MICROSCOPIC EVALUATION OF A POLYIMIDE (PMR15)-GRAPHITE COMPOSITE

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This work is part of an effort to evaluate the high temperature performance of a polyimide (PMR15)-graphite composite which consists of several plies of woven strands of carbon fibers (see fig. 1). Further details of the material are given in the background section. The longterm effect of high temperature on the dry material was studied by exposing polished test specimens of 473°F in a oven for nearly 400 hours. Periodically the specimens were removed and observed microscopically. Gradually surface cracks began to appear and the number of cracks increased over time. At the conclusion of the exposire the specimens were gradually ground down and observed in order to determine the depth of the cracks into the interior of the material. This procedure was repeated at an exposure temperature of 550°F.

The effect of absorbed moisture in the material being rapidly driven off by a sharp temperature gradient was studied by equilibrating polished specimens to an 80% R.H. environment, then thermally cycling them between room temperature and 473°F. Microscopic observations of the specimens were made following the cycling process.

Optical microscopy was used for the majority of the material observations made during this study. Since repeated observations of the same areas of composite specimens were to be made following various exposure intervals, the gold surface coating required for scanning election microscopy was not desirable for it may have interfered with the composite's surface properties during exposure. Some observations were made using a scanning election microscope, following the conclusion of the exposure periods.

BACKGROUND

The carbon fiber-polyimide composite materials studied are comprized of several plies. Each ply consists of woven structure of carbon fiber strands. In the weave pattern, strands which are oriented in one direction, interlock with only every eigth bundle oriented in the perpendicular direction.

Thus, each ply consists of two distinct layers. One layer is dominated by fiber strands oriented in one direction, while the other layer is dominated by strands oriented perpendicular to the strands of the first layers (see Fig. 2). With this structure, observations of the cross section reveal that for each ply there are two distinct rows of fibers with only an occasional crossover which indicates an interlocking of strands.

Composite specimens with two different ply sequences were investigated. One was a 2.90mm. thick, 8 ply material consisting of plies whose fibers were oriented only in 0° and 90° directions. The other composite was a 1.35mm. thick, 4 ply material consisting of two outer plies whose fibers are oriented in the 0° and 90° directions and two inner plies whose fibers are oriented in the ± 45° directions. The 8 ply composite has essentially zero void volume, whereas the 4 ply composite has nearly a 3% void volume fraction.

Most of the observations of the specimen's surfaces were along the cross section oriented in the 0° direction. Upon observing this cross section, the fibers oriented in the 0° direction (running the length of the cross section) appear as long thin strands. The cross section of the fibers oriented in the 90° direction are observed from this surface and appear roughly as hexagons (circular at low magnification). Fibers oriented in the ± 45° directions appear as elongated hexagons (ovals at low magnification) with the length in the 0° direction being 1.4 times the width in the transverse direction.

EXPERIMENTAL

Sample Preparation

Composite specimens which were observed microscopically were cut from a panel into pieces approximately 1.5cm in length by 1.2cm in height. The lengths of the pieces were oriented along the 0° fiber direction. In order to microscopically observe a given surface of the specimen, that surface had to be highly polished. Polishing was accomplished by rough grading the surface using a series of SiC abrasive papers (320,400, and 600 grit), then fine polishing the surface with alumina powders on a motorized polishing wheel. Using the larger powders first, the specimens polished with 9.5μ, 1.0μ, 0.3μ, and 0.05μ powders.

Thermal Exposure

The subjection of specimens to 400 hours of either 473°F or 550°F was accomplished by placing them on an aluminum block in a preheated oven. An iron-constantan thermocouple was taped to the surface of the block in order to accurately monitor the temperature. When a specimen was removed from the oven for periodic observations it was placed on a cool aluminum block in order to facilitate rapid cooling.

Specimens equilibrated to 80% R.H. and thermally cycled, were cycled by being placed for a given period of time on an aluminum block in an oven heated to 473°F. The cycle was then completed by removing the specimens from the oven and cooling them on an aluminum block for a time equal to the exposure time. The 4 ply pieces were exposed for periods of 2 minutes, and the thicker 8 ply pieces for periods of 4 minutes. This cycle was repeated 50 times, except occasionally specimens were removed for longer periods of time in order to make microscopic observations.

Microscopy

Microscopic observations were made with a Zeiss universal microscope. Photographs were taken with the aid of a Polariod camera attachment. Polaroid Type 52 medium contrast black and white film was used.

RESULTS AND DISCUSSION

Initial Specimen Condition

The initial condition of both sets of specimens (4 and 8 ply) appeared to be good. Only a few hairline cracks were observed prior to exposure. The 8 ply material has virtually no voids. The rare voids that were found were always located in resin pockets, between bundles. The 4 ply material has nearly a 3% void content. In addition to the larger voids found in resin pockets, areas within the fiber bundles were found which contained many small voids (see fig. 3).

400 Hour Exposure at 473°F

Specimens from both composite materials were subjected to 473°F exposure for 391 hours. The specimens were removed 7 times during the exposure in order to examine the extent of the damage to the material as a function of time. The behavior of the 8 ply material will be discussed first.

8 Ply Test Panel Two material samples were observed and photographed along the cross section oriented in the 0° direction. The first observation of the material after the beginning the exposure was made after 17 hours of exposure. The couple of very thin cracks which had been present initially had now widened slightly. The only other noticable change was that in the regions between 90° fibers (perpendicular to the surface) very shallow depressions in the resin could be seen (see fig. 4a) indicating a slight degradation and loss of resin. After 38 hours of exposure no other change or damage was observed except for a slight increase in the loss of resin from the surface. The first new crack in one sample did not appear until after 169 hours. Only after 258 hours of exposure did several cracks appear in both specimens (see fig. 5). In every case the cracks are located in the 90° fiber areas and run transverse to the 0° direction, never along it. The lengths of the cracks are dictated by the width of the 90° fibers bundles. In most every case the crack runs the entire width of the 90° fiber areas (about 0.35mm. maximum), but never beyond into 0° fiber areas where cracks would have to cut through carbon fibers in order to propagate. The few cracks which had developed earlier had now widened noticably. The loss of resin from the surface still appeared to be continuing slowly. After 324 hours of exposure many more cracks had formed and there was continued lengthening and widening of old cracks. The maximum widths of the cracks was approximately 13μ. The depressing which were due to resin loss were only a few microns deep (see fig. 4d) and thus this damage seems minimal.

After 391 hours of exposure or at 473°F the cross section appears to be heavily cracked and damaged (see fig. 6), but the real extent of the damage was not known until the depth of the cracks into the interior was determined. In order to determine the depth of the cracks into the material, the cross section of the specimen was gradually ground down and periodically examined for the extent of cracking.

After about 0.1mm. had been ground down most of the cracks, which had formed during the exposure, had been removed. Thus most all the cracks observed along the cross section were less than 0.1mm. deep. After 0.3mm had been ground down from the surface only a couple of cracks still remained and these were two cracks which were present in the material before exposure began.

4 Ply Test Panel: These specimens were first cut and observed along the 0° cross section as were the 8 ply specimens. During exposure, the loss of resin from the surface was similar to the behavior of the 8 ply material. Depressions in the resin, as observed in the areas between 90° fibers, are easily observable, but after 391 hours of exposure at 473°F are only a few microns deep.

The cracking behavior of the 4 ply material was different than that of the 8 ply material in several ways. First, the onset of surface cracking appeared sooner in the 4 ply panel than in the 8 ply panel. After only 50 hours of exposure a couple of cracks were observed in 90° fiber areas. From 50 to 313 hours of exposure there was a slow, steady increase in the number of surface cracks that did not appear in the 8 ply material until after 108 to 170 hours of exposure. As in the 8 ply material, cracks started as being short and thin and grew with additional exposure. In this material the maximum width of the 90° areas is smaller than in the 8 ply composite thus the maximum length of cracks, which run transverse to the 0° direction in the 90° fiber regions, are shorter (0.20mm) than in the 8 ply composite (0.35mm). The cracks grew to maximum widths of about 7μ. Also the cracks generated in the 4 ply material, almost without exception, originated in areas containing a high concentration of small voids intermixed in between the 90° fibers (see fig. 7). The 8 ply composite did not have void filled areas such as this.

Another difference between the two materials is that, although the 4 ply composite began crack formation earlier in the exposure period than did the 8 ply material, the 4 ply specimens do have a noticeably smaller final crack density than do the 8 ply specimens (see fig. 8). Also noticeable in figure 8, is that the cracks in the 4 ply material have formed only in the 90° fiber strand areas, which are in the outer two plies. As with the 8 ply material, one would not expect to crack formation in the 0° strands at the 0° cross section. Yet, it might be expected that cracks would form in the ± 45° fiber regions. Cracks could form and propagate between fibers in the transverse direction and still be observed along the 0° cross section, yet no cracks are found in these areas.

In order to determine whether the stresses as a whole are significantly less in the interior plies of the 4 ply material than in the 8 ply material or whether the stresses which produce cracks are governed by the orientation of the fibers with respect to the cross section, a new specimen was cut which had 4 cross-sectional surfaces prepared for observation. One side was cut along the 0° axis and perpendicular to the 90° fibers (as before), another was cut along the +45° axis and perpendicular to the -45° fibers, another was cut along the 90° axis and perpendicular to the 0° fibers, and the last surface was cut along the -45° axis and perpendicular to the +45° fibers. As this specimen was subject to 473°F exposure, it became evident that cracking occurred only in regions where the fibers were perpendicular to the exposed cross-sectional surface. Areas with fibers in the -45° direction, now produced cracking behavior when the cross section was cut in the +45° direction (see fig. 9). Like, this occurred in areas of +45° fibers with a -45° cross-sectional surface (see fig. 10).

The cross section which was cut along the + 45° direction showed the greatest amount of cracking. In this cross section the -45° fiber areas from both of the inner plies are adjacent to each other and perpendicular to the surface. Many of the cracks extended across the full width of the combined -45° fiber area (see fig. 9). The -45° area is bounded on both sides by the +45° strands whose fibers run perpendicular to the -45° fibers and only the axis of the cross section. The cross section with the least number of cracks is the one cut along the 90° direction. Here the 0° fiber regions are perpendicular to the surface and are in the outermost regions of the specimen. The other side of the 0° fiber area is bounded by a 90° fiber region (see fig. 9). The only cracks found during the exposure were located in 0° fiber areas where the 0° and 90° fiber strands had crossed over, resulting in the 0° bundle being shifted from the outside of the specimen to the interior and vice-versa for the 90° bundle. No cracks were formed during exposure in the areas where the 0° fibers were in the outermost portions of the material. The couple of cracks in this region, as seen in figure 9, were present before exposure began. The cross sections which were oriented along the 0° and -45° directions and which had 90° and +45° fibers perpendicular to their respective surfaces exhibited an intermediate amount of crack formation. The strands, in which cracking occurred were bounded on one side by fibers running perpendicular to them along the axis of the cross section and on the other side by bundles oriented 45° from the axis of the cross section (see fig. 10).

From the study of this 4 cross-section specimen, it is clear that cross-sectional surface cracking occurred only in areas where the fibers were perpendicular to the cross section. The extent of cracking appears to be dependent on the orientation of the adjacent fiber strands. Areas of cracking which are bounded on both sides by fibers oriented perpendicular to them along the cross section have a greater extent of cracking than areas in which one side is bounded by fibers perpendicular to them and the other side is bounded by fibers oriented 45° from them.On the surfaces where the perpendicular fibers were on the outside of the specimen and bounded only on one side by fibers perpendicular to them, virtually no cracking occurred. The 8 ply material consists of only perpendicular fiber regions bounded on both sides by 0° fibers, thus the crack density of this material was greater than that of the 4 ply material where this pattern never occurs then the specimen is cut along the 0° axis.

After the exposure was completed it was also noticed that cracks had formed along the outside surfaces of the 4 ply specimen as well as the cracks observed along the cross sections. Since these cracks were more difficult to observe and less prevalent than the cross-sectional ones, they were at first unnoticed. These cracks run along the length of the fibers found on the outside of the material. These cracks are long compared to the cracks in the cross section, whose lengths are limited by the widths of the perpendicular fiber bundles. The longest cracks observed were only about 3mm. long. Close-ups of a few of thses cracks can be seen in figure 11. A sketch of the crack arrangement on the outer surface is shown in figure 12. At the outer surface the 0° fibers are dominent so most of the cracks are also oriented in that direction. Cracks are also found perpendicular to these in the regions where the 90° strands have crossed over in the weave and are on the outside.

Although it appears as if the material is significantly damaged, a grinding down of the material was necessary to determine if any damage occurred to the interior of the material

One of the outer surfaces of the specimen which was initially 1.3mm. thick was gradually ground down and periodic examinations of the surface were made. The cracks from the outermost surface were observed on the ground surface until 0.15mm. had been removed. The midpoint of the outer ply had been reached. Beyond this point, going deeper into the specimen, the orientation of the fibers shifts 90°. The 90° fiber strands at the outer surface, instead of being present at an occassional cross-over are now the dominent fibers, and the 0° strands are now the occassional cross-over fibers. At this depth into the interior of the material, no cracks were found covering the outer surface as had been observed in the outer half of the outer ply. The only cracks found on this surface orignated at the intersection of the 0° cross section and ran along the direction of the 90° fibers. The cracks were all short, less than 0.5mm. in length. From figure 13, it can be seen that the cracks observed from the 0° cross section penetrate very little into the material and that the vast majority of the interior has remained undamaged.

The grinding down of the sample was continued through the next ply to the midpoint of the specimen. Similar to the 0°, 90° ply mentioned above, the ± 45° ply showed only short cracks along the +45° fibers at the -45° cross section when the +45° strands were dominent and along the -45° fibers at the +45° cross section when the -45° strands were dominent.

In the interior of the material, cavities were observed running along the axis of the fibers, but these are due to the voids present in the material. An unexposed sample was ground down and its interior possessed the same cavity structure. Thus the only damage to the material appears to be cracks in the outer half of the outer plies and along the exposed cross section. The cracks in the cross section are all less than 0.5mm. deep and most are approximately 0.1mm. deep.

400 Hour 550°F Exposure

8 Ply Test Panel A specimen was cut and polished for observation along the 0° cross section as had been done for the 473° exposure. A couple of cracks were initially present along the 15mm. length of material. Another specimen was prepared and polished along one of the outer surfaces. During the course of the exposure, observations and photographs were made of a localized area of this outer surface, but due to the fact that there is a smaller crack density on the outer surface than on the cross section, no cracks happened to form in this area. Following the exposure the entire outer surface was scanned carefully and the crack pattern sketched. The results will be discussed later.

The cross section of the 8 ply material responded very similarly to the 550°F exposure as it had to the 473°F exposure. After only 16 hours there was a slight but noticable loss of resin from the surface. After 240 hours of exposure the loss of resin from the surface appeared to have stopped. The depressions left in the surface appear to be no deeper than those formed during the 473°F exposure. Cracks began to appear in the 90° fiber areas after 98 hours of exposure. This is somewhat accelerated from the 473° exposure in which several cracks did not form until after approximately 160 hours of exposure. The number of cracks increased over time until 300 hours of exposure when no additional cracking occurred. The final crack density of the 550°F exposed material appears virtually indistinguishable from that of the 473°F exposed material. The lengths and widths of the cracks in both specimens also appeared identical.

The entire polished outer surface of the other specimen exposed to 550°F was examined and its crack pattern carefully sketched (see fig. 14). The surface appears very similar to the 4-ply material following 473° exposure. The longest of the cracks are approximately 3.5mm. long and the crack density is comparable to that of the 4 ply specimen. As with the 4 ply material, the surface was ground down in order to determine the extent of damage to the interior of the material. Once approximately 0.18mm. had been removed from the original thickness of the material (at the midpoint of the outer ply) all of the cracks had been removed except the short cracks at the cross-sectional surface. Along with the 4 ply material, this shows that crack formation is a surface phenomenon and does not effect the interior of the composite. Many cracks were formed on the outer surfaces, but were limited to just the outer half of the outside plies. The cross-sectional surface was also heavily cracked, but as can be observed from grinding down the specimens, most of the cracks are only about 0.3mm. deep into the material, with an occassional crack extending about 0.7mm. into the interior. These cracks are somewhat longer than the cracks formed during the 473°F exposure, yet the majority of the interior of the composite has been undamaged due to the 550°F exposure.

Thermal Cycling

Both 4 and 8 ply specimens which had been equilibrated to an 80% R.H. environment were thermally cycled between room temperature and 473°F as described in the experimental section. The 8 ply material was subjected to 50 cycles of 4 mintues heating time and 4 mintues of cooling time. The thinner 4 ply material was subjected to 50 cycles of 2 mintues heating time and 2 mintues of cooling time. Due to the cycling process the absorbed moisture near the outer surface was quickly driven off while the interior of the specimens retained a significant fraction of its original moisture content (see fig. 15).

During the cycling process of the 8 ply specimen, the specimen is removed after 1,5,10,20 and 50 cycles for microscopic observation. It was thought that if any cracking or other damage was to occur, it would occur early in the cycling process when the surface moisture was being rapidly driven off. Yet no signs of damage were observed either early in the process or after the 50 cycles exposure. The only noticable change occuring at the surface was the condensation of what appeared to be moisture into small beads at the ends of the specimen where dirt particles had collected. These (water beads?) were observed after 5, 10, and 20 cycles of exposure, but not after the full 50 cycles.

The 4 ply specimen was removed after only 20 and 50 cycles for observation since no damage occurred to the 8 ply material. As with the 8 ply material, no cracking or other damage was observed on the surface of the specimen. Thermal cycling of specimens equilibrated to 80% R.H. apparently has no noticable effect on the appearance of the composite surface.

CONCLUSIONS

The 400 hour exposure of the polyimide-graphite composite to 473°F did result in considerable surface cracking, both at the cross-sectional surfaces of the specimen and at the outer surfaces of the material. On the cross-sectional surfaces the cracks appeared only within the strands which were oriented perpendicular to the surface. The 4 ply composite exhibited crack formation somewhat earlier in the exposure process than the 8 ply material, yet its final crack density along the cross section was less than that of the 8 ply composite.

There was also considerable cracking along the outside surfaces of the specimens. Although the amount of cracking appears to be considerable, the extent of damage to the interior of the material was shown to be minimal. Most of the cracks from the cross-sectional surface extended only about 0.1mm. into the interior, while a few cracks did extend about 0.5mm deep. The cracks from the outer surfaces extended only to the midpoint of the outer plies. Thus, for the 4 ply material, 75% of the interior contains no cracking behavior, and for the 8 ply material, 88% of the interior is crack free. There was also a slight loss of resin from the surface which was noticed from the depressions that were formed between the fibers perpendicular to the surface. These depressions (observed with the aid of an election microscope) are only a couple of microns deep, thus the loss of resin appears to be minimal.

The 400 hour exposure at 550°F produced similar results as with the 473°F exposure. The amount of cracking on both the cross-sectional and outer surfaces was comparable to that of the 473°F exposure. The only noticable differences were that the initial cracking occurred somewhat sooner during the 550°F exposure and that the depth of the cracks from the cross section into the interior were slightly greater than those formed during the 473°F exposure. Yet, as with the 473°F exposed specimens, the only observable damage occurred at the outer portions of the material and the majority of the interior remained undamaged.

Thermally cycling composite materials, equilibrated at 80% R.H., from room temperature to 473°F produced no observable damage. During this period, moisture is rapidly driven from the outer regions of the composite while the center of the material still retains a large portion of its original moisture content. If any significant damage was to be produced due to thermal cycling, it would have been expected to occur within the first portion of this cycling process when the rate of moisture loss was at its greatest.

From the observations made during this study, the PMR15-graphite composite material in question appears to be satisfactory for operations at these temperatures (up to 550°F). This study has shown that for these given exposure times and temperatures, cracking is entirely a surface phenomenon and that the damage due to cracking will be minimal. Cracks can be expected to develop in the outer surfaces of the material, but these cracks will penetrate only to the midpoint of the outer ply. Since this cracking behavior, along with the slight loss of resin from the surface were only forms of damage observed (no evidence of debonding, delamination, or other damage were found), it would be expected that there would be some loss of material properties following thermal exposure, but that these losses would be quite small.

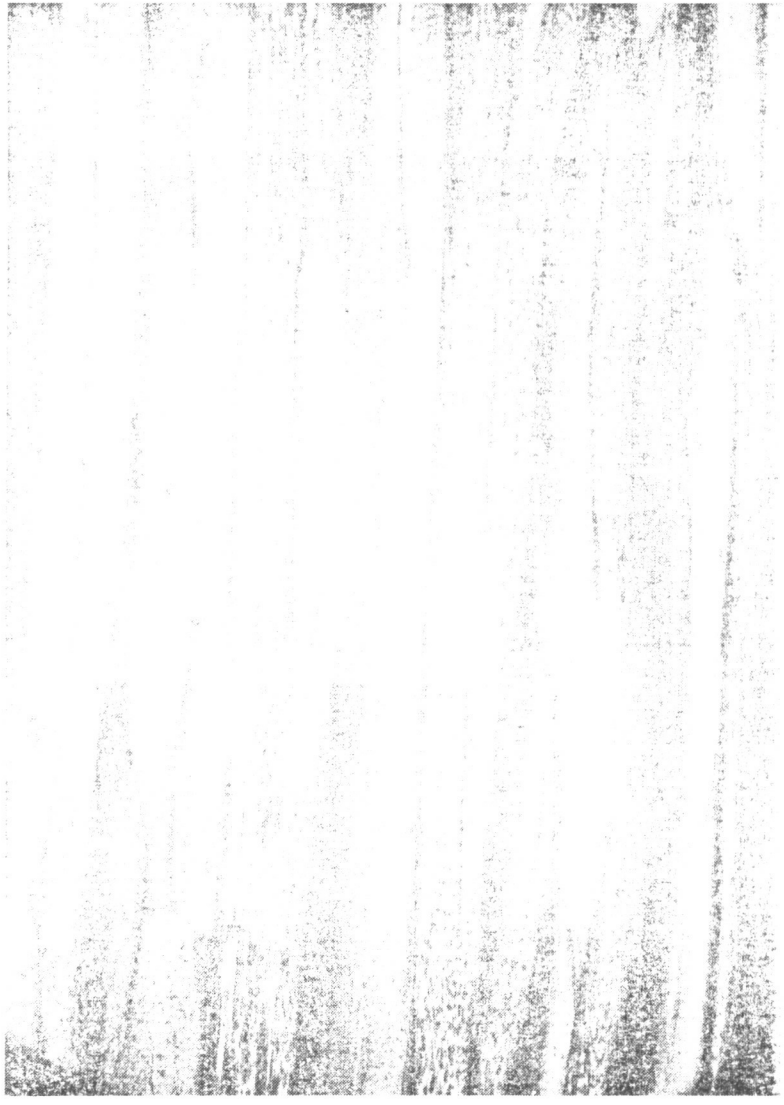

Figure 1. - Cross section of 8 ply material.

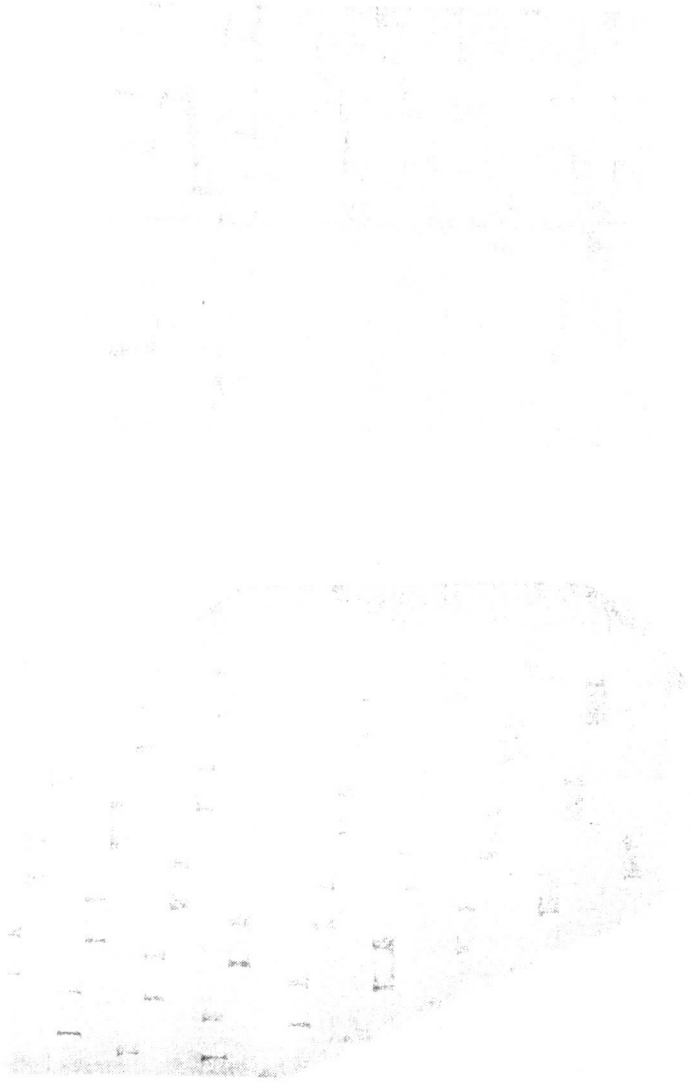

Figure 2. - Weave pattern in composite.

Figure 3. - Initial condition of 4 ply material.

Figure 4. - Loss of resin from composite surface.

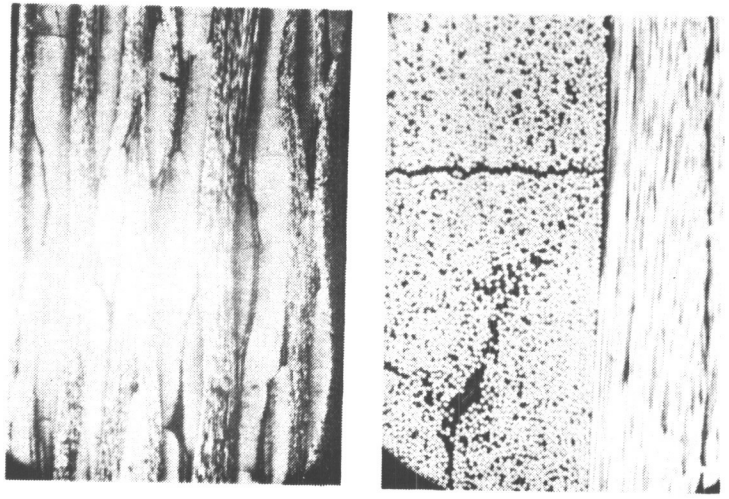

Figure 5. - 8 ply specimen after 258 hours of exposure at 473°F.

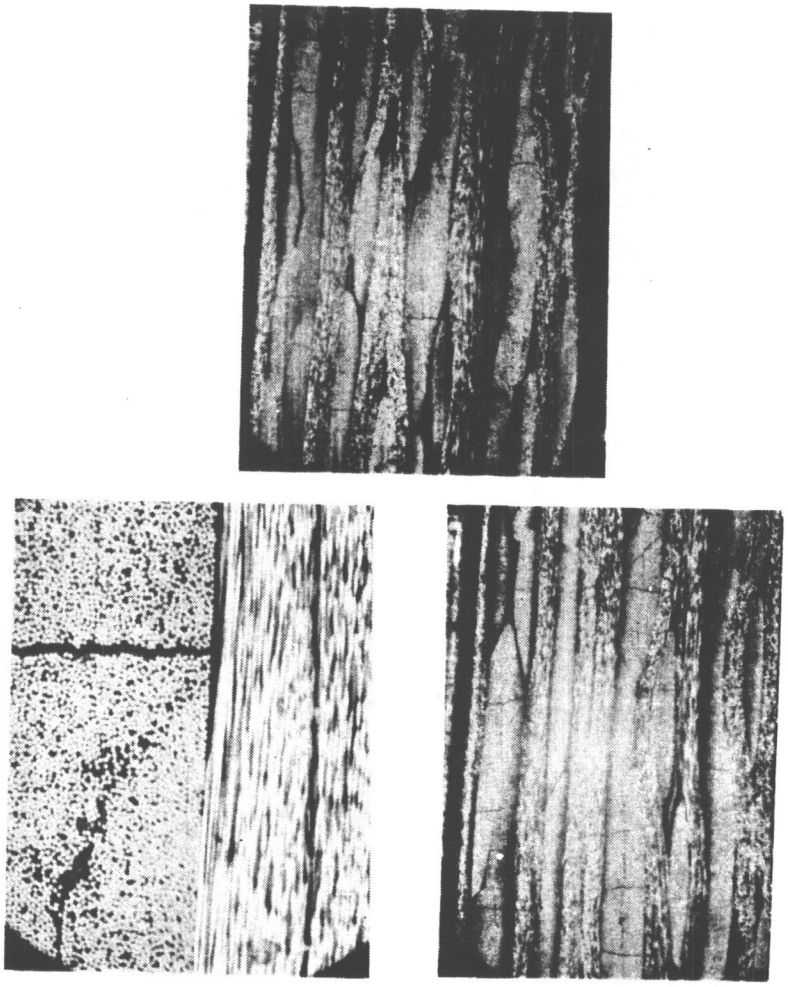

Figure 6. - 8 ply specimen after 391 hours of exposure at 473°F.

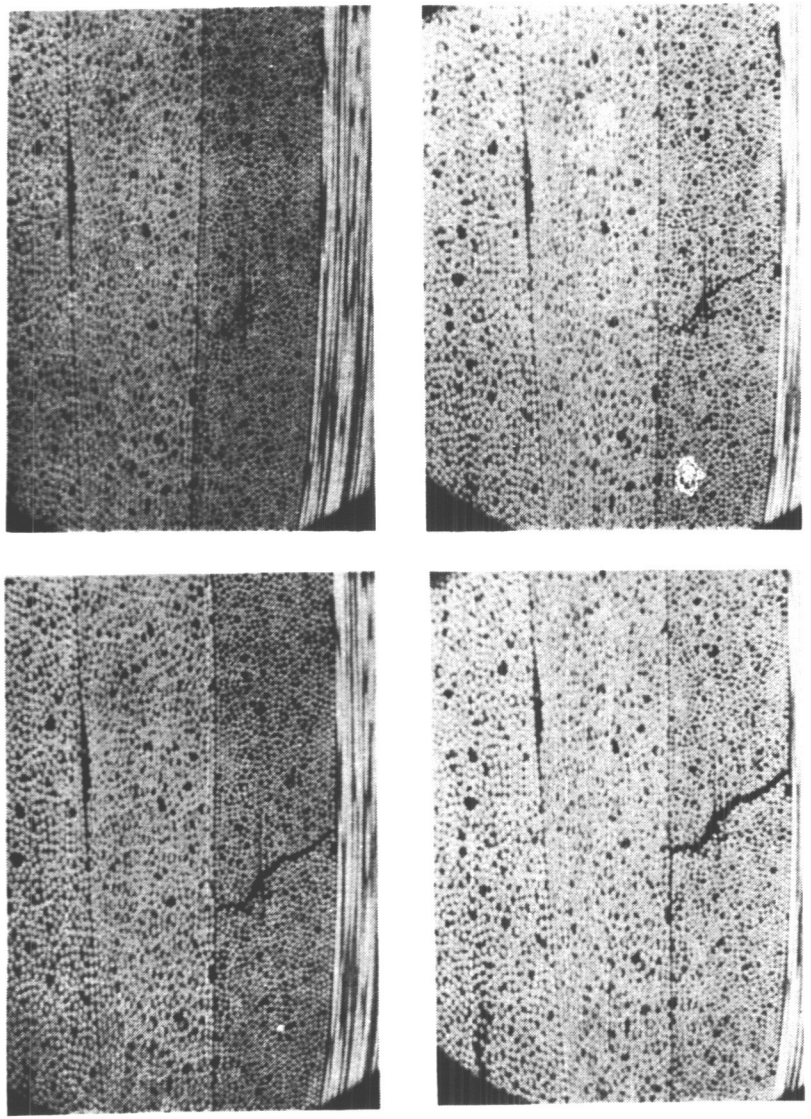

Figure 7. - Crack formation in 4 ply composite.

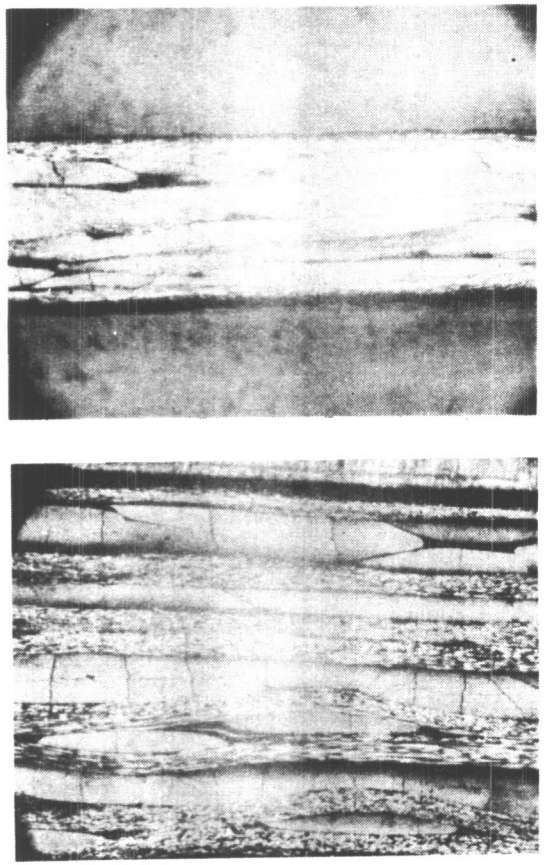

Figure 8. - 4 and 8 ply specimens following exposure at 473°F.

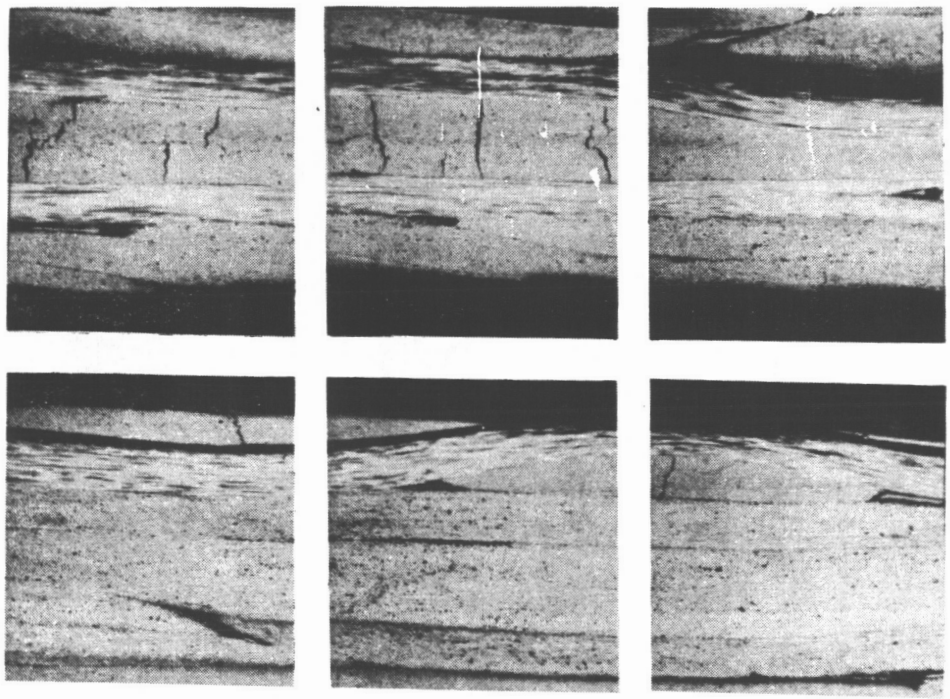

Figure 9. - 4 ply composite following exposure at 473°F.
(Top: Along +45° axis. Bottom: Along 90° axis.)

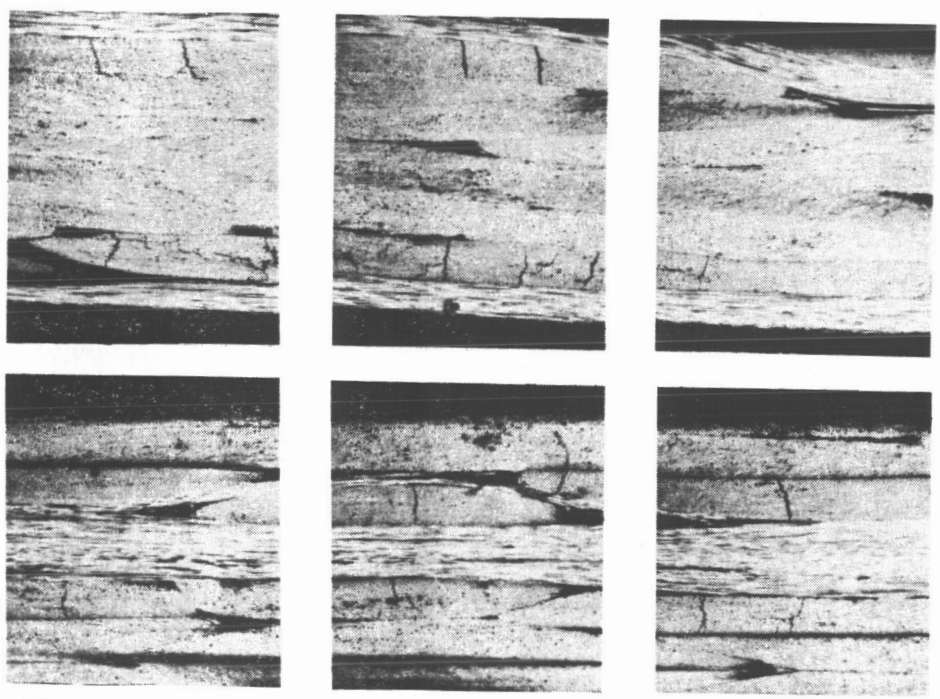

Figure 10. - 4 ply composite following exposure at 473°F.
(Top: Along 0° axis. Bottom: Along -45° axis.)

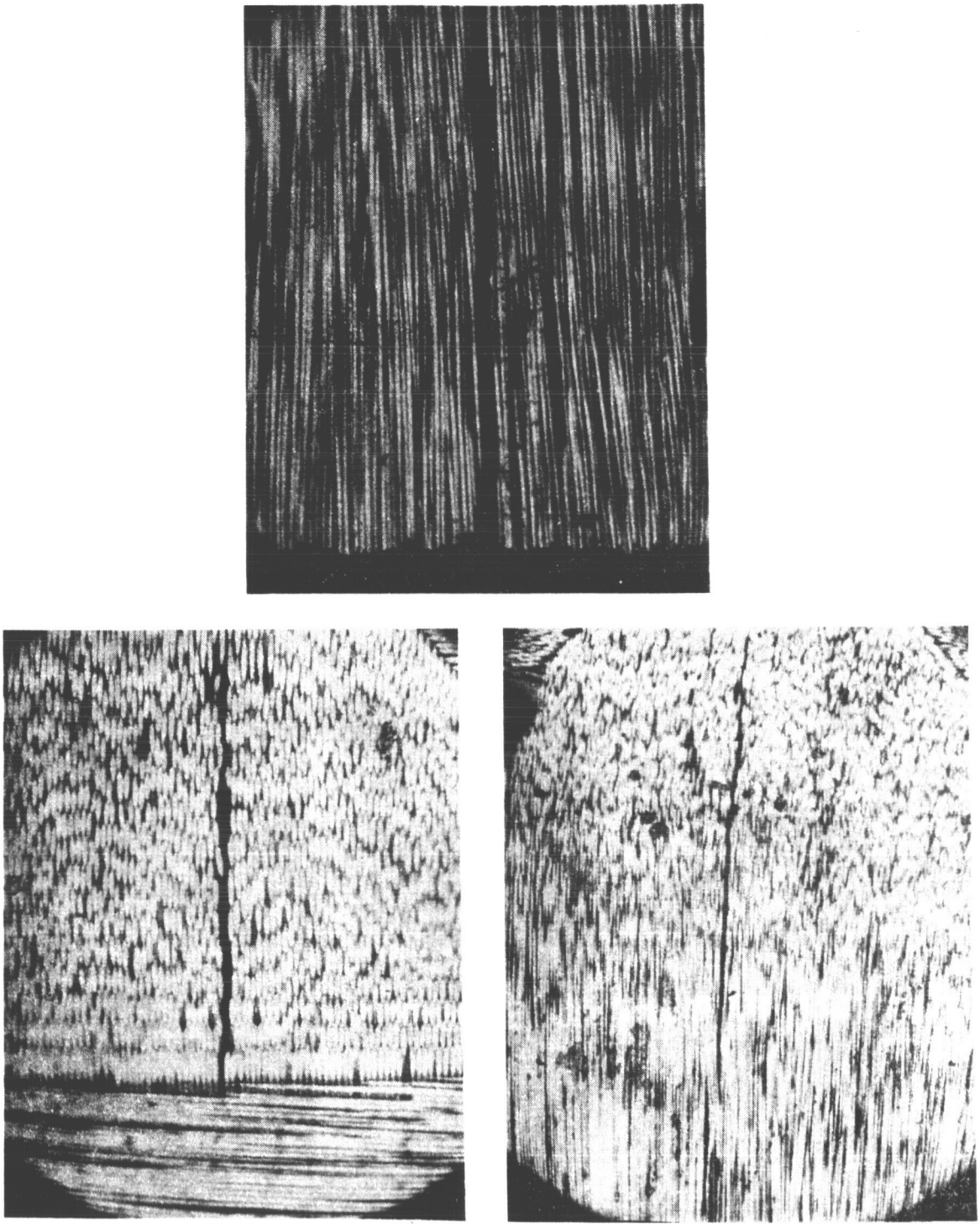

Figure 11. - Cracks along the outer surface following exposure at 473°F.

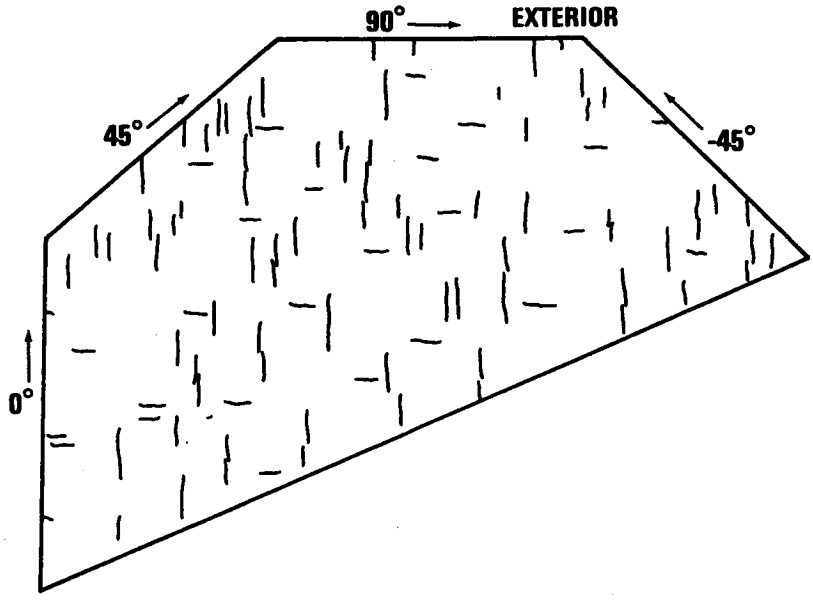

Figure 12. - 4 ply specimen after 400 hour exposure at 473°F.

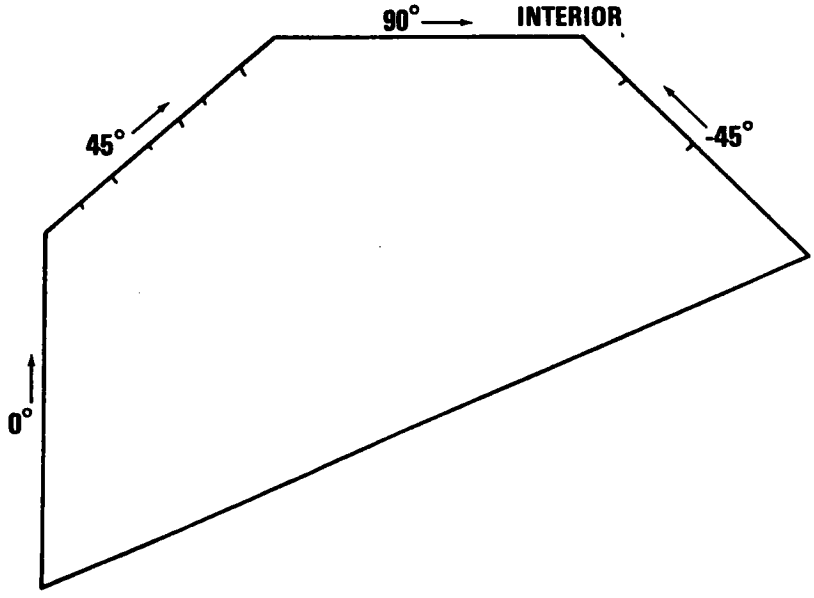

Figure 13. - 4 ply specimen after 400 hour exposure at 473°F.

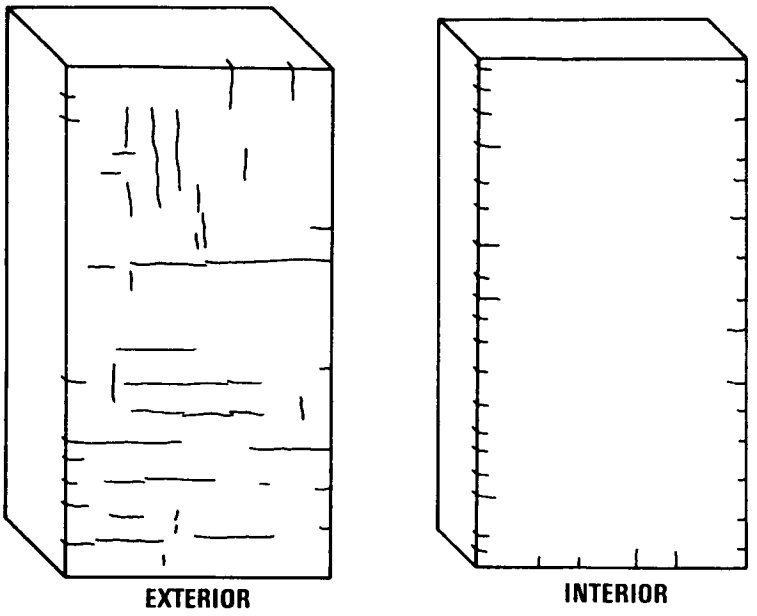

Figure 14. - 8 ply specimen after 400 hour exposure at 550°F.

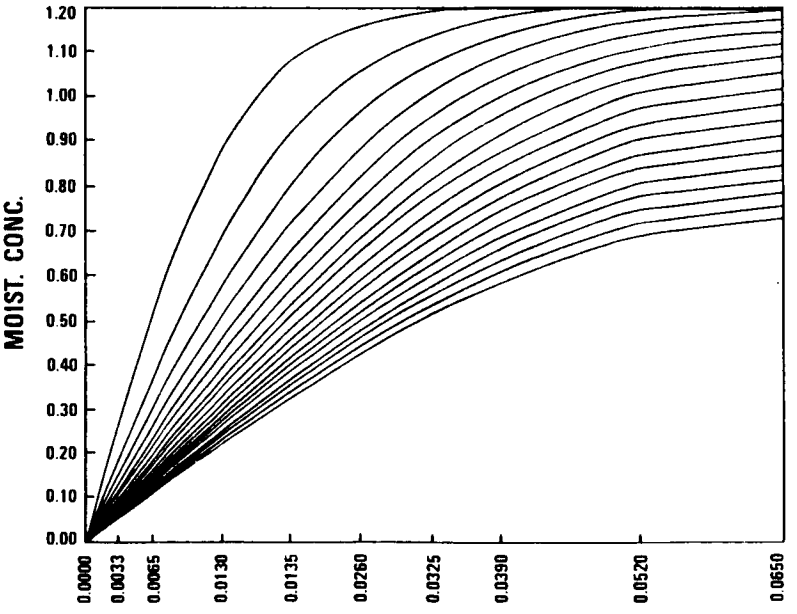

Figure 15. - Moisture concentration profile of a 4 ply specimen during thermal cycling.