrix. The 1.5-percent weight loss exhibited by the AS–4G fiber in the bare state was not evidident in the composite. The significance of this degradation in determining the usable lifetime of these matatterials in structures is not apparent from the data presented herein. Because composite lifetime is detetermined by the magnitude of the retained mechanical properties during the thermal aging process, the TOOS data presented herein do not really indicate the allowable lifetime for structures fabricated from thesese materials. Studies are now being conducted at our laboratory to address this issue.

It is important to note the mechanism of composite degradation during aging at elevated temmperatures. The process is clearly illustrated in the series of photomicrographs in Figure 5. As the agining time increased, a distinct layer of degraded matrix formed at the uncut surfaces and advanced into the e composite. As a result of the layer growth, cracking initiated perpendicular to these surfaces and grew inwaard between the reinforcement fibers. This cracking degraded those composite mechanical properties thatat are matrix dependent or surface-dependent properties such as flexural strength. This layer growth wasis similar to that observed in neat resin during aging at elevated temperatures[6] except that the cracking doeses not always occur at all temperatures in neat-resin samples.

The weight loss rates per unit area from smaller A–4-fiber-reinforced, unidirectional composites are commpared with that of the PMR–15 neat resin in Figure 6. Weight loss rates for the neat resin and the commposite samples were nearly identical for the first 200 hr of aging. Although it appears that the weight lossis rates of the composites can be related to that of the neat resin, the minimum rates for the three commposites did not reach that of the neat resin. As time elapsed, the rates for the composites increased

significantly but the neat-resin rate stayed constant. These curves indicate that the edge effects started dominating the oxidation rates at 288 °C after 200 hr of aging.

Figure 7 shows another aspect of the thermo-oxidative stability of unidirectional, graphite-fiber-reinforced composites. Specimen size has an important influence on the TOS of polymer matrix composites. This figure shows weight losses for PMR–15 neat resin and for three different sizes of A–4-fiber-reinforced composite specimens. Also included in the figure are dashed lines denoting the neat-resin data and the rule-of-mixtures weight loss for a composite with a fiber volume percent of 60. In evaluating the results of isothermal aging TOS tests, allowances must be made for the accelerated oxidation that occurs along the cut surfaces of the specimens.[1-5] It is evident in Figure 7 that, as the surface-area-to-volume A/V ratio increased and as the percentage of cut-edge surfaces to total surface area C/T decreased, the composite weight loss on a surface area basis approached the rule-of-mixture value. Figure 7 also indicates that as time elapsed, the small 7.6- by 2.54- by 0.33-cm specimens actually oxidized at a faster rate than the neat resin because of the accelerated oxidation at the cut edges. Because most of the uncut specimen surfaces were resin rich, the initial weight loss from these surfaces would be expected to mirror that of the neat resin. It has been shown (Figures 5 and 6) that the thermal degradation of the matrix resin took place in a layer on the specimen surface. When the specimen contained reinforcement fibers, the amount of matrix available for degradation in the layer at the resin-rich surface was the same as the resin content of the composite.

Table 2 presents interlaminar shear strength measurements for composites having the three different fibers as reinforcement. These measurements reflect the relative bonding strengths of the three different fibers. For the data generated during this study a ranking of thermal stability according to fiber surface finish or interfacial bonding strength was dependent on the specimen size. The smaller specimens' stabilities were significantly influenced by the cut edges and the fiber ends.[1-5] This suggests that the TOS of the small specimens may be dependent on the interfacial bonding because the AU–4-reinforced composite had the least stability of the small specimens as indicated in Figure 8. On the other hand the

AS–4G-reinforced large specimens fared the worst in TOS ranking according to Figure 8. The reason may be that the degradation of the epoxy sizing significantly influenced the TOS when the edge effects were reduced. The amount of sizing was unusually large. More study is needed in this area.

Crossplied Composites

The edge effect phenomenon is dramatically illustrated by the results of the 288 °C isothermal aging tests of three different sizes of AS–4/PMR–15 crossplied (±45°) composites. The sizes were 7.6- by 2.54- by 0.33-cm, 2.54- by 2.54- by 0.33-cm, and 7.6- by 0.51- by 0.33-cm. The crossply design yielded a material with the greatest amount of interlaminar residual stresses because of the large mismatch in the coefficients of thermal expansion (CTE) between the adjacent plies. Although the cut edges of unidirectional, graphite-fiber-reinforced composites did undergo enhanced oxidation, the edges of the crossplied composites were subjected to a much more accelerated oxidative attack due to the presence of interply and intraply cracks produced by these high residual stresses. The results of the isothermal aging of the three sizes of 45° crossplied composites are shown in Figure 9. The weight loss data, measured at 288 °C, are shown as weight loss rate per unit specimen area and also as weight loss rate per unit volume at 288 °C. It is evident from the figure that, in the first 300 hr of aging, the weight loss rates per unit surface area of three different-size composite specimens were approximately equal. This suggests that oxidation was occurring at the specimen surfaces as was observed for the neat resin and the unidirectional composite specimens. The curves relating weight loss rate to specimen volume show different rates for the three different-size specimens over this same time period. The data show that after the first 300 hr had elapsed the relationship with the surface area was deteriorating, since the curves are starting to diverge. At the same time the weight loss rate was starting to become a function of specimen volume. Eventually, after 450 hr and on the basis of specimen volume, the three curves coincide. This result is totally different from the long-term aging results that were observed for the neat resin and the unidirectional composites reinforced with graphite fibers.

The aged specimens were examined to determine the reason for this change in the mode of oxidative degradation. The crossplied composite specimens were removed from the aging ovens at time intervals of 96, 264, 768, and 1000 hr. The specimens were inspected by x-radiography enhanced with 1,4 diiodobutane and also by standard metallography procedures. Figure 10 shows x-radiographs of the specimens that were aged in air for 96, 264, 768, and 1000 hr at 288 °C. The measured weight losses from these specimens were 1.1, 2.9, 9.5, and 11.8 percent, respectively. It is clearly evident that the gray density of the resultant x-radiograph increased with aging time, indicating that the amount of absorbed 1,4 diiodobutane increased with aging time. One of the x-radiographs was enlarged (Figure 11) to show the individual flaws more clearly. The straight lines indicate the presence of cracks that have probably formed between the fibers throughout the specimens. The distances between cracks were measured by using a Nikon Measurescope, which indexes displacements in the x and y directions. It appeared that the aging time did not affect the number of flaws within the samples. From the observations made with this instrument, if changes did occur, they were very small and played an insignificant part in the deepening of the gray tone as aging progressed.

The samples that were examined by x rays were then cut through the centers parallel to one set of edges, and the freshly cut surfaces were examined by using standard metallographic procedures. The results are shown in Figure 12. One significant observation is obtained by comparing Figures 12(a) and (d). The interior cracks in adjacent plies (Figure 12(d)) did not connect to provide a continuous path from the uncut, resin-rich surfaces into the interior of the composite. The air did not penetrate into the interior through continuous paths from the uncut surfaces. These cracks only enhanced the access of the air to the interior during aging through a path beginning at the cracked cut edges. Increased internal oxidation resulted as corroborated by Figure 13. The metallographic mounts shown in Figure 13 were photographed by using fluorescence microscopy.[9] The specimens were mounted in fluorescent epoxy, and the epoxy was vacuum infiltrated into the specimens. The fluorescent method, using filters to differentiate

the difference between the color of the specimen and the fluorescent dye, enhanced the differences in the microstructure. The unfilled, isolated voids and cracks are dark black in the photographs. The cracks and voids that have been infiltrated by the fluorescent epoxy are the white areas. It is evident that infiltration progressed with aging time, indicating the increase in interconnected cracks and pores.

It is interesting to note that the spacing between cracks was greater in the surface plies than in the interior plies. Prior to aging, very few cracks were observed in the outer plies of the composites (see Figures 11 and 12(a)). Studies of microcracking due to thermal cycling have indicated that the microcracks begin at the outer plies of a polymer matrix composite and proceed inward toward the center of the composite. The x-radiographs indicate that as the aging time increased some intraply cracking began, the existing cracks widened, and numerous voids nucleated and grew. The voids appeared at the fiber/matrix interface and expanded to envelop increasing numbers of fibers as aging increased. From these photomicrographs the increase in 4,1 diiodobutane within the specimens, as shown in Figure 10, appears to be due to connected, interpenetrating cracks and voids, emanating from the cut edges, which appear and grow during aging. They allow the oxygen in the air to eventually completely penetrate the interior of the crossplied specimens through the edges and to cause internal oxidation. Thus, the weight loss eventually becomes dependent on the volume rather than the surface area, as was seen previously in Figure 9.

SUMMARY

The purpose of this study was to look at some variables that could affect the thermo-oxidative stability (TOS) of PMR–15 composites. Three areas were investigated. The first was the effect of fiber/matrix interfacial bond strength on the isothermal aging weight loss of composites. Using the type-A graphite fibers produced by Hercules, we were able to study composites reinforced with fibers that were processed to receive different surface treatments which produced three significantly different interfacial bond strengths. Differences in active site analyses of the fiber surfaces were limited to nitrogen content. The epoxy sizing on the AS–4G fiber was quickly removed from the bare fiber surfaces at 288, 316, and

343 °C. The weight loss due to the removal of the sizing was constant at 1.5 percent. This initial weight loss was not observed in TOS studies of composites. The PMR–15 matrix satisfactorily protected the reinforcement at all three temperatures.

The aging degradation of PMR–15 neat resin and its unidirectional composites is a reaction that is controlled by the exposed surface area of the specimens. The degradation takes place when a surface layer grows and penetrates into the interior of the resin and the composite. In the unidirectional composite the growth is accompanied by the initiation of interfiber cracking perpendicular to the surfaces.

The correlation between the neat-resin TOS and the unidirectional composite TOS varied as the specimen size changed. The data from this study indicate that as the cut-edge surface area decreased in relation to the total composite surface area, the weight loss rate per unit of surface area approached the value calculated by the rule of mixtures based on the weight loss rate calculated for the neat PMR–15 resin. This result applied for the AS–4G-reinforced specimens probably because of the sizing on the fiber surface. A specimen size of 20.3 by 7.6 by 0.33 cm exhibited weight loss rates nearly equivalent to the rule-of-mixtures value, and this size should be considered as a standardized test specimen size.

Smaller TOS specimens of crossplied composites exhibited weight loss rates that were more dependent on residual stress damage than on the TOS behavior of the matrix resin. Initially, the composite weight loss rate depended on the surface area and the PMR–15 weight loss rate, but after a few hundred hours of aging there was an unstable period during which the mechanism changed from a surface-area-controlled oxidative degradation to one controlled by the specimen volume. The mechanism was still surface driven, but the active surfaces began to include internal cracks (and voids as the cracks became wider) and to promote nucleation of internal voids that grew and multiplied. Access paths to the interiors of the specimens were created by oxidation-induced widening of the edge cracks. Great care and extensive characterization of crossplied composite TOS specimens would be necessary to elicit more significant conclusions from the tests.

CONCLUSIONS

The results of this study have yielded information that allows some significant conclusions to be drawn. Under certain conditions some relationship exists between PMR–15 thermo-oxidative stability (TOS) and unidirectional, graphite-fiber-reinforced composite TOS. Smaller unidirectional composite specimens never attain weight loss rates as low as those of the neat matrix resin because the effect of the cut edges controls the degradation mechanism after the first few hundred hours of aging. Larger unidirectional specimens with small ratios of cut surface area to total surface area give TOS values close to rule-of-mixture predictions based on weight loss data of the neat PMR–15 matrix resin. Fiber surface treatment can affect the TOS of the larger composite specimens. Specimens reinforced with sized fibers exhibited accelerated weight loss, but it is unclear whether the cause was bonding due to surface treatment or the presence of less thermally stable epoxy sizing. The TOS of crossplied composites is influenced strongly by internal oxidation of the specimen. The oxidative damage proceeds through edge cracks initiated by coefficient-of-thermal-expansion-induced strains, resulting in weight loss rates much greater than those observed for unidirectional composites. It has not been determined what effect the fiber/matrix interfacial bonding has on the initiation and number of edge cracks. A close examination of microcracking data should clarify this point.

Table 1. Elemental concentrations on surfaces of different fibers and after different aging times at 316 °C for AU–4 fibers

Element	Fiber				
	AU–4	AU–4 after 0.38% weight loss	AU–4 after 7.86% weight loss	AS–4	AS–4G
	Concentration, wt %				
Carbon	82.96	78.26	76.40	83.04	82.19
Oxygen	11.17	10.17	16.06	9.36	12.92
Nitrogen	(a)	3.69	1.86	5.20	2.17
Sulfur	1.18	.61	.87	.30	.18
Chlorine	1.27	.94	.72	(a)	.64
Sodium	.79	.34	.56	.38	(a)
Silicon	1.69	2.70	(a)	1.72	1.36
Phosphorus	.96	1.51	(a)	(a)	(a)

[a]No detectable amount.

Table 2. Interlaminar shear strength of type-A-fiber-reinforced PMR–15 unidirectional composites measured at room temperature

Fiber	Interlaminar shear strength	
	MPa	ksi
AU–4	49.9	7.2
AS–4	65.6	9.5
AS–4G	99.3	14.4

REFERENCES

1. K.J. Bowles and A. Meyers, "Specimen Geometry Effects on Graphite/PMR-15 Composites During Thermo-Oxidative Aging," 31st International SAMPE Symposium and Exhibition (1986) 1285.
2. K.J. Bowles and G. Nowak, *Journal of Composite Materials*, 22 (1988) 966.
3. K.J.Bowles, *SAMPE Quarterly*, 21, 4 (1990) 6.
4. F.J. Magendie, "Thermal Stability of Ceramic and Carbon Fiber Reinforced Bismaleimide Matrix Composites," Master's Thesis, Department of Chemical Engineering, University of Washington, Seattle, WA, 1990.
5. J.D. Nam and J.C. Seferis, *SAMPE Quarterly*, 24, 1 (1992) 10.
6. K.J. Bowles, D. Jayne, and T.A. Leonhardt, *SAMPE Quarterly*, 24, 2 (1993) 2.
7. J.D.H. Hughes, *Composites Science and Technology*, 41 (1991) 13.
8. C. Kozlowski and P.M.A. Sherwood, *Carbon*, 24, 3 (1986) 357.
9. K.W. Street and T.A. Leonhardt, *Microstructural Science*, 19 (1992) 69.

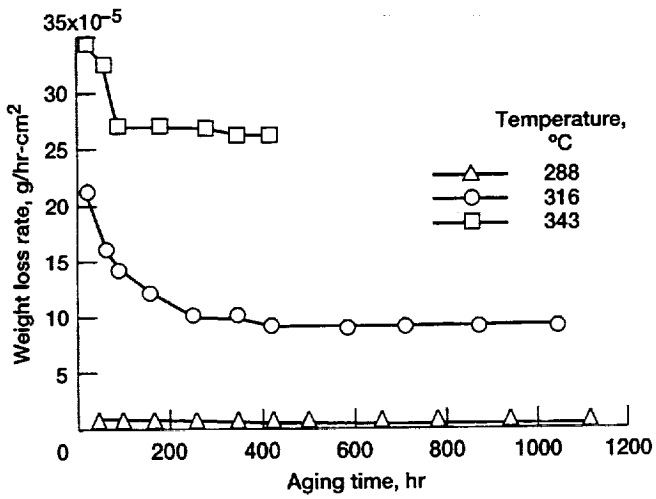


Figure 1.—Weight loss rates of PMR–15 in air at different temperatures.

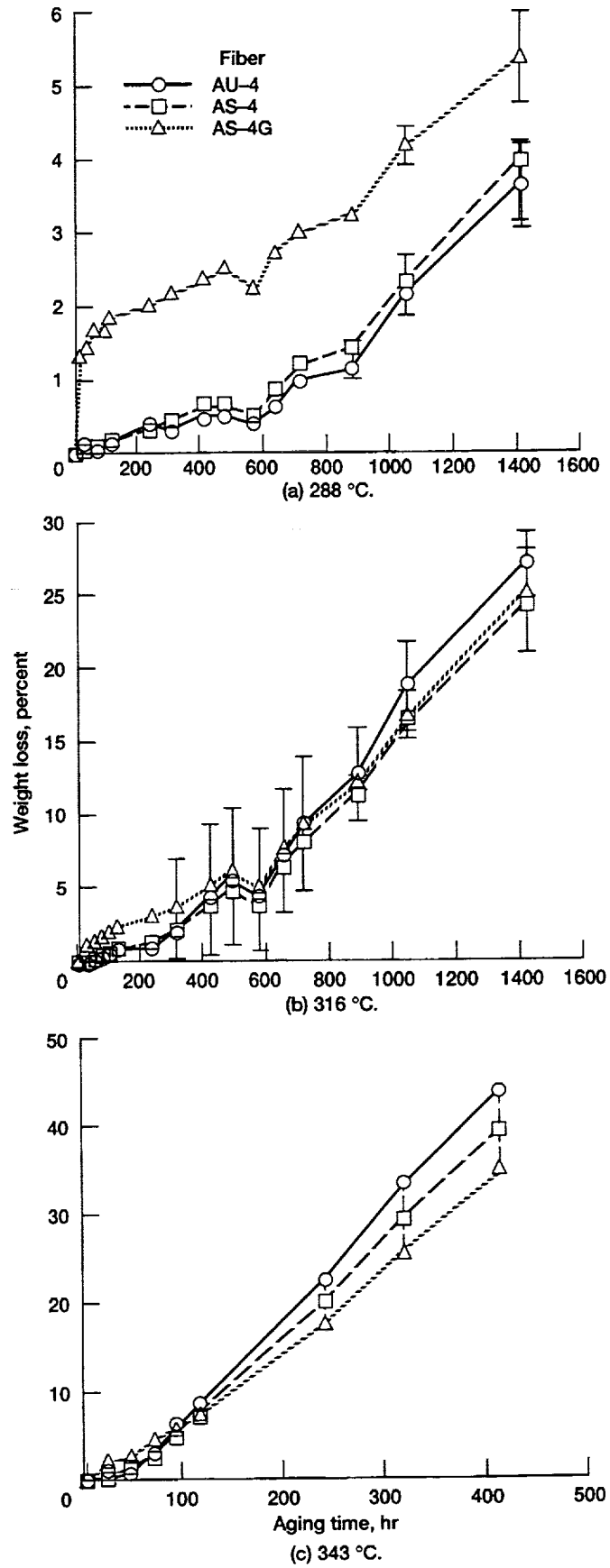
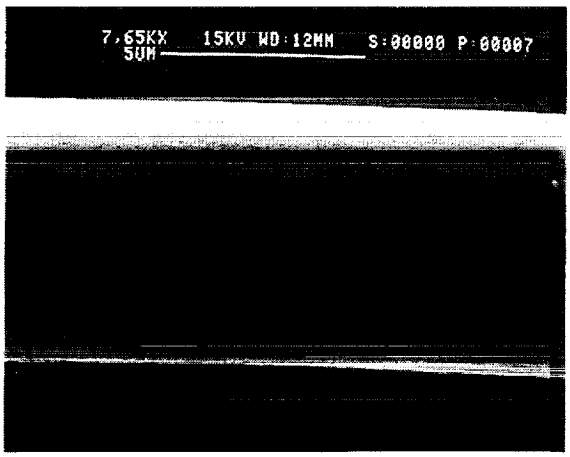
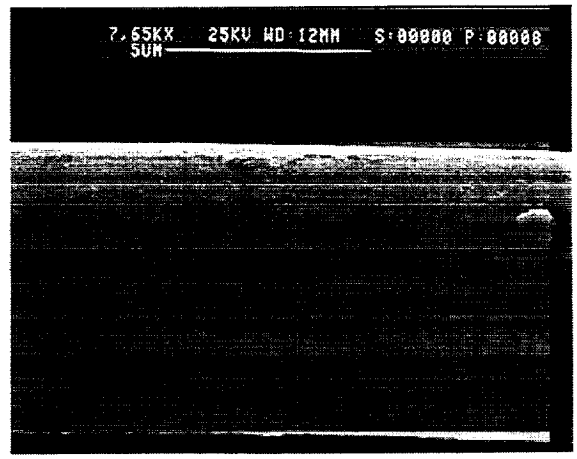


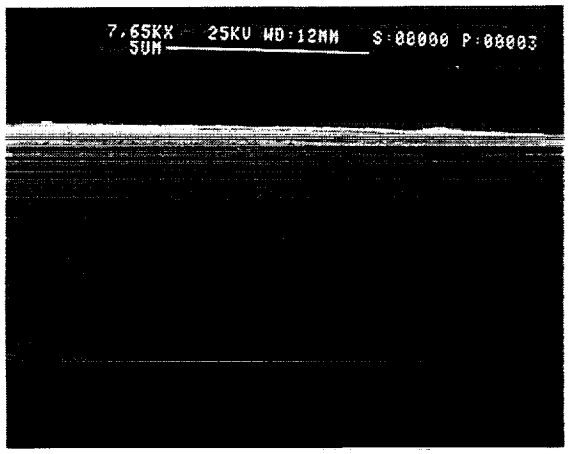
Figure 2.—Thermo-oxidative stability tests of graphite fibers.



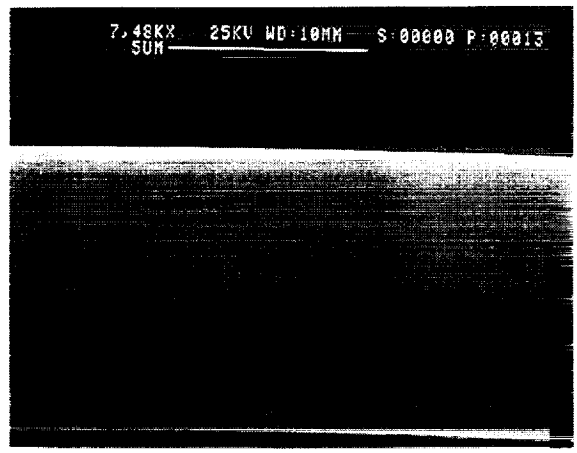
(a) AS–4G fiber after 32.3-percent weight loss.



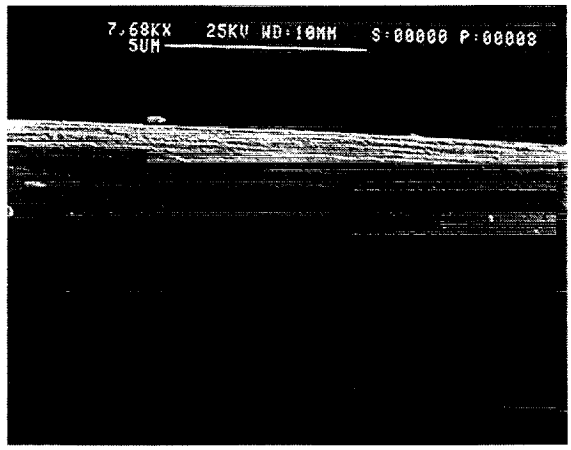
(b) AU–4 fiber as received.



(c) AU–4 fiber after 36.9-percent weight loss.



(d) AS–4 fiber as received.



(e) AS–4 fiber after 30.6-percent weight loss.

Figure 3.—Type A fiber topographies as received and after aging at 316 °C.

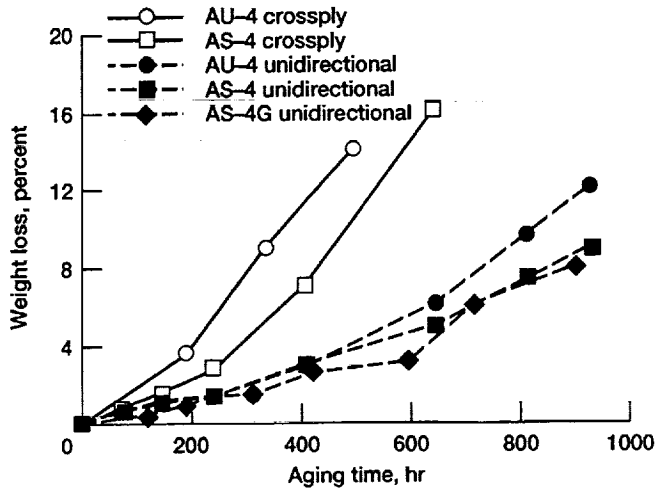
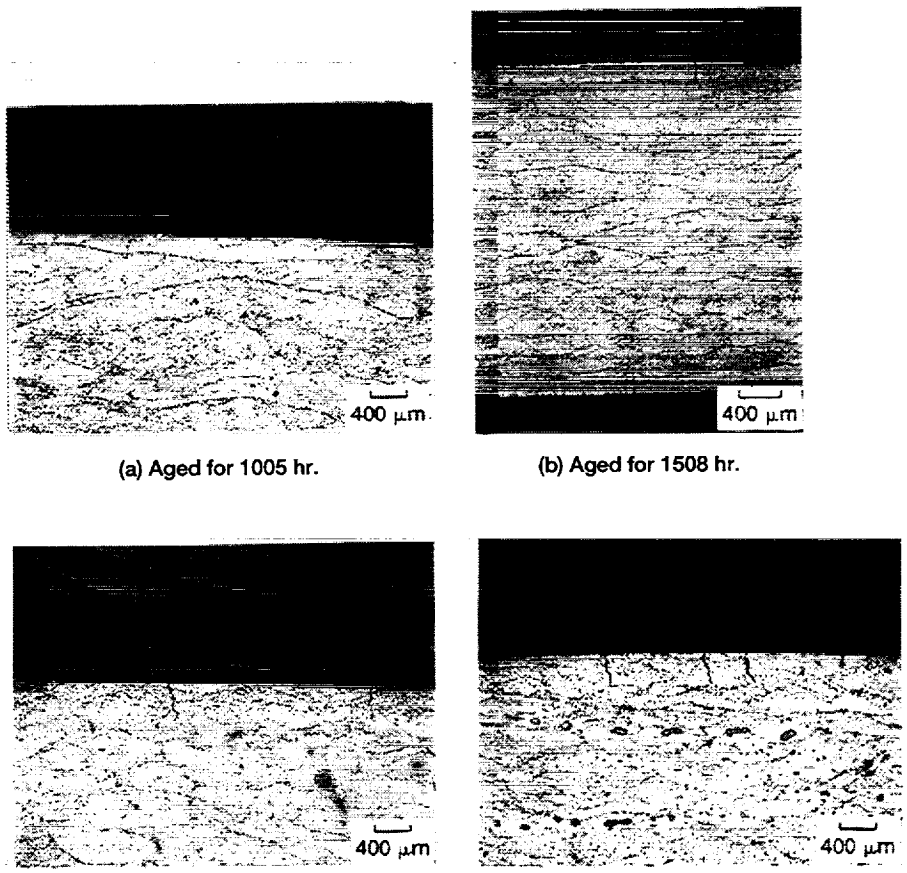


Figure 4.—Weight loss of PMR–15 composites aged in air at 316 °C. (all specimens measure 2.54 by 7.6 by 0.36 cm.)



(a) Aged for 1005 hr.

(b) Aged for 1508 hr.

(c) Aged for 2002 hr.

(d) Aged for 2514 hr.

Figure 5.—AS–4/PMR–15 unidirectional composites aged in air for various times at 288 °C.

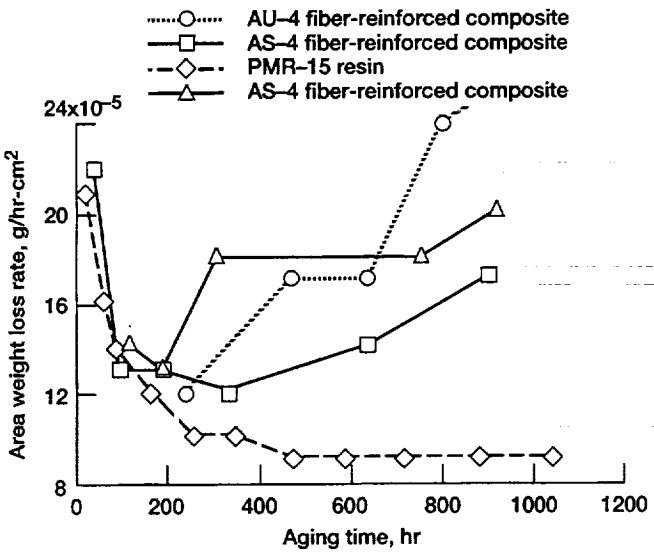


Figure 6.—PMR–15 and unidirectional composite weight loss rates at 288 °C for 7.6- by 2.54-cm composite specimens.

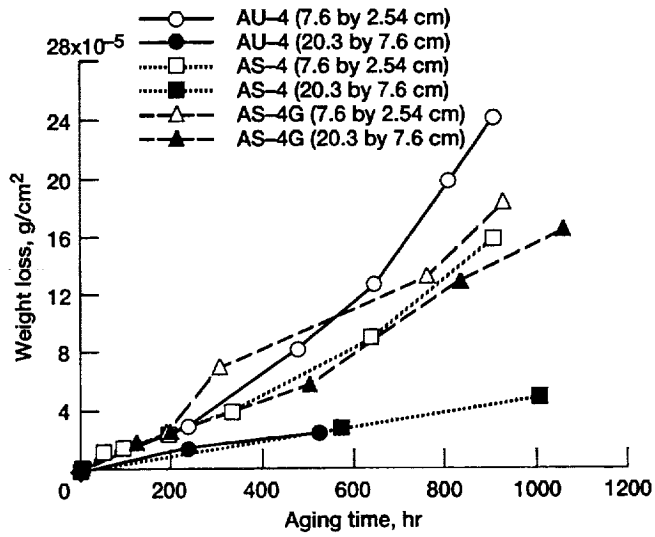


Figure 8.—Thermo-oxidative stability of PMR–15 composites reinforced with unidirectional graphite fibers with different surface treatments. Aging temperature, 316 °C.

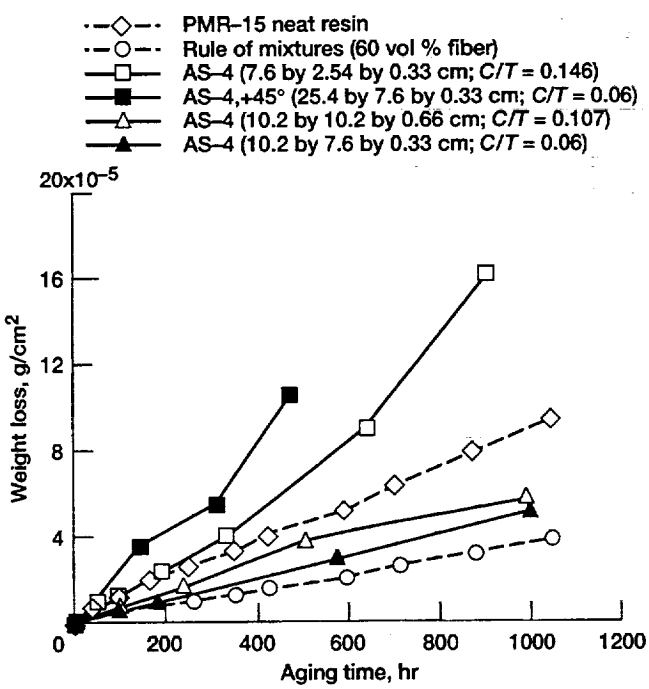


Figure 7.—Weight loss for AS–4-fiber-reinforced composites with different proportions of cut-edge surfaces. (*C/T* denotes ratio of cut surface area to total area.)

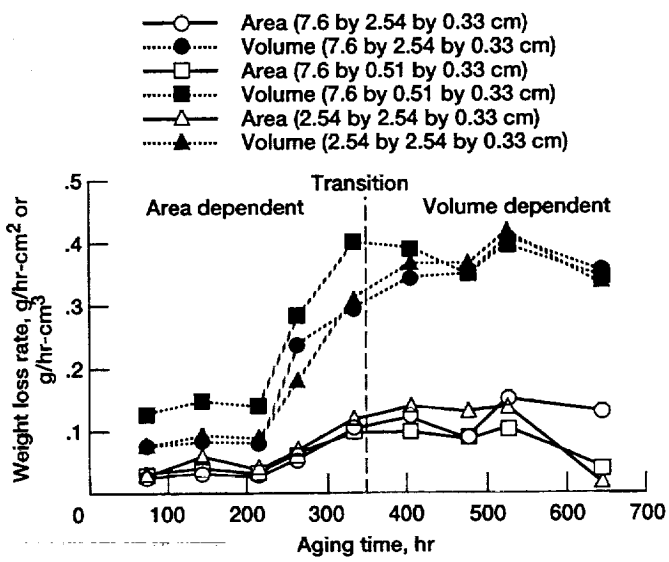
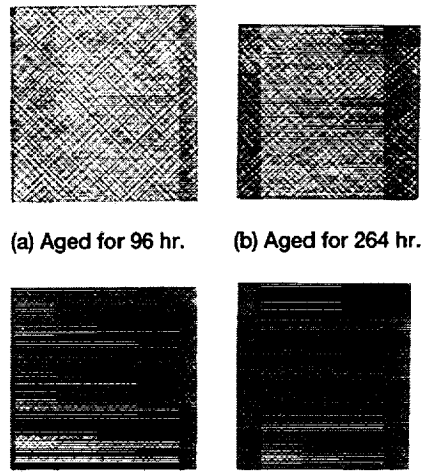


Figure 9.—Weight loss rates of crossplied composites as functions of surface area and volume for AS/PMR–15 composites aged at 288 °C.



(a) Aged for 96 hr. (b) Aged for 264 hr.

(c) Aged for 768 hr. (d) Aged for 1000 hr.

Figure 10.—X-radiographs of 2.54- by 2.54-cm AS–4±45° composites that were aged in air at 288 °C. (X-radiographs enhanced with diiodobutane.)

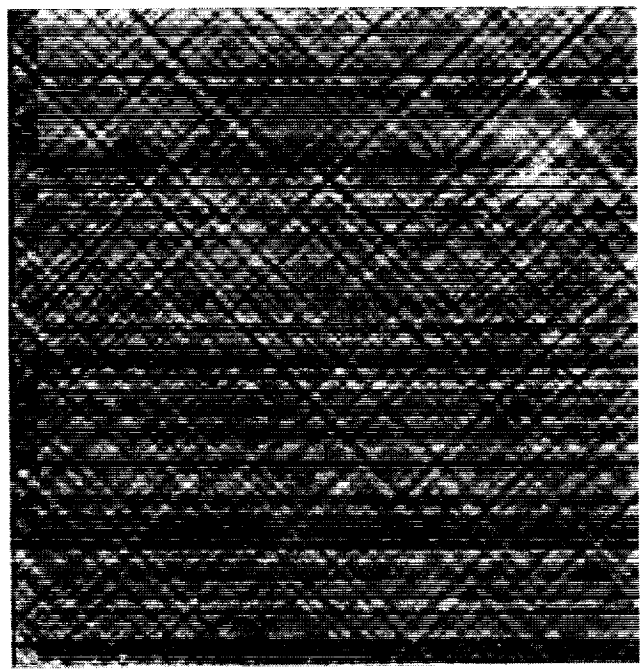
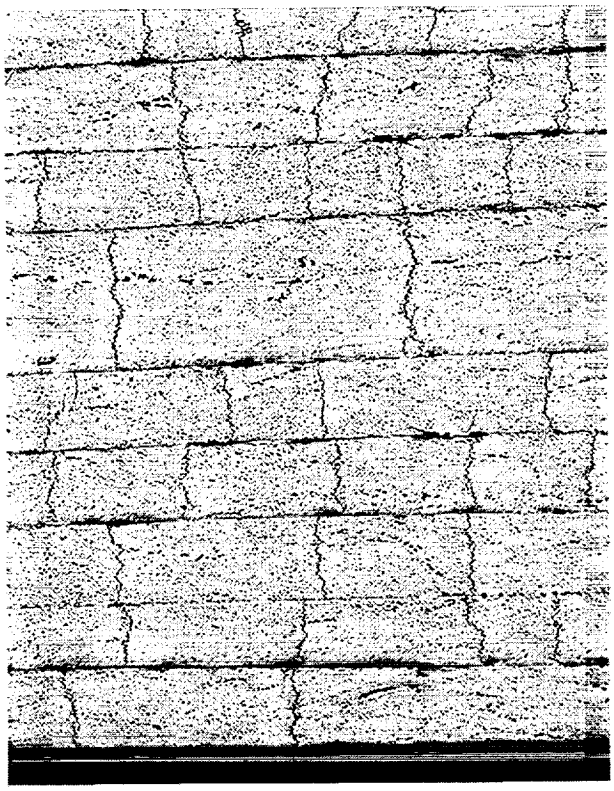
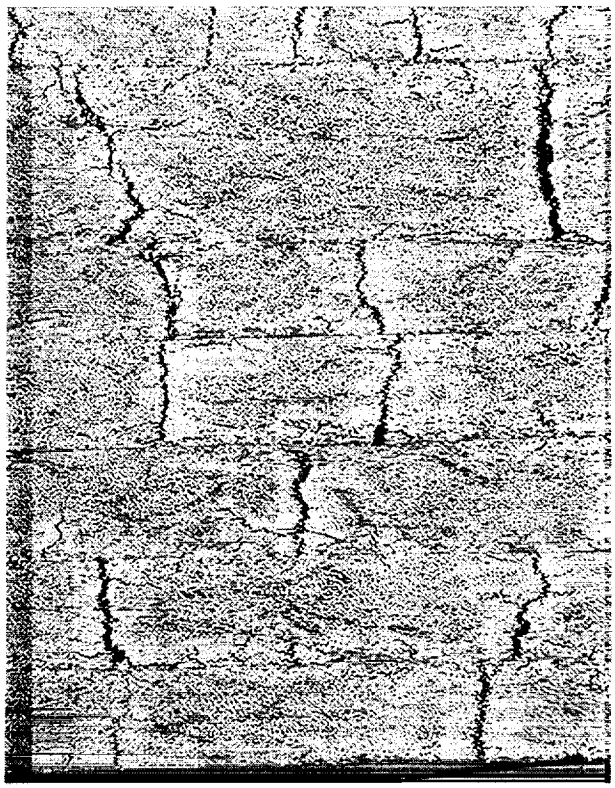


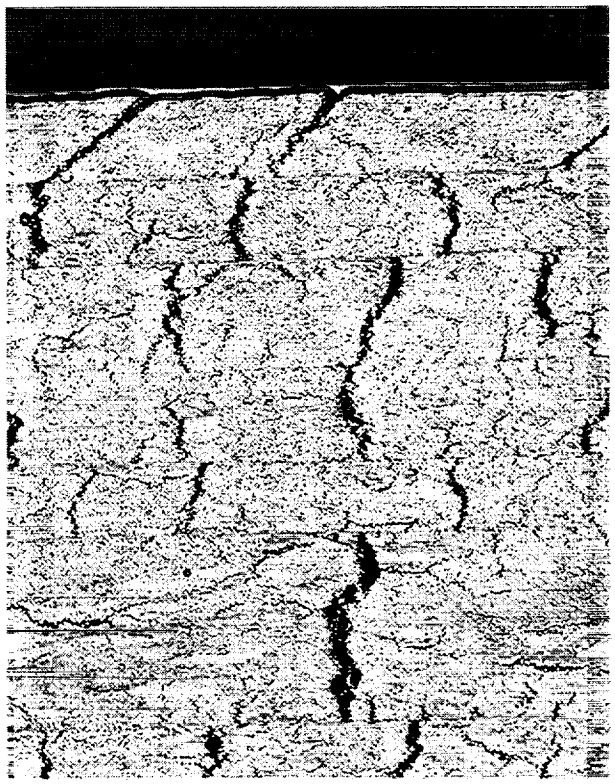
Figure 11.—Enlargement (x4) of diiodobutane-enhanced x-radiograph of 45° crossplied AS–4-reinforced composite aged in air for 96 hr at 288 °C.



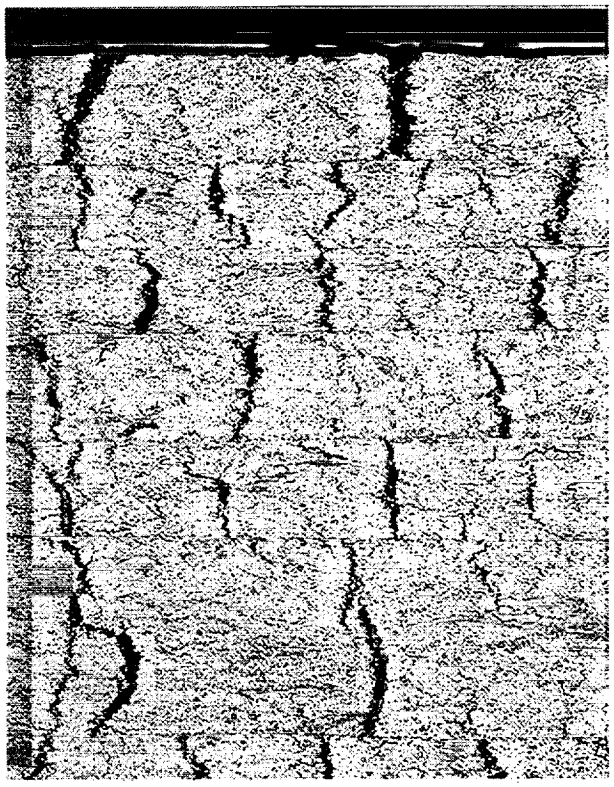
(a) No aging.



(b) Aged for 264 hr.

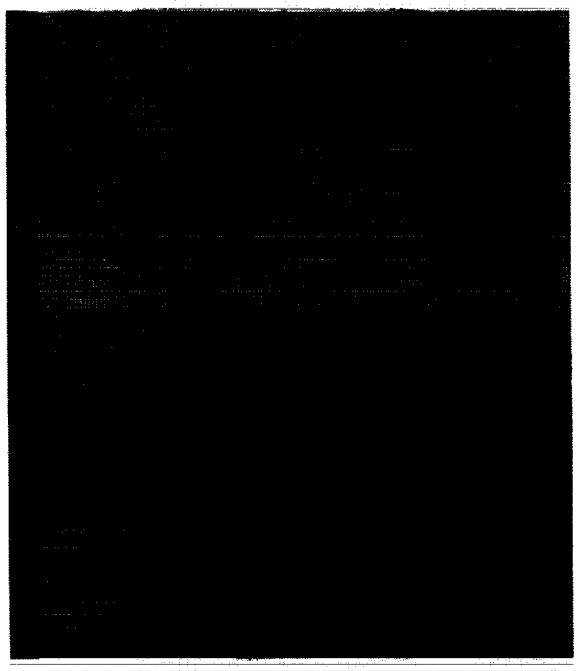


(c) Aged for 768 hr.

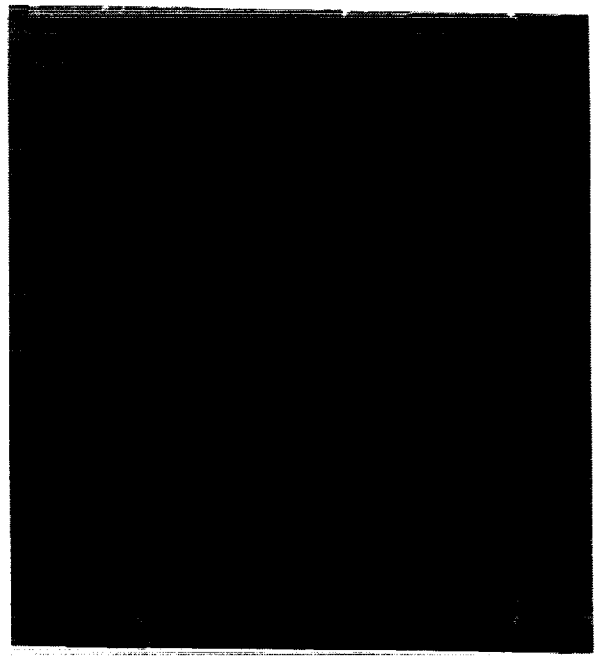


(d) Aged for 1000 hr.

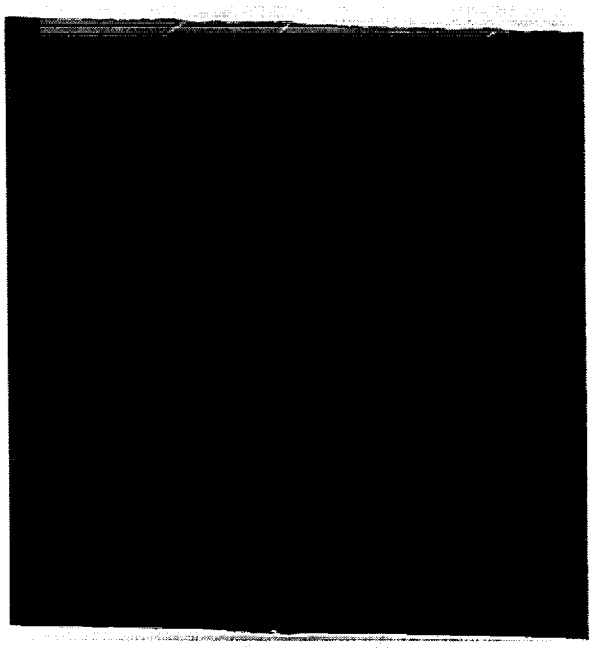
Figure 12.—AS–4-reinforced, crossplied composite aged at 288 °C for various times, x35.



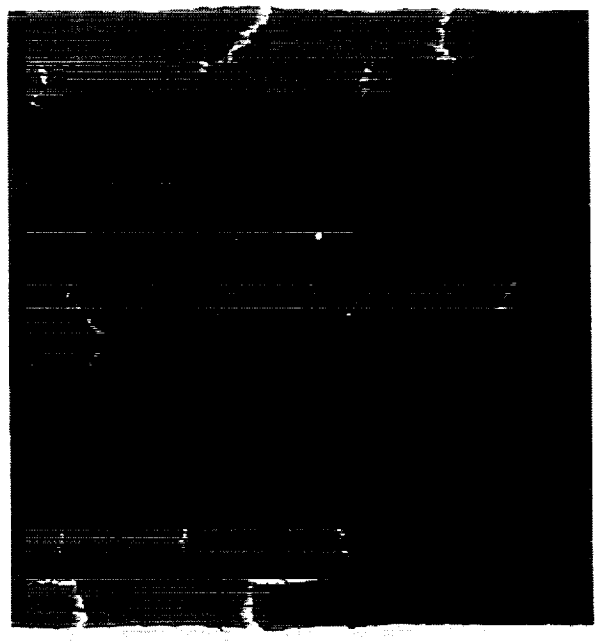
(a) Aged for 96 hr.



(b) Aged for 264 hr.



(c) Aged for 768 hr.



(d) Aged for 1000 hr.

Figure 13.—Fluorescent-aided photomicrographs of AS–4-fiber-reinforced, crossplied composite aged at 288 °C for different times, x25.

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13. ABSTRACT (*Maximum 200 words*)

A study was conducted to investigate the relationships between the thermo-oxidative stability of PMR–15 matrix resin and the stability of graphite-fiber-reinforced composites that contain this resin as the matrix material. Three areas were investigated. The first was the effect of fiber/matrix interfacial bond strength on the isothermal aging weight loss of composites. By using type-A graphite fibers produced by Hercules, it was possible to study composites reinforced with fibers that were processed to receive different surface treatments. One of the fibers was untreated, a second fiber was treated by oxidation to enhance fiber/matrix bonding, and the third type of fiber was coated with an epoxy sizing. These treatments produced three significantly different interfacial bond strengths. The epoxy sizing on the third fiber was quickly oxidized from the bare fiber surfaces at 288, 316, and 343 °C. The weight loss due to the removal of the sizing was constant at 1.5 percent. This initial weight loss was not observed in thermo-oxidative stability studies of composites. The PMR–15 matrix satisfactorily protected the reinforcement at all three temperatures.

14. SUBJECT TERMS
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