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THE ROLE OF SURFACE FUNCTIONAL GROUPS IN ADHESIVE  
BONDING AT THE ARAMID-EPOXY INTERFACE(U) MIDWEST  
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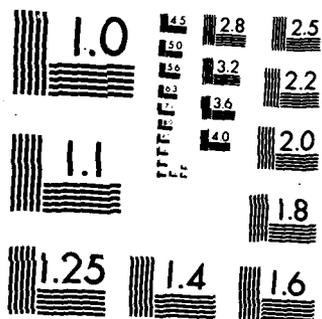
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THE ROLE OF SURFACE FUNCTIONAL GROUPS  
IN ADHESIVE BONDING AT THE ARAMID-EPOXY INTERFACE

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The Role of Surface Functional Groups in Adhesive Bonding  
at the Aramid- Epoxy Interface

( Penn, Byerley, and Liao)

Abstract

In polymeric composites, reactive functional groups on the fiber surface are assumed to greatly enhance the mechanical strength of the fiber-matrix interface 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  $100\text{\AA}^2$  of fiber surface, a level that agrees well with the theoretical amount. Surprisingly, 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.

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The Role of Surface Functional Groups in Adhesive  
Bonding at the Aramid-Epoxy Interface

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INTRODUCTION

In polymeric composites, the presence of reactive functional groups on the fiber surface is expected to greatly enhance the mechanical strength of the fiber-matrix interface 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. Only in the case of glass-reinforced composites has direct evidence of covalent bond formation been provided. This was accomplished in a series of experiments (1-3), some of which used glass particles in place of glass fibers.

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 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

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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 uniformity and the crystallinity of the fiber suggest that under the proper experimental conditions, the smooth surface topography can be retained. Furthermore, the organic nature of the fiber offers the possibility that attachment of organic functional groups 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).

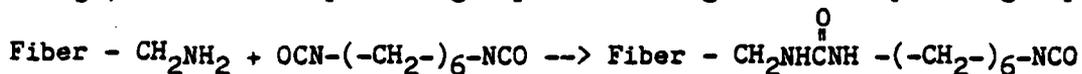
In the work described in this paper, we sought to promote covalent bonding at the interface by attaching flexible reactive pendent groups to the fiber surface while keeping the fiber surface topography and surface energetics constant. In principle, holding these two factors constant should permit a clearer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



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



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  $\text{Na}_2\text{HPO}_4$  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.

Plasma treatment: To attach aminomethyl groups,  $-\text{CH}_2\text{NH}_2$ , 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. 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 a dessicator in the dark.

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.

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. Specimens were stored in dark, ambient environment.

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 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. Both 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.

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. 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, and areas 2 mm in diameter were sampled to a depth of 20 Å. 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 regions) were obtained.

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 accurately weighed and 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  $\text{Na}_2\text{HPO}_4$  solution was used to rinse the fiber specimen and <sup>this</sup> was also added to the volumetric. The contents were diluted to volume with 0.2 M  $\text{Na}_2\text{HPO}_4$ , as required for the subsequent fluorescence assay conducted at pH 9.1. Fiber specimens were rinsed with acetone and vacuum-dried prior to weighing and storing in the dark in a dessicator.

Quantitative analysis of cleaved product: A fluorescence assay specific for primary amines was used to analyze the above 0.2 M  $\text{Na}_2\text{HPO}_4$  solution for the cleavage product 1,6-diaminohexane (15). 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 fibers 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 (16). To insure realistic moisture content, fibers were allowed to equilibrate with laboratory air for a minimum of two weeks. 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 did not leave irregular 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 1.

TABLE 1: CONTACT ANGLE COSINES OF WATER ON CONTROL AND TREATED FIBER

<u>Fiber</u>	<u>Cos<math>\theta_r</math></u>	<u>Cos<math>\theta_a</math></u>	<u>N</u>
Control	0.822 $\pm$ 0.106	0.407 $\pm$ 0.136	15
2-min plasma plus NCO	0.744 $\pm$ 0.107	0.255 $\pm$ 0.114	13

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 oleophilic six-carbon segments in the pendent groups. 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. Each of the three fiber types displayed unique spectral characteristics. The spectrum of the control fiber contained a distinct peak at 3300  $\text{cm}^{-1}$ , attributed to hydroxyl group, that was totally absent in the spectrum of the fully-treated fiber. The presence of the peak indicates that the control (untreated) fiber contained hydroxyls. The disappearance of this peak in the spectrum of the fully-treated fiber can be explained by the occurrence of a chemical reaction between hydroxyl and isocyanate groups when NCO was added, a reaction well-documented in both

homogeneous and heterogeneous phases (15). The spectrum of the fiber with the plasma treatment only was similar to that of the control in that it contained the peak at  $3300\text{ cm}^{-1}$ , attributed to hydroxyl. However, it also contained a distinct peak at  $3600\text{ cm}^{-1}$ , attributed to amine groups. As was the case with the hydroxyl peak, this peak vanished from the spectrum when NCO was added, indicating chemical reaction with, rather than burial by, the NCO.

A strong peak at  $2900\text{ cm}^{-1}$ , attributed to aliphatic carbon groups, appeared in the spectrum of fully-treated fiber but was barely perceptible in the spectra of both control and plasma-treated fibers. This peak is undoubtedly due to the six-carbon aliphatic segment added by the NCO treatment.

XPS: Since the XPS technique's sampling depth is  $20\text{ \AA}$ , the results presented in Table 2 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 as much as 30% from the absolute atom percent. However, within a specimen, the relative accuracy is within 5%. The top portion (A) of Table 2 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.

TABLE 2. XPS ANALYSIS OF FIBER SURFACE

A. Estimated Atomic Compositions (%) Within 20 Angstrom Analyzed Layer

<u>Specimen</u>	<u>C</u>	<u>N</u>	<u>O</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Ca</u>	<u>Sn</u>
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

<u>Specimen</u>	<u>N/C</u>	<u>O/C</u>	<u>N/O</u>	<u>O/N</u>
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

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 2. The surface of the control fiber contained more than the theoretical oxygen atom content for the pure poly-p-phenylene terephthalamide polymer, an observation made by others (7,17). The infrared results presented previously indicate that some of this oxygen is in the form of hydroxyl groups. The plasma treatment further oxidized the fiber surface even though the treatment was carried out on dry fiber in the absence of air. It is probable that the 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 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 very limited ability to distinguish the functional group in which a given atom resides. It can only distinguish oxidized from reduced atoms. The high resolution spectra (not presented) showed that all specimens

contained both unoxidized and oxidized carbon but contained only unoxidized nitrogen (e.g., amines or amides).

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 primary amine cleavage product from the fiber polymer might be sufficient to interfere with the quantitative analysis of the pendent group. While acid (18) or basic (19,20) hydrolysis of the urea linkage is known, strong acid (21) or base (21,22) also have been found to extensively cleave the amide linkage of the aramid polymer. Seeking a compromise, we tested the ability of mild base (0.2 M  $\text{Na}_2\text{HPO}_4$ , pH 9.1) at reflux to hydrolyze 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 (23) 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  $8.80 \pm 3.48$  ppm, a low level with small variation.

Analysis of pendent groups: Results of fluorescence analysis for fully-

treated fiber types are presented in Figure 2, 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  $8.80 \pm 3.48$  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).

The final conclusion that can be drawn from Figure 2 is that there is no real difference between the three plasma treatment times used to initially activate the fiber surface. 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  $-\text{CH}_2\text{NH}_2$  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 (17), diameter, and right cylinder geometry. The resultant factor of 0.0883 converts the values 17-55 ppm shown in Figure 2 to 1.5-4.5 pendent groups per  $100 \text{ \AA}^2$  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 (24). The result is that a maximum of 4 pendent groups can be attached per  $100 \text{ \AA}^2$  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  $100 \text{ \AA}^2$ .

Other surface reactions: Several observations 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 combined IR and XPS data indicated the presence of hydroxyl groups on the surface of both untreated and plasma-treated fiber. Second, the rapid reaction of NCO with the hydroxyl groups on a solid surface is a well-documented reaction (15). Finally, and most importantly, as Figure 2 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. Thus, we postulated that all the aromatic rings on the surface of the fiber contained either aminomethyl or hydroxyl attachment sites and that the NCO reacted with either of these to form pendent groups with either urea or urethane linkages, respectively. Like pendent groups with a urea linkage, pendent groups with

a urethane linkage should be stable to mild base but readily hydrolyzed by the steam hydrolysis procedure to produce diaminoethane.

To check for evidence of the second type of pendent group, 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 ( $0.2 \text{ M Na}_2\text{HPO}_4$ ) 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 3, are similar in every way to those in Figure 2. This is conclusive evidence that there are covalently attached pendent groups formed by the reaction of NCO with existing hydroxyl groups on the fiber surface.

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 3. 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.

TABLE 3. FLUORESCENCE ASSAY RESULTS FROM TWO GROUPS OF FIBER SPECIMENS - UNEXPOSED AND EXPOSED (\*) TO EPOXY

<u>Fiber Specimen</u>	<u>ppm</u>
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*

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 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 3 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 (25). 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. First, large scatter (20-30%) is typical of results obtained in adhesive tests using

single filaments (4,5,16,26-31). This is due to tremendous local variation in surface energetics possessed by all materials (32), 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. Second, the interfacial bond strength values obtained in the single filament test are not independent of imbedment depth (33,34). Therefore, for strictly valid comparisons, results only 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 4.

TABLE 4. INTERFACIAL BOND STRENGTHS (Ave.  $\pm$  1 S.D.) FOR CONTROL AND FULLY-TREATED ARAMID FIBERS IN EPOXY MATRIX

<u>Fiber Treatment</u>	<u>Interfacial Bond Strength,psi</u>	<u>No. specimens, N</u>
None (control)	4940 $\pm$ 820	26
2-min plasma plus NCO	4960 $\pm$ 1040	23
5-min plasma plus NCO	4650 $\pm$ 1140	45
15-min plasma plus NCO	4520 $\pm$ 1160	32

The table shows that the adhesive bond strength at the fiber-matrix 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 the hydroxyl groups 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<sup>2</sup>, agreeing with the theoretical maximum of 4 groups/100 Å<sup>2</sup>.
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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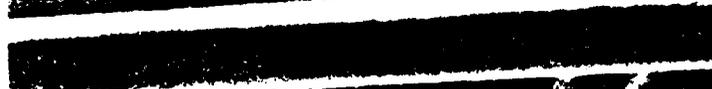
FIGURE CAPTIONS

Figure 1. Scanning electron micrographs of aramid fiber showing that surface smoothness is retained after treatments. Top - control; middle - 5-min plasma without NCO; bottom - 2-min plasma plus NCO. Original magnification - 1000X.

Figure 2. 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:  $\pm 1$  S.D.). Background is shown as shaded horizontal band. A dotted line tracks each group of specimens through the cycles of cleavage and regeneration.

Figure 3. 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:  $\pm 1$  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.

-23-  
FIGURE 1



-2A-  
FIGURE 2

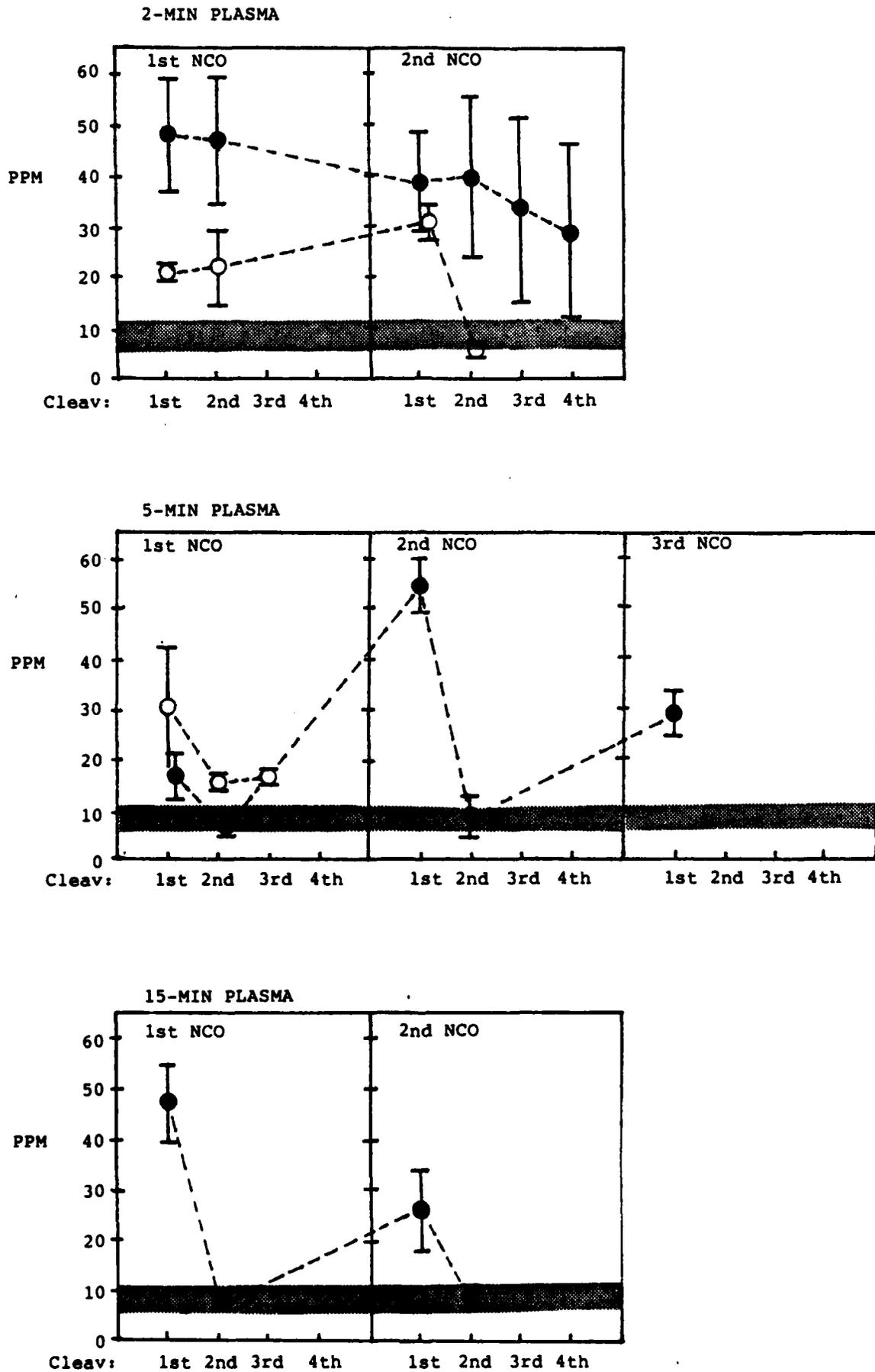
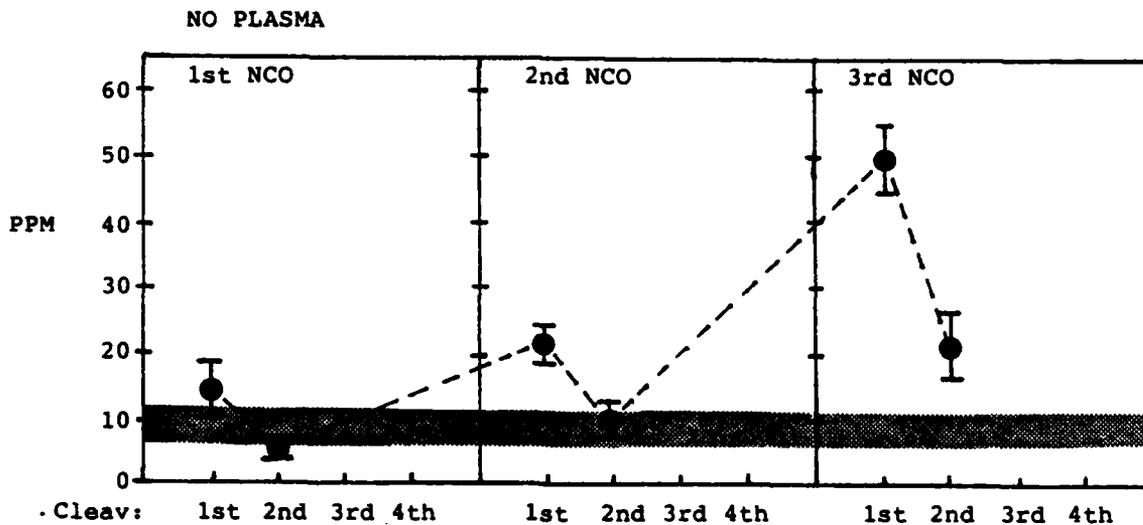


FIGURE 3



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