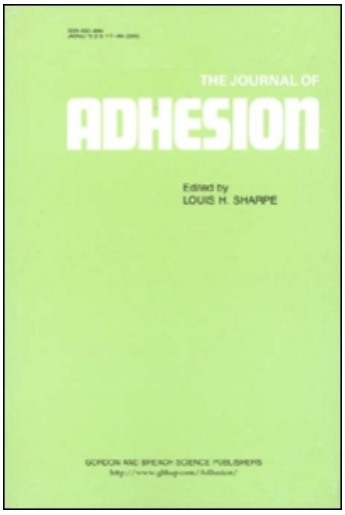

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The Study of Reactive Functional Groups in Adhesive Bonding at the Aramid-Epoxy Interface†

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In polymeric composites, reactive functional groups on the fiber surface are assumed to enhance the mechanical strength of the fiber-matrix interface greatly by forming covalent bonds with the matrix. To test this assumption, we sought to promote covalent bonding at the aramid fiber-epoxy matrix interface by attaching flexible reactive pendent groups to the fiber surface. Other factors that could affect interfacial adhesion were kept constant, *i.e.*, surface energy and surface topography. Quantitative analysis showed a pendent group attachment level of 1.5 to 4.5 groups per 100 $Å^2$ of fiber surface, a level that agrees well with the theoretical amount. Surprisingly, in adhesive performance tests, the presence of these reactive pendent groups did not improve the fiber-matrix interface strength. Specific chemical tests for covalent bond formation between the terminal amine of the pendent group and the epoxy molecule showed that covalent bonding did not occur, thus explaining the unexpected lack of improvement in adhesive performance.

KEY WORDS Chemical bonding at interface; quantitative analysis of surface; aramid fiber-epoxy adhesion; single filament pull-out test; functional groups on fiber surface; reactive pendent groups.

INTRODUCTION

In polymeric composites, the presence of reactive functional groups on the fiber surface is expected to enhance the mechanical strength

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of the fiber-matrix interface greatly through a covalent bonding mechanism. The advent of sophisticated surface analysis techniques has permitted the identification of atoms and, in some cases, of specific functional groups on fiber surfaces. However, whether the functional groups actually form covalent bonds with a reactive matrix has not been clarified. The only exceptions to this are the investigations which addressed glass-reinforced composites, where in some cases silicate particles were used as high surface area models for glass fibers. In these, direct evidence was provided for covalent bond formation between the glass substrate and the silane coupling agents and also between amino silane coupling agents and epoxy resin.[1–2]

Practical problems have hindered meaningful study of the role of covalent bonding at the interface. One major problem is that the interface represents a very small portion of the material in a bulk composite and is buried within the solid. This makes *in situ* spectroscopic investigations difficult even with modern instruments. Another severe problem is that the various factors that contribute to interface bonding are difficult to control and quantify. Experiments are needed where the functional group content, *i.e.*, the covalent bonding capability, of the fiber surface is used as a variable while the surface topography and the surface energy are held constant.

The aramid fiber, Kevlar 49® (poly-p-phenylene terephthalamide), appears to offer the opportunity for such controlled experiments. Although the fiber is chemically inert under normal conditions, reactive functional groups have been attached covalently to its surface by reactive gas plasma treatment. Such attached groups could serve as a basis for subsequent covalent bonding at the fiber-matrix interface. The high degree of crystallinity of the fiber suggests that under the proper experimental conditions, the gross smoothness of the surface topography can be retained.[3] Furthermore, the organic nature of the fiber offers the possibility that attachment of organic functional groups to the surface can be accomplished without significant change in atomic composition, and therefore, that fiber surface energetics can be maintained constant. The latter can occur because a key determinant of surface energetics is atomic composition. For example, the surface energetics of polymers containing only C, H are similar to each other, whereas

the surface energetics of polymers containing C, H, N, O are similar to each other but different from the C, H polymers. This concept has been demonstrated specifically for modified and unmodified aramid fiber surface.[4,5]

In the work described in this paper, we sought to promote covalent bonding at the interface by attaching flexible reactive pendent groups to the fiber surface while keeping the fiber surface topography and surface energetics constant. In principle, holding these two factors constant should permit a clearer assessment of the role of fiber surface functional groups in fiber-matrix adhesion.

BACKGROUND

The first step in attaching pendent groups is to activate the relatively inert aramid fiber surface by plasma treatment. This affects only the surface and does not degrade the bulk properties of the fiber. Previous studies[6–10] provide evidence that either the plasma treatment itself or the associated procedures (*e.g.*, vacuum) cause the fiber surface to form a better adhesive bond with the matrix in the fiber composite. Since these investigations have shown that chemical changes,[6–8] surface etching,[9] formation of persistent free radicals,[9] and moisture desorption[10] can all occur as a result of plasma treatment, it is difficult to determine the specific cause of the improved fiber-matrix interface. In our application of plasma treatment we wished to eliminate all the effects mentioned above except the surface chemical changes.

Monomethyl amine plasma has been reported to attach the aminomethyl group to the aromatic ring of the fiber polymer chain.[7,8] One attached, each aminomethyl group can be extended by chemical reaction with an aliphatic diisocyanate. A heterogeneous chemical reaction between the aminomethyl group on the fiber surface and the isocyanate in the liquid phase will form, through a urea linkage, an extended pendent group terminating in an isocyanate group.

$$\text{Fiber} - CH_2NH_2 + OCN\text{—}(\text{—}CH_2\text{—})_6\text{—}NCO \rightarrow$$

$$\text{Fiber} - CH_2NHC(=O)NH\text{—}(\text{—}CH_2\text{—})_6\text{—}NCO$$

Exposure to moist air will convert the terminal isocyanate to a primary amine with liberation of carbon dioxide giving the desired pendent group.

$$\text{Fiber} - CH_2NHC(=O)NH-(-CH_2-)_6-NH_2$$

Conversion of isocyanate groups on solid surfaces by moist air has been confirmed spectroscopically.[11]

The aliphatic segment of the pendent group is intended to make the terminal primary amine much more accessible for reaction with the epoxy molecules when the fiber and matrix are joined to make the fiber composite. The effectiveness of six-carbon aliphatic segments in increasing the accessibility of terminal functional groups at solid-liquid interfaces has been demonstrated previously.[12,13]

An attractive feature of the proposed pendent group is that it can be cleaved at the urea linkage for quantitative analysis of the cleavage product in solution. For small amounts of material, quantitative analysis is accomplished much more accurately by solution techniques than by solid phase surface analysis techniques. Another advantage of the proposed pendent group is that it would not be expected to alter significantly the fiber surface energetics since it, like the fiber, is composed of C, H, N, and O atoms.

Once the pendent groups have been added to the fiber surface, determination must be made of their surface concentration, permanence, configuration, and extent of chemical reaction with epoxide functional groups. In addition, the strength of the adhesive bond between the modified fiber and the epoxy matrix must be assessed and compared to that of the control fiber. The most direct method for measuring fiber-matrix adhesion is the single filament pull-out test. It is conceptually simple and provides a valid comparison of fiber-matrix systems when only the interface is modified but not the bulk fiber and matrix. A good correlation between interfacial adhesive strength and the fiber surface pendent group content would be strong evidence for the presence of covalent bonding at the interface.

The following section provides the experimental details of fiber treatment procedures, the analysis of the fiber surface, the test for reaction with epoxide groups, and the mechanical testing of the interfacial bond.

EXPERIMENTAL

Fiber cleaning: Unbound, absorbed matter was removed from the as-received aramid fiber, Kevlar 49, by a three-step procedure. A 24-hr washing in 0.2 M Na_2HPO_4 solution (pH 9.1) at reflux was followed by a thorough rinse in deionized water. The final step was a rinse in spectroscopic grade anhydrous acetone to remove excess water. The clean fiber was vacuum-dried at 80°C and stored in a dessicator in the dark. Vacuum drying the fiber at this stage greatly reduced the time required to achieve the high vacuum conditions necessary to begin the plasma treatment of the fiber in the next step. Dark storage was important at all times during the program to avoid possible sunlight damage to the fiber.

Plasma treatment: To attach aminomethyl groups, —CH_2NH_2, to the surface, fiber specimens were exposed to monomethyl amine plasma. The exposure times of 2, 5, and 15 minutes covered a range selected to achieve a measurable level of pendent group attachment without fiber strength degradation or surface etching. The minimum was selected using Allred's data[7] while the maximum was determined by trial and error in our laboratory on the basis of fiber tensile strength. The plasma treatment was carried out in a tubular glass reactor containing a glass frame to support the fiber. The rf energy (27.1 MHz) was supplied by a Tomac Dithery unit, model 1565, with a power setting of 100 W and was inductively coupled with a 20-cm diameter two-turn coil perpendicular to the length of the reactor. Prior to each plasma treatment, the reactor containing the sample was evacuated until sample outgassing stopped and a stable low pressure less than 10^{-3} torr was reached. This ensured the removal of residual moisture and air from the fiber which could possibly interfere with the plasma treatment. A steady state flow of monomethyl amine gas from a reservoir was then established in the reactor. The gas pressure was maintained at 0.2 torr by a diffusion pump system while the rf field was on, creating the plasma. After treatment, the fiber was stored in the dark. Dry storage was not necessary at this point.

Post-plasma wash: To ensure the removal of any unbound, adsorbed material and to ensure decay of any persistent free radicals resulting from the plasma treatment, the fiber was washed, dried, and stored as described above. The functional groups

attached by the plasma to the fiber surface were extended chemically as described below. Dryness was very important at this point in order that the reaction below not be poisoned by moisture.

Extension of pendent group with 1,6-*diisocyanatohexane*: Degassed 1,6-diisocyanatohexane (NCO) in neat liquid form was exposed to plasma-treated fiber for 48 hr at room temperature in the presence of a catalytic amount (1 drop) of dibutyl tin dilaurate. Unreacted NCO was removed from the fiber by two separate Soxhlet extractions. Dry nonpolar methylene chloride or Skelly B was used first to remove the excess NCO without causing moisture-induced side reactions involving chemically-bound groups on the fiber surface. Acetone was used to remove any adsorbed polar species remaining. After exposure to moist air, the fiber surface was assumed to contain covalently attached pendent groups, each with a urea linkage, a six-carbon aliphatic segment, and a terminal primary amine. Once the pendent groups were attached, there was no reason to keep the fiber in a dessicator. The fiber is known to absorb moisture rapidly, making it difficult to keep moisture-free during ordinary laboratory operations and testing. Therefore, to ensure that all further testing be carried out on fiber having a stable moisture content, we allowed the NCO-treated fiber to equilibrate at ambient conditions. However, the specimens were still stored in the dark to avoid sunlight.

Surface topography evaluation: A JEOL 35 scanning electron microscope was used to monitor surface topography of the fiber at selected stages of treatment. Fibers exposed to the 2-min plasma treatment (without NCO) and to the 5-min plasma treatment (without NCO) were examined to determine if undesired plasma etching had occurred. Fibers subjected to 2-min plasma plus NCO were examined to determine if undesirable globules of polymer had been deposited as a result of NCO addition. All were compared to control fiber surface.

Surface energetics evaluation: The surface energetics of untreated (control) fiber and of one type of fully-treated fiber (2-min plasma plus NCO) were evaluated and compared by the Wilhelmy wetting force method from which contact angle cosines are computed.[14] Water was used as the probe liquid since it is the most sensitive of all liquids to changes in surface polarity. Testing was carried out at ambient conditions.

Infrared analysis: A computerized Perkin-Elmer 283 spectrophotometer was used with an attenuated total reflectance attachment and KRS5 crystal to obtain spectra of control, 2-min plasma-treated, and fully-treated (2-min plasma plus NCO) fiber surfaces, all at ambient conditions. The signal-to-noise ratio was enhanced by averaging multiple scans.

X-ray photoelectron spectroscopy (XPS): Analysis of the atom content of fiber surfaces was carried out by Structure Probe, Inc., of Metuchen, New Jersey, on a Perkin–Elmer Model 549-XPS/AES/SAM. The specimens were in the form of woven swatches, mounted on aluminum specimen holders. They were placed in the sample chamber which was evacuated to 10^{-7} torr and areas 2 mm in diameter were sampled to a depth of 20 Å. Standard spectra for elements pertinent to this study were obtained from Handbook of X-Ray Photoelectron Spectroscopy.[15] Empirically derived atomic sensitivity factors from the same handbook were used. Besides evaluating the control fiber and one of the fully-treated fiber types (2-min plasma plus NCO), we evaluated fiber with different plasma treatment times and no NCO to check for progressive plasma modification of the surface. Both survey spectra and high resolution spectra (C, N, O region) were obtained. High resolution XPS data were corrected for surface charge shift by referencing the C1s photoelectron line due to aromatic hydrocarbon species at 284.5 eV. A consequence of the high vacuum conditions of the XPS specimen chamber is that adsorbed or absorbed moisture is removed from the specimen just before the spectrum is taken.

Cleavage of pendent groups from the fibers: For quantitative analysis, the pendent groups were hydrolytically cleaved at the urea linkage by a high-pressure steam procedure that we developed. Each fiber specimen of nominal 2-g mass was vacuum-dried for accurate determination of the dry weight and subsequently placed in its own 32-ml cylindrical steel bomb along with 20 ml of deaerated, deionized water. The contents were blanketed with argon gas to displace all oxygen and the tightly sealed bomb was placed in hot oil at 200°C for 30-min (225 psi computed steam pressure). The sealed bomb was dropped into cold water to quench the reaction after which the liquid contents were transferred to a 100 ml volumetric flask. Some 0.2 M Na_2HPO_4 solution was used to rinse the fiber

specimen and this was also added to the volumetric. The contents were diluted to volume with 0.2 M Na_2HPO_4, as required for the subsequent fluorescence assay conducted at pH 9.1. Fiber specimens were rinsed with acetone and vacuum-dried for accurate determination of the dry weight. After weighing, they were stored in the dark at ambient conditions.

Quantitative analysis of cleaved product: A fluorescence assay specific for primary amines was used to analyze the above 0.2 M Na_2HPO_4 solution for the cleavage product 1,6-diaminohexane.[16] A Perkin–Elmer LS-5 luminescence spectrometer provided sensitive detection of the fluorescamine-amine fluorescent complex. Since, theoretically, cleavage of one pendent group simultaneously produces one molecule of 1,6-diaminohexane and one residual aminomethyl group on the fiber, we arbitrarily decided to convert the fluorescence assay result from a mass of diaminohexane to mass of aminomethyl group using the molecular weight ratio. Our results are tabulated as parts per million (micrograms of aminomethyl group per gram of fiber).

Reaction of pendent groups with epoxide groups: From a batch of ten fully-treated specimens (5-min plasma plus NCO) five specimens were selected for pendent group quantitative analysis by the hydrolytic cleavage and fluorescence assay procedures described above. The other five specimens were exposed individually to neat butyl glycidyl ether, a reactive epoxy, at room temperature for 24 hr. After Soxhlet extraction with Skelly B and then with acetone to remove excess unreacted epoxy, these fiber specimens were also subjected to hydrolytic cleavage and fluorescence assay.

Fiber-matrix interfacial bond strength: The adhesive bond strength at the interface was evaluated directly by a single filament pull-out test.[17] To insure stable and realistic moisture content, the fibers used for this test were also allowed to equilibrate with ambient laboratory atmosphere. The matrix resin used was Ciba–Geigy's 6010 epoxy, cured with Ciba–Geigy's 956 triethylenetetramine. Curing was carried out at atmospheric pressure for 3 hr at 120°C. Single filament pull-out tests were conducted on specimens made from control (clean, untreated) fiber and from three fully-treated fiber types: 2-min plasma plus NCO, 5-min plasma plus NCO, and 15-min plasma plus NCO. Pulled-out filaments were checked microscopically to verify that the locus of failure was at the fiber-matrix interface.

RESULTS AND DISCUSSION

Surface topography: Scanning electron micrographs (Figure 1) of typical fibers at selected stages of treatment showed that the smooth surface topography of the control fiber (top) was retained as desired. The plasma treatment did not etch or pit the surface (middle) and the NCO addition to plasma-treated fiber left only small scale low profile deposits (bottom).

Surface energetics: The advancing and receding contact angle cosines, $\cos\theta_a$ and $\cos\theta_r$, obtained for control fiber and for fully-treated fiber, are shown in Table I.

For the two fiber types there is no difference between the $\cos\theta_r$ values but there is a statistically significant difference between the $\cos\theta_a$ values (Student t-test at $\alpha = 0.995$). The fact that the treatment lowered $\cos\theta_a$ but not $\cos\theta_r$ indicates that the treatment produced microscopic regions of reduced polarity on the fiber surface. We attribute the reduced polarity to the presence of the pendent groups' aliphatic six-carbon segments which are large nonpolar segments. A change in surface polarity of the modest magnitude detected here has been found to have no effect on fiber-matrix adhesion in similar situations.[4,5] Because the wettability method tests a surface layer less than 5 Å deep, the results obtained on the fiber with the 2-min plasma plus NCO can be assumed to be representative of any fully-treated surface with similar pendent group concentration.

Infrared analysis: The attenuated total reflectance technique with its 10,000-Å sampling depth (10% of fiber diameter) is not as surface-sensitive as XPS or wettability analysis. The signals from the functional groups on the fiber surface are diluted by the signals from the large amount of bulk organic fiber present in the sampling volume. Dominated by the underlying bulk fiber, the spectra of treated and nontreated specimens were so similar that no distinct conclusions could be drawn from them regarding changes in the surface functional groups.

XPS: Since the XPS technique's sampling depth is 20 Å, the results presented in Table II represent surface plus some subsurface material. The estimated atom percent values shown in part A (top) cannot be taken as absolute because XPS does not analyze for hydrogen. Atom percents are computed only on the basis of analyzed elements and, therefore, can deviate substantially from the

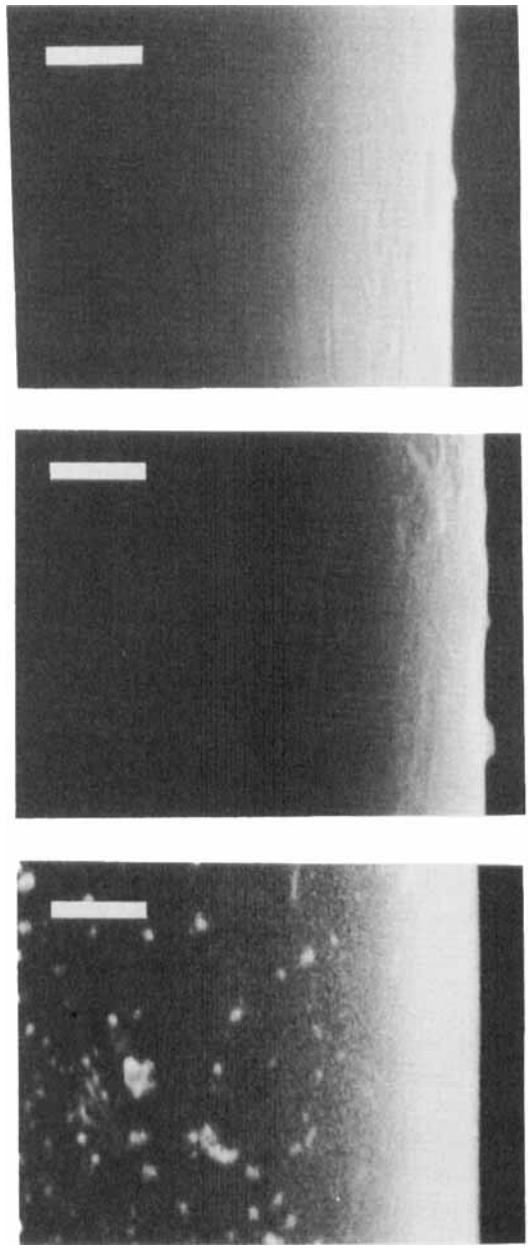

TABLE I
Contact angle cosines of water on control and treated fiber

Fiber	Cos θ_r	Cos θ_a	N
Control	0.822 ± 0.106	0.407 ± 0.136	15
2-min plasma plus NCO	0.744 ± 0.107	0.255 ± 0.114	13

TABLE II
XPS analysis of fiber surface

A. Estimated atomic compositions (%) within 20 Angstrom analyzed layer

Specimen	C	N	O	Si	P	S	Ca	Sn
Theoretical aramid polymer	78.0	11.0	11.0	0.0	0.0	0.0	0.0	0.0
Control	74.2	7.8	17.3	—	—	0.7?	—	—
2-min plasma	66.0	4.5	21.7	6.2	—	—	1.7	—
5-min plasma	63.1	4.6	22.9	6.9	—	—	2.5	—
15-min plasma	66.6	6.9	20.1	3.5	0.8	—	2.2	—
2-min plasma + NCO	67.9	10.3	18.4	1.5	0.7	—	1.0	0.3

B. Relative amounts of key surface atoms in analyzed layer

Specimen	N/C	O/C	N/O	O/N
Theoretical	0.143	0.143	1.000	1.000
Control	0.105	0.233	0.451	2.22
2-min plasma	0.068	0.329	0.207	4.82
5-min plasma	0.073	0.363	0.201	4.98
15-min plasma	0.104	0.302	0.343	2.91
2-min plasma + NCO	0.152	0.271	0.560	1.79

absolute atom percent when hydrogen is present. However, within a specimen, the relative accuracy is within 5%. The top portion (A) of Table II shows introduction of Si and Ca into the fiber surface at longer plasma treatment times, probably from the glass reactor walls. It is also evident that the post-plasma wash removed (or the NCO treatment buried) these species.

FIGURE 1 Scanning electron micrographs of aramid fiber showing that surface smoothness is retained after treatments. Top—control; middle—2-min plasma without NCO (5-min plasma treatment gave identical results); bottom—2-min plasma plus NCO. Original magnification—18,000 ×. White bars each represent 1 micron.

For meaningful comparison of the changes in C, N, and O at the fiber surface, ratios of the atoms within a specimen were computed from part A and are shown in part B of Table II. The surface of the control fiber contained more than the theoretical oxygen atom content computed for the pure poly-p-phenylene terephthalamide polymer, an observation also made by others.[7,18] This has been interpreted to mean that the fiber surface is somewhat oxidized by the manufacturing process. The plasma treatment oxidized the fiber surface even further, although the treatment was carried out on dry fiber in the absence of air. It is probable that this oxidation actually occurred when the fiber was removed from the plasma reactor and residual surface free radicals reacted with oxygen from the air.

The Table shows that when NCO was added to the plasma-treated fiber, the oxygen in the analyzed depth diminished relative to both C and N while the nitrogen increased relative to C and O, consistent with expected consequences of NCO treatment. It is not possible to draw additional conclusions from the atom content data because the treatments to which the fiber was subjected could have caused both addition and removal (by burial or ablation) of atoms from the 20-Å deep surface layer.

XPS has a limited ability to distinguish the functional group in which a given atom resides. When carried out at high resolution, XPS can distinguish oxidized from reduced atoms by means of their small binding energy shifts. The high resolution spectra, while not able to indicate specific functional groups, can yield helpful information, as discussed below.

The nitrogen spectrum for each and all specimens showed that the nitrogen atom was in reduced form (*e.g.*, amide, amine). This means that the oxidation that occurred both during manufacture and as a result of plasma treatment did not involve the amide nitrogen of the fiber's polymer chains.

The high resolution carbon spectrum for each and all specimens showed a dominant species at 284.5 eV corresponding to the aromatic ring carbon (reduced). Two carbon species at higher binding energies (oxidized) were present, one of which was assumed to be the carbonyl carbon. Located as shoulders on the dominant peak, they grew with plasma treatment time (Figure 2). For the fully treated fiber, 2-min plasma plus NCO, the six aliphatic carbons (reduced) of the pendent group chemically attached to the surface

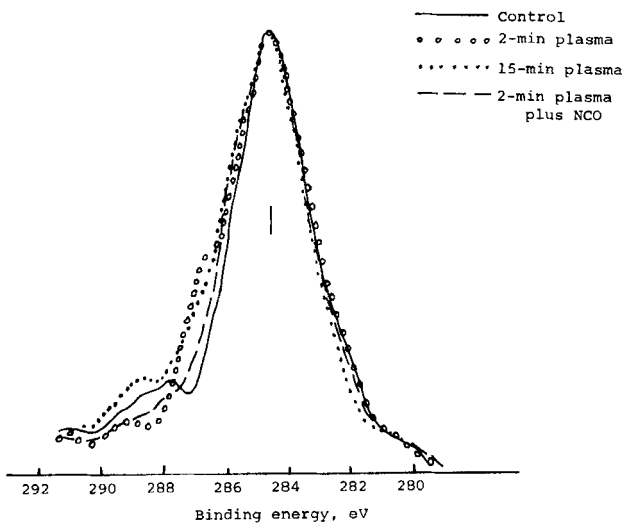

FIGURE 2 High resolution XPS spectrum for carbon atom. Spectra from four fiber specimens are superimposed to show differences. The dominant peak is aromatic ring carbon. Shoulders at higher binding energies are oxidized species. Note increases in oxidized species relative to ring carbons at longer plasma treatment times. Also note diminution in relative amount of oxidized carbon after pendent group attachment (2-min plasma plus NCO), as expected.

have almost exactly the same binding energy as the aromatic carbons.[15] Therefore, their only effect on the spectrum would be to diminish the relative contribution of the oxidized carbons, as Figure 2 shows. The high resolution oxygen spectra for all specimens showed a dominant contribution from carbonyl oxygen at 531–532 eV,[7,15] surrounded by contributions from species of both higher and lower binding energies. The NCO treatment, as might be expected, seemed to reduce the relative contributions of all oxygen species other than the carbonyl at 531.7 eV (Figure 3).

In sum, the high resolution XPS data shed some light on the nature of the surface oxidation and are consistent with attachment of the proposed pendent group.

Cleavage of pendent groups: It was important that the pendent group's urea linkage be cleaved without significant cleavage of the amide linkages in the fiber polymer itself. Even a limited release of

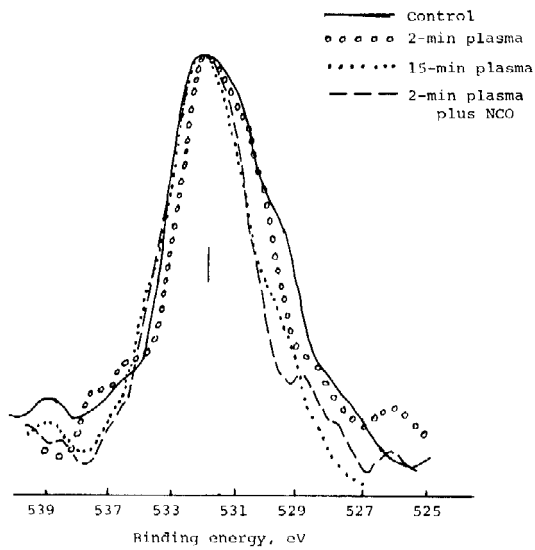

FIGURE 3 High resolution XPS spectrum for oxygen atom. Spectra from four fiber specimens are superimposed to show differences. The dominant peak is the carbonyl carbon of the amide linkage in the fiber polymer chain. Other oxygen species are present in all spectra. Note the diminution in relative amount of the other oxygen species after pendent group attachment (2-min plasma plus NCO), as expected.

primary amine cleavage product from the fiber polymer might be sufficient to interfere with the quantitative analysis of the pendent group. While acid[19] or basic[20,21] hydrolysis of the urea linkage is known, strong acid[22] or base[22,23] also have been found to cleave extensively the amide linkage of the aramid polymer. Seeking a compromise, we tested the ability of mild base (0.2 M Na_2HPO_4, pH 9.1) at reflux to hydrolyxe the fiber pendent groups. Known to be harmless to the fiber itself, the mild base was found by fluorescence assay also to be ineffective in cleaving pendent groups. Therefore, using a reference to steam hydrolysis of urea in waste water[24] as a starting point, we developed conditions for selective hydrolytic cleavage.

The effectiveness of the steam hydrolysis procedure in cleaving the urea linkage of the pendent group without cleaving the amide linkage of the fiber polymer was carefully checked on model

compounds bis(benzyl urea)hexane and N-phenylbenzamide. The cleavage conditions developed succeeded in hydrolyzing 95% of the urea model compound to primary amine while hydrolyzing less than 7% of the amide model compound. Survivability of primary amine under the cleavage conditions was also checked and found to be >80%.

Control fiber (no plasma, no NCO) specimens were subjected to the steam hydrolysis procedure to establish the background level of primary amine issuing from fiber with no pendent groups. From 23 replicates, this value was found to be 8.30 ± 3.48 ppm, a low level with small variation.

Analysis of pendent groups: Results of fluorescence analysis for fully-treated fiber types are presented in Figure 4, in three separate charts corresponding to the three different plasma treatment times before NCO addition. The charts display ppm —CH_2NH_2 group for each hydrolytic cleavage conducted on the fiber. The background level of 8.80 ± 3.48 ppm obtained for control fiber (no plasma, no NCO) is shown as a shaded band for comparison. Multiple additions of NCO were carried out, each addition followed by more than one cleavage procedure to determine completeness of pendent group removal. The second or third NCO additions were designed to test the ability of the fiber's cleaved surface to react with NCO again.

The quantitative analysis results show the presence of a substantial number of pendent groups on the fibers' surfaces. The analysis values are wide-ranging, as is often the case for sensitive quantitative analysis of surface species, but significantly above background. The source of variation is the fiber surface rather than the fluorescence assay technique, since replicate assays of the same specimen routinely gave <2% variation. In most cases, all or nearly all of the pendent groups were removed by the first hydrolytic cleavage, as indicated by the much lower values (close or equal to background) obtained in the second cleavage. We have no explanation for the behavior of one group of specimens with 2-min plasma plus NCO which showed continued release of pendent groups through several cleavage procedures.

The data also show that pendent groups can be reestablished on the hydrolytically-cleaved surface of the fiber by another addition of NCO (return to high ppm levels of 2nd and 3rd NCO). Through the

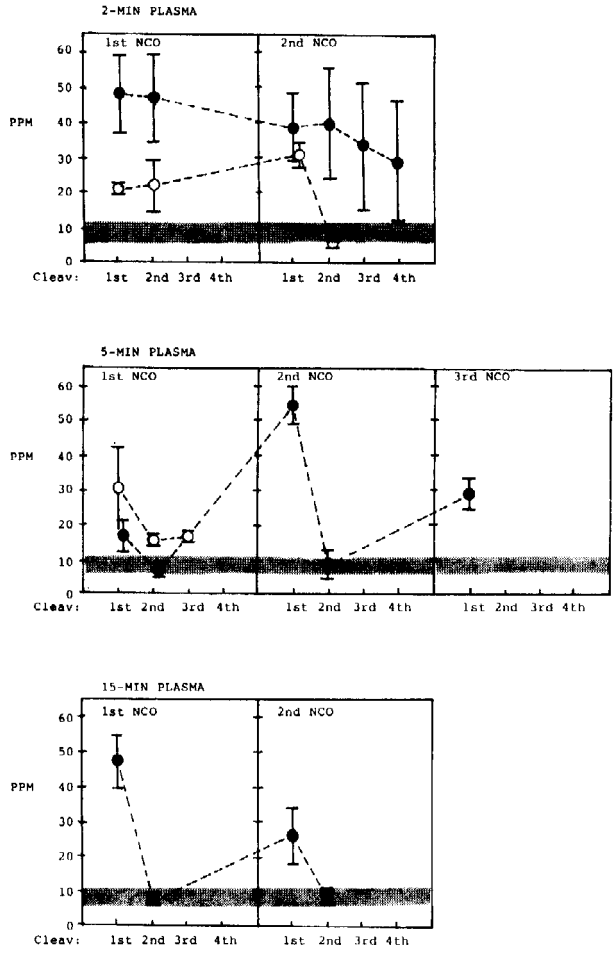

FIGURE 4 Fluorescence assay results for fiber surface pendent groups showing they can be cleaved and regenerated repeatedly. Data for fibers with different plasma treatment times are shown on separate charts. Open and closed circles are averages of groups of 5 to 10 fiber specimens (error bars: ±1 S.D.). Background is shown as shaded horizontal band. A dotted line tracks each group of specimens through the cycles of cleavage and regeneration.

many cycles of pendent group addition and cleavage, the mass of the fiber remained unchanged within the 100 ppm sensitivity of the analytical balance. This sensitivity was insufficient to detect the 17–55 ppm increases due to pendent group addition but was sufficient to show that there was no gross mass loss or increase over many treatment cycles.

The final conclusion that can be drawn from Figure 4 is that there is no real difference between the three plasma treatment times used to activate the fiber surface initially. Addition of NCO to all three types of fibers produced surface pendent group concentrations in the same wide range of 17–55 ppm.

The meaning of these analysis values on a molecular scale can be visualized by converting micrograms of $—CH_2NH_2$ per gram of fiber to number of pendent groups per unit surface area. The mass of aminomethyl group is changed to number using group molecular weight and Avogadro's number. The surface area per gram of fiber is computed using known fiber density,[18] diameter, and right cylinder geometry (computation shown in Appendix). The resultant factor of 0.0883 converts the values 17–55 ppm shown in Figure 2 to 1.5–4.5 pendent groups per 100 $Å^2$ of fiber surface area. We can make an estimate of the reasonableness of these values. In each aromatic ring, if the poly-p-phenylene terephthalamide polymer is assumed to offer one site for pendent group attachment, the sites per unit fiber surface area can be computed from known crystal structure.[25] The result is that a maximum of 4 pendent groups can be attached per 100 $Å^2$ of fiber surface. The experimentally obtained range of pendent group attachment agrees well with the theoretically predicted value of up to 4 pendent groups per 100 $Å^2$.

Other surface reactions: Several considerations suggested to us that another reaction might have taken place at the fiber surface besides the assumed coupling of NCO with aminomethyl groups. First, the high resolution XPS data indicated the presence of oxygens other than carbonyl oxygens on the surface of both untreated and plasma-treated fiber. This opens the possibility that some of the other oxygens are in the form of hydroxyl groups. The rapid reaction of NCO with the hydroxyl groups on a solid surface is a well-documented reaction.[16] Second, it may be a misconception to regard the secondary amide group in the fiber polymer chain as a relatively non-reactive group. The reaction of such N-substituted

amides with isocyanates is documented in the literature.[26] Finally, and most importantly, as Figure 4 showed, there was no distinction in pendent group content between fibers with different plasma treatment times. All plasma-treated fibers behaved as though they offered the maximum of 4 attachment sites for NCO per 100 $Å^2$. Thus, we postulated that the active sites available on the untreated or plasma-treated fiber could include hydroxyl and secondary amide as well as aminomethyl. The urethane and substituted urea linkages formed by reaction of NCO with hydroxyl and secondary amide, respectively, should be stable to mild base but readily hydrolyzed by the steam hydrolysis procedure to produce diaminohexane.

To check for evidence of pendent group *via* an active site other than aminomethyl, we exposed control fiber (no plasma-treatment) to NCO as described for plasma-treated fiber. Fiber specimens treated in this way showed complete stability to mild base (0.2 M Na_2HPO_4) at reflux, releasing no primary amine. However, when NCO-treated fiber was subjected to the steam hydrolysis procedure, the fluorescence assay was positive. The results, shown in Figure 5, are similar in every way to those in Figure 4. This is conclusive evidence that there are covalently attached pendent groups formed by the reaction of NCO with existing reactive groups on the fiber surface. No efforts at specific identification of the reactive groups were made in this research program. Such identification is the subject of future research.

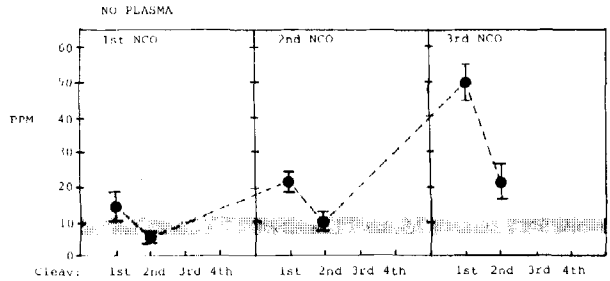

FIGURE 5 Fluorescence assay results for fiber surface pendent groups on fiber with no plasma treatment. Closed circles are averages of a group of five specimens (error bars: ±1 S.D.). Background is shown as a shaded horizontal band. Data points show repeated cleavage and regeneration of pendent groups, similar to that of plasma-treated fibers.

For the plasma-treated fiber, the question of what portion, if any, of the pendent groups were formed from the reaction of NCO with aminomethyl group cannot be answered. The fluorescence assay we used detected only cleaved primary amine, and both types of pendent groups would give the same amine as hydrolytic-cleavage product.

Reaction with epoxy: The fluorescence assay results for ten fully-treated fiber specimens (5-min plasma plus NCO), five of which were exposed to reactive liquid epoxy, are shown in Table III. The epoxy, a monofunctional model of those used in matrix resins, was used without curing agent to eliminate competitive curing reaction. Occurrence of chemical reaction between the epoxide ring of the epoxy molecule and the terminal primary amine of the pendent group would transform the primary amine to secondary amine which cannot be detected by our fluorescence assay method. Therefore, a reduction in fluorescence assay values would signify that reaction has occurred.

The results from the two groups are identical (29.6 ± 4.67 ppm for unexposed, 29.0 ± 4.80 ppm for exposed) indicating that there was no reaction between the pendent groups and the epoxy. This unexpected result is one of the most important findings of this work.

As an explanation for the lack of reaction with epoxy, it is tempting to postulate that, in the establishment of the pendent

TABLE III
Fluorescence assay results from two groups of fiber specimens—unexposed and exposed (*) to epoxy

Fiber specimen	ppm
1	29.8
2	23.6*
3	37.2
4	30.4*
5	28.9
6	33.6*
7	24.7
8	24.2*
9	27.4
10	33.1*

groups earlier, both ends of the NCO molecule covalently attached to the hydroxyl or aminomethyl groups on the fiber surface. However, because the configurational requirements are severe it is unlikely that this would have happened to any great extent, and yet the results in Table III indicate 100 percent unavailability of terminal amine. A more likely explanation is that the flexible pendent groups arranged themselves in a configuration to minimize the fiber surface energy and in doing so made the terminal amine groups inaccessible to epoxy. This type of behavior has been found in surface vibrational spectroscopy studies of fatty acids on metal surfaces.[27] Exactly what has happened to the surface pendent groups in the work presented here is a subject for future research.

Strength of the fiber-matrix interface: Before presenting the results, two important features of single filament testing must be mentioned. Firstly, large scatter (20–30%) is typical of results obtained in adhesive tests using single filaments.[4,5,17,28–33] This is due to tremendous local variation in surface energetics possessed by all materials,[34] incapable of being averaged out as much in small diameter fibers. These local variations are manifested as large scatter in adhesive bond strength values when the volume of material being tested is small. Secondly, the interfacial bond strength values obtained in the single filament test are not independent of imbedment depth.[35,36] Therefore, for strictly valid comparisons, only results from specimens with the same imbedment depth can be used. Because we could not control the imbedment depth, but could measure it after test, results from specimens with an imbedment depth of 0.25 mm were selected from a much larger pool of results. They are presented below in Table IV.

The Table shows that the adhesive bond strength at the fiber-matrix

TABLE IV
Interfacial bond strengths (Ave. ± 1 S.D.) for control and fully-treated aramid fibers in epoxy matrix

Fiber treatment	Interfacial bond strength, psi	No. specimens, N
None (control)	4940 ± 820	26
2-min plasma plus NCO	4960 ± 1040	23
5-min plasma plus NCO	4650 ± 1140	45
15-min plasma plus NCO	4520 ± 1160	32

interface was not improved by the presence of the flexible reactive pendent groups. This is consistent with the negative chemical reaction results described above.

SUMMARY AND CONCLUSIONS

The key findings of this work are summarized briefly below.

1) Pendent groups, each containing a flexible six-carbon aliphatic segment and a terminal primary amine, were covalently attached to the aramid fiber surface.

2) The groups were chemically attached through a functional group found to be already present on the untreated fiber surface or through the aminomethyl groups placed on the surface by plasma activation or through both.

3) Quantitative analysis of pendent groups showed surface attachment levels of 1.5–4.5 groups/100 $Å^2$, agreeing with the theoretical maximum of 4 groups/100 $Å^2$.

4) Mechanical tests of the adhesive bond strength between fiber with pendent groups and epoxy matrix showed no improvement over the adhesive strength between control fiber and epoxy matrix.

5) Specific chemical tests for the reaction of pendent groups with epoxy molecules showed that no reaction took place.

The general conclusion to be drawn from these findings is that, contrary to common assumption, reactive functional groups on a fiber surface do not necessarily form covalent bonds with a reactive matrix. In the case reported here, the fact that there was no chemical reaction between the pendent groups and the epoxy molecule precluded the improvement of fiber-matrix adhesion by a covalent bonding mechanism. It is, of course, still reasonable to assume that if covalent bonding between the fiber and matrix could be achieved, adhesive bonding would be improved.

The question that remains from this work is why the particular pendent groups, designed to be accessible and reactive, did not react with the epoxy. As suggested earlier, a preferred conformation may have rendered the terminal amines inaccessible. This question is the subject of continuing research.

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References

1. H. Ishida and J. L. Koenig, *J. Colloid Interface Sci.* **64,** 555 (1978).
2. S. R. Culler, H. Ishida, and J. L. Koenig, *ibid.* **109,** 1 (1986).
3. M. G. Northolt, *Polymer* **21,** 1199 (1980).
4. L. S. Penn, F. A. Bystry, and H. J. Marchionni, *Polymer Composites* **4,** 26 (1983).
5. L. S. Penn and T. K. Liao, *Composites Technol. Rev.* **6,** 133 (1984).
6. E. M. Petrie and J. C. Chottiner, in *Proc. 40th Annual SPE Tech. Conf. and Exhib: ANTEC* 1982, (Soc. Plast. Engr., St. Louis, MO, U.S.A., May, 1982), p. 777.
7. R. E. Allred, "Surface Chemical Modification of Polyaramid Filaments", Dissertation for D.Sc., Massachusetts Institute of Technology, Cambridge, MA, U.S.A. (1983).
8. R. E. Allred, "XPS Analysis of Amine-Plasma Treated Polyaramid Filaments", *Abstracts of the Seventh Annual Meeting of the Adhesion Society* held in Jacksonville, FL, February 13–15, 1984.
9. M. R. Wertheimer and H. P. Schreiber, *J. Appl. Poly. Sci.* **26,** 2087 (1981).
10. R. Tira, "Continuous Plasma Treatment and Resin Impregnation of a High Strength Fiber Material", Bendix Report BDC-613-2983, Bendix Corp., Kansas City, MO, September, 1983.
11. D. Allara, Bell Communications Research, personal communication, 1986.
12. I. Parikh and P. Cuatrecasas, *Chem. Eng. News* August 26, 1985, p. 17.
13. A. S. Hoffman, G. Schmer, C. Harris, and W. G. Kraft, *Trans. Amer. Soc. Artif. Int. Organs* **18,** 10 (1972).
14. B. Miller, L. S. Penn, and S. Hedvat, *Colloids and Surfaces* **6,** 49 (1983).
15. C. D. Wagner, *et al., Handbook of X-Ray Photoelectron Spectroscopy* (Perkin–Elmer Corp., Physical Electronics Division, Eden Prairie, MN, U.S.A., 1979).
16. S. V. Caro, Jr., C. S. Paik Sung, and E. W. Merrill, *J. Appl. Polym. Sci.* **20** 3241 (1976).
17. L. S. Penn, and S. M. Lee, *Fibre Science Technol.* **17,** 91 (1982).
18. L. Penn and F. Larsen, *J. Appl. Polym. Sci.* **23,** 59 (1979).
19. D. W. Farlow and R. B. Moodie, *J. Chem. Soc.* (*B*), 407 (1971).
20. R. W. Frei, J. F. Lawrence, and D. S. LeGay, *Analyst* **98,** 9 (1973).
21. C. J. Giffney and C. J. O'Connor, *J.C.S. Perkin II*, p. 362 (1975).
22. T. S. Keller, A. S. Hoffman, B. D. Ratner, and B. J. McElroy, *Proceedings of the International Symposium of Physicochemical Aspects of Polymer Surfaces, Vol.* 2, K. L. Mittal, Ed. (Plenum Press, New York, 1983), p. 861.
23. L. Penn, H. A. Newey, and T. T. Chiao, *J. Mat. Sci.* **11,** 190 (1976).
24. N. J. Landis, U.S. Patent 4,341,640, "Urea Hydrolysis," July 1982, to Standard Oil Co.
25. M. G. Northolt, *European Polym. J.* **10,** 799 (1974).
26. P. F. Wiley, *J. Amer. Chem. Soc.* **71,** 3746 (1949).
27. D. Allara, "Spectroscopic Characterization of Modified Surfaces," *Abstracts of the Eighth Annual Meeting of the Adhesion Society,* held in Savannah, GA, U.S.A., February 24–27, 1985.

28. J. P. Favre and M. C. Merienne, *Int. J. Adhesion and Adhesives* **1,** 311 (1981).
29. R. J. Gray, *ibid.*, **3,** 197 (1983).
30. P. S. Chua and M. R. Piggott, *Comp. Sci. Technol.* **22,** 33 (1985).
31. L. T. Drzal, M. J. Rich, J. D. Camping, and W. J. Park, in *Proceedings of the 35th Annual Technical Conference,* Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Section 20-C (1980).
32. S. J. DeTeresa, R. J. Farris, and R. S. Porter, "Fracture and Interface Studies of Aramid Reinforced Polyamide Composites: Compressive Effects and Critical Length Measurements", Office of Naval Research Report 18 on Contract No. N00014-75-C-0686, Project NR 356-584, October 20, 1981, available from DTIC as No. ADA109506.
33. A. T. DiBenedetto, "Evaluation of Fiber Adhesion in Composites," in *NATO Conference Series* 6, *Vol.* 3, 113 (1981).
34. L. S. Penn and B. Miller, *J. Colloid Interface Sci.* **78,** 238 (1980).
35. M. R. Piggott and P. S. Chua, *Ind. Eng. Chem., Prod. Res. Devel.*, in press (1987).
36. L. S. Penn and S. M. Lee, "Interpretation of Experimental Results in the Single Filament Pull-out Test Results", submitted to *Composites Technol. and Research,* 1987.

Appendix

The computation used to convert micrograms of $—CH_2NH_2$ groups per gram of bulk fiber (expressed in the text as ppm) to number of pendent groups per 100 Å^2 of fiber surface area is shown below:

Given: a) Specific surface area = 0.227 m^2/g
from B.E.T. measurements (Ref. 7).
b) Mol. wt. of $—CH_2NH_2$ group = 30.05 g/mole
c) Avogadro's number = 6.023×10^{23} groups/mole

Let Q = dimensionless numerical value of ppm.

To convert Q into number of groups/g fiber:

$$\frac{Q \times 10^{-6}\ \text{g}}{1\ \text{g fiber}} \times \frac{(6.023 \times 10^{23}\ \text{groups/mole})}{(30.05\ \text{g/mole})} = \frac{Q \times 0.200 \times 10^{17}\ \text{groups}}{1\ \text{g fiber}}$$

To convert from groups/1 g to groups/100 Å^2:

$$\frac{Q \times 0.200 \times 10^{17}\ \text{groups}}{1\ \text{g fiber}} \times \frac{100}{\left(\frac{0.227\ \text{m}^2}{1\ \text{g fiber}}\right)\left(\frac{10^{20}\ \text{Å}^2}{\text{m}^2}\right)} = \frac{Q \times 0.0883\ \text{groups}}{100\ \text{Å}^2}$$