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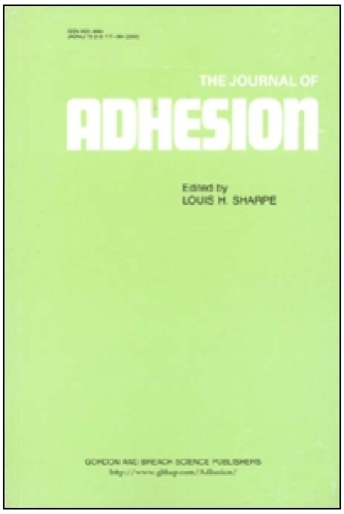

**The Journal of Adhesion**
Publication details, including instructions for authors and subscription information:
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# The Effect of Pendent Groups at the Fiber Surface on Interfacial Adhesion

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**To cite this Article** Penn, L. S. and Jutis, B.(1989) 'The Effect of Pendent Groups at the Fiber Surface on Interfacial Adhesion', The Journal of Adhesion, 30: 1, 67 — 81
**To link to this Article: DOI:** 10.1080/00218468908048196
**URL:** http://dx.doi.org/10.1080/00218468908048196

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*J. Adhesion*, 1989, Vol. 30, pp. 67–81
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# The Effect of Pendent Groups at the Fiber Surface on Interfacial Adhesion

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*(Received December 27, 1988; in final form March 28, 1989)*

Amine-terminated hexyl pendent groups were attached by direct chemical reaction to the surface of aramid engineering fiber. The number of groups attached was evaluated by two different methods of quantitative analysis, with parts per million sensitivity, and good agreement was found. Separate tests found no evidence for reaction of pendent groups with simple epoxy. A single filament pull-out test was used to assess directly the effect of the pendent groups on the fiber-matrix bond strength. The increased adhesive performance brought about by the presence of the pendent groups was ascribed either to a decrease in the initial crack size at the interface or to an increase in matrix modulus near the interface.

KEY WORDS Surface modification; fiber-matrix interface; quantitative surface analysis; single filament pull-out test; interfacial fracture energy; aramid composite.

## INTRODUCTION

Surface treatment of engineering fibers used in fiber composites has been motivated by the desire to manipulate the interaction at the fiber-matrix interface. Treatments such as acid oxidation or exposure to reactive plasma have had some success in attaching chemical functionalities to the fiber surface.[1–4] Treatments have also been shown to have some effect on the interface-sensitive properties of composite laminates.[4–9] However, the progress in developing a useful and comprehensive correlation between surface modification and the adhesion at the fiber-matrix interface has been slowed by two major difficulties.

The first difficulty is that of quantifying the surface modification produced by a given treatment. Instrumental analysis techniques such as infrared spectroscopy, which can be quantitative when used in transmission with internal standards, are only qualitative when applied to surface or interface analysis. Other modern instrumental techniques, such as X-ray photoelectron spectroscopy, are semi-quantitative at best.

The second difficulty is in adequately assessing the adhesive performance itself. Tests on composite laminates provide only an indirect measure of fiber-matrix adhesion, and the results are not immune to other effects. Examples of the latter are void content and resin content, which are difficult to control exactly from one laminate to the next, and can easily cause misleading conclusions to be drawn.

This paper describes our efforts to overcome these difficulties. Key features of the work are the use of quantitative wet chemical surface analysis and the use of an adhesive performance test that measures interfacial adhesion directly.

## BACKGROUND

Controlled functionalizing of aramid fiber surface has been used recently by us and others to affect the adhesive bonding at the interface between the fiber and the matrix.[9–14] The aramid fibers (e.g., Kevlar® 29 and 49) are ideal for these studies because they appear to undergo surface reaction without bulk degradation. These research efforts all featured attempts to quantify the implanted functional groups and to relate them in some way to adhesive performance.

Efforts in our laboratory have focused on the attachment of linear chains which terminate in a reactive functional group. Pendent groups such as these offer the possibility of increasing the fiber-matrix adhesion by diffusion into the matrix or by chemical reaction with a suitably chosen matrix.

In previously-reported work, we "activated" the surface of the inert fiber Kevlar 49 with a reactive gas plasma treatment prior to attachment of the linear chain.[12] Plasma treatment was followed by chemical treatment to attach covalently a primary amine-terminated hexyl chain to the fiber surface. The successful attachment of the pendent group was demonstrated by a lengthy fluorescent dye assay.

In the work reported here, we sought to attach pendent groups to the fiber surface directly, without the complications of plasma treatment. Plasma treatment of surfaces comprises a multitude of events which are often poorly understood (e.g., ubiquitous oxidation even when oxygen has been excluded from the system) or not even totally identified. To eliminate extraneous processes, we wished to attach the pendent groups to the fiber surface by a chemical approach alone, using well-understood chemical reactions with documented solution analogues. Earlier preliminary trials using direct chemical reaction without plasma treatment had indicated the possible success of this approach.[12] It was hoped that use of a direct approach would allow a more clear connection to be drawn between surface treatment and adhesive performance.

For the work described in this paper, a reaction scheme was used which involved exposure of the aramid fiber to diisocyanatohexane reagent to attach pendent groups. The proposed reaction sequence is shown in Figure 1. We assume that the isocyanate group reacts directly with the secondary amide groups on the fiber surface, since a solution analogue exists for the reaction of aliphatic isocyanate with secondary amide.[15]

The fiber, with the amine-terminated pendent groups presumably attached, was then subjected to a visible dye colorimetric analysis. The results from this analysis method were compared with results from the fluorescent dye method adapted

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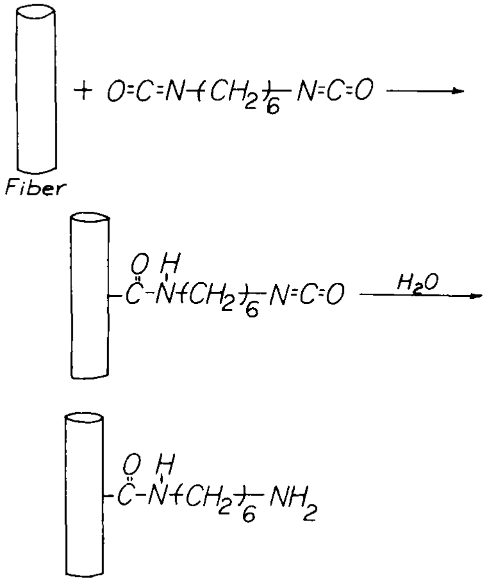

FIGURE 1 Proposed reaction sequence for attaching pendent groups to fiber surface. One end of diisocyanate reacts chemically with site (perhaps secondary amide) on fiber surface. Subsequent exposure to moisture converts remaining isocyanate to primary amine.

previously for surface analysis of the aramid fiber.[12] The comparison of one method of analysis with another becomes important when sensitivity at the parts per million level is required, as it is for fiber surfaces. To our knowledge, a comparison under controlled conditions has not been previously made on the aramid fiber.

In addition to quantitative analysis, adhesive performance tests were conducted

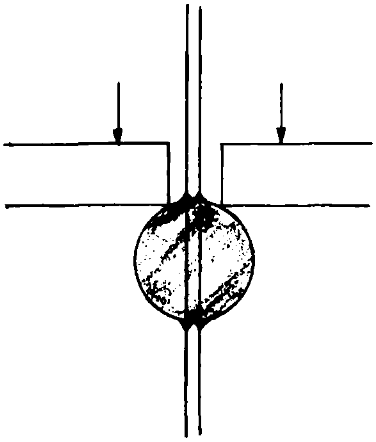

FIGURE 2 Single filament pull-out test specimen. The cured matrix surrounding the fiber is gripped and pushed downward so that the fiber, attached to a load cell at top end, is pulled out.

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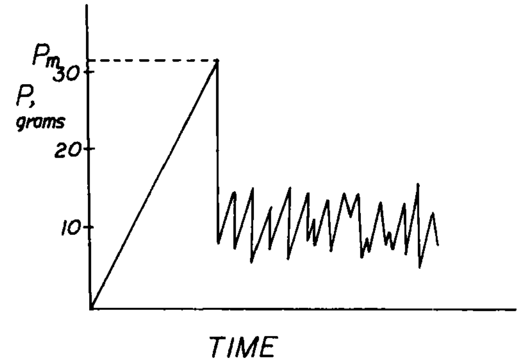

FIGURE 3 Typical load *versus* time trace for pull-out test. The load maximum $P_m$, is the debond load, while the erratic trace to the right is the frictional load as the fiber moves up through the matrix hole before the test is stopped.

on both treated and untreated fiber. The test used was the single filament pull-out test, which gives a direct measure of interfacial adhesion without the complicating effects present in a composite laminate. The test specimen configuration is shown in Figure 2. Pulling the fiber upward while restraining the matrix causes debonding at the fiber-matrix interface followed by fiber pull-out. A typical load *versus* time trace is shown in Figure 3.

## EXPERIMENTAL

### Modification of fiber surface

Kevlar 49 fabric (style 352, 1140 denier) from Clark Schwebel was washed thoroughly in mild detergent. After water rinsing, the fabric was further cleaned by a series of extractions in a Soxhlet. Solvents were used in increasing order of polarity: hexane, acetone, and water. The cleaned fabric was vacuum-dried and stored in a dessicator for further use. Some of the fabric was to serve as "experimental," i.e., to receive the surface modification treatment, and some was to serve as "control," i.e., without surface modification.

For attachment of pendent groups, fabric specimens of approximately 2 grams each were placed in test tubes in a dry nitrogen environment. They were flushed with dry nitrogen to eliminate all traces of moist air before being covered with neat diisocyanatohexane (Aldrich) in the presence of a small amount of dibutyl tin dilaurate (Aldrich) catalyst. Reaction was allowed to proceed at room temperature for 12 hours.

Excess diisocyanatohexane was removed from each fabric specimen by rinsing twice with hexane under dry nitrogen. Rinsed specimens were then subjected to a series of extractions in a Soxhlet to ensure removal of all diisocyanatohexane not chemically bonded to the fiber. These extractions were exhaustive, starting with hexane under dry nitrogen, followed by acetone and then distilled water, both in

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air. Use of water as a final solvent ensured all isocyanate groups were converted to primary amine.

### Dye assay of treated fiber

Each treated fabric specimen was separately subjected to the analysis procedure described next.

The fabric specimen was soaked for 1 h in a 1.0 N solution of HCl to protonate the primary amine groups on the fiber surface. This was followed by a rinse in 0.0010 N HCl solution (pH 3) to remove the excess 1.0 N HCl without deprotonating the amine. The specimen was then soaked in fresh Poinceau 3R dye (Curtis Matheson) solution for 1 h at 25°C to allow complex formation between the dye and the protonated primary amine. Excess dye molecules were removed by copious rinsing with 0.10 N acetic acid. (Use of a mild acid insured removal of excess dye without uncoupling any of the dye attached to primary amine.)

To cleave the attached dye for analysis, the drained specimen was soaked in 0.10 N NaOH solution for 1 h at 25°C. The NaOH supernatant was drained from the specimen and preserved in a collection flask. This cleavage step was repeated with fresh base until the supernatant was colorless. Each aliquot was added to the collection flask. The accumulated aliquots of supernatant from the specimen were reduced in volume to approximately 5 ml (use of a vacuum oven at 80°C speeded the process) and were transferred carefully to a 10-ml volumetric flask. The contents of the flask were acidified with 0.5 ml of 12 N HCl and diluted to the mark. This acidified cleavage medium, originating from a specimen of fabric of known mass, was then assayed for concentration of dye molecules.

Concentration of dye was determined by visible spectrometer measurements made on a Carey Model 14C spectrophotometer. Absorbance readings were made at 499 nanometers, using distilled water as a blank. The concentration of dye in the medium from each specimen was determined by comparison with a calibration curve of pure Poinceau 3R dye solution acidified to pH 3. Each molecule of dye found was taken to represent one pendent group on the fiber surface. Therefore, determinations of molecules of dye per gram of fiber could be converted to number of pendent groups per unit area of fiber surface.

The same dye analysis procedure was also conducted on control fabric, which had not been subjected to surface modification.

### Adhesive performance testing

Single filaments of the Kevlar fiber were teased from the fiber bundles of the fabric for preparation of single filament pull-out specimens. To form a pull-out specimen, each end of a filament about 75 mm long was affixed with double backed tape to a frame which allowed the central 50 mm of length to be suspended horizontally over open space. To serve as an end tab, a small metal loop was glued to each end of the filament with Hobby Epoxy®. Then a droplet of uncured epoxy resin, diglycidyl ether of bisphenol A (Shell Epon 826) mixed

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with triethylene tetramine (Aldrich) in the proportion by weight of 7.35:1.00, was deposited near the center of the filament's length with the aid of a very small diameter glass rod. The droplet, being liquid, assumed an approximately spherical shape which was retained during cure. Several of these specimens were prepared simultaneously on the frame, and were cured in a convection oven at 80°C for 5 h. Because the droplet size could not be controlled exactly during preparation, the embedded length of fiber was measured for each specimen under the microscope after cure.

For testing, the specimen was removed from the frame and attached by either end tab to the hook of a load cell in a universal test machine (Instron Table Model with A cell). The end tab on the other end of the filament served as a weight to keep the filament plumb. The jaws of a miniature vise attached to the crosshead of the test machine were positioned around the filament just above the droplet, and were closed to a distance smaller than the droplet diameter but just larger than the fiber diameter. When the downward crosshead motion was started, the vise jaws slowly descended to contact the top of the droplet and to apply the downward force necessary to debond the droplet from the fiber by shear and push it down the fiber.

Large numbers of control (no fiber surface treatment) and experimental (fiber surface treated) specimens were prepared and tested, covering a range of embedded lengths.

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## RESULTS AND DISCUSSION

### Attachment of Pendent Groups

The results of the quantitative analysis are shown in Table I, expressed as the number of primary amine groups detected per 100 Å$^2$ of fiber surface. Results using both visible dye analysis (Poinceau 3R) and fluorescent dye analysis (fluorescamine) are presented. Comparison of the control values with the

TABLE I
Quantitative analysis results for amine-terminated pendent groups on fiber surface

| | Control | Experimental |
|---|---|---|
| Visible Dye Method: | | |
| No. specimens | 20 | 36 |
| Ave. no. amine groups per 100 Å$^2$ | 0.156 | 0.795 |
| Std. dev. | 0.0573 | 0.630 |
| Std. error mean | 0.0128 | 0.105 |
| Fluorescence Dye Method: | | |
| No. specimens | 23 | 5 |
| Ave. no. amine groups per 100 Å$^2$ | 0.777 | 1.30 |
| Std. dev. | 0.307 | 0.295 |
| Std. error mean | 0.0641 | 0.132 |

experimental values indicates that the direct chemical treatment, with no prior plasma treatment, has indeed attached amine-containing groups to the fiber surface. The experimental values are different from the control values at the 99% level of confidence using the Student "*t*" test.

Comparison of the two experimental values after subtracting the appropriate controls shows that there is good agreement between the two methods of analysis. The corrected values for pendent groups attached are 0.639 and 0.523 groups per 100 Å$^2$ for the visible dye and the fluorescent dye methods, respectively.

The good agreement between two very different dye analysis methods used on fiber subjected to exactly the same surface treatment procedure is heartening. Not only does it suggest that both methods are accurate, but it means that the choice of method can be made on convenience alone. On this basis, the visible dye method using Poinceau 3R is much preferred over the lengthy fluorescent dye method which involves carefully timed, high pressure steam cleavage of the pendent group with the chromophore attached.

The reasonableness of the values in Table I can be evaluated by considering the theoretical maximum number of reactive sites (the secondary amides) on the surface of the fiber, computed from the known crystal structure of aramid polymer,[16] depicted in Figure 4. The maximum number of sites is 3 or 4 per 100 Å$^2$ of surface, a number which is likely to be diminished by the known surface oxidation of the aramid fiber.[17] Experimental values could conceivably vary from near zero (for no pendent groups attached), to many orders of magnitude higher than the theoretical maximum (for attachment with a branching polymerization). Because the actual results are within an order of magnitude of the theoretical maximum, they must be considered quite reasonable.

It is instructive to summarize the work of several researchers wherein chemical groups were attached to the aramid fiber surface by various treatment procedures. Allred attached primary amine groups by an ammonia plasma treatment,[9] with results ranging from 1.0 to 2.5 groups per 100 Å$^2$. Wu and Tesoro used a nitration and reduction sequence to produce chemically bonded primary amine on

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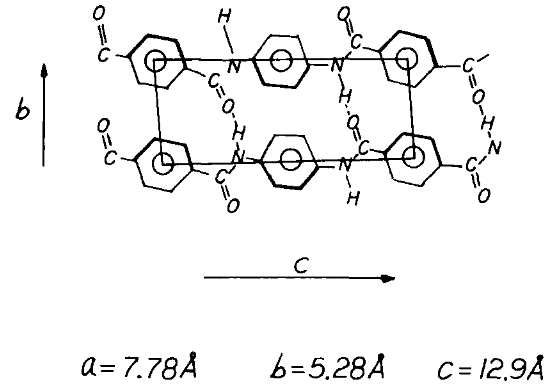

FIGURE 4 Crystal structure of the aramid polymer composing the fiber. The view shown depicts about 70 Å$^2$, according to the unit cell dimensions stated.

the aramid fiber surface,[11] with results ranging from 0.48 to 0.60 groups per 100 Å$^2$. Use of bromination followed by ammonolysis to form primary amine groups, gave similar results, 0.47 to 0.86 groups per 100 Å$^2$. Penn *et al.* attached primary amine terminated hexyl groups to the fiber surface using chemical reagent preceded by a plasma treatment,[12] and obtained results ranging from 1.5 to 4.5 groups per 100 Å$^2$.

All of this work, plus our present data on attaching primary amine-containing hexyl groups without plasma, allows a conclusion to be drawn about the number of sites available for attachment on the aramid fiber surface. Active sites seem to be pinned in the range 0.45 to 4.5 sites per 100 Å$^2$, with treatments involving plasma activation producing values at the higher end. That is, the attachment levels achieved using chemistry alone are lower than the levels achieved when the plasma treatment is involved. This suggests that the chemical treatments depend on existing reactive sites on the fiber surface, whereas plasma treatment may create new ones.

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### Adhesion at the Interface

The results of the single filament pull-out test are best presented in the form of a plot of debond load $P_m$ *versus* initial embedded length $l$. Typically, a plot of $P_m$ *versus* $l$ over a wide range of $l$ shows an increasing region at low $l$ followed by a plateau region at higher $l$.[18] This behavior makes it obvious that a unique value of interfacial bond strength using debond load divided by interfacial area is not defined. However, the experimenter can make an effective comparison of the adhesive performance of treated fiber with that of untreated fiber by examining the full range of behavior from a complete $P_m$ *versus* $l$ plot.

To interpret the test results, many authors e.g., References 19, 20, 21 have considered the mechanics of the single filament pull-out test. Penn and Lee[18] have developed an interpretation which accounts for both the rising and the plateau region seen experimentally. Their final result, based upon an energy balance approach, is given by the expression shown below for pull-out load:

$$P_m = \frac{2\pi r(rG_cE_f)^{1/2}}{\{1+\operatorname{csch}^2[n(l-a)/r]\}^{1/2}} \qquad (1)$$

where

$$n^2 = \frac{E_m}{E_f(1+v_m)\ln(R/r)}$$

and $E_f$ = fiber modulus,
$E_m$ = matrix modulus,
$v_m$ = matrix Poisson's ratio,
$r$ = fiber radius,
$R$ = radius of deformed portion of matrix which surrounds fiber,

$G_c$ = critical strain energy relase rate equivalent to fracture energy per unit interface, and

$a$ = length of tiny crack or flaw where fiber enters matrix, much smaller than the embedded length.

The trigonometric nature of the equation originates in the nonuniform stress distribution at the fiber-matrix interface. Refs. 19 to 21, ending with Ref. 18, provide the development in a chronological fashion.

At small values of $l$, $\operatorname{csch}[n(l-a)/r]$ increases to infinity and Eq. (1) approximates a sinh function:

$$P_m = 2\pi r(rG_cE_f)^{1/2}\sinh[n(l-a)/r] \tag{2}$$

Equation (2) shows that $P_m$ rises nonlinearly from zero, and depends not only on fiber-related quantities, such as $E_f$, but also on and the matrix-related quantities contained within $n$.

On the other hand, for large $l$, the denominator in Eq. (1) simplifies to 1, resulting in:

$$P_m = \frac{2\pi r(rG_cE_f)^{1/2}}{1} \tag{3}$$

As per Eq. (3), $P_m$ depends only on fiber-related quantities and the interfacial fracture energy $G_c$, and is independent of $l$. Thus, at large values of $l$, $P_m$ vs. $l$ appears as a straight horizontal line, from which $G_c$ can be computed directly.

The shapes of Eqs. (2) and (3) are shown in Figure 5 as dotted lines. the actual data would be expected to make a smooth transition from one to the other as shown by the solid line in Figure 5.

The experimental results obtained from the single filament pull-out test are shown in Figure 6. Both plots show a rising region followed by a plateau region, thereby conforming to the predicted shape. It should be noted that a high data scatter is typical of small-scale mechanical tests where averaging effects within the material cannot take place as they can for traditional size laboratory specimens. To offset this and to allow reliable determination of trends, a large number of individual tests was performed.

The $l$ value separating rising from plateau region of each plot was estimated

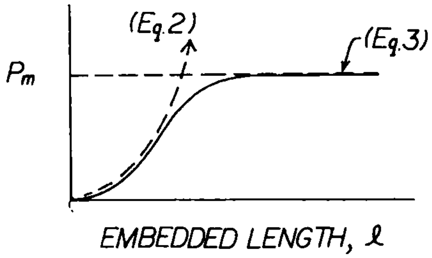

FIGURE 5 Predicted $P_m$ *versus* $l$ function. Dotted lines for $P_m$ at small $l$ and at large $l$ are shown. Actual data would be expected to make a smooth transition from one behavior to the other as shown by solid line.

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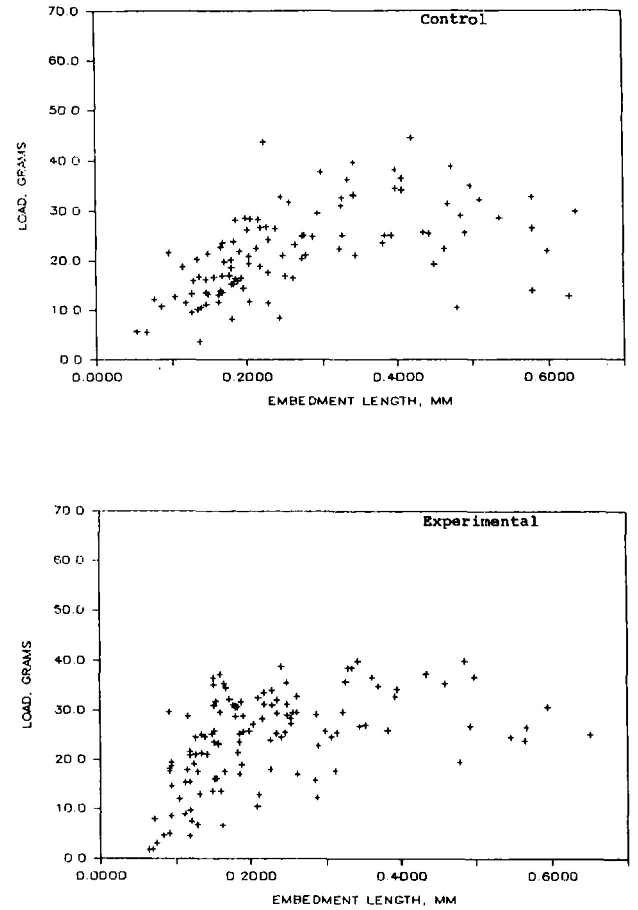

FIGURE 6 Experimental results from single filament pull-out tests on control and experimental fiber. Note that both plots give rising and plateau regions. For experimental fiber the rising region rises more steeply than for control fiber, but the plateau region is at the same level as the control.

visually, and was designated $l_c$, or "critical" $l$. Comparisons were then made separately between the plateau regions of control and experimental populations and between the rising regions of control and experimental populations.

For a quantitative comparison of the plateau regions, the average debond load $P_m$ was computed for each plot. Table II shows these average values for control and experimental populations. Slight differences in choice of $l_c$ made no difference to the computed average. The most important result shown in Table II is that there is no difference in plateau region debond load between the control and the experimental populations. This fact, used with Eq. (3) where $E_f$ and $r$ are constants with respect to fiber surface treatment, leads to the conclusion that the fiber treatment did not modify the value of the interfacial fracture energy $G_c$, computed as 143 J/m$^2$. Since a lack of change in $G_c$ was a rather unexpected result, we sought additional evidence to support this result.

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TABLE II
Debond load in the plateau region for treated and untreated aramid fiber in epoxy resin matrix

| Untreated fiber (control) | | | |
|---|---|---|---|
| Chosen $l_c$, mm | 0.229 | 0.300 | 0.345 |
| No. data points | 51 | 36 | 27 |
| Ave. debond load, g | 28.9 | 30.4 | 30.6 |
| Std. dev. | 6.98 | 6.32 | 6.79 |
| Std. error mean | 0.977 | 1.05 | 1.13 |
| **Treated fiber (experimental)** | | | |
| Chosen, $l_c$, mm | 0.211 | 0.236 | 0.262 |
| No. data points | 53 | 43 | 31 |
| Ave. debond load, g | 29.0 | 29.0 | 29.0 |
| Std. dev. | 6.46 | 6.80 | 7.33 |
| Std. error mean | 0.887 | 1.03 | 1.32 |

A form of independent confirmation was obtained by examining the frequency of occurrence of fiber tensile failures in the plateau region during the course of the testing. As $l$ is increased, the loads required to debond the fiber from the matrix approach the fiber failure load. Therefore, in the plateau region, many fiber tensile failures occur in preference to fiber-matrix interfacial debonding. In this situation, any fiber treatment that changed the interfacial fracture energy would be expected also to change the per cent of fiber failures that occurred.

The data in Table III show that the per cent occurrence of fiber tensile failure was not affected by the fiber surface treatment used in this work. This is consistent with the finding that the average debond load in the plateau region (Table II), and therefore the $G_c$ value, was not affected by the fiber surface treatment.

Parenthetically, Table IV offers information about the effect of surface treatment on the fiber tensile strength, which is a separate matter from interfacial debonding data. Possible damage to the fiber's load-bearing capability as a result

TABLE III
Fiber tensile failures *versus* pull-outs in the plateau region for treated and untreated aramid fiber in epoxy resin matrix

| Untreated fiber (control) | | | |
|---|---|---|---|
| Chosen $l_c$, mm | 0.229 | 0.300 | 0.345 |
| No. fiber failures | 25 | 25 | 24 |
| No. pull-outs | 51 | 36 | 27 |
| Sum | 76 | 61 | 51 |
| % fiber failures | 32.9 | 41.0 | 47.1 |
| **Treated fiber (experimental)** | | | |
| Chosen $l_c$, mm | 0.211 | 0.236 | 0.262 |
| No. fiber failures | 28 | 26 | 24 |
| No. pull-outs | 53 | 43 | 31 |
| Sum | 81 | 69 | 55 |
| % fiber failures | 32.9 | 37.7 | 43.6 |

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TABLE IV
Fiber tensile failure load in the plateau region for treated and untreated aramid fiber in epoxy resin matrix

| Untreated fiber (control) | | | |
|---|---|---|---|
| Chosen $l_c$, mm | 0.229 | 0.300 | 0.345 |
| No. tensile failures | 25 | 25 | 24 |
| Ave. tensile failure load, g | 29.4 | 29.4 | 29.3 |
| Std. dev. | 9.14 | 9.14 | 9.31 |
| Std. error mean | 1.83 | 1.83 | 1.90 |
| **Treated fiber (experimental)** | | | |
| Chosen $l_c$, mm | 0.211 | 0.236 | 0.262 |
| No. tensile failures | 28 | 26 | 24 |
| Ave. tensile failutre load, g | 31.2 | 31.2 | 31.0 |
| Std. dev. | 8.05 | 8.11 | 8.24 |
| Std. error mean | 1.52 | 1.59 | 1.68 |

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of surface treatment is always a concern. The fact that, in this case, the treated and untreated fiber populations show the same value for fiber tensile strength confirms that the chemical treatment did not degrade the fiber.

Another reassuring finding supporting the unchanged value of $G_c$ is the apparent lack of chemical reaction between the experimental (treated) fiber and the epoxy resin matrix, even though one might be expected. Auxiliary experiments were conducted involving the exposure of experimental fiber to butyl glycidyl ether, a simple liquid epoxy, followed by thorough rinsing and quantitative dye analysis using Poinceau 3*R*.[22] Analyses of repeated runs showed that the number of pendent amine groups on the fiber surface was undiminished, results that we also found in our earlier work.[12] If no reaction occurs under these favorable conditions, it is not likely that reaction occurs at the fiber-matrix interface of the single filament pull-out specimen. Thus, a major driving force for the increase of $G_c$ can be ruled out.

The rising regions of the $P_m$ *versus* $l$ plots were also compared to check for differences between control and experimental populations. Although Eq. (2) indicates that the rising region should be nonlinear, the actual data cannot be distinguished from linearity. Therefore, for a convenient quantitative comparison, the plots below $l_c$ were regarded as linear, and interfacial shear strength values were computed from each point using $P_m/2\pi rl$. The average interfacial shear strengths are shown in Table V.

In contrast to the plateau regions, the rising regions of experimental and control populations indicate that the treatment did increase the adhesive performance. Control and experimental samples are different at the 99% level of confidence, for all choices of $l_c$, according to the Student "$t$" test. The increase of about 30% is an amount that seems large enough to be important.

The fact that the rising region shows an increase in interface strength with treatment while the plateau region shows that $G_c$ was unchanged by the surface treatment simply underscores the difference between interfacial fracture energy

TABLE V
Interfacial shear strength in the rising region for treated and untreated aramid fiber in epoxy resin matrix

| | | | |
|---|---|---|---|
| Untreated fiber (control) | | | |
| Chosen $l_c$, mm | 0.229 | 0.300 | 0.345 |
| No. data points | 60 | 75 | 84 |
| Shear strength, MPa | 2.80 | 2.76 | 2.72 |
| Std. dev. | 0.888 | 0.878 | 0.844 |
| Std. error mean | 0.115 | 0.101 | 0.0921 |
| Treated fiber (experimental) | | | |
| Chosen $l_c$, mm | 0.211 | 0.236 | 0.262 |
| No. data points | 73 | 83 | 95 |
| Shear strength, MPa | 3.80 | 3.76 | 3.70 |
| Std. dev. | 1.55 | 1.48 | 1.40 |
| Std. error mean | 0.182 | 0.162 | 0.140 |

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and adhesive performance. From these results we must conclude that the higher $P_m$ values in the rising region of the experimental population are due to quantities within $\sinh[n(l-a)/r]$, since $G_c$ and other quantities are unchanged. There are only two quantities within $\sinh[n(l-a)/r]$ that could possibly change as a result of fiber surface treatment. These quantities are "$a$" and $n$.

Let us first consider "$a$," the small initial crack of flaw presumed to exist at the interface where the fiber enters the matrix. According to Eq. (2), for a given value of $l$, a smaller "$a$" would increase $P_m$. While we cannot see or measure the size of "$a$," it is conceivable that surface treatment could somehow bring about a smaller average "$a$," which could then serve to raise $P_m$ in the experimental population.

We must also consider an increase in $n$ as the possible cause of higher $P_m$ in the experimental population at low $l$. Recall the definition:

$$n^2 = \frac{E_m}{E_f(1+\nu_m)\ln(R/r)}$$

Increased $n$ can arise only from changes in the matrix-related quantities $E_m$, $\nu_m$, or $R$, since $E_f$ and $r$ are constant with respect to fiber surface treatment. Here we emphasize that the quantities $E_m$, $\nu_m$, and $R$ in this definition refer only to that portion of the matrix that is deformed and, therefore, is storing energy during specimen loading. The undeformed matrix remote from the interface is irrelevant.

Reasoning suggests that changes in $n$ are linked much more strongly to the behavior of $E_m$ than to $\nu_m$ or $R$. In ploymeric materials that behave normally, the quantities $E_m$, $\nu_m$, and $R$, are not likely to vary independently; an increase in $E_m$ would be accompained by a decrease in $\nu_m$ and an increase in $R$. However, Poisson's ratio $\nu_m$ can only change within a limited range (0.2 to 0.5), and a substantial percentage increase in $R$ would bring about only a small increase in

$\ln(R/r)$. This leaves $E_m$ as the dominant variable within $n$, and it would have to increase to bring about the higher $P_m$ values found for the experimental fiber.

Unfortunately, we cannot make *in situ* modulus measurements of the cured matrix directly adjacent to the fiber. However, there are reports in the literature of changes in this region brought about by fiber treatment.[23,24] Because of preferential adsorption or other factors, the epoxy-curing agent ratio adjacent to the fiber is different from that in the bulk and different cure kinetics and final properties result. Furthermore, it has been shown that moving the epoxy-curing agent ratio in either direction from 1:1 stoichiometry results in an increase in matrix modulus.[24,25]

For our case, chemically sound arguments probably could be made for either an epoxide-rich or an amine-rich layer adjaent to the treated fiber. Evidence cited above indicates that either situation would produce an increased matrix modulus, leading to the observed higher adhesive performance at low values of $l$. In addition, improvement could arise from a simultaneous increase in $E_m$ and decrease in "$a$." Further insight must await the results of future work.

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## CONCLUSIONS

The main findings of this work can be summarized as follows:

Direct chemical treatment successfully attached amine-terminated pendent groups to the fiber surface.

The level of attachment was found to be about 0.8 groups per 100 Å$^2$, a reasonable value, lower than the theoretical maximum of 3–4 groups per 100 Å$^2$.

A cross check of the surface quantitative analysis results using two different methods gave good agreement.

Separate experiments indicated that the terminal amine of the pendent group apparently fails to react with epoxide.

The presence of the pendent groups on the fiber surface did not change the interfacial fracture energy $Gc$.

The presence of the pendent groups did increase the adhesive performance at low embedded lengths.

The improved adhesive performance can be attributed to an increase in matrix modulus near the interface, to a reduction in flaw size at the interface, or to a combination of both.

### Acknowledgements

The authors thank Mr C. T. Chou for valuable assistance.

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