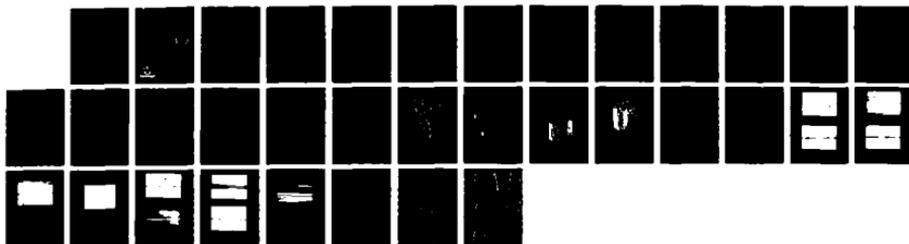
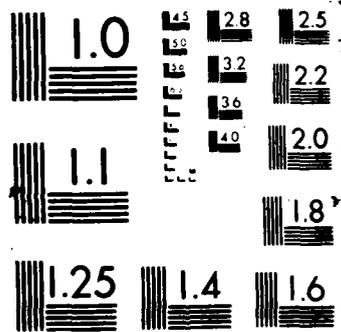


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FINAL TECHNICAL REPORT

"INTERFACIAL SHEAR STRENGTH OF PITCH AND HIGH STRAIN PAN FIBERS IN AN EPOXY MATRIX

by

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ABSTRACT

→ In advanced polymeric composites reinforced with fibers of glass, carbon, or graphite the ability to effectively use the strength and stiffness of these reinforcing fiber depends on the properties of the matrix material and the degree of bonding between fiber and matrix.

This work uses the embedded fiber method to directly determine the interfacial shear strength between 1) PAN high strain carbon fibers (Apollo 38-750) with different surface modifications and 2) mesophase pitch-based carbon fibers of various moduli and surface modifications with an epoxy matrix (D.E.R. #331 resin with MPDA (1,3-phenylenediamine) as the curing agent). The effect of the various surface modifications on the interfacial shear strength was evaluated in an attempt to determine their interrelationships.

The results show that sizing of the fiber increases the interfacial shear strength by 23% over an unsized fiber while an oxidative surface treatment produces an increase of over 200% over the untreated PAN carbon fiber. The mesophase pitch-based fibers showed a general decrease in the interfacial shear strength with an increasing fiber modulus. These results are in agreement with previous work on similar systems.

INTRODUCTION

Composite design requires a determination of the bond strength between the fiber and matrix. Although there is no satisfactory method of measuring composite bond strength, the single fiber interfacial shear strength method does provide a sensitive reproducible measure of

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fiber-matrix adhesion in shear without the complicating factors of composite geometry and macrodefects which may obscure interfacial effects. This work seeks to determine the relationship between surface treatment and shear strength for two different carbon fibers in a typical structural epoxy matrix.

FIBER STRUCTURE AND BULK PROPERTIES

In order to understand the effect of surface treatment on fiber-matrix shear strength, knowledge of the fiber structure and its production are required.

Graphite is a crystalline form of carbon having a hexagonal layered structure with covalent bonding between the carbon atoms within the plane. When a polymer fiber is partially converted to carbon and graphite during carbonization, a fiber with the potential for having the highest absolute modulus, modulus density, and theoretical tensile strength of all known materials results.

The structure of the carbon fiber is made up of ribbons or columns of graphite crystallites which lie approximately parallel to the fiber axis (Figure 1)^[8]. The superior fiber properties are due to the alignment of the layered planes with their strong sp^2 orbital bonding in the hexagonal layer planes parallel to the fiber axis. The bonding between planes is weak due to dispersive bonding and produces a low shear modulus and cross plane Young's modulus. When the hexagonal layer planes are off-axis the low shear modulus between the planes greatly decreases fiber stiffness resulting in lower modulus.



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The processing of carbon fibers can affect the fiber structure (Figure 2). To introduce the preferred orientation of the hexagonal layer planes commercial processes use high temperature and plastic deformation such as a hot stretching process.

The graphite basal planes form layered structures called crystallites which form the ribbon.^[11] A lower graphitization temperature with hot stretching results in a fiber surface with small graphite crystallites which have more edges and corners exposed on the fiber surface (Figure 3).^[9] A higher graphitization temperature and hot stretching result in a surface of large graphitic crystallites oriented more parallel to the fiber axis which means fewer edges with less exposure due to alignment.

One model of the PAN fiber bulk and surface structure suggests that the arrangement of the layers of the basal planes becomes less organized further into the fiber.^[11] This would suggest a "skin/core" ratio dependent on the final carbonization temperature, where higher temperatures would produce a thicker skin and consequently a more "onion skin" type of structure (Figure 4).^[9] A low modulus fiber doesn't have this gradient of preferred orientation.

Mesophase pitch-based fiber orientation is different from that of the PAN based fibers. The graphitic ribbons formed under the carbonization and graphitization steps produce a high axial alignment but also a more radial alignment of the ribbons. The fiber tensile modulus also increases with high temperature heat treatment, but as a natural consequence of the liquid crystalline order there is no gradient

in orientation. The concentration of corners and edges of graphitic crystallites would be expected to be different than that achieved for the PAN fiber.

These ideal models don't take into account the transitions that occur during graphitization. During graphitization the polyacrylonitrile polymer decomposes and the carbon atoms form the graphite structure. The result is the formation and release of volatiles (gases) from the core and surface of the fiber. Since solidification probably occurs from the surface inward the escaping gases must pass through the forming surface. The resulting structure would have a defect filled outer surface. Combining the ideal structural model with the events of graphitization results in a defect laden outer skin with preferentially aligned graphitic crystallites along the fiber direction. Studies have shown that this structure does in fact occur on the fiber surface and that it appears to be quite different from the structure of the interior of the fiber.^[2]

CARBON FIBER PRODUCTION

The majority of carbon fiber production today (Figure 5) starts with PAN (polyacrylonitrile) fiber precursor but rayon and pitch precursors are also used for large-scale production. The essential features of the processes for each precursor are similar, they are:

- a stabilization treatment to prevent melting of the fiber
- a carbonizing heat treatment to eliminate the noncarbon elements
- a high-temperature graphitizing treatment to enhance the mechanical properties of the final carbon fiber

A technique to improve the mechanical properties of PAN fibers is "hot stretching" of the fiber during the graphitization treatment. This was first done by Bacon and Schalamon.^[1] The temperature of the graphitization treatment and hot stretching further align the graphite layer orientation with the fiber axis.

Mesophase pitch-based carbon fibers also have the same sequence of production, ie; oxidation, carbonization, and graphitization. A "hot stretching" technique is also used and is carried out by spinning the pitch under stress at a low temperature. The resulting mesophase pitch fibers have a high-modulus without stress graphitization. ^[8]

FACTORS AFFECTING INTERFACIAL & BULK PROPERTIES

SURFACE TREATMENTS:

The most commonly used continuous production surface treatments are air oxidation and electrolytic oxidation.^[2] Surface treatments act to improve the bonding capability of the fiber to the matrix by removing some of the weak defective outer skin and by adding oxygen to the fiber surface.^[9] The weak defective skin reduces shear transfer between fiber and matrix because the defective layer can't support the shear loads, thus failure occurs in the fiber surface layers.

OXYGEN ADDITION:

The corners and edges of the graphitic crystallites are sites for oxidative attack.^[3] Since the higher temperature graphitization of the high modulus fibers produces larger crystallites, the result is a lowering of the edge area. Also the crystallites have better alignment, which exposes fewer edges and corners to oxidative attack. Thus the

bonding capability is lower in a high modulus fiber.^[3] Studies have shown that addition of surface groups (O₂,N) only increase the interfacial shear strength by about 10%.

DEFECT LAYER REMOVAL:

The second result of surface treatments is the removal of the defective surface layers of a fiber, leaving a structurally sound fiber surface.^[9] The defective surface cannot support shear loads resulting in interfacial failure in the fiber surface. Studies have shown that the removal of the defective layer is the major factor of increasing the interfacial shear strength.^[9]

SIZING:

Sizing is usually a thin polymeric coating applied to a carbon fiber to increase bond strength, for surface protection and to hold fiber tows (bundles) together during fabrication. The increased bond strength to sized fibers is due to the formation of a brittle interphase region.^[12] The brittle region has a higher modulus than the matrix since the polymer (epoxy) has cured with very little curing agent present. The brittle region increases stress transfer between fiber and matrix, but it also promotes crack growth into the matrix due to lower fracture toughness of this interphase region.^[7,10] The greatest increase of interfacial shear strength is due to the formation of the sound structural fiber surface and the creation of the brittle zone by the sizing.^[10]

INTERFACIAL SHEAR STRENGTH DETERMINATION

The single fiber interfacial shear strength method is a direct measure of the adhesion between a fiber and matrix. The method requires embedding a single fiber totally in the epoxy matrix. The fiber is

mounted axially within the test specimen (figure 6). Once in the fixture under tensile load, shear forces are transferred to the fiber. The primary purpose of the ductile epoxy matrix is to transfer stress to the brittle filaments. Failure of the fiber occurs when the local tensile strength of the fiber is exceeded.^[2] The fiber breaks within the epoxy and the fragments can be seen with polarized and unpolarized light. The tensile load is increased gradually and the process continues until the pieces of fiber remaining are not long enough to support sufficient shearing forces to exceed the fiber tensile strength. These fragments represent the critical transfer length (L_c) for reinforcement.^[4,2] The relationship between the fiber diameter (d) and fiber tensile strength (σ) at the critical length with the interfacial shear strength (τ) is:

$$\tau = \frac{\sigma}{2} \left(\frac{d}{L_c} \right)$$

In this work the fiber tensile strength at the critical length was assumed a constant (see Further Studies).

There are several advantages to this method of measurement:

- the state of stress is very similar to that of an actual composite
- the interfacial shear strength upper limit is that of the matrix
- easy observation, photography, and measurement with a trinocular microscope
- comparison of fibers with different surface treatments and assessment of the actual interfacial shear strength of the fiber and matrix.

EXPERIMENTAL PROCEDURE

A) The fabrication of a test specimen.

Fiber Lay-up In Silicone Dogbone Molds:

1. Place carbon fiber across the silicone mold so the fiber lays in the sprue slot of the mold.
2. Fill the sprue slot with rubber cement to hold the fiber taut in the mold.
3. Allow the cement to cure overnight.
4. Weight out Dow D.E.R. #331 epoxy resin, using 14.5% of the resin weight as the amount of m-PDA (curing agent) to add. The m-PDA (1,3-phenylenediamine) is solid a room temperature.
5. Heat the epoxy and m-PDA to 60-70⁰C to melt the m-PDA and insure that a good mix will occur. Also heat silicone molds to this temperature.
6. Mix the epoxy and m-PDA.
7. Apply vacuum at (29 in.Hg) and heat (60-70+oC) for approximately 2 minutes.
8. Pour epoxy\m-PDA mixture into mold.
9. Cure in circulating air oven for: 75⁰C for 2 hours then, 125⁰C for 2 hours then, turn off oven and allow to oven cool to room temperature.

*Note: The m-PDA and D.E.R. #331 were refrigerated to prevent deterioration.

B) Interfacial Shear Strength Testing Procedure:

1. Calibrate of filar eyepiece at 50X and 500X.
2. Load specimen in fixture.
3. Measure fiber diameter at 500X.
4. Apply load to find critical length
 - a) by 0.4% strain increments
 - b) counting of breaks at each increment
 - c) continue loading until there's no increase in breaks
5. Measure breaks at 50X.

*Note: The experimental procedure was repeated until a consistency of results was established for the Apollo fibers. A statistical evaluation of the fiber length data could have been used instead of the multiple measurement method.

FIBERS TESTED AND THEIR KNOWN PROPERTIES

Fibers from two different precursors were used in this experiment.

The PAN based fiber was described as Apollo 38-750 whose properties include:

Modulus.....38 Mpsi
Tensile strength.....750 kpsi
Strain.....2%

The surface treatments on the Apollo fiber were:

Fiber#1.....untreated and unsized
Fiber#2.....treated and unsized
Fiber#3.....treated and sized

The mesophase pitch-based fibers used had the following properties and were labeled:^[4]

- P-25 25 Mpsi, about 200 kpsi tensile strength,
untreated and unsized
- P-55 55 Mpsi, about 300 kpsi tensile strength,
untreated and sized (UC-318 finish
- P-75S 75 Mpsi modulus, 300-350 kpsi tensile
strength, treated and sized (UC-320)
- P-100 100 Mpsi modulus, about 350 kpsi tensile
strength, untreated PVA sized.

EXPERIMENTAL RESULTS AND ANALYSIS

PAN High Strain Fibers

The specimen fabrication was done by a batch process where one batch consisted of 5-15 specimens of the same fiber and surface treatment. The variation of specimen numbers was dependent on the number of "good" specimens in the batch.

With the PAN based fiber batches the average aspect ratio for the batch was determined as well as the percent standard deviation of the aspect ratios and the coefficient of variation.

A total average aspect ratio, percent standard deviation, and coefficient of variation were then calculated for all of the batches of that fiber surface. The interfacial shear strength was then calculated. The PAN based fiber results are listed in Table 1.

Table 1.

Interfacial Shear Strength for PAN Fibers

	Average Aspect Ratio	Interfacial Shear Str.
fiber #1	115.25	3.25 kpsi
fiber #2	53.08	7.06 kpsi
fiber #3	43.20	8.68 kpsi

Transmitted polarized light was used to observe the stresses occurring in the fiber-matrix interphase. Qualitative differences in the stress pattern resulting from interphase changes could be observed as were found in previous studies.^[9] The interphase changes are related to changes in fiber surface treatment.

The failure mode in Apollo fibers for both the untreated and the surface treated fibers was observed to be crack growth parallel to the fiber-matrix interphase (Figures 7-10). This was similar to the failure mode observed for untreated and surface treated fibers studied earlier.^[9,12] The surface finished fiber gave a more intense photoelastic stress pattern (Figure 11) and also indicated a change in failure mode from interfacial to matrix (Figure 12). Apparently the presence of the finish layer is acting to produce a brittle interphase which fails in shear under the stress concentrations acting at the fiber ends.

Mesophase Pitch Fibers

The data collected for the mesophase pitch-base fibers was tabulated in the same manner as was the PAN fiber data. (Table 2) In general a definite trend to

Table 2.

Interfacial Shear Strength for Pitch Fibers		
	Average Aspect Ratio	Interfacial Shear Str.
P-25	50.02	2.0 kpsi
P-55	96.10	1.56 kpsi
P-75S	90.96	1.79 kpsi
P-100	133.59	1.31 kpsi

decreasing the interfacial shear strength with increasing modulus was noted. The deviation from this general trend were due to surface treatment which was applied to one fiber (P-75S). The application of the finish to P-55 and P-100 did not have as great an influence as might be expected from the Apollo fiber results. This is due to the fact that the finish was applied to an untreated fiber making its performance limited to the intrinsic shear strength of the native surface. This was also observed in a previous study.^[9]

The interfacial failure modes for all of the pitch fibers were similar. Figures 13-17 show the stressed interface for various pitch fibers. The photoelastic stress patterns observed for these specimens all indicated interfacial failure. All indicate interfacial failure with low levels of adhesion.

The results of this study confirm the basic conclusions proposed earlier about the effect of fiber surface treatment and fiber surface finish. Figure 18 is a plot of the interfacial shear strength data obtained in this program with that obtained in some previous efforts for PAN fibers.^[9,12] Grouping the fibers by surface treatment shows a parallelism in behavior irregardless of precursor and surface treatment.

The increases within each set are the same. (The absolute values for the XA fibers will be modified once the strength versus length data is available. This would shift the data for the XA fibers upward making for a closer agreement with the other two sets.) For all three sets of PAN fibers, the surface treated fibers increase their level of interfacial shear strength with surface treatment by the largest amount. Surface finish or sizing application further increases the level of interfacial shear strength obtained but at the expense of changing the failure mode from interfacial to matrix.

Figure 19 is a plot of the interfacial shear strength obtained with the pitch fibers compared to some data obtained earlier^[9] for PAN based low (A) and high (HM) modulus untreated fibers. The values obtained for the pitch fibers (P-25, -55, -74S, -100) are uniformly low and show a decrease with increasing modulus. The possibility of improvement in these values with surface treatment is indicated by the higher value obtained for the surface treated HM fiber (HMS). The low values obtained for the low modulus fibers may be reflective of the radial orientation of the pitch fiber. A morphology of this type would not be altered much as the graphite size increases with increasing processing temperature as much as it would for a circumferentially oriented PAN based fiber.

CONCLUSIONS

For the Apollo PAN fibers, it can be concluded that surface treatment improves the effective interfacial shear strength of the Apollo 38-750 fiber in an epoxy matrix by over 200% from that of an untreated and unsized fiber. (fiber #1 vs fiber #2) The application of a

resin sizing to the surface treated fiber improves the effective interfacial shear strength by an additional 23% (fiber #3 vs fiber #2). These results indicate the removal of the outer fiber surface layer with surface treatment is the most important factor in surface treatments and that the brittle interphase created by the sizing plays a smaller but nonetheless significant part in increasing the interfacial shear strength. Other studies have also shown similar improvements of interfacial shear strength due to sizing and surface treatments. In general these results for the PAN fibers confirm earlier results published by the author.[9]

The mesophase pitch-based fibers display a decrease in interfacial shear strength with increasing modulus even with treatments and sizing on the higher modulus fibers. This behavior is consistent with the model of the surface structure of the pitch fiber. As the modulus increases there are less matrix-fiber bonding sites due to larger graphite crystallites and better crystallite alignment.

FUTURE WORK

While the results of this work seem to fit into the surface structure-property relationships developed previously, further research is warranted to confirm this conclusion. In particular, the interfacial shear strength of a fiber in a matrix requires that the tensile strength at the critical length of the fiber be known. Surface treatments and finishes could have unexpected effects on the fiber tensile strength as a function of length and consequently could affect the calculations made here. Likewise, the surface energetics of the fiber itself can strongly influence the adhesion and the structure of the interphase region.

Determination of the locus of failure at the molecular level is necessary to confirm the validity of the interfacial mechanisms being postulated.

Acknowledgment A portion of the research reported here was included as part of the senior research project of T. Gendron and was published separately in "Relationship Between Surface Treatments and Bond Strength of High Strain Carbon Fibers and Mesophase Pitch-based Carbon Fibers with Epoxy Resins" as a senior research project for course number MMM 499 in partial fulfillment of the requirements for the degree of bachelor of science from the department of Mechanics, Metallurgy, and Material Science at Michigan State University. Additional data was provided by M. Waterbury. Partial funding for this project was provided under ONR Contract No. N00014-86- K-0393 Dr. Larry H. Peebles, Jr., Project Monitor.

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↑ AXIAL DIRECTION

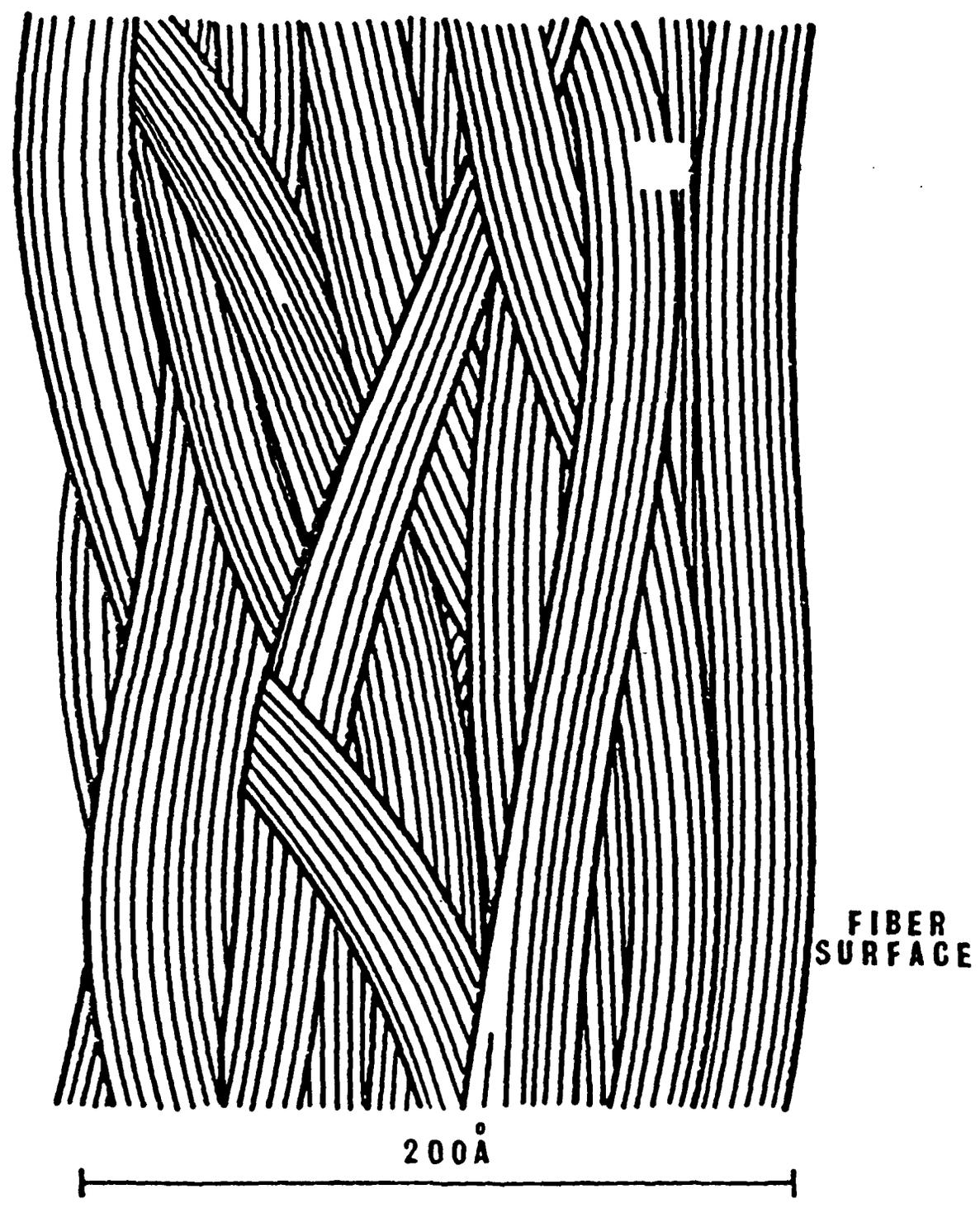


Figure 1 Ribbons of graphite crystallites from a 57 Mpsi modulus PAN carbon fiber. ⁸

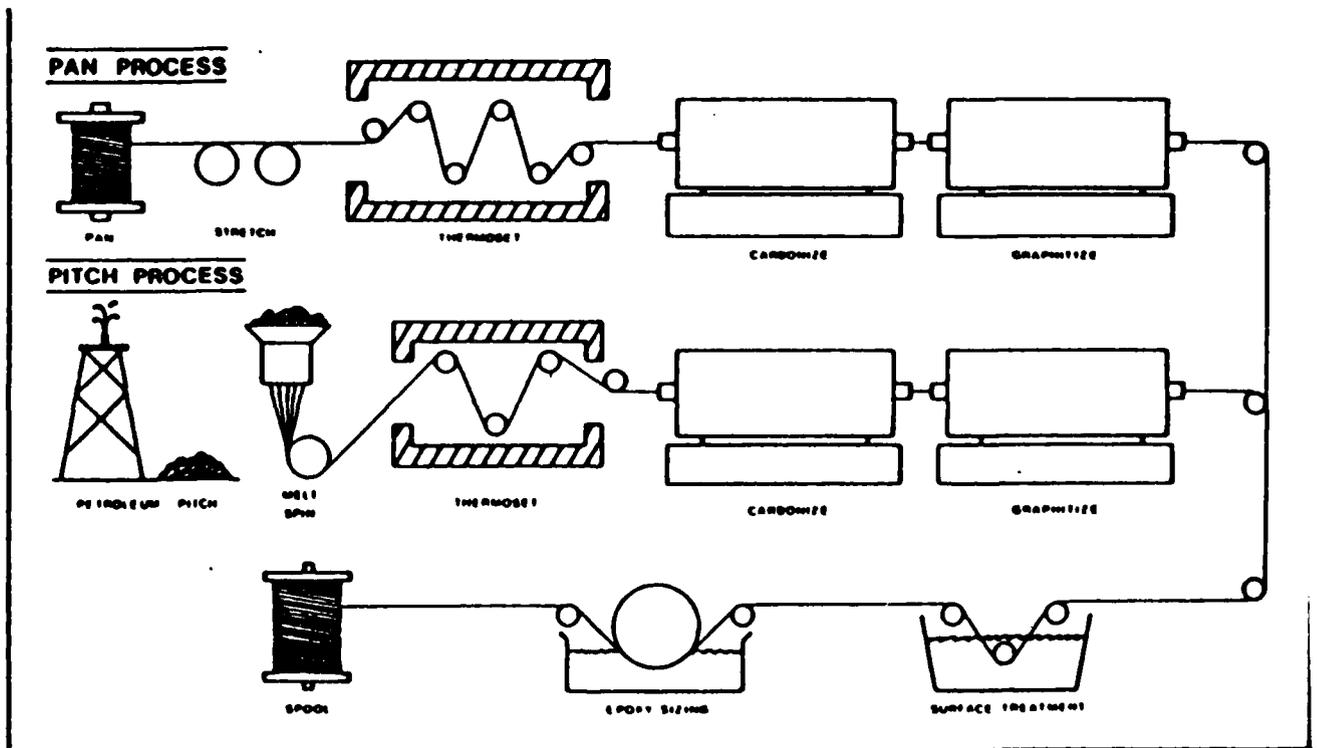


Figure 2 PAN and pitch-based carbon fiber processing with "hot stretching". [8]

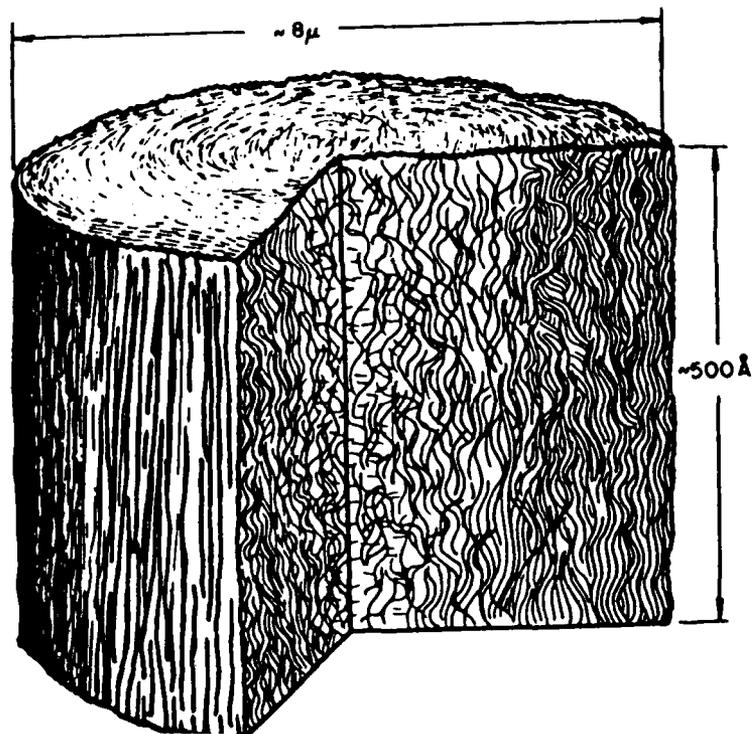


Figure 3 Schematic 3-D structural model of a PAN based fiber of intermediate modulus (35 Mpsi). [9]

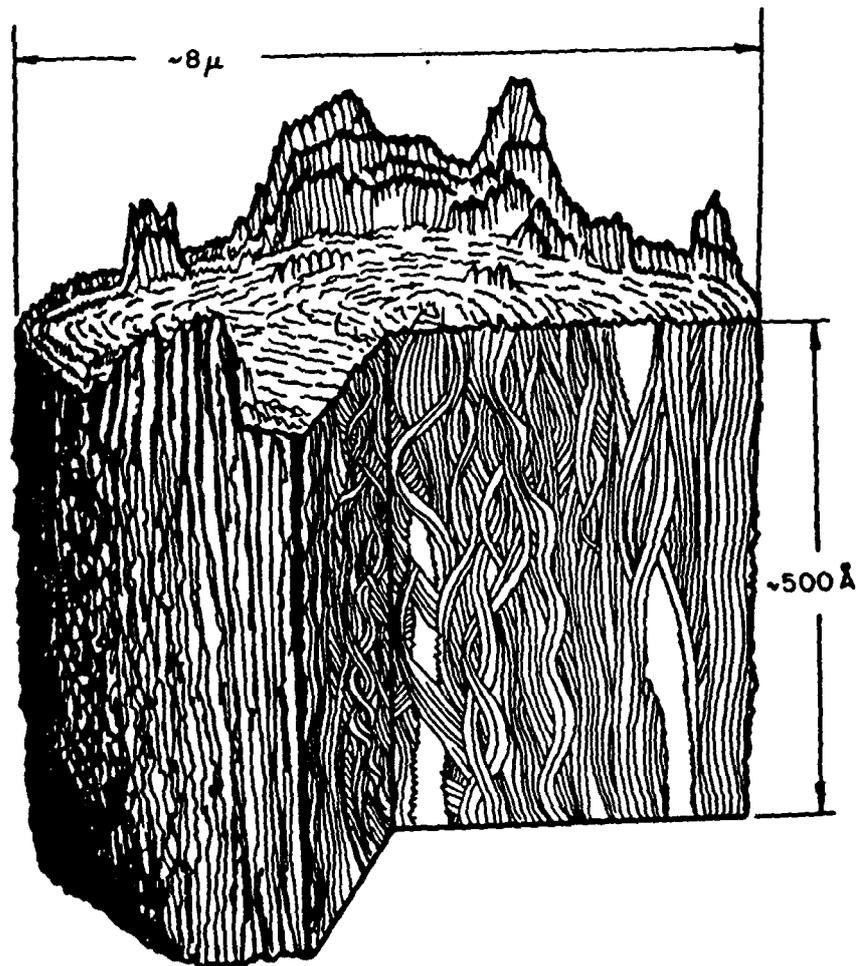


Figure 4 Schematic 3-D structural model of PAN based fiber of high modulus (51 Mpsi).^[9]

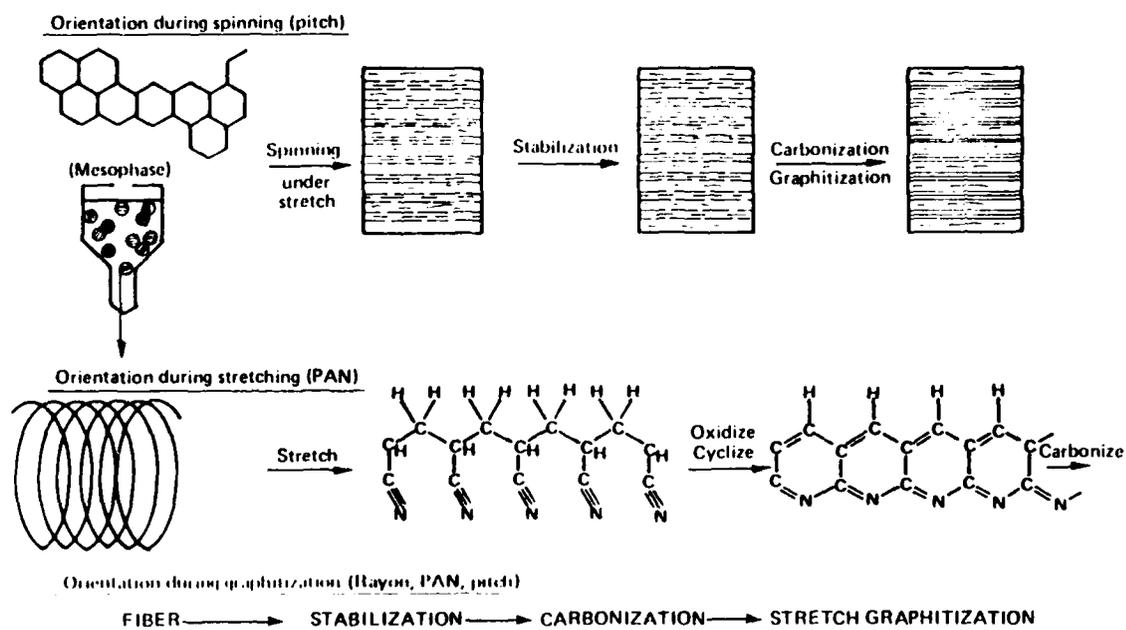
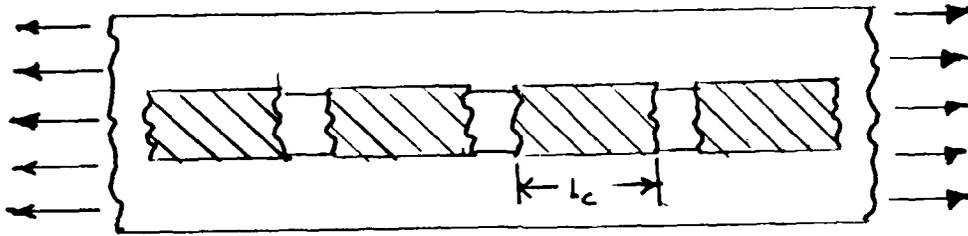


Figure 5 Schematic representation of carbon fiber preparation. [1]



$$\tau = \frac{\sigma_F}{2} \left(\frac{d}{l_c} \right)$$

Figure 6 Interfacial Shear Strength Specimen. [2,4]

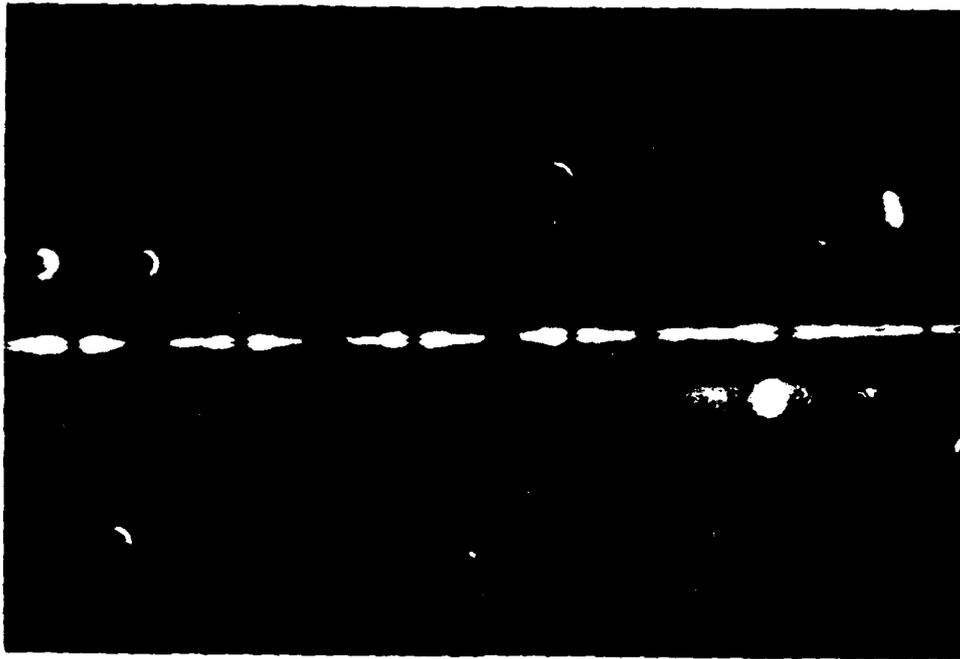


Figure 7 Apollo fiber #1 @ 82.5X, polarized, untreated and unsized.

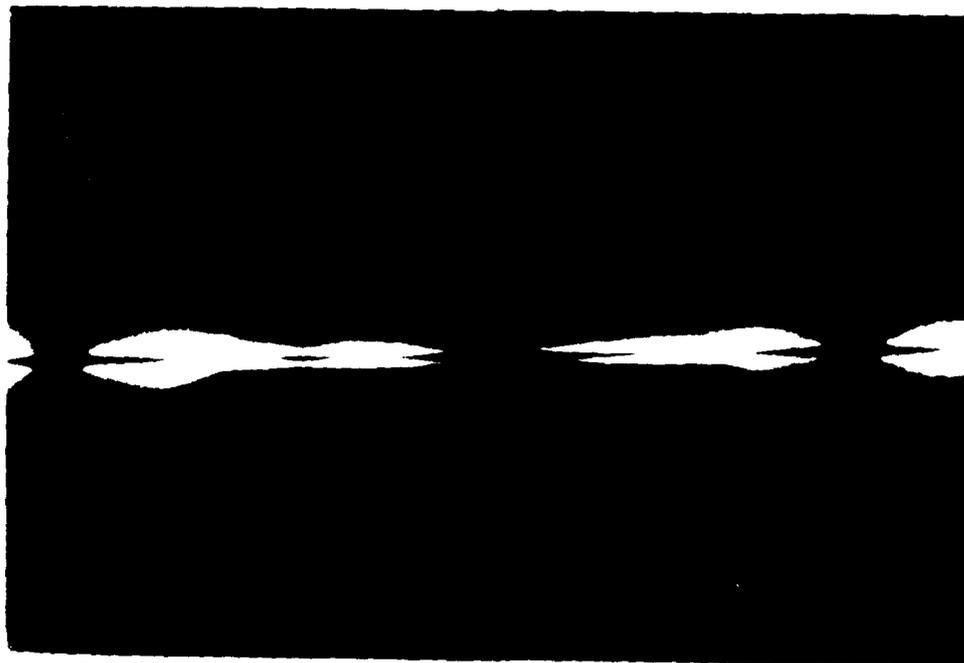


Figure 8 Apollo fiber #1 @ 330X, polarized.

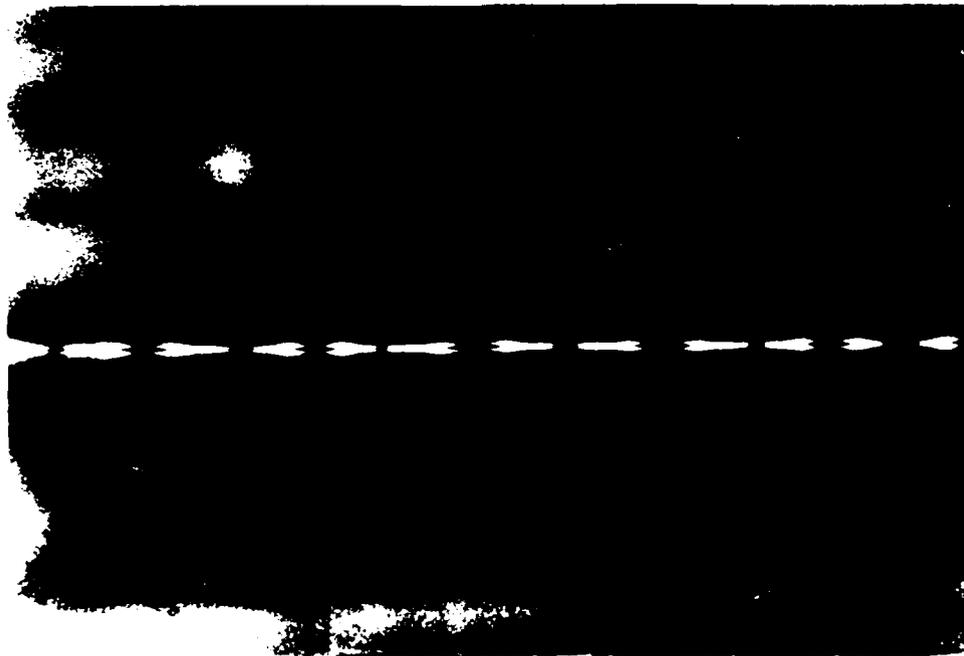


Figure 9 Apollo fiber #2 @ 82.5X, polarized, the narrow photoelastic region between the elliptical region and the break is due to frictional stresses where the crack has already separated the fiber from the matrix.

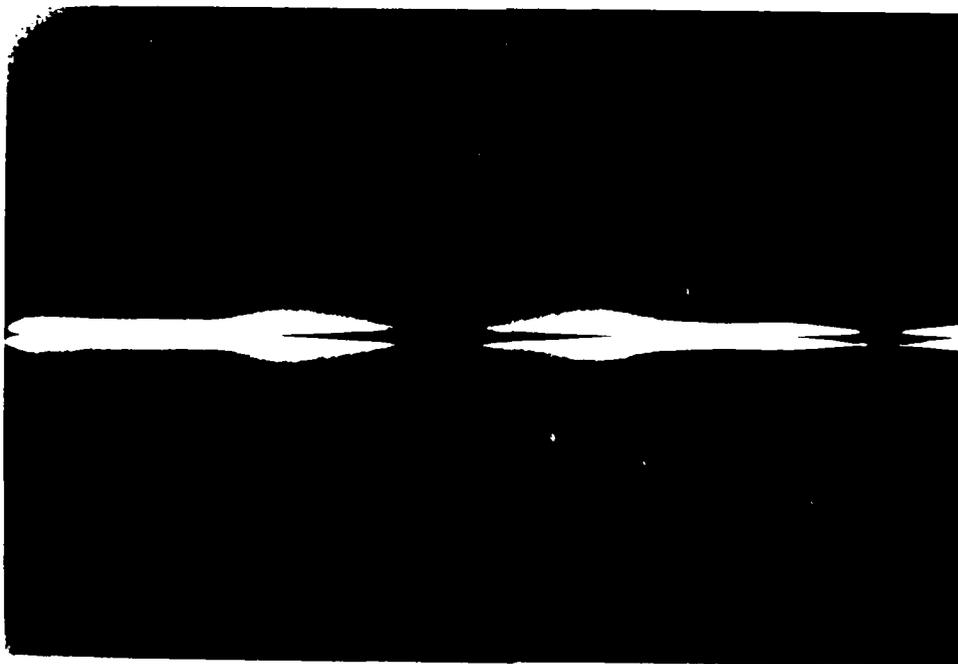


Figure 10 Apollo fiber #2 @ 330X, polarized, treated and unsized.

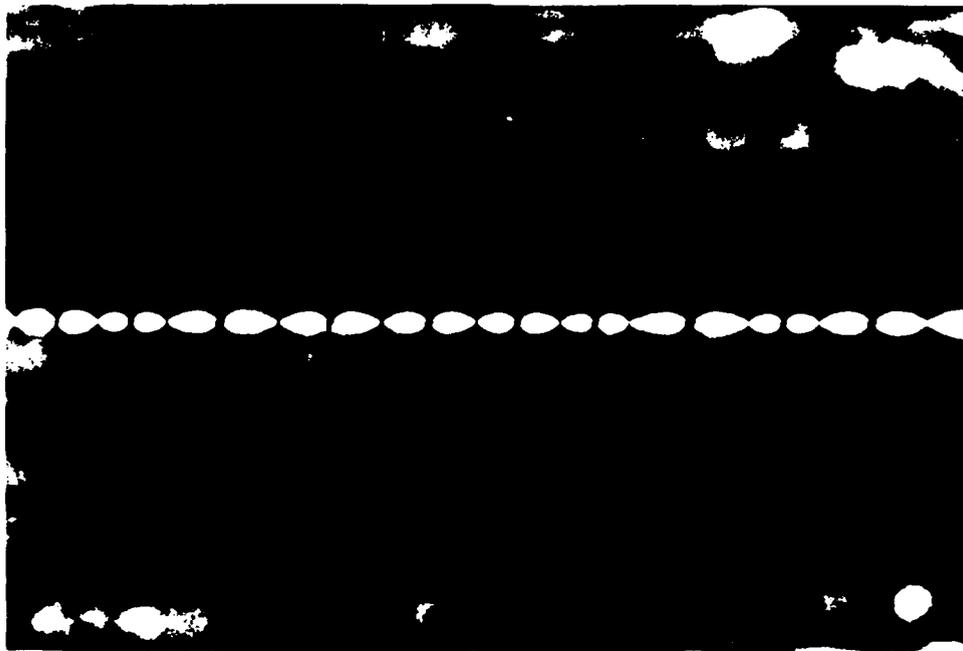


Figure 11 Apollo fiber #3 @ 82.5, polarized, treated and sized.

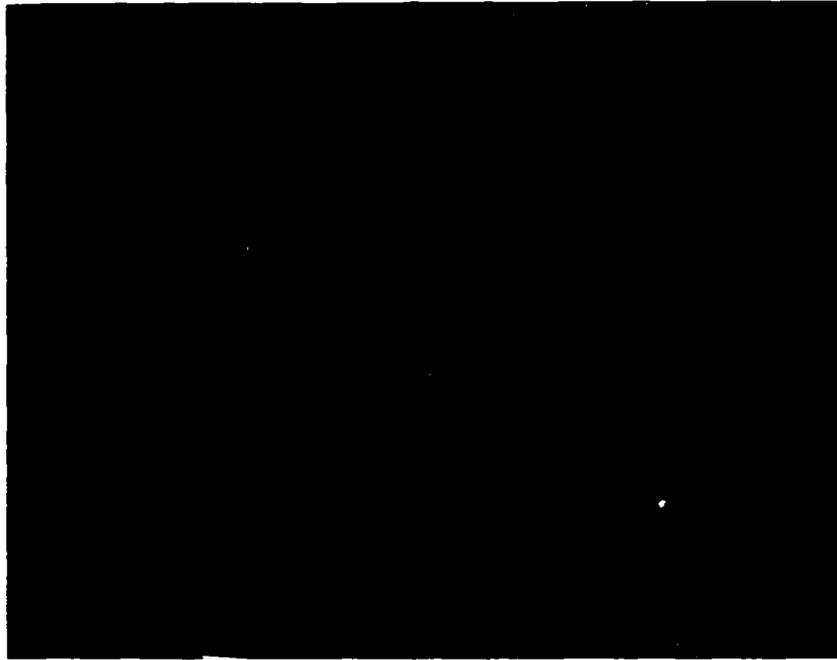


Figure 12 Apollo fiber #3 @ 750X, unpolarized, note: matrix crack perpendicular to fiber axis.

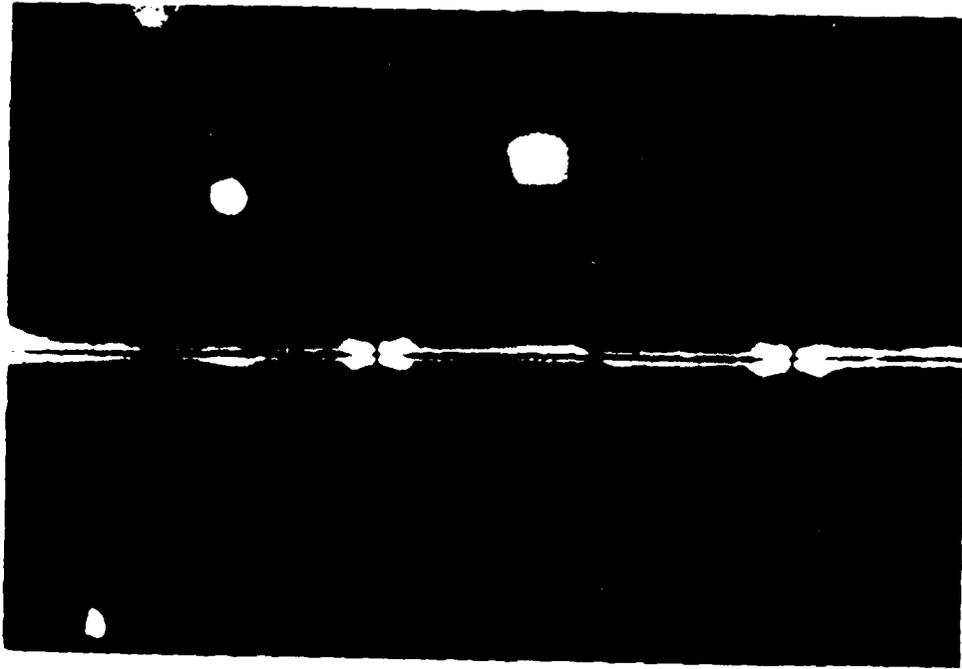


Figure 13 p-25 @ 82.5X, polarized light, note: breaks are at the darker points along fiber.

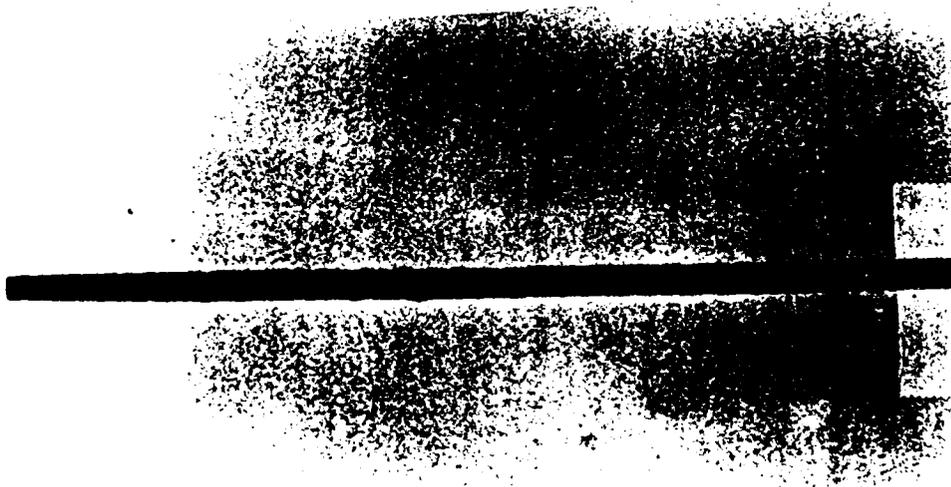


Figure 14 p-25 @ 330X, unpolarized, note: cylindrical cavity forming at fiber break.

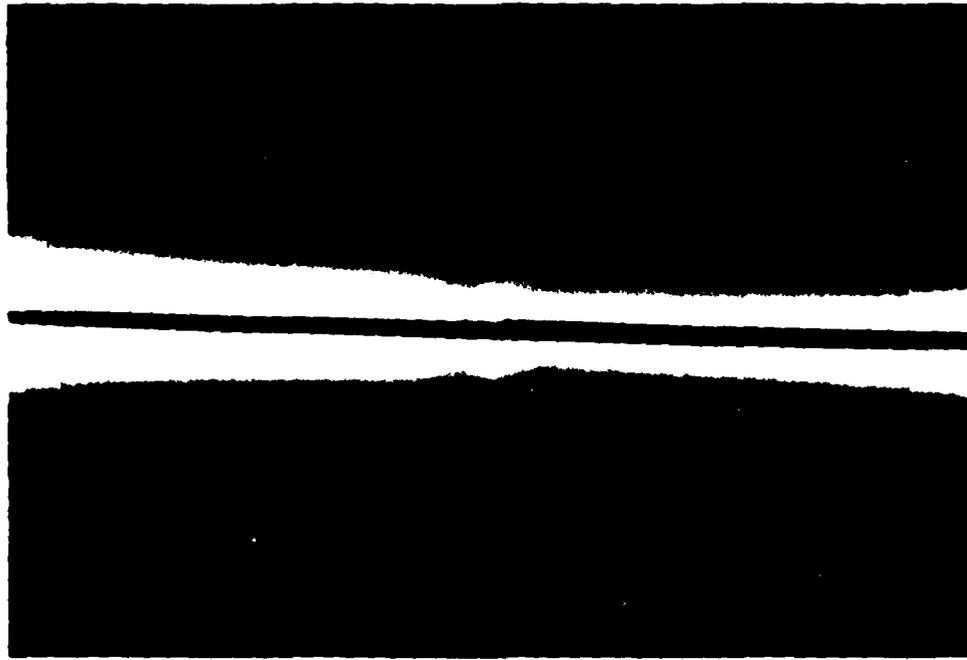


Figure 15 p-55 @ 330X, polarized, note: stress pattern is due to interfacial crack growth.

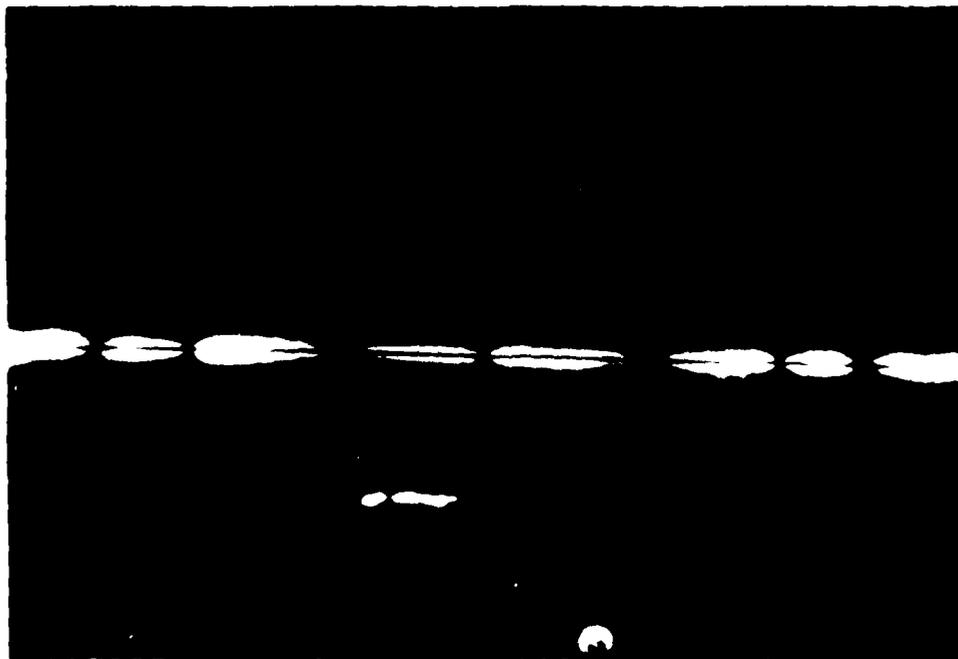


Figure 16 p-75 @ 82.5X, polarized, note: the stress pattern is relieved at the breaks due to better bonding.



Figure 17 p-100 @ 330X, unpolarized, note: cylindrical cavity forming at break.

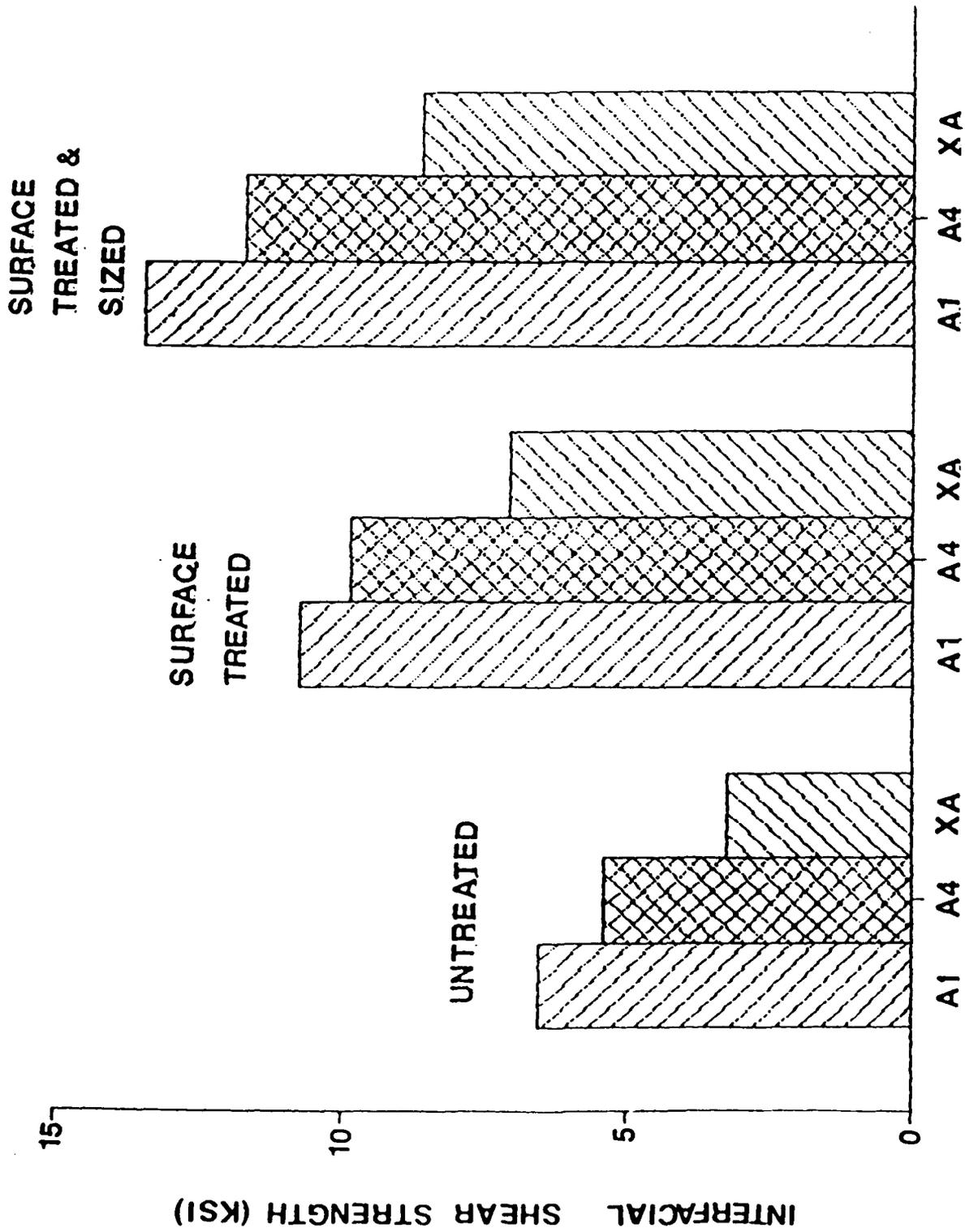


Figure 18 Interfacial Shear Strengths of A-1, A-4 and XA Fibers untreated, surface treated and sized.

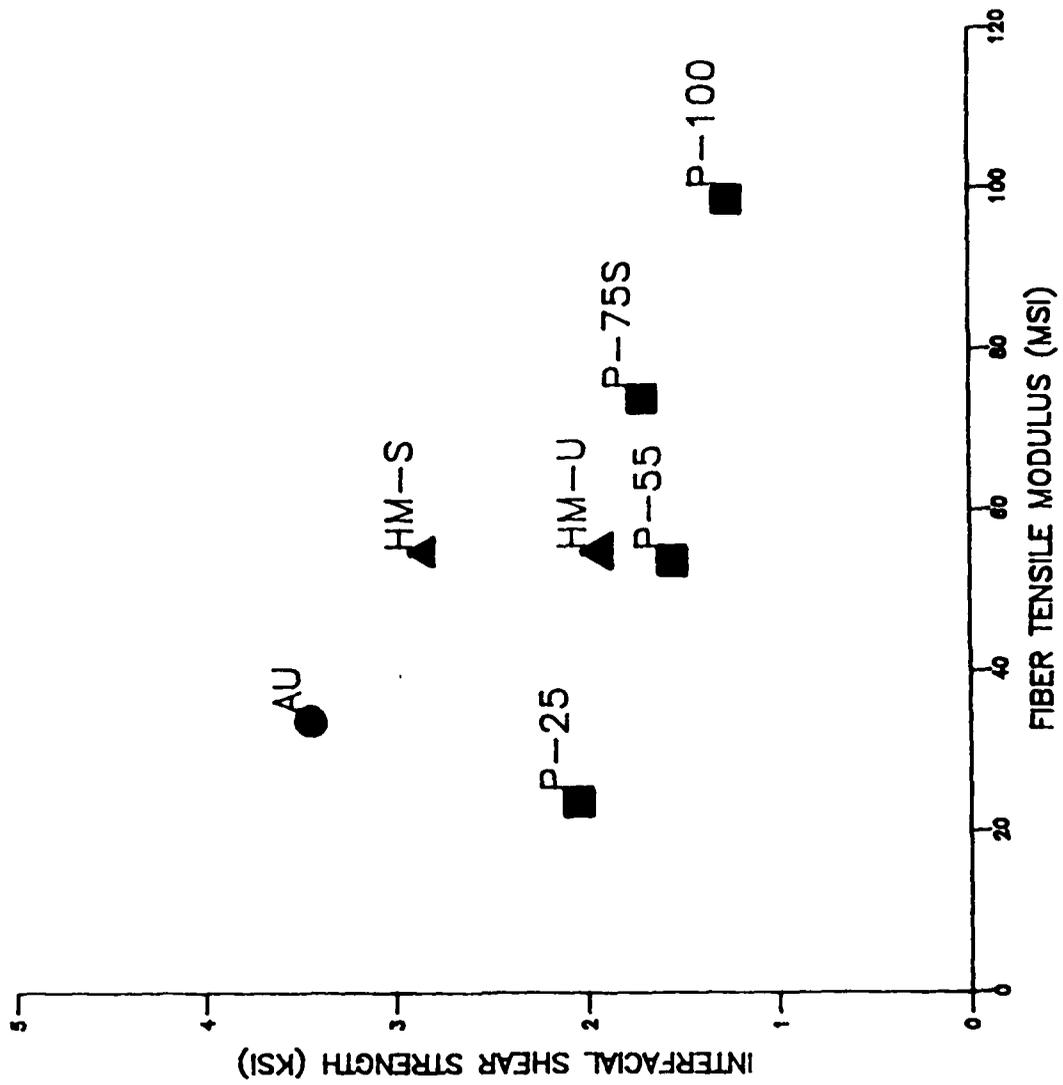


Figure 19 Interfacial Shear Strengths of HM and Pitch Fibers unsized.

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