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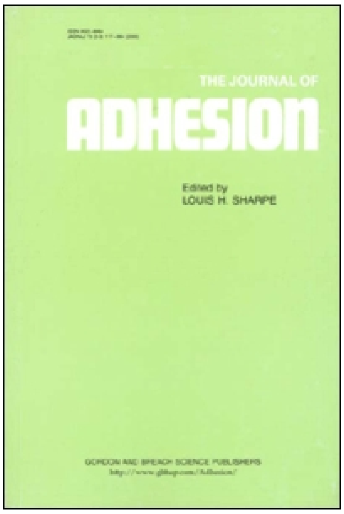

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Chemical Bonding and Physical Interaction by Attached Chains at the Fiber-Matrix Interface

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Molecular chains with different chemical structures were attached to the surface of aramid engineering fiber, and their effect on the fiber's adhesion to epoxy matrix was measured. Adhesive performance increases up to 65% were achieved, depending on the structure of the attached chains. Increases were attributed to chemical bonding between the terminal reactive group of the chain and the epoxide molecule used in the matrix, and to a length-related physical interaction between the chain and epoxy matrix.

KEY WORDS fiber-matrix interface; chemical bonding; adhesion; attached chains; composite; aramid fiber; epoxy matrix.

INTRODUCTION

The importance of the interface in composite materials has been emphasized in many research studies.[1-7] Aspects of composite behavior such as shear strength, durability, and damage accumulation are greatly related to the interactions between fiber and matrix at the interface. Researchers in composite materials have learned how to manipulate the fiber-matrix interface by means of fiber surface oxidation treatments[8-11] and coupling agents. Plasma treatments and chemical reagents also have been used to introduce functional groups to the surface of engineering fibers.[12-18]

Some progress has been made in characterization of the molecular details at the interface in some materials systems. For example, the interface in glass-polymer systems[19-21] and carbon-polymer systems[22] has been elucidated considerably by modern techniques such as Fourier transform infrared spectroscopy (FTIR). Obviously, true understanding of how to tailor the interface effectively requires both characterization of the molecular details at the interface and correlation of these details with their effect on the fiber-matrix adhesion.

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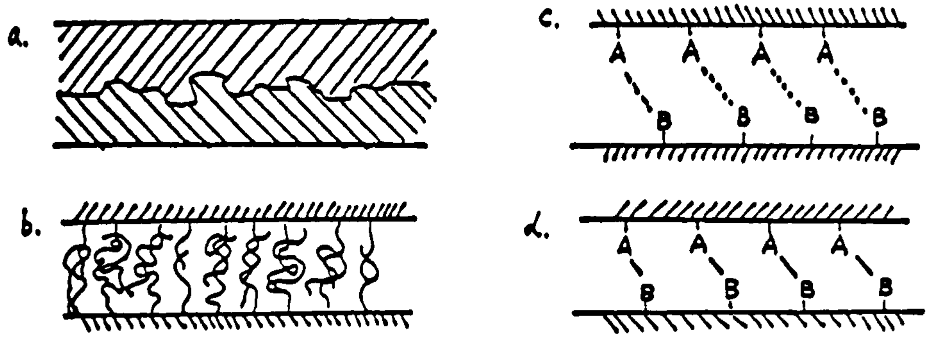

FIGURE 1 Schematic illustration of the mechanisms of adhesion. Different fundamental mechanisms can be categorized as (a) mechanical interlocking, (b) molecular chain interdiffusion or penetration, (c) intermolecular interaction, and (d) chemical bonding.

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The focus of our research has been the relation between the molecular details and the adhesive performance at the fiber-matrix interface. Our approach is to attach carefully designed molecular chains directly to the surface of an engineering fiber prior to making the fiber-matrix adhesive bond. The chemical structures of the attached chains are selected to exploit one or more of the fundamental mechanisms of adhesion. As illustrated schematically in Figure 1, these mechanisms can be categorized as mechanical interactions, interdiffusion, intermolecular interactions, and chemical bonding.[23,24]

Aramid engineering fiber was selected for these studies because its surface contains active sites to which molecular chains can be attached by chemical reaction. The bulk fiber is relatively inert, allowing chemical treatments to modify the surface without degrading the bulk mechanical properties. In addition, the fiber surface's smoothness down to the microscopic level eliminates mechanical lock and key interactions as a variable, thereby simplifying our study.

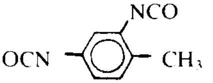
Treated and untreated fibers were characterized by surface-sensitive techniques to verify the attachment of the molecular chains. Adhesive performance was evaluated directly by a mechanical test, and the results are explained in terms of intermolecular interactions between the original fiber surface and the matrix, chemical bonding between the attached chains and the matrix, and physical interaction between the chains and the matrix.

EXPERIMENTAL

Attachment of Pendent Chains by Isocyanate Reactions

Molecular chains were attached to the surface of clean, dry aramid fiber (Kevlar 29,® Dupont, Wilmington, DE, U.S.A.) by catalyzed, heterogeneous phase reactions involving isocyanate reagents. The isocyanate reagents used are shown in Table I. The reaction conditions and procedures described in reference 25 were used to achieve chemical reaction between the isocyanate reagents and the active

TABLE I
The isocyanate and diisocyanate reagents used

Reagent	Source
$OCN—(CH_2)_6—NCO$ Diisocyanatohexane	Aldrich
$OCN—(CH_2)_3—CH_3$ n-Butylisocyanate	Aldrich
 Tolylene 2,4-diisocyanate	Aldrich
$OCN—(CH_2)_3—Cl$ Chloropropylisocyanate	Aldrich

sites on the fiber surface. Where desired, chains terminating in primary amine groups were extended in length by additional reaction cycles with fresh isocyanate reagent. The extension reactions proceeded with high yield.

Colorimetric Analysis

The colorimetric analysis involved exposure of the fiber to the primary amine-specific dye, Ponceau 3R, for complexation. The full procedure, which included complex formation, complex cleavage, and quantitative analysis of the cleaved dye by visible spectrometry, was the same as used previously.[25] Each fiber treatment batch was sampled by taking several replicate fiber specimens, each approximately 2 g, for analysis. Results, determined as number of primary amine groups per gram of fiber, were converted to number of amine groups per 100 A^2 of fiber surface with the use of specific surface area value 0.180 m^2/g.

Differences between control and experimental samples were evaluated for statistical significance with the Student t test. When the difference between two samples was not significant at the 0.01 level, the samples were considered to be the same.

X-Ray Photoelectron Spectroscopy

Control fiber and fiber treated with 3-chloropropyl isocyanate were analyzed by XPS to verify the attachment of chloropropyl pendent chains. The X-ray photoelectron spectroscopy was conducted by Structure Probe (Metuchen, NJ) using a Perkin-Elmer Model 549 XPS/AES/SAM surface analysis system (Eden Prairie, MN). Survey spectra were collected from two replicate specimens of both experimental and control fiber samples.

Scanning Electron Microscope Study

Treated fibers and the debonded regions of single filament pull-out specimens were examined with an Amray AMR Model 1200 scanning electron microscope (Bedford, MA). Specimens were coated with a thin film of platinum to provide the conductive surface necessary to prevent charging effects in the beam.

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Chemical Reaction with Epoxy

Fibers having primary amine-terminated pendent chains attached to their surfaces were exposed to a 50% solution of the monomeric epoxide, diglycidyl ether of bisphenol A (DGEBA) from Ciba Geigy (Ardsley, NY) in acetone. The reaction mixture was heated under reflux for 66 hours. After this, all unreacted DGEBA was removed from the fiber surface by Soxhlet extraction with acetone. The extent of reaction between primary amine and DGEBA was determined by colorimetric analysis for unreacted primary amine.

Single Filament Pull-Out Test

Specimens were prepared by depositing small droplets of uncured resin on single filaments and allowing the droplets to cure. The preparation and testing details are described in references 25 and 26. The chemical structures and proportions of the epoxide and curing agent used as the matrix are shown in Table II. Although the epoxy resin was nominally a room temperature-curable system, we subjected it to a mild elevated temperature cure, 40°C for 6 days.

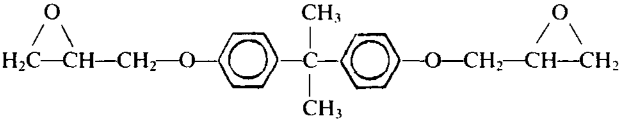
The Student t test was used to evaluate sample differences. The samples were considered to be from different populations when the difference between them was statistically significant at the 0.01 level.

RESULTS AND DISCUSSION

Attachment of Chains

The most likely moiety on the fiber surface to serve as an active site with respect to isocyanate reagent is the secondary amide group linking the aromatic rings of the aramid polymer. An addition reaction between the amide linkage and the isocyanate group of the reagent attaches one end of the reagent molecule to the fiber surface. When a diisocyanate instead of a monoisocyanate is used as a reagent, one of the isocyanate groups remains unattached and is converted subsequently to a primary amine by contact with water. The reaction sequence is shown in Figure 2, for a diisocyanate.

TABLE II
The chemical structures and proportions of matrix resin constituents

Constituent	Structure	Parts by weight
Epoxide: diglycidyl ether of bisphenol A (Ciba Geigy's 6010)		100
Curing agent: Triethylene tetramine (Aldrich)	$H_2N—CH_2CH_2—NH—CH_2CH_2—NH—CH_2CH_2—NH_2$	13.6

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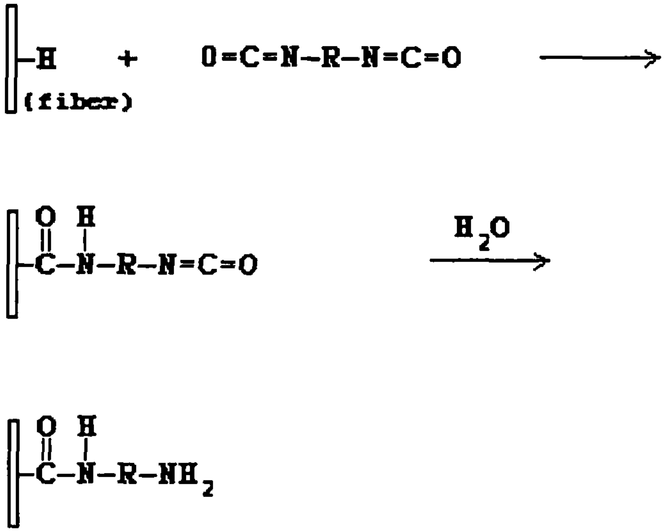

FIGURE 2 The covalent attachment of the molecular chain to the aramid fiber surface. Chemical reaction occurs between the amide hydrogen on the fiber and the isocyanate group of the reagent. R- is varied to create different attached chains. When a diisocyanate reagent is used, a primary amine-terminated attached chain results.

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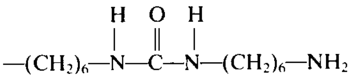
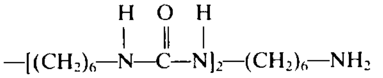
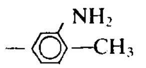
Colorimetric analysis results verifying the attachment of molecular chains to the fiber surface are presented in Table III. The analysis is primary amine-specific, *i.e.*, detects only those chains containing a primary amine group. On a sample weight basis, the species being detected are present in parts per million, a level at which high scatter is unavoidable. Statements in the discussion as to the equality or difference between samples have taken the scatter into account (see experimental section). Results are expressed as the number of primary amine groups per 100 $Å^2$ of fiber surface.

We emphasize that the work-up of the fiber specimens prior to colorimetric analysis was vigorous, involving extraction by a series of different solvents under reflux as well as changes in pH. Therefore, the molecular chains detected by the colorimetric analysis can be assumed to be covalently attached—not merely physically adsorbed.

The control fiber, expected to have a value of zero, showed a low but nonzero value. Whether this "background" indicates primary amine on the untreated fiber surface, or is a systematic error in the analysis technique is discussed later. The primary amine concentration of experimental samples E-1, E-2, and E-3 significantly exceeded that of the control, confirming the attachment of primary amine-terminated molecular chains.

Samples E-2 and E-3 were prepared from E-1 by chain extension, and although the colorimetric analysis showed their amine concentrations to be statistically the same, this does not prove chain extension. To verify the latter, auxiliary experiments were conducted: E-1 was exposed separately to n-butyl- and n-octadecyl-monoisocyanate reagents. The analysis that followed for primary amine revealed by differ-

TABLE III
Colorimetric analysis results (ave. ± std. dev.)

Sample	Attached chain	N*	No. primary amines per 100 Å^2
Control	none	8	0.190 ± 0.020
E-1	$-(CH_2)_6-NH_2$	10	0.887 ± 0.234
E-2	 $-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-NH_2$	5	0.559 ± 0.181
E-3	 $-[(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}]_2-(CH_2)_6-NH_2$	4	1.147 ± 0.324
E-4	$-(CH_2)_3-CH_3$	5	0.036 ± 0.014
E-14		3	0.131 ± 0.044
E-1-ep	$-(CH_2)_6-NH-$epoxide	7	0.379 ± 0.128

*Number of specimens

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ence that, for both reagents, 75–80% of the primary amine-terminated chains of E-1 had been "chain-extended" by reaction with monoisocyanate.

Sample E-4, whose attached chains contained no primary amine and therefore were expected to be the same as the control, showed an even lower value than the control. The (statistically significant) discrepancy between control and E-4 was caused by surface sites that not only coupled with the primary amine-specific dye but also were consumed by ready reaction with a relatively small isocyanate molecule. While these facts together make it seem likely that these sites are indeed primary amines, we have no insight as to why there would be this amount of primary amine on the surface of the unmodified fiber.

The E-14 sample, treated with the normally very reactive 2,4-tolylene diisocyanate (TDI) reagent, was expected to give results equivalent to E-1, E-2, and E-3. However, E-14's results were the same as the control, indicating that TDI did not attach covalently to the fiber surface. It is possible that the rigidity and bulkiness of the TDI molecule prevented its adequate positioning for reaction with the active sites on the fiber surface.

The last entry in Table III shows the results of the exposure of sample E-1, with its amine-terminated pendent chains, to diglycidyl ether of bisphenol A. Reaction between the epoxide reagent and the terminal primary amines was the expected result (see Figure 3), because the analogous homogeneous phase reaction between epoxide and aliphatic primary amine is known to proceed rapidly, even at room temperature. The colorimetric analysis value dropped significantly after exposure, indicating that the epoxide reacted with the terminal primary amines to end-cap them, rendering them undetectable by colorimetric analysis. The extent of reaction between epoxide molecule and terminal primary amine was computed to be, after subtraction of background, about 73%. This is strong indirect evidence for chemical bond formation between the curing matrix resin and the modified fiber.

Earlier attempts by us to demonstrate the occurrence of the epoxide-amine reac-

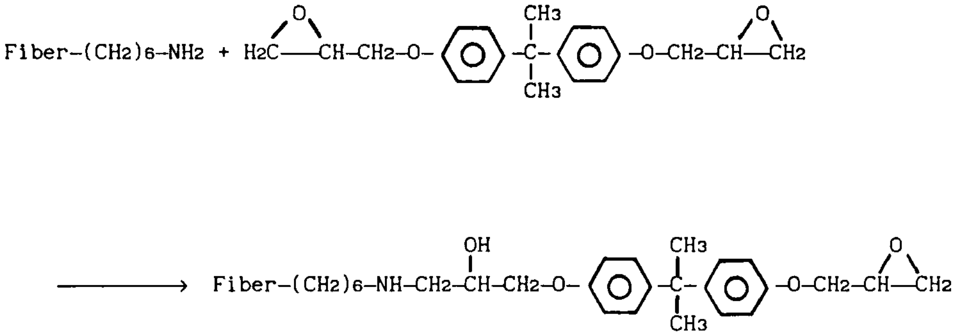

FIGURE 3 The chemical reaction between the epoxide molecule and the terminal primary amine of the attached chain. The epoxide "end-caps" the attached chain, making it undetectable by colorimetric analysis.

tion in heterogeneous phase failed. In previous work, we had exposed the E-1 fiber to the very reactive butyl glycidyl ether, and had found that no end-capping of the terminal primary amines occurred.[15,25] However, follow-up work done later revealed that the relatively unstable butyl glycidyl ether was an inappropriate choice of epoxide for end-capping. Gas chromatographic analysis of the liquid phase of the reaction mixture showed that butyl glycidyl ether underwent decomposition and self-reaction to produce a wide variety of species, none of which apparently reacted with primary amine.

From Table III, the surface concentration of attached chains can be expressed roundly as 1 chain per 100 Å^2 when scatter is considered. This applies to E-1, E-2, and E-3 by direct analysis, and to E-4 by difference. The concentration of attached chains did not ever reach the theoretical maximum of approximately 3 chains per 100 Å^2, a value based on the number of secondary amide groups that would reside in the surface of a fiber composed of crystalline aramid polymer, as shown in Figure 4.[27] The shortfall can be attributed to the slightly oxidized nature of the fiber surface, whose chemistry differs somewhat from the bulk.[13-15,28-30]

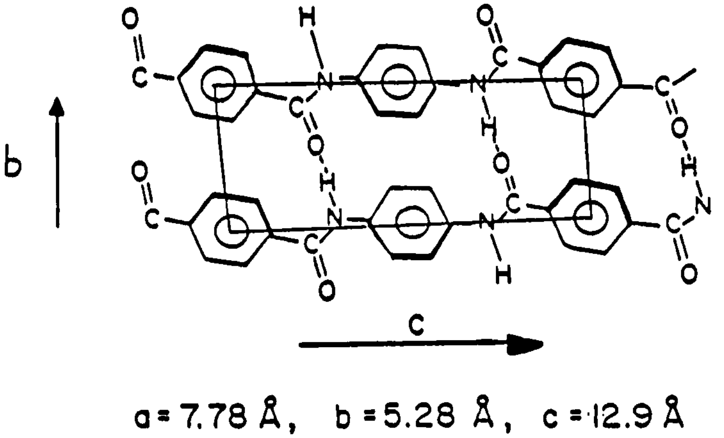

FIGURE 4 The chemical and crystal structure of aramid fiber. This model is used for computation of the theoretical number of attachment sites for attached chains. Area shown is slightly less than 100 Å^2.

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X-Ray Photoelectron Spectroscopy

The purpose of using XPS analysis in this work was to obtain proof of molecular chain attachment by a second analysis technique, completely different from the wet chemical (colorimetric) analysis described above. To use XPS in the most definitive way, we attached molecular chains containing a heteroatom (an atomic species not present in the original surface) to the fiber surface. Table IV shows the atom content data obtained from control fiber and from fiber treated with chloropropyl isocyanate, where chlorine was intended to serve as the heteroatom.

The atom content of the control fiber surface (20-Å thick layer) was in agreement with that reported in the literature by other workers.[13–15,28–30] The treated fiber surface showed the presence of a small amount of chlorine, as expected. This chlorine value can be converted from atom % in a surface layer 20 Å thick to number of chloropropyl chains per 100 Å^2 of fiber surface by using the fiber's chemical and crystal structure (Figure 4). This results in a value of approximately 0.4 chains per 100 Å^2, which agrees fairly well with colorimetric analysis values reported earlier for chain attachment.

Unfortunately, definitive conclusions are hindered by the fact that the treated fiber surface also showed other changes with respect to the control: sodium, sulfur, and additional oxygen. These three are often found together in aramid fiber specimens, and are indicative of residual Na_2SO_4 from the sulfuric acid and sodium carbonate used in fiber manufacture. The Na_2SO_4 has been reported in widely varying amounts from one analysis to another.[28–30]

When constituents, such as sodium and sulfur, from the manufacturing process are shown to be present as contaminants from time to time, and to vary randomly in the material, it becomes impossible to conclude definitively that the heteroatom chlorine is not also a mere contaminant, its concentration in agreement with the predicted value by coincidence alone. The most that can be said about the XPS data in Table IV is that they are consistent with the attachment of chloropropyl chains to the fiber surface, but they are not definitive proof.

Scanning Electronic Microscopy (SEM)

SEM studies at 500X of fiber from each experimental group showed that the treatment procedures did not roughen the surface. Studies reported previously showed treated surfaces to be smooth at 18,000 ×.[15] The retention of the smooth surface topography meant that mechanical interlocking did not need to be considered as a variable in this study.

Additional SEM studies identified the interface as the locus of failure for every treatment group. The debonded areas of tested single filament pull-out specimens

TABLE IV
Estimated atomic compositions (%) within 20 Å analyzed layer

Sample	C	N	O	S	Na	Cl
Control	76.5	7.5	16.0	—	—	—
$-CH_2CH_2CH_2Cl$	65.6	6.0	21.8	4.9	1.2	0.5

showed neither residual matrix material on the fiber surface nor damage to the fiber surface. Figure 5 presents a typical scanning electron micrograph of a single filament pull-out specimen after test, showing the previously bonded surface of the fiber to be clean and smooth.

Adhesive Performance

The single filament pull-out test (Figure 6), ideal when only small amounts of treated fiber are available, was used to evaluate adhesive performance. The detailed analysis of this test based on the energy balance approach, and the demonstration that interfacial failure is by crack propagation, has been presented elsewhere.[31] Typically, experimental values for pull-out load, P, are plotted against measured length, l, of the fiber-matrix interface. Although the relation between P and l is not linear, it closely approximates linearity at low values of l. By considering only the data in the region of low l the experimenter can make valid comparisons of adhesive performance among samples.

Table V presents the adhesive performance data for control and experimental samples. Since the surface concentrations of the attached chains are essentially the same, as discussed earlier, differences in adhesive performance can be assumed to

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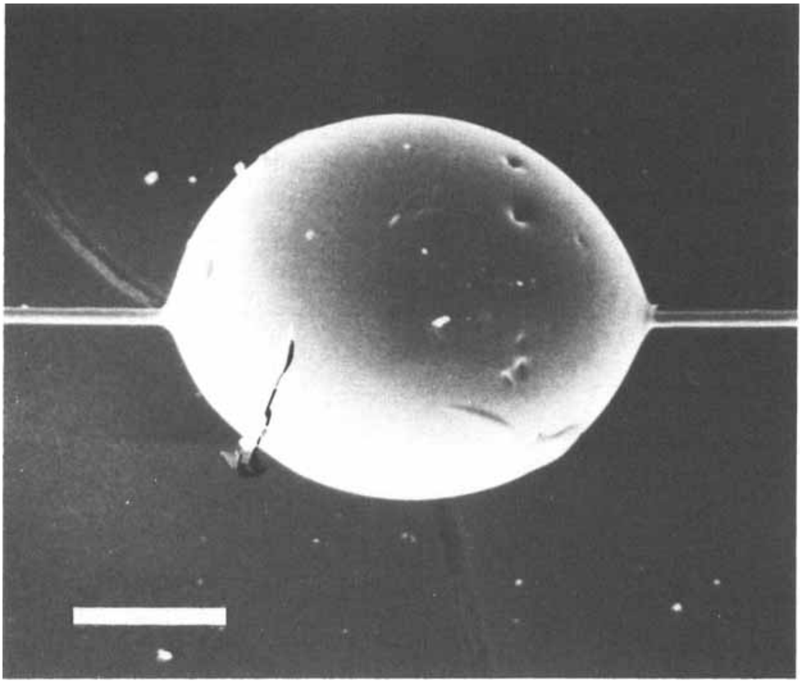

FIGURE 5 Typical scanning electron micrograph (65 ×) of matrix droplet on fiber, after debonding. The fiber was pulled to the right to debond the interface. The fiber surface immediately to the right of the droplet, although previously bonded to the matrix, appears clean and undamaged, indicating interfacial failure. The bar is 100 μm.

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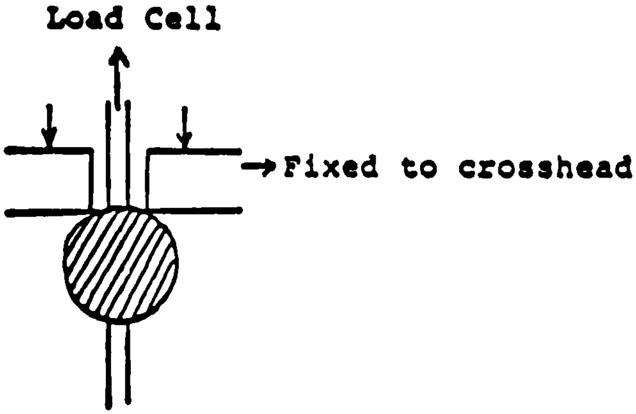


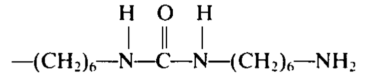
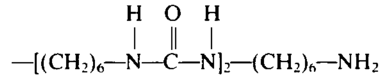
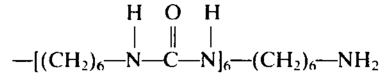
FIGURE 6 Single filament pull-out test configuration. The slotted fixture is moved downward to snag the matrix droplet and debond it from the fiber. The top end of the fiber is attached to a load cell to record the debond load.

depend only on chain structure. The adhesive performance is expressed as $P/2\pi rl$, a quantity that has the dimensions of interfacial shear strength, but strictly speaking is only a performance index. It should not be regarded as a true shear strength as would result from uniform yielding of the interface.

The chains attached to the fiber surface in E-1 and E-4 samples were both short, aliphatic chains. The short chains of E-4 did not bring about any increase in adhesive performance with respect to the control. However, E-1's chains, shown earlier to be capable of reacting with epoxide molecules, increased the adhesive performance 20%. We feel that this improvement can be attributed to the formation of covalent bonds between pendent chains and matrix, especially in light of the null result of E-4. Reassurance that the improvement was because of covalent bonding and not

TABLE V

Adhesive performance results (Ave. ± std. error of mean)

Sample	Attached chain	N*	Interfacial shear strength, MPa	Change in adhes. (%)
Control	none	142	21.6 ± 0.51	—
E-1	$-(CH_2)_6-NH_2$	74	25.8 ± 1.01	20
E-4	$-(CH_2)_3-CH_3$	86	21.7 ± 0.66	0
E-2	 $-(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}-(CH_2)_6-NH_2$	43	28.1 ± 0.76	30
E-3	 $-[(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}]_2-(CH_2)_6-NH_2$	117	30.7 ± 0.79	43
E-7	 $-[(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}]_6-(CH_2)_6-NH_2$	55	35.6 ± 1.26	65

*Number of specimens

simply because the chains of E-1 were three atoms longer than E-4 was provided by supplementary adhesive performance data; fiber whose attached chains were similar to E-4 (aliphatic, nonreactive) but 18 carbons long showed no better adhesion to epoxy matrix than E-4.

The adhesive performance of E-4 also sheds light on the longstanding question of whether the control fiber surface reacts chemically with epoxy resin matrix. In E-4, the active sites of the control surface have been replaced by an attached chain that is incapable of reacting with the matrix. The equivalence of the control to E-4 in terms of adhesive performance suggests that the control, like E-4, does not form any chemical bonds with the matrix. Thus, the adhesion of the control fiber to the matrix can be attributed entirely to nonchemically bonded intermolecular interactions.

The comparison of samples E-2, E-3, and E-7 involves attached chains that are similar in structure but very different in length. The increases in adhesive performance shown by these samples cannot be attributed to increases in the surface energy, since contact angle measurements indicated only a slight change, and that was a reduction.[32] Rather, the increases appear to be achieved by a combination of chemical bonding and physical interaction with the matrix. (Affinity between the chains' polar substituted urea groups and the polar epoxy resin can be assumed to drive the chains to extend into the matrix.) If a constant 4 MPa of adhesive performance is assigned to chemical bonding between the matrix and the terminal primary amine for E-2, E-3, and E-7, the remainder of the improvement is related to chain length, longer chains bringing about greater improvement.

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Attachment of chains to the fiber surface is a way of bringing different mechanisms of adhesion into play at the interface. The nonchemically bonded intermolecular interactions between the control fiber surface and the matrix—the van der Waals interactions, dipole-dipole interactions, etc.—can be regarded as supplying the baseline adhesion. Depending on their structure, the attached chains can introduce, on top of this, chemical bonding and a physical interaction based on chain length. The exact nature of this length-related physical interaction (*e.g.*, penetration into the matrix, molecular friction, specific enthalpic interactions, etc.) is the subject of ongoing work.

Because it has often been proposed, without data, that chemical bonding at the interface should make huge increases in adhesive performance, the less-than-huge increases found in this work deserve some discussion. Over-optimistic expectations arise from comparing the energy to rupture a chemical bond with the reversible work of separation rather than with the total (reversible plus irreversible) work of separation at an interface. The reversible work of separation at an interface is simply the work of adhesion, a thermodynamic quantity readily estimated from surface energies of the two adhering materials or determined directly by measuring the contact angle made by one of the materials in liquid form on the other material in solid form.[33,34] For the aramid-epoxy interface, the work of adhesion is estimated to be about 100 mJ/m^2.[31]

The rupture of a C—N bond (bond energy 50 kcal/mol) present at the level of 0.66 per 100 Å^2 of interface (since 75% of the 0.88 attached chains react with epoxide) requires 230 mJ/m^2. The value of 230 mJ/m^2 added to 100 mJ/m^2 of reversible work suggests a 230% increase in adhesive performance. However, the energy to rupture the chemical bond must be added to the total work of separation, not just to the reversible portion. The total work is dominated by irreversible contributions that can be orders of magnitude larger than the reversible portion. Thus, increases would be expected to be much smaller than 230%. Furthermore, any assessment of chemical bond rupture energy with respect to total interfacial separation energy must be converted to failure load per unit interfacial area, a conversion that is not usually direct. Thus, quantitative predictions of the effect of chemical bonding on adhesive performance cannot be made by simple estimate.

CONCLUSIONS

This study demonstrated the covalent attachment of a variety of different molecular chains to the surface of an engineering fiber. Depending on the structure of the chains, the adhesive performance between the fiber and an epoxy matrix could be significantly affected. Short, inert chains did not alter the fiber-matrix adhesion. Chains capable of chemically bonding with the matrix increased the adhesion significantly. Long chains containing polarities also enhanced the adhesion, by an amount that increased with chain length.

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