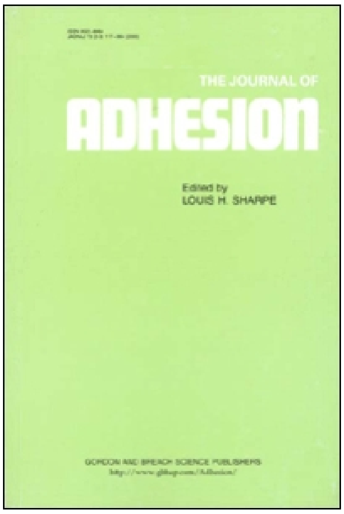

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# Adhesion of Graphite Fibers to Epoxy Matrices. III. The Effect of Hygrothermal Exposure

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# Adhesion of Graphite Fibers to Epoxy Matrices.
# III. The Effect of Hygrothermal Exposure†

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Surface treatments have been used to promote shear strength between graphite fibers and epoxy matrices by adding polar surface groups to increase the attraction between the fiber surface and the polar epoxy matrix. Because of the polar interactions between fiber and matrix, interfacial bonding may be susceptible to moisture attack resulting in permanent loss of fiber matrix bonding with a resultant loss in composite shear strength. Fiber "finishes" are also used to improve the processability of surface treated graphite fibers. These "finish" layers may not respond to hygrothermal exposure in the same manner as the matrix.

Type AS1 surface treated graphite fibers and surface treated and "finished" (ASIC) for improved adhesion to epoxy matrices were used in this study. Single fibers were encapsulated in an epoxy-mPDA matrix so that interfacial shear strength and matrix response to shear loading could be quantified and observed microscopically with polarized light as a function of moisture exposure of the samples. Moisture was sorbed into the coupons at 20°C, 70°C, and 125°C until saturation was reached. The interfacial shear

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strength was measured under saturated conditions and after dehydration to the initial weight in an attempt to isolate matrix plasticization effects from interface effects.

For epoxy matrices and fiber finishes which consist of a layer of epoxy without curing agent, the following conclusions can be made:

At temperatures below the wet glass transition temperature of the matrix, matrix properties are reduced by the sorption of moisture but can be restored to their original values by reversibly removing the moisture. The fiber surface is not affected by hygrothermal exposure at these conditions. The interfacial shear strength loss is primarily due to the plasticization of the matrix.

At temperatures above the wet glass transition temperature of the matrix, some irreversible changes in matrix properties occurred which affected the interfacial shear strength through matrix shear transfer.

A substantial difference in interfacial shear strength alteration with hygrothermal exposure was detected at all conditions between the surface treated and the surface treated and "finished" fibers. In all cases the "finished" fibers retained a higher absolute value for the interfacial shear strength after hygrothermal exposure. This was attributed to the creation of an interphase region in the "finish" layer that was more brittle but had a lower Tg than the matrix. The presence of this layer at low temperatures promoted better stress transfer but at higher temperatures in the wet state acted like a compliant zone that reduced irreversible damage occurring at the fiber-matrix interface.

## INTRODUCTION

Moisture and temperature are two environments that can have deleterious effects on advanced graphite-epoxy composite performance. Published data seeking to elucidate the role of water and temperature on composite mechanical properties have been concerned with measuring moisture absorption into the neat matrix material or into the fabricated composite.[1-6] Conclusions drawn from these studies have speculated that the degradation mechanisms are completely reversible with moisture and temperature; have an irreversible and a reversible component; or are totally irreversible. The plasticization of the matrix with its concommittant lowering of Tg is reversible on removal of the sorbed moisture if the water is removed without inducing matrix damage, that is, if the composite has not been subjected to extended mechanical or thermal excursions during its saturated condition[4] or does not contain hydrophilic impurities.[6] The irreversible portion of the loss in mechanical properties has been speculated to be due to a loss in fiber-epoxy interfacial shear strength.[1]

The purpose of this study is to isolate the fiber-matrix interfacial changes occuring with hygrothermal exposure from the effects of the same exposure on the matrix. Success in this effort can provide guidance as to the selection of fiber treatments and matrix selection necessary to minimize hygrothermal degradation of advanced composite materials.

# EXPERIMENTAL

## A. Materials

A diglycidyl ether of Bisphenol-A (EPON 828) cured with 14.5 parts per hundred by weight (phr) of meta-phenylene diamine (m-PDA) was chosen as the epoxy matrix for this study. This system has been used in previous research efforts in combination with this fiber. The epoxy was mixed, debulked under vacuum for two minutes and air-cured for two hours at 75°C and two hours at 125°C. Details of the exact procedure have been published elsewhere.[7] The matrix cured in this manner has an initial tensile modulus of 525 ksi and a tensile strength of around 13 ksi.

The fibers used in this study were Hercules ASl graphite fibers. They were from the same lot of material and were surface treated (ASl) to promote adhesion to an epoxy matrix. Graphite fibers are also sold with a "finish" layer applied over the surface treatment. Previous work has shown that the "finish" layer has an effect on the interfacial properties and mode of failure.[8] A portion of the surface treated ASl fibers was further treated with the application of a surface "finish" (ASlC). This was a 100 nm thick coating of the epoxy resin without the curing agent applied to the fiber surface from solution. Mechanical properties of the surface treated (ASl) and surface treated and "finished" (ASlC) fibers were measured and the modulus and strength values agreed. The fiber tensile strength was measured at decreasing gauge length from 25 mm to 0.3 mm. A semi-logarithmic relationship between strength and gauge length was observed and within experimental error, differences in the tensile strength between the ASl and ASlC fiber could not be detected.

## B. Hygrothermal Exposure

The tensile coupons containing a single fiber were conditioned in water vapor at 20°C, 70°C or 125°C at 100% RH. Immersion of the specimens was not used to preclude leaching out of matrix material or artifactual moisture ingression.[9,10] Samples were removed from the chamber periodically for weight measurements. Saturation was achieved when the plot of weight increase *versus* the square root of time approached a plateau. Desorption was accomplished by simply reversing the absorption conditions. Because of the long equilibrium times, *e.g.* ~ 12 months at 20°C, a higher temperature, *i.e.* 50°C, was used to accelerate the dehydration of the 20°C sample but vacuum was not used.

All interfacial shear strength and matrix property determinations were done at 20°C. A master batch of samples was prepared. A portion of these samples was placed under the desired hygrothermal exposure. Some samples were withdrawn after equilibrium for testing wet (WET) and the remainder were dehydrated (WET/DEHYD) to their initial weight before testing. In addition at the 20°C and 70°C hygrothermal exposure, one group of samples was equilibrated with moisture and strained to 5%, then dehydrated and again tested for interfacial shear strength (WET ($\sigma$)/DEHYD).

## C. XPS Analysis

Analysis of the fiber surface chemical composition was conducted by means of x-ray photoelectron spectroscopy (XPS), also known as ESCA. Measurements were made using a KRATOS ES300 XPS system equipped with a magnesium x-ray source. The analyzer was set at a fixed pass energy of 65 eV and 1.3 eV resolution for these analyses. Data were accumulated in the pulse counting mode on an LSI-11/03 minicomputer. Surface compositions were calculated using integrated peak areas which were corrected for photoelectric cross-section[11], analyzer transmission and mean-free path.[12] Comparisons were made between the fiber surfaces before and after various treatments.

Fibers were conditioned at 70°C or 125°C in distilled water for two weeks and dried in argon at 15 psia and 70°C for two hours prior to analysis. Samples of these fibers were cut and aligned in a mechanical fixture using handling procedures which precluded sample contamination. These samples were transferred to the XPS system for analysis.

Peak binding energies were normalized to 284.6 eV for the C1s peak. The accuracy of the surface concentration values on an absolute basis is dependent on the assumptions used in reducing the spectra. For these fibers the surface concentration values are estimated to be accurate to +/− 20%.

## D. Matrix Properties

Matrix properties were measured at 20°C after hygrothermal exposure at 20°C, 70°C and 125°C. Initial tensile modulus measurements were made on strain gauged samples having a one inch gauge length. The epoxy Tg was measured on a TMA apparatus with a heating rate of 10°C/minute. Water saturated samples were run initially at the saturated condition. Moisture loss during the TMA runs was unavoidable so that values of Tg are therefore not absolutely correct. These results should be taken as a qualitative indicator of the changes in Tg with hygrothermal conditioning for this epoxy.

## E. Interfacial Shear Strength

A single filament interfacial shear strength test was chosen to provide a mechanical parameter sensitive to interfacial properties. Although this is a single filament test, it has been shown to parallel composite interfacial property changes and at the same time allow fundamental mechanistic information about the fiber-matrix interphase to be determined.[13]

The method for measuring the fiber-matrix interfacial shear strength involves encapsulating a single graphite fiber in an epoxy tensile coupon, stressing the coupon to near its point of fracture and then measuring the graphite fiber fragment lengths inside of the specimen. Since the graphite fibers have a low strain to failure they will fracture within the coupon because of stress transferred to them by shear at the fiber-matrix interface. However the fragments will approach a lower limit in length which is dependent on the fiber fracture strength ($\sigma$), the fiber diameter (d) and the interfacial shear strength ($\tau$). These variables can be related through the expression

$$\tau = \frac{\sigma}{2}\left(\frac{d}{l}\right) \tag{1}$$

In practice a distribution of lengths is measured and Weibull statistics are used to evaluate the mean value of the critical length which, when substituted in equation (1), gives rise to the expression

$$\tau = \frac{\sigma}{2\beta}\,\Gamma\left(1 - \frac{1}{\alpha}\right) \tag{2}$$

where ($\alpha$) is the Weilbull shape factor, ($\beta$) is the scale factor and ($\Gamma$) is the Gamma function.

A single parameter like the interfacial shear strength is of limited value by itself in explaining interfacial phenomena when the mode of failure between fiber and matrix is changing. Additional insight can be gained by observing the interfacial shear strength specimen under transmitted polarized light with the aid of a microscope. The highly stressed epoxy polymer near the ends of the fiber fragments is birefringent and changes in the micrographs of this region can be related to changes in the fracture mode and interfacial shear strength.

## RESULTS AND DISCUSSION

### A. Matrix Properties

The matrix properties are affected by the absorption of moisture as indicated by the data in Table 1. The absorption of moisture follows Fickian diffusion initially and approaches an equilibrium level at a fixed temperature. The water has a plasticization effect on the matrix. Water molecules diffuse into the free volume present in the epoxy[14] and can associate with hydroxyl groups present in the network.[15,24] This reduces the intramolecular interactions between segments thereby decreasing the modulus and lowering the Tg.[16]

Hygrothermal exposure at 20°C can be seen to reduce the initial tensile modulus and the Tg of the 14.5 phr epoxy. Removal of the water allows the intramolecular interactions within the epoxy to be re-established and both the modulus and Tg increase to their dry state values.

At hygrothermal exposures at or above the wet Tg of the epoxy, irreversible changes occur in the material. The modulus and Tg are reduced in the wet state but the modulus is not recovered after drying

TABLE I
Epoxy Properties as a Function of Hygrothermal Conditioning

| Composition | Condition | T°C | Modulus | Tg° |
|---|---|---|---|---|
| 14.5 phr mPDA | DRY | 20°C | 525 ksi | 166°C |
| 14.5 phr mPDA | WET | 20°C | 446 ksi | 146°C |
| 14.5 phr mPDA | WET/DEHYD | 20°C | 522 ksi | 150°C |
| 14.5 phr mPDA | WET | 70°C | 500 ksi | 145°C |
| 14.5 phr mPDA | WET/DEHYD | 70°C | 516 ksi | 170°C |
| 14.5 phr mPDA | WET | 125°C | 426 ksi | 129°C |
| 14.5 phr mPDA | WET/DEHYD | 125°C | 452 ksi | 162°C |
| 7.5 phr mPDA | DRY | 125°C | 695 ksi | 62°C |
| 7.5 phr mPDA | WET | 125°C | 600 ksi | 67°C |
| 7.5 phr mPDA | WET/DEHYD | 125°C | 595 ksi | 88°C |

indicating that some irreversible damage had taken place in the polymer.

The presence of an epoxy rich "finish" layer between the fiber and the stoichiometric matrix results in an amine deficient layer around the fiber after cure. Previous work[8] has shown that this layer is more brittle than the stoichiometric matrix and that its composition can be modelled by a 7.5 phr epoxy-amine composition. This composition has a higher modulus than the stoichiometric epoxy but a much lower Tg. When this composition is hygrothermally treated above its wet Tg it also exhibits an irreversible loss in modulus. The combination of exposure to water and temperature apparently causes some additional reaction within the epoxy as detected by an increase in Tg after this treatment.

## B. Fiber Surface Analysis

Nine AS fiber tow sections were analyzed using XPS: seven were samples in the "as-received" state and dry, one was a section of tow that had

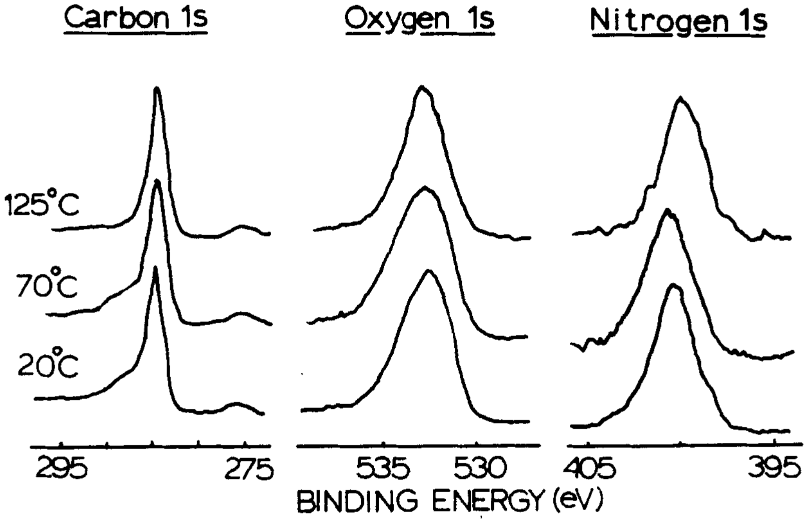

FIGURE 1 XPS Spectra of the Carbon 1s, Oxygen 1s and Nitrogen 1s regions for Three Hygrothermal Conditions: a) AS1 fiber "as-received" at 20°C b) AS1 Fiber after 70°C Treatment and c) AS1 Fiber after 125°C Treatment.

TABLE II
XPS Analysis of Graphite Fibers

| | Carbon 1s | Oxygen 1s | Nitrogen 1s |
|---|---|---|---|
| ASl (AVG.) | (83+/−2%) 284.6,288.1eV | (11+/−1%) 531.9eV | (4.5%) 399.8eV |
| ASl H2O 70 C | (86%) 284.5,288.1eV | (10%) 531.8eV | (2.5%) 399.8eV |
| ASl H2O 125 C | (89%) 284.6eV | (8.5%) 532.5eV | (1%) 399.3eV |

been exposed to 70°C and 100% RH and then dehydrated and one was exposed to 125°C and 100% RH and then dehydrated. The exposure was immersion in liquid water in a closed container. The carbon 1s, oxygen 1s and nitrogen 1s spectra are shown in Figure 1 and these results are summarized in Table 2. The range for the seven "as-received" specimens is listed in Table 2.

From these data we can see that some change has occurred in the surface composition due to the 70°C hygrothermal treatment. The nitrogen has decreased. The line shapes and positions of the major constituents (*i.e.* carbon 1s and oxygen 1s peaks) remain largely unaltered. These factors together imply that the majority of the functional groups on the surface remain unaffected by the hygrothermal exposure.

On the other hand, exposure to the 125°C hygrothermal treatment produced far greater changes in the fiber surface chemistry. The shift in line positions and narrowing of the carbon and oxygen peaks implies that the surface functional groups are being reduced. The appearance of a nitrogen 1s component peak at lower binding energy is indicative of the formation of amine-type groups on the fiber surface and hence supports the carbon and oxygen data.

## C. Work of Adhesion

The basic attraction of the epoxy resin for the fiber surface and its alteration with moisture exposure can be evaluated thermodynamically. The Work of Adhesion, Wa, for the epoxy resin to the graphite fiber in the dry state and in the presence of moisture can be determined through evaluation of expressions for Wa as proposed by Kinloch[17] and others. A positive value for Wa indicates thermodynamic stability while a negative value indicates a thermodynamic driving force for spontaneous separation. The polar and dispersive components of the surface free energy of the fiber, the epoxy and water are necessary for evaluation of Wa. These quantities were measured in previously reported work.[18] The Wa for the dry ASl fiber-epoxy interface is 84.5 mJ/m$^2$ which decreases to 18.3 mJ/m$^2$ for the wet case. While the work of adhesion decreases when the interface is wet, it will not spontaneously separate. This agrees with results on a similar system determined by Kaelble.[19]

## D. Interfacial Shear Strength

The results of the interfacial shear strength determinations are tabulated in Table 3 as a function of the hygrothermal conditioning. The first and second columns list the epoxy encapsulated fiber and its hygrothermal history prior to the interfacial shear strength measurements. Column 3 is the critical length to diameter ratio of the fiber fragment length. Column 4 is the fiber tensile strength at the critical length. Column 5 is the calculated (20°C) interfacial shear strength and column

TABLE III
Room Temperature (20°C) Interfacial Shear Strength ($\tau$) as a Function of Hygrothermal Conditioning

| | *Exposure Temp* | $\beta$ | $\sigma_f(1/d)$ | $\tau(20°C)$ | *% Change* |
|---|---|---|---|---|---|
| *ASl Fiber* | | | | | |
| DRY | 20°C | 38.8 | 650 ksi | 10.7 ksi | — |
| WET | 20°C | 49.5 | 615 ksi | 7.8 ksi | −27% |
| WET/DEHYD | 20°C | 43.5 | 630 ksi | 9.4 ksi | −12% |
| WET ($\sigma$)/DEHYD | 20°C | 49.5 | 615 ksi | 7.8 ksi | −27% |
| WET (Na) | 20°C | 85.6 | 630 ksi | 4.9 ksi | −54% |
| WET | 70°C | 61.2 | 580 ksi | 6.2 ksi | −42% |
| WET/DEHYD | 70°C | 46.1 | 625 ksi | 8.6 ksi | −20% |
| WET($\sigma$)DEHYD | 70°C | 61.2 | 580 ksi | 6.2 ksi | −42% |
| WET | 125°C | 216 | 570 ksi | 2.0 ksi | −81% |
| WET/DEHYD | 125°C | 83.1 | 630 ksi | 4.8 ksi | −55% |
| *ASlC Fiber* | | | | | |
| DRY | 20°C | 26.8 | 675 ksi | 16.0 ksi | — |
| WET | 20°C | 40.7 | 650 ksi | 10.2 ksi | −36% |
| WET/DEHYD | 20°C | 32.0 | 665 ksi | 12.8 ksi | −20% |
| WET($\sigma$)/DEHYD | 20°C | 40.7 | 650 ksi | 10.2 ksi | −36% |
| WET | 70°C | 47.8 | 625 ksi | 8.2 ksi | −49% |
| WET/DEHYD | 70°C | 45.0 | 620 ksi | 8.5 ksi | −47% |
| WET ($\sigma$)/DEHYD | 70°C | 47.8 | 625 ksi | 8.2 ksi | −49% |
| WET | 125°C | 45.9 | 650 ksi | 9.0 ksi | −44% |
| WET/DEHYD | 125°C | 46.7 | 650 ksi | 9.1 ksi | −43% |

6 is the percent reduction in interfacial shear strength relative to the dry state. The two fibers chosen for this study establish the baseline interfacial shear strength values for their respective interfaces in the DRY state. As the data in the rows labelled DRY for the ASl and the ASlC fibers indicate, the fiber that has the epoxy "finish" layer present achieves a higher value for the interfacial shear strength (*viz.* ASl—10.7 ksi *vs.* ASlC—16.0 ksi). The difference in attainable interfacial shear strength is attributable to the formation of a brittle interphase layer around the "finished" fiber. This layer has a higher modulus than the bulk matrix and allows more efficient stress transfer to be made between the matrix and the fiber.[8]

Polarized light photomicrographs of the ASl and the ASlC fiber in this epoxy matrix illustrate the difference in interfacial behavior. (Figure 2) The stress pattern for the ASl fiber is typical for growth of an interfacial crack along the fiber away from the point where the fiber has broken in the matrix. The transmitted light micrograph shows where the fiber has broken and separated slightly under the loading conditions. In contrast, the ASlC fiber forms a matrix crack perpendicular to the fiber axis at the point of fracture under the same loading conditions. This is due to the low fracture toughness of the interphase layer which has less than the stoichiometric amount of amine crosslinking agent. A mixture of 7.5 phr mPDA in Epon 828 has been chosen as a model of the properties of the matrix in the interphase zone for discussion purposes in this paper.

## 1. Hygrothermal Exposure at 20°C

*ASl*: Comparisons of the interfacial shear strength with hygrothermal exposure and with fiber surface condition are illustrated graphically in Figure 3. Hygrothermal conditioning at 100% RH and 20°C causes the interfacial shear strength to decrease by 27% over that attainable with a dry ASl fiber in a dry epoxy (*i.e.* 7.8 ksi WET *vs.* 10.7 ksi DRY). The wet matrix has been plasticized by the water and the stresses at the fiber-matrix interface are reduced as indicated by the transmitted polarized light micrograph in Figure 4 (WET). The polarized light micrograph shows a narrow lower intensity region in the same area where an intense pattern was detected for the ASl fiber in its dry state as shown in Figure 2. (Part of the decreased photoelastic intensity may be due to the reduced birefringence of the matrix due to the presence

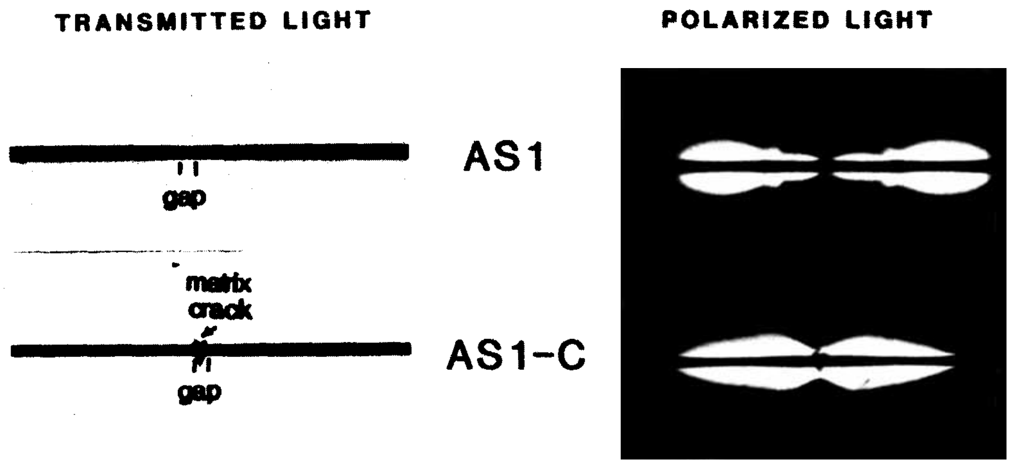

FIGURE 2 Polarized and Transmitted Light Micrographs at 400x of the AS1 and AS1C Fibres Encapsulated in Epoxy Resin, Under $\sim 4\%$ Strain in the DRY State.

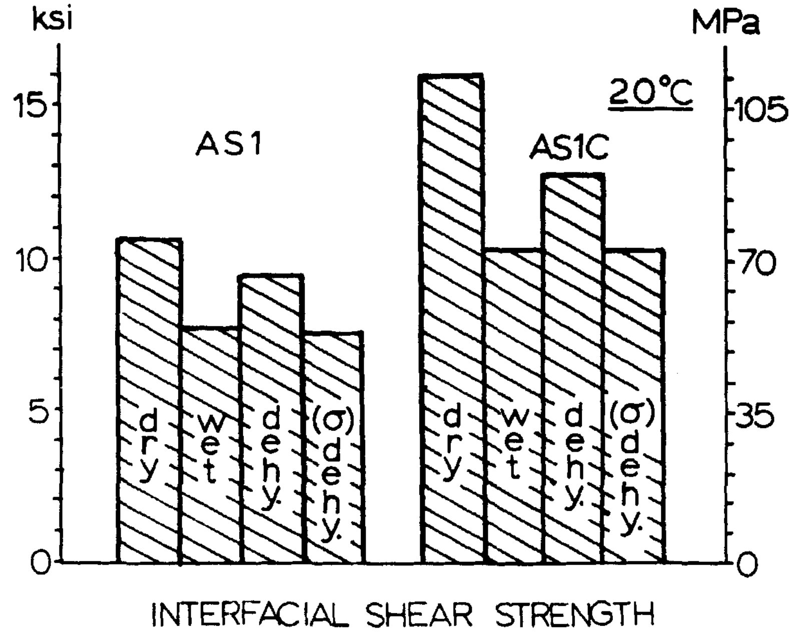

FIGURE 3 Interfacial Shear Strength Measured at 20°C, of the ASI and ASIC Fibers in EPON 828/14.5 phr mPDA Matrix a) Dry, b) Wet, Saturated with Moisture at 20°C, c) Dehydrated to the Dry State and d) Dehydrated after being Stressed in the Wet State.

of water. All photoelastic micrographs were taken under identical conditions to mitigate some of this effect.)

Rosen[20] and others have published micromechanical analyses of a single fiber fragment in an infinite matrix. A dependence of interfacial shear strength on the shear modulus of the matrix adjacent to the fiber surface was proposed in these models. The shear modulus of this epoxy at 14.5 phr and 7.5 phr mPDA has been measured at 20°C and 1.6 Hz both in the dry and wet states.[21] The results of these measurements are summarized in Table 4. The data for the shear modulus in Table 4 indicate a drop of 25% with moisture absorption. Since the stresses on the fiber are due to shear transfer at the interphase, the decrease in modulus detected in the epoxy in the wet state would be expected to reduce the interfacial shear strength.

When the sample is dehydrated back to its original dry state, the interfacial shear strength is increased to within 12% of its original level

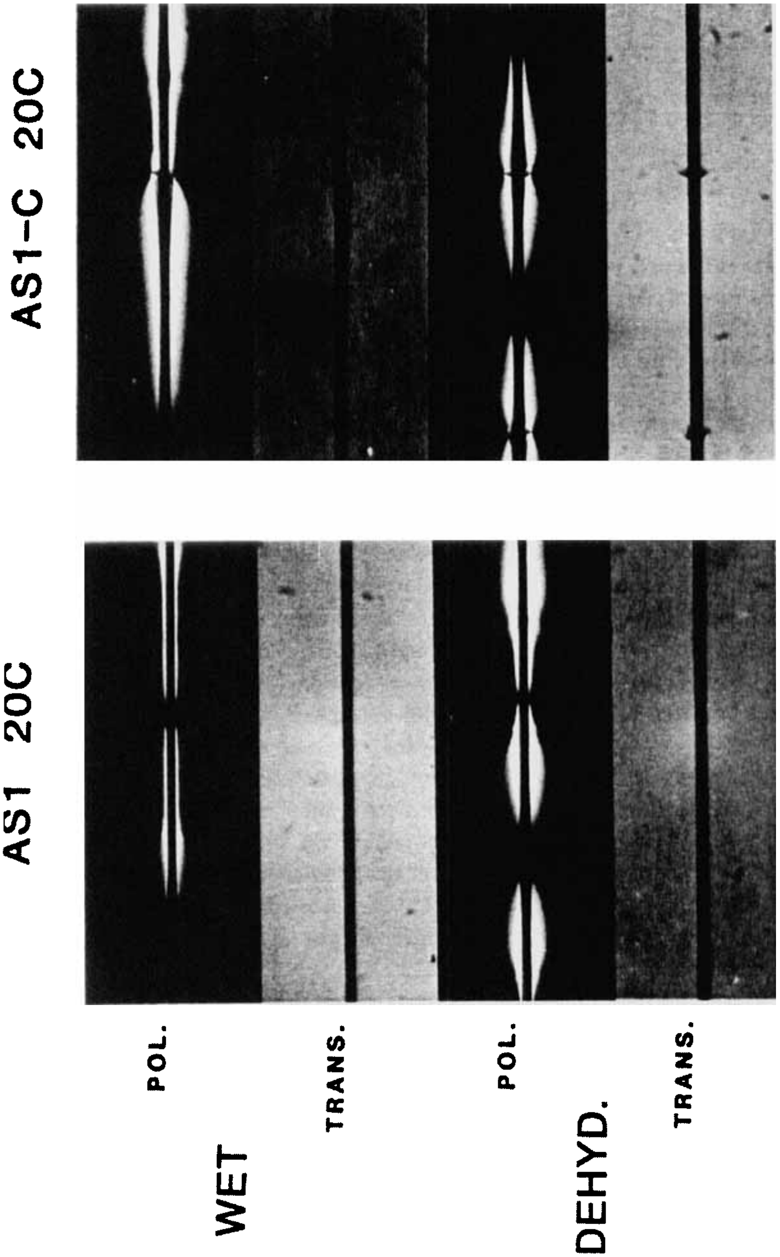

FIGURE 4 Polarized and Transmitted Light Micrographs at 400x of the ASL and ASIC Fibers Encapsulated in Epoxy Resin, under Stress After Hygrothermal Conditioning at 100% RH and 20°C.

TABLE IV
Shear Modulus of Epoxy Matrices

| 7.5 phr mPDA + Epon 828 | 14.5 phr mPDA + Epon 828 |
|---|---|
| DRY 1.5 GPa (218 Ksi) | DRY 1.16 GPa (168 Ksi) |
| Wet 1.36 GPa (197 Ksi) | WET 0.88 GPa (128 Ksi) |

(*i.e.* 9.4 ksi DEHYD). The matrix regained most of its dry state properties after the moisture was removed. This suggests that some irreversible degradation of the interface has occurred even though the room temperature measured bulk modulus has returned to its original value. Inspection of the wet sample showed that the stresses induced by expansion at 100% RH and 20°C were not of sufficient magnitude to induce any fiber breaks in the specimen. Independent measurements of the coefficient of thermal expansion of the stoichiometric sample before and after hygrothermal exposure showed no difference compared to the dry expansion properties of the same epoxy.[14] Differential expansion then would not be expected to induce any appreciable additional stress in the fiber. The micrograph of Figure 4 (DEHYDRATED) also reflects the reversibility of the matrix and interfacial conditions. A more intense polarized light micrograph is obtained after dehydration of the sample. This agrees very closely with the photoelastic behavior of the matrix in the dry state as shown in Figure 2.

One set of water saturated samples stressed at 20°C WET for interfacial shear strength measurements was dehydrated and strained again (WET($\sigma$)/DEHYD) to measure interfacial shear strength. This is in contrast to the WET/DEHYD set where no straining occurred in the wet state. The results of this stress applied when the sample is wet are shown in the fourth row of Table 3. After dehydration, the full recovery of the interfacial shear strength cannot be realized (*i.e.* 7.8 ksi WET ($\sigma$)/DEHYD *vs.* 9.4 ksi WET/DEHYD). This indicates that some irreversible damage was done by the application of stress to the interface region while in the wet state. If the effect was only on the matrix, drying would restore the interfacial shear strength to its original value. The extent of the irreversible interfacial damage caused by the application of stress in the wet state is greater than that produced by moisture saturation without the concurrent application of additional stress. Morgan[22] has shown that moisture absorption under stress can change the mechanical response of epoxies to a mode which enhances failure by a cavitation mechanism.

An interesting observation was coincidentally made on the response to hygrothermal exposure of an older AS fiber that had been surface characterized in an earlier work.[23] This older AS fiber had a large amount of residual sodium present in the fiber which was shown to be capable of migration to the fiber surface and capable of being extracted with water. Specimens of this fiber gave interfacial shear strengths identical with the ASl fiber in the DRY state and in the WET/ DEHYDRATED state. However, as row 6 of Table 3 shows, in the wet state the interfacial shear strength drops to 54% of its dry value. The presence of the hygroscopic sodium must be responsible for the observed difference in the wet state. Ashbee[6] has shown that hygroscopic inclusions such as salts can cause the generation of local defects in the matrix and at the interface from the osmotic pressures associated with such materials.

*AS1C*: The addition of a 100 nm "finish" layer around the AS1 fiber to form the ASlC fiber causes a dramatic difference in interfacial behavior after hygrothermal exposure for all conditions. The data from Table 3, shown graphically in Figure 3, illustrates the reduction in the interfacial shear strength with hygrothermal exposure at 20°C. In the wet state the interfacial shear strength decreases by 36% from the dry value. The photomicrographs of Figure 4 indicate that the mode of failure in the brittle interphase zone has not been altered from matrix cracking even in the wet state. The shear modulus of the matrix represented by the 14.5 phr data has decreased 25% in the wet state but the 7.5 phr data representing the interphase region has only decreased 10%. The absolute value of the shear modulus for the 7.5 phr interphase material is slightly greater than the dry value for the 14.5 phr matrix. The plasticization of the matrix by water is responsible for the reduction in the interfacial shear strength but the presence of the interphase matrix prevents this stiffness reduction from causing the low levels of interfacial shear strength obtained in the system without the fiber "finish".

Dehydration of the sample causes the interfacial shear strength to rise to within 80% of the dry state value. Since little change was detected in the surface chemistry of the fibers with hygrothermal exposure at these conditions (Figure 1), most of the observed changes for unstressed specimens are due to the plasticization of the interphase and matrix polymer. Some irreversible damage to the interface does occur however, as indicated by the permanent 20% reduction in interfacial shear strength.

Application of stress to the ASIC specimens in the wet state followed by dehydration produces a detectable reduction in WET($\sigma$)/DEHYD interfacial shear strength. Again the maximum value of interfacial shear strength attainable after dehydration is equal to the value obtained for a WET specimen. This behavior is similar to the results obtained for the ASI fiber under the same conditions.

## 2. Hygrothermal Exposure at 70°C

*AS*1: The 70°C treatment was selected to provide a hygrothermal exposure that was well below the wet Tg of the 14.5 phr matrix but at the wet Tg of the 7.5 phr interphase polymer. The interfacial shear strengths graphed in Figure 5 show a larger effect due to hygrothermal exposure at 70°C than at 20°C. The ASI interfacial shear strength is reduced by 42% from its dry value when the sample is saturated with moisture at 70°C. This is a larger decrease than at 20°C (42% vs. 27%).

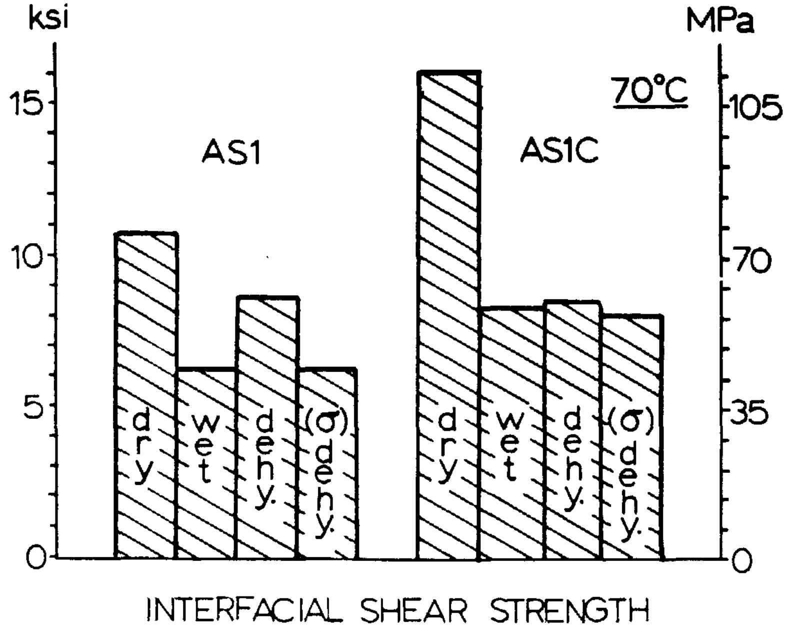

FIGURE 5 Interfacial Shear Strength Measured at 20°C, of the ASI and ASIC Fibers in EPON 828/14.5 phr mPDA Matrix a) Dry, b) Wet, Saturated with Moisture at 70°C, c) Dehydrated to the Dry State and d) Dehydrated after being Stressed in the Wet State.

The photoelastic stress patterns displayed in Figure 6 indicate a reduced intensity reflecting the lowering of the shear modulus of the matrix in the wet state. Examination of the sample in the wet state showed no evidence of fiber breakage due to the increased expansion of the matrix over the fiber. Both thermal and moisture effects would be expected to be additive in placing the fiber under tension.

Dehydration of the sample causes the interfacial shear strength to return to within 20% of the dry state value. The matrix itself is unaffected by the hygrothermal exposure at 70°C as indicated by the data in Table 1. Both the Tg and tensile modulus of the matrix return to their original values after dehydration. The photomicrographs of Figure 6 show, as in the case for the 20°C exposure, an increase in intensity of the stress pattern after dehydration.

The application of stress to the sample in the wet state causes irreversible damage to the interface. Dehydration of the sample does not return the level of interfacial shear strength to that attained when additional stress is not applied in the wet state. The interfacial shear strength attained after the WET($\sigma$)/DEHYD procedure is only equal to that obtained in the fully saturated state.

*AS1C*: The presence of the "finish" layer around the fiber alters the interfacial response to hygrothermal exposure when compared to the unfinished fiber. The 70°C hygrothermal exposure is near the wet Tg of the interphase material as modeled by the 7.5 phr epoxy. Therefore this layer would become more compliant than the 14.5 phr matrix. A more compliant interphase would be expected to reduce the stress transfer from the matrix to the fiber resulting in a lower interfacial shear strength. The interfacial shear strength does decrease by 49% from the dry strength value (*i.e.* 8.2 ksi) for this specimen. Concurrently a change in failure mode is detected also. The micrographs for the AS1C fiber (WET) in Figure 6 show a pattern characteristic of interfacial failure rather than matrix failure as observed in the dry state or at 20°C wet. The transmitted light micrograph of the same region shows no evidence of matrix failure at the fiber breaks.

Dehydration of this specimen does not increase the interfacial shear strength over the value obtained in the wet case, even though the matrix has fully regained its modulus and Tg. Irreversible damage to the interface has occurred after this exposure. The DEHYD photomicrograph of the AS1C fiber shows a return to the stress pattern characteristic of matrix failure and the transmitted light micrograph does show the presence of a matrix crack at the fiber break after dehydration.

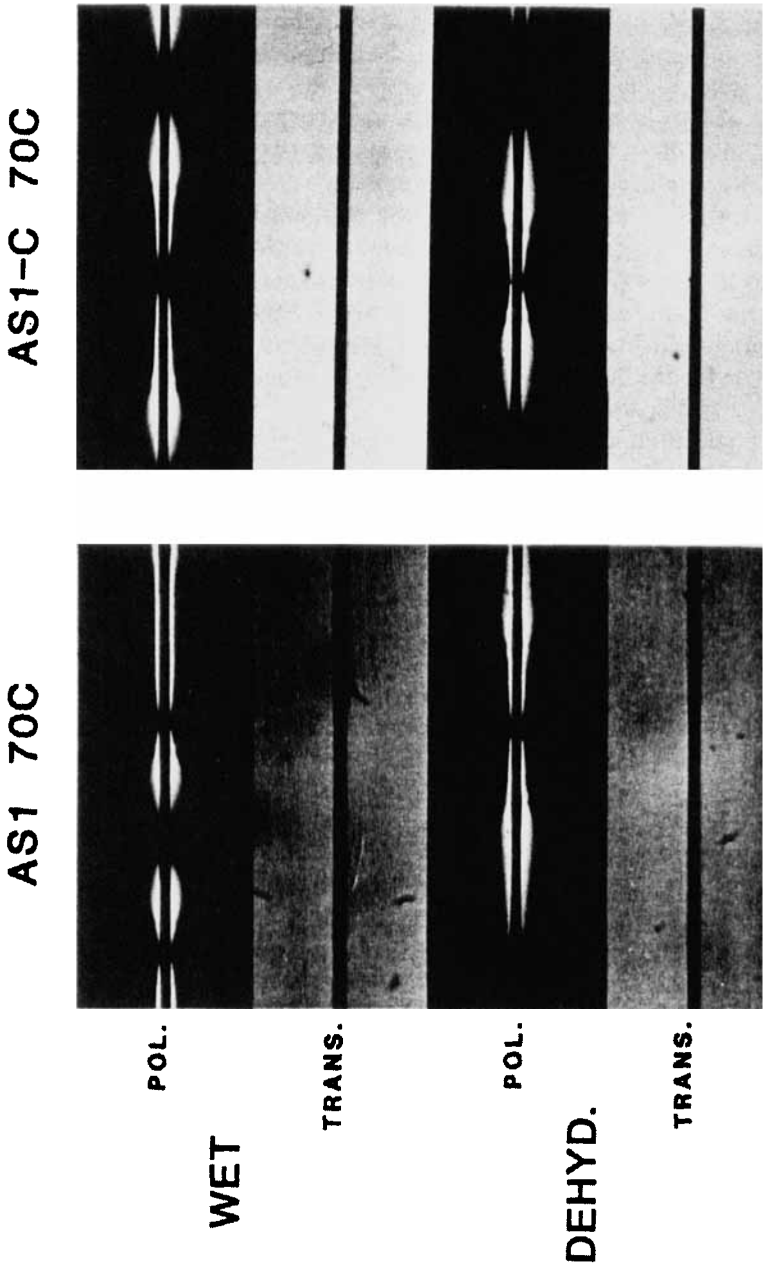

FIGURE 6 Polarized and Transmitted Light Micrographs at 400x of the AS1 and AS1C Fibers Encapsulated in Epoxy Resin, Under Stress After Hygrothermal Conditioning at 100% RH and 70°C.

Carisella *et al.*[25] measured the plane strain fracture toughness of a similar epoxy network as a function of hygrothermal exposure conditions and found that at 75°C the fracture toughness almost doubled over the 25°C values.

Application of stress to the wet specimen does not reduce the interfacial shear strength. The value obtained is equal to the WET and WET/DEHYD values. Apparently the combination of thermal and moisture induced stress on the interphase matrix above its Tg causes some irreversible changes to take place which are not recoverable after dehydration. It must be noted, however, that the absolute value of the interfacial shear strength is equal to that of the unfinished fiber after dehydration and greater than the unfinished fiber in the wet state.

### 3. Hygrothermal Exposure at 125°C

*AS*1: As the data of Table 1 indicate, the Tg of the epoxy can be reduced

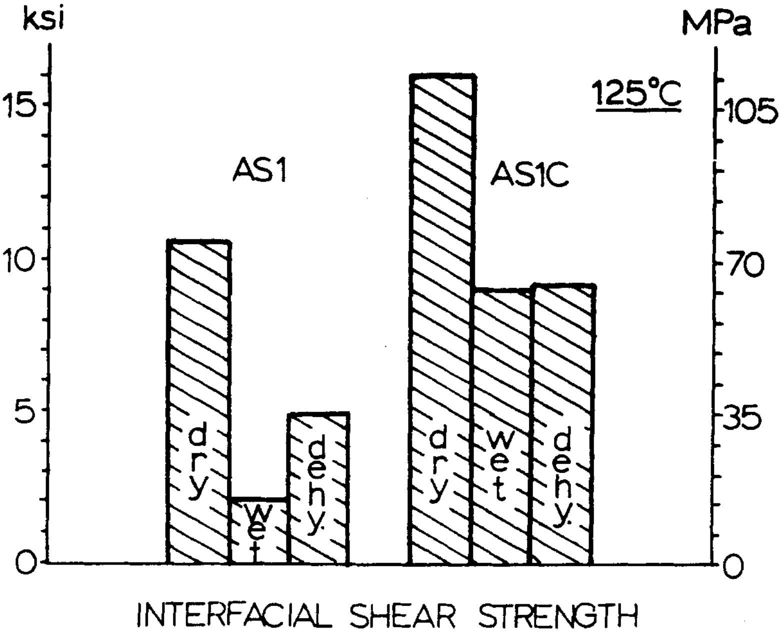

FIGURE 7 Interfacial Shear Strength Measured at 20°C, of the ASI and ASIC Fibers in EPON 828/14.5 phr mPDA Matrix a) Dry, b) Wet, Saturated with Moisture at 125°C and c) Dehydrated to the Dry State.

to near 125°C by moisture absorption at 125°C. The samples conditioned at 125°C exhibited a precipitous increase in the critical transfer length corresponding to an 80% drop in interfacial shear strength over the dry unexposed sample (*i.e.* 2.0 ksi WET *vs.* 10.7 ksi DRY) as shown in Figure 7. The stress pattern in Figure 8 is indicative of very low stress levels at the interface in the wet state. This is to be expected because of the plasticization effect of water on the matrix and the exposure at a temperature above the wet Tg of the matrix. The low level of interfacial shear stress can be seen in the transmitted light micrograph of Figure 8 which shows that the fiber fragments separate at increasing loads to the largest distances observed in this series of tests.

Dehydration of the matrix results in recovery of some of the interfacial shear strength in the sample but only to about one-half of that attainable in the dry state (*i.e.* 4.8 ksi DEHYD *vs.* 10.7 ksi DRY). The photoelastic stress pattern in Figure 8 also confirms that the interfacial response is characteristic of a poorly bonded system.

The matrix is irreversibly damaged by hygrothermal exposure at 125°C. The data in Table 1 indicate that neither the Tg nor the tensile modulus of the matrix returns to their dry state values. The XPS analysis of the graphite fiber after 125°C treatment shows an alteration both in surface composition and in the molecular environment of the surface species. Both the fiber surface and the matrix are themselves irreversibly altered by this exposure.

*AS1C*: The results of the interfacial shear strength evaluation after the 125°C hygrothermal treatment show a difference for the AS1C "finished" fiber versus the surface treated but unfinished AS1 fiber. After 125°C hygrothermal conditioning, the value for interfacial shear strength has dropped by 44% to 9.0 ksi. (Figure 7). Subsequent dehydration does not alter this value (*i.e.* 9.1 ksi DEHYD *vs.* 9.0 ksi WET). Although this forty-four percent drop in shear strength is large, the absolute value of interfacial shear strength is a factor of 4.5 greater than that attainable for the same AS1 unfinished fiber in the same epoxy matrix after the same hygrothermal exposure.

The micrographs in Figure 8 show that a different interface response exists in the wet *versus* dehydrated state. Normally the AS1C fiber in the dry state causes growth of radial cracks into the matrix at sites of fiber fracture in the interfacial shear strength specimen. After 125°C wet exposure, the fiber breaks do not act as sites for radial crack growth. The polarized and transmitted light micrographs of Figure 8 indicate that interfacial crack growth is occurring while stress is applied after

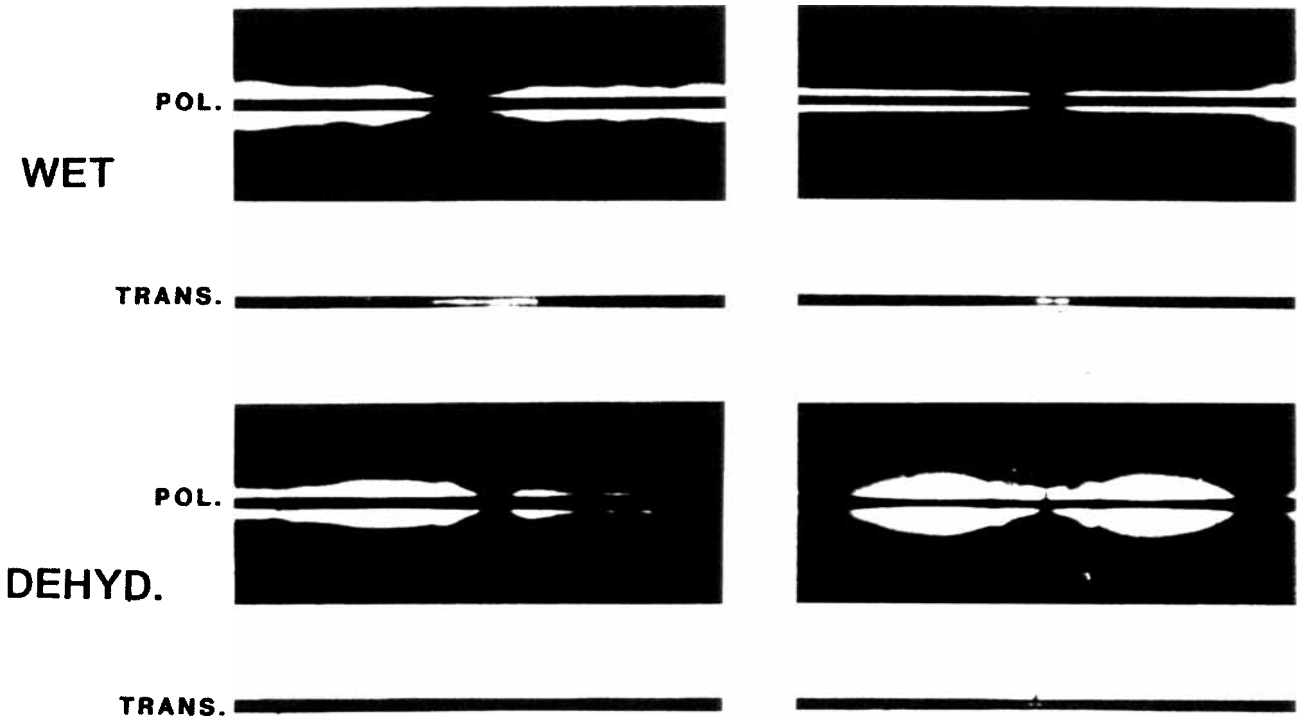

FIGURE 8 Polarized and Transmitted Light Micrographs at 400x of the ASl and ASlC Fibers Encapsulated in Epoxy Resin, Under Stress After Hygrothermal Conditioning at 100% RH and 125°C.

being conditioned wet at 125°C. After dehydration at 125°C the polarized and transmitted light micrographs of Figure 8 show that the stresses have increased in intensity at the fiber breaks and that radial cracking is again observable although to a much lesser degree than in the dry state.

The presence of the 100 nanometer thick brittle epoxy "finish" has not prevented a reduction in interfacial shear strength over the surface treated but "unfinished" fiber. However, it has reduced the magnitude of the loss in interfacial shear strength. It is believed that the compliant nature of this interphase at these hygrothermal conditions prevents high interfacial stresses from developing under the combination of thermal and moisture expansion of the matrix and this allows for more substantial stress transfer after dehydration.

The permanent reduction in interfacial shear strength that results from the application of stress to the moisture saturated specimens is taken to mean that the local material properties of the interphase have been exceeded irreversibly. It is also possible that the interphase regions which have been subjected to shear yielding during this additional application of stress may not have fully dehydrated. Since bulk sample weight measurements were used to establish fully saturated and dehydrated conditions, small amounts of water in the interfacial regions could remain there and be undetected by these measurements. Plasticization of the interphase matrix could then be possible due to the presence of water even after the sample had dehydrated as determined by bulk measurements.

## CONCLUSIONS

The response of the graphite fiber-epoxy interface to hygrothermal conditioning has both a reversible and irreversible component which depends on the temperature of the hygrothermal exposure, the presence of additional externally applied stress and the presence of an interphase coating created by a fiber "finish". When that finish consists of an epoxy-rich layer and is used in conjunction with an epoxy matrix, the following conclusions can be made.

At 20°C under moisture saturated conditions, the interfacial shear strength is reduced. Surface chemical changes are not responsible for this change. Plasticization of the matrix reduces stress transfer at the interface and the concurrent loss in matrix stiffness is responsible for the reduction in interfacial shear strength. Application of stress to the interface in the wet state causes an irreversible loss in interfacial shear strength which is not recoverable by simply drying the matrix. The presence of an epoxy "finish" on the fiber creates an interphase which mitigates the level of interfacial shear strength reduction.

At 70°C under moisture saturated conditions, the "finished" fiber is slightly less affected than the "unfinished" fiber. In both cases the interfacial shear strength is reduced substantially upon exposure to moisture. However, the interphase matrix of the "finished" fiber has a lower Tg than the bulk matrix and becomes more compliant under these hygrothermal conditions. The "finished" fiber undergoes a permanent reduction in interfacial shear strength which is not reversible after dehydration of the sample. The absolute value of the interfacial shear strength is, however, greater than that of the 'unfinished' fiber.

Hygrothermal exposure at 125°C causes a substantial irrecoverable loss in the interfacial shear strength of the "unfinished" fiber but only a moderate loss for the "finished" fiber. The combination of temperature and moisture reduced the interfacial shear strength to 19% of its dry state value for the unfinished fiber but to only 56% for the "finished" fiber. Dehydration does not restore the interfacial shear strength to greater than 45% of the dry value for the "unfinished" fiber. The "finished" fiber does not recover any of its interfacial shear strength but its absolute value remains over twice that of the "unfinished" fiber. Both the matrix and the interface are altered irreversibly by these hygrothermal conditions.

The epoxy rich fiber "finish" acts to promote better stress transfer and consequently increases the interfacial shear strength in the dry state. Wet, this interphase matrix becomes more compliant than the matrix and acts to reduce the extent of irreversible damage to the interface.

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