Chemical Modification of Kevlar Fiber Surfaces and of Model Diamides

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Synopsis

Organic reactions of aromatic diamides as models for PPTA fibers have been investigated to select reagents and conditions suitable for surface-controlled heterogeneous reactions on Kevlar filaments and fabrics. Amine functional groups have been incorporated into fiber surfaces by bromination followed by ammonolysis and by nitration followed by reduction. Modification of filaments has been attained without impairment of fiber properties. Preliminary experiments have also shown that the presence of amino groups on Kevlar fabric can provide remarkably improved peel strength and apparent interlaminar shear strength in epoxy laminates, suggesting a significant role of covalent bonding in improving adhesion in aramid-epoxy composites.

INTRODUCTION

The importance of Kevlar aramid [PPTA; poly(p-phenylene terephthalamide)] fibers in the development of high-strength, light-weight composites for aircraft and other advanced applications has been recognized for a decade (e.g. Ref. 1) and has stimulated many aspects of research activity in the field of composites.[2] The role of the fiber/matrix interface in the deformation and failure mode of Kevlar-epoxy composites has been the subject of numerous investigations,[2,3] and specific problems associated with interfacial adhesion have been defined, in part employing approaches and knowledge derived from the investigation of other systems. In the case of glass fiber-epoxy and, in some measure, of graphite fiber-epoxy composites, significant progress has been made in the chemical characterization of fiber/matrix interfaces.

Covalent bonding of fiber surfaces and resin matrix is currently accepted as one valid mechanism for enhancing interfacial adhesion in epoxy composites reinforced with glass or graphite fibers. In the case of PPTA fibers, the absence of reactive functional groups has suggested the necessity for investigation of other approaches for example, pretreatment of the fibers or fabric with a polymeric sizing or coating prior to preparation of the epoxy composite.[3-6] The chemical composition of the sizing agents evaluated and the type of Kevlar (49 or 29) were not described in these publications, and improvements attained in a preliminary evaluation of mechanical properties in these instances are thus of limited significance as a bases for working hypotheses.

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Promising results have been reported in the chemical modification of PPTA fiber surfaces by plasma treatments designed to provide a functional group for covalent bonding with epoxy resins in composites. For example, Wertheimer and Schreiber investigated effects of several types of microwave plasma,[7] and Allred and coworkers reported[8,9] the results of an extensive study of surface chemistry and bonding of plasma-aminated aramid filaments. In one aspect of this work, the latter authors showed that stable, reactive amine functional groups on surfaces of PPTA filaments can improve the interlaminar strength of epoxy composite laminates, suggesting the formation of covalent bonds between surface amino groups and the epoxy network at the interface.

With this consideration in mind, the objective of the work reported in the present paper has been to introduce functional groups on the surface of PPTA fibers by reactions of the macromolecule based on classic organic chemistry, under conditions that would not impair the mechanical properties of the fiber—and that, in principle at least, would not require specialized instrumentation or processes. This is a complex and difficult task, because the chemical inertness of PPTA, coupled with the exceedingly high crystallinity of the fiber,[10] poses formidable obstacles to swelling and penetration by reagents beneath the ultimate surface.

A recent report[11] describes attempts to attain amine sites on Kevlar 49 fiber surfaces by hydrolytic scission of amide groups. Decreases in fiber strength upon treatment with strong base and with acid and adsorption of acid dye from hydrolyzed samples showed that hydrolysis was not limited to the surface, and approaches based on selective cleavage of surface macromolecules do not seem promising.

In the work reported here, an extensive study of reactions of model compounds (para-diamides) has been carried out in order to evaluate the feasibility of specific reactions and conditions for heterogeneous, surface-limited reactions that could be subsequently carried out on PPTA fiber (or fabric) without chain scission and without disruption of microstructural order. Two approaches studied on model compounds were then evaluated for the modification of Kevlar 49 filament and fabric, and promising results have been obtained in the initial evaluation of modified fibers and of epoxy laminates prepared from modified fabric.

EXPERIMENTAL

Materials

Fiber: Kevlar 49, 1140 denier, T-968 (E. I. Du Pont De Nemour & Co., March 1983) Fabric: Kevlar 49, Style 181, 4.9 oz/yd^2, 50 × 50 count (Hi-Pro, Form Fabrics, Newark, Delaware) Dye: Ponceau 3R, azo dye, Color Index 16155 (MCB Manufacturing Chemists, Inc., Gibbstown, N. J.)

Model Compound Synthesis

The diamides MC-1 and MC-2 shown in Figure 1 were prepared by the Schotten-Baumann reaction of the corresponding acid chloride and amine in dimethylacetamide (DMAC) and recrystallized from DMAC. The yield,
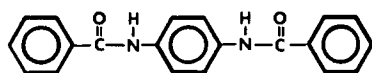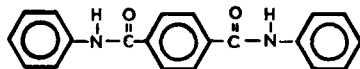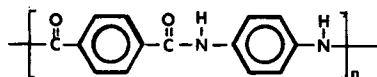
melting point, and elemental analysis are shown in Table I. The reaction schemes selected for reactions of the model compounds are summarized in Table II. The preferred reaction conditions selected on the basis of optimization studies in the context of the work to follow on surface reaction of fibers are described below for MC-1. Slight modifications were made in the case of MC-2, which is somewhat less stable and requires milder reaction conditions.

Bromination[12,13]

After 1 mmol (0.316 g) of MC-1 was dissolved in 10 ml of DMAC and 2.2 mmol of N-bromosuccinimide (NBS), 0.002 g of benzoyl peroxide and 0.002 g of N, N'-dimethyl benzylamine were added. The mixture was stirred at 85°C for 10–30 min under nitrogen, quenched in 100 ml of distilled water and filtered. The solid was washed with large amounts of distilled water (at 50–60°C) and then with methylene chloride, dried in a vacuum oven at 110°C, and recrystallized from DMAC. The products were characterized by
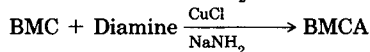
TABLE I
Model Compounds

	MP[a] (°C)	Element analysis[b]			Yield (%)
		C%	H%	N%	
MC-1	349.2	75.93 / 75.81	5.10 / 5.09	8.85 / 8.78	79
MC-2	344.1	75.93 / 75.89	5.10 / 5.20	8.85 / 8.84	78

[a] The melting point was measured by the DuPont 1090 instrument, DSC model, at 10°C/min and peak temperature was taken for MP.
[b] Values are calculated over found.

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TABLE II

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                    ┌─────────────────────┐
        ┌───────────│   MODEL COMPOUND    │───────────┐
        │           └─────────────────────┘           │
        │                                              │
    Bromination                                    Nitration
        │                                              │
 ┌──────────────┐                            ┌──────────────┐
 │  BROMINATED  │                            │   NITRATED   │
 │MODEL COMPOUND│                            │MODEL COMPOUND│
 └──────────────┘                            └──────────────┘
        │                                              │
    Ammonolysis                                   Reduction
        │                                              │
        │           ┌─────────────────────┐           │
        └───────────│     AMINATED        │───────────┘
                    │  MODEL COMPOUND     │
                    └─────────────────────┘
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$$MC + NBS \xrightarrow[\text{DMAC}]{\text{BPO}} BMC$$

$$MC + HNO_3 \xrightarrow[\substack{\text{Acetic anhydride} \\ \text{heterogeneous}}]{\substack{\text{Homogeneous} \\ \text{H}_2\text{SO}_4}} NMC$$

$$NMC + NaBH_4 \xrightarrow[\text{EtOH H}_2\text{O}]{\text{Cocomplex}} NMCA$$

$$BMC + Diamine \xrightarrow[\text{NaNH}_2]{\text{CuCl}} BMCA$$
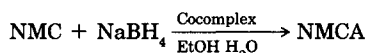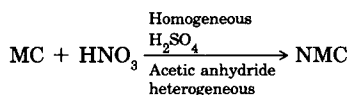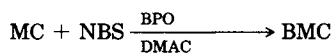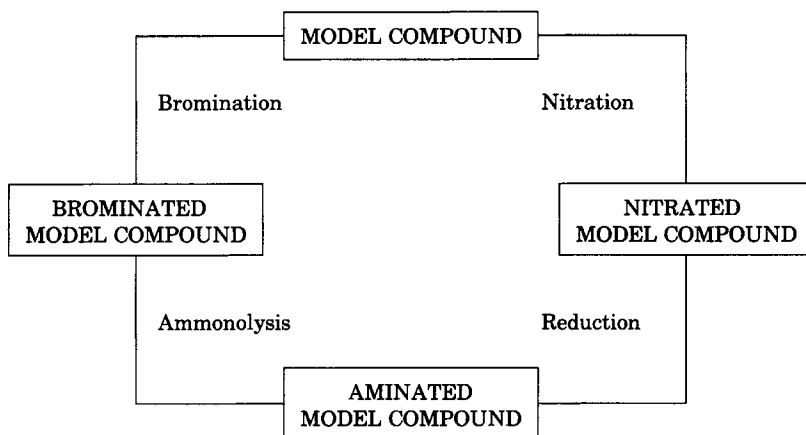
elemental analysis and by the infrared spectrum. The product obtained by bromination of MC-1 was identical with the compound prepared by the Schotten-Baumann reaction of terephthaloyl chloride with p-bromoaniline. Two crystalline fractions of identical composition but different infrared spectrum and melting point were obtained in the bromination of MC-1 (see Table III). Characterization of the different crystalline forms of brominated MC-1 will require further study.

Ammonolysis[4-17]

To 1 mmol of brominated model compounds (BMC-1) added to a solution of a trace of cuprous chloride in 10 ml of ethylene diamine, 40 mg of sodium amide were added. The mixture was refluxed under nitrogen for 1 h, followed by addition of 0.5 g of ammonium chloride and quenching in 200 ml of distilled water. The solid was filtered, washed with large amounts of distilled water, and dried in a vacuum oven at 110°C for 2 h. The yellow solid was characterized by elemental analysis and by its infrared spectrum. (The presence of primary amino groups was confirmed by ion-exchange analysis with Ponceau 3R).

Nitration[13,19]

Two procedures were used for the nitration of model compounds MC-1 and MC-2 (see Table II).
In homogeneous nitration, 5 mmol of MC-1 were dissolved in 9 ml of

concentrated H_2SO_4. Then 2.5 ml of mixed acid (1.25 ml concentrated H_2SO_4 + 1.25 ml of fuming HNO_3) were added dropwise with stirring and cooling in an ice bath, maintaining the temperature at 5–10°C, over a period of 20 min. The mixture was stirred for an additional 20 min, then poured into 250 ml of cracked ice. The solid was filtered, washed with distilled water until the wash water was neutral, dried for 2 h in a vacuum oven at 110°C, and recrystallized from DMAC.

The nitrated products (characteristically yellow) were characterized by elemental analysis and by their infrared spectra. They were identical with the compounds prepared by reaction of acid chlorides with the corresponding nitroanilines.

In heterogeneous nitration, 1 g of well-ground model compound (MC-1 or MC-2) was suspended in 10 ml of a 9:1 mixture (*v/v*) of acetic anhydride and glacial acetic acid, and 10 ml of nitrating mixture (6:1:3 by volume acetic anhydride, glacial acetic acid, and fuming nitric acid) were then added dropwise with stirring and cooling at 10–15°C. The mixture was stirred for 15 min after addition was completed. After filtering and washing, 1.1 g of yellow solid was isolated from the reaction mixture.

Reduction[20,21]

To 1 g of well-ground nitrated compound (NMC-1 or NMC-2) suspended in 100 ml of aqueous ethanol (50% by volume), buffered to pH 6.5–7.0 with KH_2PO_4-K_2HPO_4, 50 mg of a cobalt-bipyridyl complex $[Co(bipy)_3(ClO_4)_3]$ catalyst were added. With gentle stirring, 1 g of sodium borohydride was then added in portions over a period of 4–5 h, and stirring was continued overnight. The solid was filtered and washed with large volumes of distilled water and dried in a vacuum oven at 110°C for 2 h. The yellow color of the nitro compound disappeared, and the grayish solid obtained showed the presence of amino groups in ion-exchange tests with Ponceau 3R.
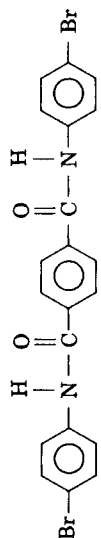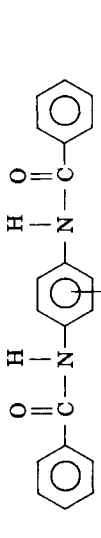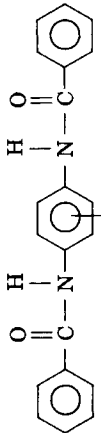
Note: The reaction conditions described above have entailed extensive modifications of methods reported in the literature. The references cited in each case thus correspond to the approach in general rather than specific terms. The compounds obtained by these reactions and discussed below have not been previously reported.

Melting points, yields, and analytic data for the new compounds prepared by bromination, ammonolysis, and nitration of the model compounds MC-1 and MC-2 are summarized in Tables III, IV, and V. Characterization of compounds obtained by reduction of nitrated model compounds has not been completed to date.

Reactions on Kevlar Filaments

Before reaction, the fiber was washed in CCl_4 at reflux for 2 h, then with large amounts of distilled water, and dried at 110°C for 2 h. Fiber samples (about 1 g) were wound around a glass cagelike support that could be placed in a reaction flask and immersed in reagent solution.

TABLE III
Structure, Composition, and Melting Point of Brominated MC

Structure	MP[a] (°C)	Elemental analysis[b]				Yield %	Remarks
		C%	H%	N%	Br%		
BMC1—α	273.8	55.66 / 55.39	2.98 / 2.76	5.91 / 5.85	33.70 / 33.25	98	Needles
BMC1—β	265.9	55.66 / 55.44	2.98 / 2.85	5.91 / 5.87	33.70 / 33.56	98	Flakes
BMC2	234.7	60.72 / 61.44	3.83 / 3.85	7.09 / 7.13	20.22 / 19.83	73	

[a] As in Table I.
[b] As in Table I.

TABLE IV
Structure, Composition, and Melting Point of Ammonolyzed BMC

Structure[a]	MP[b] (°C)	Elemental analysis[c]			Yield %
		C%	H%	N%	Br%	

			C%	H%	N%	Br%	Yield %
BMC1—A	317.1		66.64 / 65.53	6.53 / 6.71	19.43 / 19.02	0.0 / 0.1	92.5
sh,1 BMC2—A	215.9		70.57 / 72.23	5.92 / 5.58	14.96 / 12.33	0.0 / 0.1	45

[a] A = —NHCH$_2$CH$_2$NH$_2$.
[b] As in Table I.
[c] As in Table I.

TABLE V
Structure, Composition, and Melting Point of Nitrated MC

	Structure	MP[a] (°C)	Elemental analysis[b]			Yield %
			C%	H%	N%	
NMC1		296.7	48.38 48.55	2.42 2.45	16.94 16.96	100
NMC$_2$		261.2	59.11 59.20	3.45 3.30	13.79 14.00	75

[a] As in Table I.
[b] As in Table I.

After reaction, the treated fiber sample was washed as appropriate and dried. Initially, the reaction conditions were derived from results obtained on model compounds, and subsequently, modifications were made in reaction time and temperature or in reagent concentration if the visual appearance of treated fibers indicated damage (e.g., discoloration or interfilament bonding or stiffening), suggesting that the reaction conditions used were too severe. Kevlar 49 filament samples subjected to bromination (BF) bromination followed by ammonolysis (BFA), heterogeneous nitration (NF), and nitration followed by heterogeneous reduction (NFA) were tested for tensile properties. Samples containing amino groups (BFA and NFA) were analyzed quantitatively by ion exchange with Ponceau 3R to determine the concentration of amino groups on fiber surfaces.

Reactions on Kevlar Fabric

In order to prepare sufficient treated fabric for the initial evaluation of epoxy laminates, the following procedure was used. After scouring in an ultrasonic bath for 1 h at 40–50°C in 2% aqueous detergent solution, the fabric was washed thoroughly with water at 40–50°C and dried for 2 h at 120°C. A sample (7.5 × 7.5 in.) was inserted into a plastic Zip-lock bag containing the reagent mixture, and the air was evacuated. The closed bag was then placed in an ultrasonic bath containing water (to maintain motion), and the bag was also shaken manually at intervals. After reaction, the fabric was removed from the reagent medium, washed well with distilled water, and dried in a vacuum oven at 70°C. Several fabric swatches were reacted simultaneously in one bag for the preparation of laminates. The reagent medium and conditions used for fabric treatment are described below.

Bromination and Ammonolysis of Fabaric

Bromination, 500 ml DMAC, 5 g NBS, 0.15 g of benzoyl peroxide (BPO), and 10 drops benzyl dimethylamine (BDMA), were reacted at 50–60°C for 3 h under nitrogen.

In ammonolysis, 500 ml ethylene diamine (EDA), 0.003 g CuCl, and 0.3 g $NaNH_2$ (B-Fb-A-1); or 0.2 g $NaNH_2$ (B-Fb-A-2) were reacted at 50–60°C for 1 h under nitrogen.

Nitration and Reduction of Fabric

The nitration mixture (prepared immediately before use) was 160 ml of acetic anhydride, 60 ml of glacial acetic acid, 40 ml of fuming nitric acid, and 2 ml of 98% H_2SO_4; the reaction was at 10–20°C for 2 h.

For the reduction, 250 ml distilled water, 160 ml ethanol, 2.5 g KH_2PO_3, 0.6 g Na_2HPO_4, 0.5 g $[Co(biPy)_3(ClO_4)_3]$, and 1.8 g $NaBH_4$ (added in portions over a period of 2 h) were reacted at room temperature for 24 h (N-Fb-A1, N-Fb-A2).

Preparation of Laminates

For composite 1, 100 g of epoxy resin, Epon 828 (Shell Chemical), and 14 g of m-phenylenediamine were mixed, heated to 70°C with stirring for 5 min, and quickly cooled to 30°C. Fabric (approximately 25% by weight) was

laminated, freed from microvoids, and pressed (6 kg/cm^2) at 100°C for 1 h, 120°C for 2 h, and 150°C for 2 h. The laminate was then cooled to room temperature in the press.

Composite 2 was made similarly, using 18.7 g of xylylene diamine (in place of *m*-phenylenediamine) and about 35% by weight of fabric, pressing (2 kg/cm^2) for 2 h at room temperature before heating (1 h at 120°C and 2 h at 150°C).

Analysis and Testing

Elemental analyses and infrared spectra provided adequate characterization of model compounds but were not applicable in the case of fiber and fabric because of the low total concentration of functional proups introduced in surface-limited reactions. For the quantitative determination of amino groups on fiber surfaces, the ion-exchange dye method suggested by Allred et al.[8] was used with excellent results.

Tensile properties of Kevlar filaments were measured on an Instron (crosshead speed of 0.5 in./min and chart speed of 10 in./min) at 23°C and 69% RH. The T-peel test of fabric laminates was measured by ATM-1876-72 (reapproved 1978) and interlaminar shear strength of laminates (short beam) by ASTM-D-2344-76 (reapproved 1982).

Results and Discussion

Model Compounds

Results obtained on reactions of model compounds are largely defined by the analytic data summarized in Tables III, IV, and V. Certain conclusions are warranted concerning the (predictable) site of substitution in the aromatic ring for bromination and for nitration reactions and its consequences in the case of reactions carried out on PPTA. In this context, an initial comparison of the two approaches (bromination and ammonolysis versus nitration and reduction) as viable sequences for introducing amino groups on the surface of Kevlar fibers can be attempted.

The para position (to amide nitrogen) is not available for substitution in or on PPTA. It would thus appear that nitration, which can attack the ortho position more readily, would be preferable to bromination as a first reaction step in the case of fiber. However, this factor can be evaluated only in the context of further experiments on fibers, designed to establish the optimum conditions under which each reaction can be carried out to attain the desired concentration of amino groups without impairment of fiber properties.

The results obtained to date suggest that the significance of the study of model compounds has been primarily the definition of reactants and reaction conditions that are, in principle, suitable for fiber modification. It will be evident from the following discussion of results obtained on fiber and on fabric samples that the conditions established on the basis of extensive studies on model compounds, coupled with knowledge of PPTA fiber properties, have been successfully applied to reactions on fiber in this first phase of the investigation.

Surface Modification of Kevlar Fiber

For each of the reactions discussed, there are critical variables in reaction conditions which determine whether the desired concentration of amino groups can be attained on fiber surfaces without impairment of fiber properties. In the case of the ammonolysis reaction on brominated fiber, the effects of $NaNH_2$ concentration in the ethylenediamine reaction mixture, of reaction time at 70°C on amine content, and on the appearance of aminated fiber were studied in some depth.

The results of these experiments are shown in Figure 2. Visual inspection of the fiber samples obtained in the experiments, which were carried out on brominated fiber samples prepared in replicate runs, showed *no* apparent damage for amino group concentrations up to 2–3 $NH_2/100$ Å^2. Under the conditions shown, the optimum concentration of $NaNH_2$ (in EDA) for control of surface reaction was shown to be 0.02–0.03%. Higher reaction temperatures and shorter reaction times have also been investigated.

Effects of bromination and ammonolysis conditions and of the concentration of amino groups introduced on tensile properites of treated filaments are summarized in Table VI. Several points of interest are notd. There was no strength loss on bromination in these experiments (9-BF, 10-BF, and 13-BF). Ammonolysis conditions are indeed more critical, and a significant strength loss occurred in the absence of solvent (9-BFA). The exotherm observed when CCl_4 was used (13-BFA) as the medium in the ammonolysis reaction, and the high concentration of NH_2 attained in a reaction time of only 10 min may be explained by the formation of a charge transfer complex from CCl_4 and an amine (EDA) in which basicity is enchanced by the presence of $NANH_2$.[22-24]

As for correlation of NH_2 concentration with tensile properties, a significant strength loss corresponds to the high NH_2 (6.31) concentration of sample 10BFA, but a concentration of 0.86 per 100 Å^2 can be attained without altering fiber strength.

Results of tensile tests on filaments modified by nitration and reduction under various conditions are summarized in Table VII. It is noteworthy
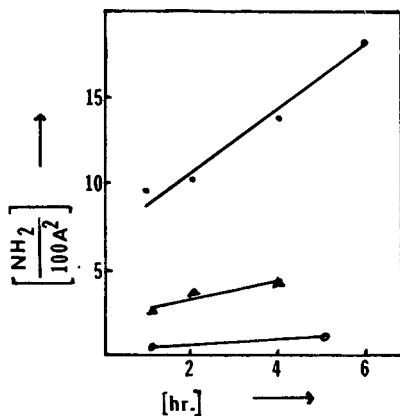
TABLE VI

Surface Amine Concentration and Tensile Properties of Kevlar Filaments After Bromination and Ammonolysis

	NH_2 per $100Å^2$	Bromination condition	Ammonolysis condition	Tensile strength (g/d)	Elongation (%)	Remarks
Control	0.05	—	—	35.9	2.84	
9-BF	—	2.87% NBS in DMAC, BPO 85°C/2 h		36.8	2.85	
9-BFA	0.47		EDA-NaNH$_2$-CuCl; reflux (118°C)/1 h	23.8	1.94	No solvent used
10-BF	—	1.5% NBS in DMAC, BPO 85–90°C/2 h		40.5	2.82	
10-BFA	6.31		EDA-DMSO-NaNH$_2$-CuCl; 100–120°C/40 min	16.0	1.52	
13-BF	—	1.0% NBS in DMAC, BPO-CHP[a] 100°C/1 h; 150°C/1 h		31.4	2.32	
13-BFA	0.86		EDA-CCl$_4$-NaNH$_2$-CuCl; 40–60°C/10 min	32.5	2.41	Exothermic reaction

[a] CHP: Cumyl hydroperoxide.

TABLE VII
Surface Amine Concentration and Tensile Properties of Kevlar Filaments After Nitration and Reduction

No.	NH$_2$ per 100Å^2	Nitration condition	Reduction condition	Tensile strength (g/d)	Elongation (%)	Remarks
Control	0.05			35.9	2.84	
7-NF	—	OAc-HOAc-HNO$_3$ = 100:28:28; RT/1 H		34.9	2.93	
7-NFA	0.48		Co-complex NaBH$_4$; RT/7 h	32.6	2.8	
8-NF	—	OAc-HOAc-HNO$_3$-H$_2$SO$_4$ = 100:37:25:1.25; RT/2 h, 40°C/15 min		37.2	2.96	
8-NFA	0.59		Co-complex NaBH$_4$; RT/24 h, 100°C/2 h	32.4	2.65	
10-NF	—	OAc-HOAc-HNO$_3$-H$_2$SO$_4$ = 100:100:25:0.5; RT/0.5 h, 40°C/0.5 h		19.7	1.61	Fiber from nitrated fabric
11-NFA	0.56	Same as 8-NF	SBH-THF^a = 0.7:100; RT/24 h, reflux/1 h	39.0	2.60	Solid on fiber surface; difficult to remove
12-NF	—	OAc-HOAc-HNO$_3$-H$_2$SO$_4$ = 100:37:32:1.6; 5–10°C/1 h, 15°C/3 h		27.1	2.01	
12-NFA	0.54		SBH-THF = 0.7:100; RT/14 h, reflux/6 h	23.2	1.72	Solid on fiber surface difficult to remove
13-NF	—	Nitrating agent was used for 12 NF; RT/3 h		38.7	2.78	Nitrating mixture reused after 12 NF

^{a} SBH-THF = sulfurated borohydride in THF.

that nitration can be carried out without strength loss (7-NF and 8-NF). reduction with sodium borohydride catalyzed by the Co complex (7-NFA and 8-NFA) results in a significant NH_2 concentration, and strength is not impaired. Sulfurated borohydride (11-NFA and 12-NFA) is also an effective reducing agent, but it leaves solid residues that are extremely difficult to remove from the fiber suraces.

A summary of tensile data on amine-containing fiber samples is presented in Table VIII. It is evident that a major strength loss was observed only in the case of the high NH_2 content produced by severe conditions of am-monolysis, in which reaction may have occurred beneath the surface after disruption of the structure.

Fabric Laminates

Composite laminates (2 plies) for preliminary evaluation of T-peel strength were prepared from fabric samples that had been modified by bromination-ammonolysis (B-Fb-A) and by nitration-reduction (N-Fb-A) re-actions. In each case, two procedures were used (composite 1 and composite 2), and laminate samples ere tested (ASTM D-1876-72, except that specimen size was 1 × 7.5 in., not 1 × 12 in. as specified). Results are summarized in Table IX. Taken at face value, these limited results suggest that an improvement is realized by the introduction of amino groups, but that higher concentrations of NH_2 would not enhance peel strength further.

T-peel fracture surfaces were examined by scanning electron microscopy, and the appearance of selected specimens (composite 1) is shown in Figures 3 through 8. There are significant differences between the failure surfaces of untreated peel specimens (Figs. 3 and 6) and those of specimens prepared from amine-modified kevlar (Figs. 4 and 7; NFb-A-1) (Figs. 5 and 8; B-Fb-A-1). However, the appearance of bonding at failure conditions in the amine-modified samples is not as good as might have been predicted from the numerical values of peel strength (Table IX). This may be interpreted as localized bonding resulting from nonuniformity of chemical reaction on fiber surfaces under the conditions of the experiments. Bonding is seemingly better for the N-Fb-A-1 sample than for the B-Fb-A-1 sample (in spite of the lower surface amino group content), and this is consistent with the postulated role of uniformity and with heterogeneous reaction medium required in ammonolysis.

For the evaluation of interlaminar shear strength of laminates from modified Kevlar fabric, reactions were carried out as described previous-ly, NFb-A-1 and B-Fb-A-1, using four swatches of fabric simultaneously in the reaction medium. Preparation of 24-plie laminates (composite 1) was as described above, with minor modifications in the conditions of heating and pressure. The resin weight fraction in the laminates was ap-proximately 40%.

Results of the test are shown in Table X. A 51.6% increase in appar-ent shear strength was obtained for the laminate prepared from nitrat-ed-reduced fabric (0.62 NH_2 per 100 Å²). This is significantly greater than reported by previous investigators for Kevlar 49 fabric treated with amine plasma to about 0.75 NH_2 per 100 Å².[9] The results for the lami-

TABLE VIII

Fiber sample	NH₂ per 100 Å²	Strength (g/d)					
		Average	CV (%)	Loss (%)	Average	CV (%)
Control	—	35.9	16.7	—	2.84	13.5
7-NFA	0.48	32.6	17.0	9.2	2.80	12.1
8-NFA	0.59	32.4	24.5	9.7	2.65	23.3
11-NFA	0.56	39.0	17.1	-8.7	2.60	16.0
9-BFA	0.47	23.8	32.8	33.7	1.94	30.1
10-BFA	6.31	16.0	27.8	55.4	1.52	22.5
13-BFA	0.86	32.5	23.5	9.5	2.41	14.1

TABLE IX

Fabric in composite	NH$_2$ per 100 Å^2 in fabric	T-peel strength (lb/in.)
Composite		
Control	—	0.6
N-Fb-A-1	0.62	1.2
B-Fb-A-1	3.12	1.3
Composite		
Control	—	0.9
N-Fb-A-2	0.65	1.1
B-Fb-A-2	1.64	1.4

Fig. 3.   Control.
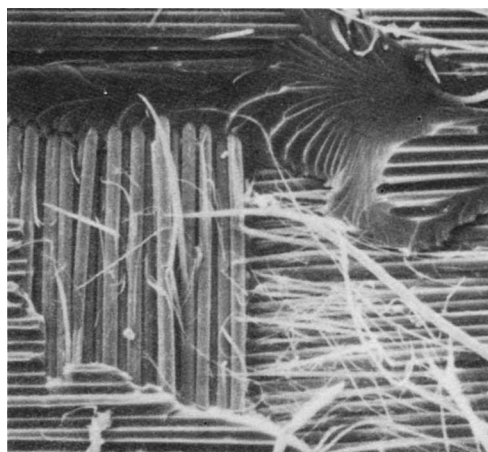
Fig. 4.   N-Fb-A-1 (0.62 NH$_2$/100 Å^2).
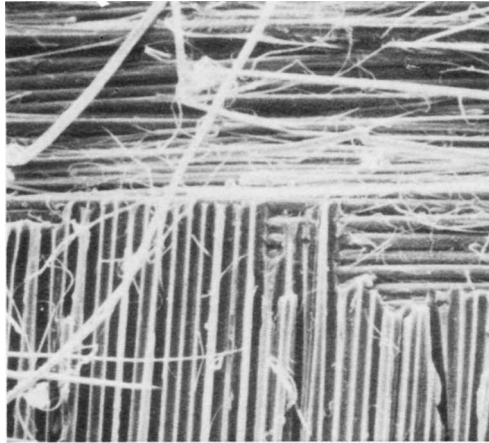
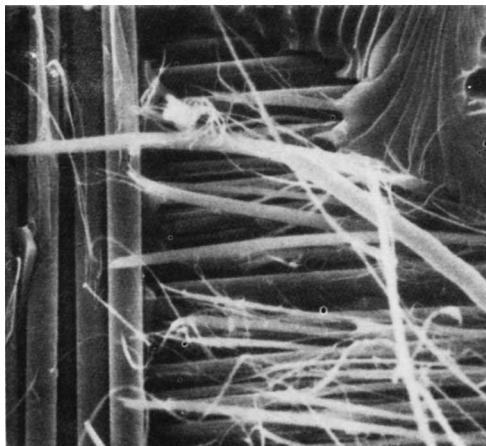Fig. 5. B-Fb-A-1 (3.12 Nh_2/100 $Å^2$).
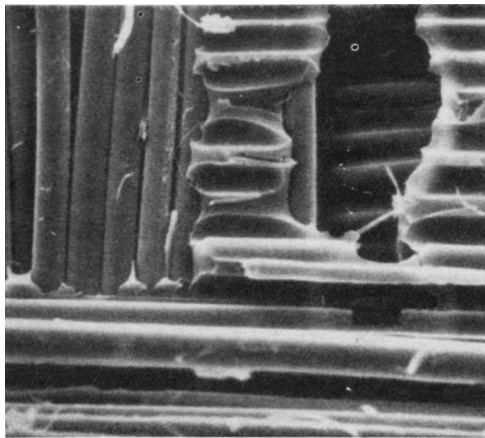
Fig. 6. Control.

Fig. 7. N-Fb-A-1 (0.62 Nh_2/100 $Å^2$).
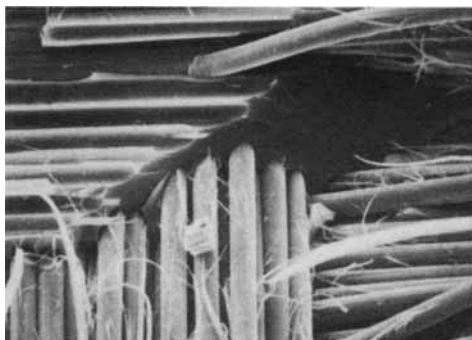
Fig. 8.   B-Fb-A-1 (3.12 NH$_2$/100 Å^2).

nate from brominated-aminated fabric of comparable amine content were
disappointingly low. We attribute this to lack of uniformity in the reac-
tions (carried out on four fabric swatches simultaneously), particularly in
the case of ammonolysis, where critical effects of reaction conditions
have been shown in other experiments. Nonuniformity was also apparent
in the case of B-Fb-A-3 samples from localized stiffening in the treated
fabric and voids noted during the preparation of laminates.

CONCLUSIONS

The study of organic reactions of aromatic diamides as models for PPTA
fibers has provided a basis for selecting viable approaches to the surface-
controlled modification of Kevlar fibers with amino groups.

Bromination followed by ammonolysis and nitration followed by reduc-
tion have been investigated on Kevlar 49 filaments, and significant con-
centrations of primary amino groups can be attained on filament surfaces
in these reactions without impairment of fiber tensile properties. Although
the optimum conditions of treatment have not been established, the results
of both reaction sequences show that further study is warranted.

Kevlar 49 fabric modified with surface amine sites by these approaches
yields epoxy laminates in which peel strength and apparent interlaminar
shear strength are remarkably improved, suggesting that covalent bonding
of epoxy resin with amino groups on fiber surfaces can be a major factor
in the adhesive strength of aramid-epoxy composites.

The results reported in this paper demonstrate that surface modification
with reactive functional groups and improved bonding of aramid fibers in
epoxy composites can be attained by organic reactions that do not require
special installations and are potentially suitable for industrial processes.

TABLE X

Fabric in laminate	NH$_2$ per 100 Å^2 in fabric	Apparent shear strength, Pa × 10^6 (kg/cm^2)	CV (%)	Δ (%)
Control	—	20.18 (205.9)	2.7	—
N-Fb-A-3	0.62	30.60 (312.2)	1.9	+51.6
B-Fb-A-3	0.63	21.46 (219.1)	3.9	+6.4

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