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STUDY OF SURFACE MODIFIED POLY(ETHYLENE) YARNS

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Abstract

Spectra® fibers and fabrics have been treated to enhance surface friction to determine if ballistic penetration resistance of Spectra fabric can be increased with improved interfiber friction. Scanning electron microscopy (SEM) has shown the extent of surface modification for plasma treated Spectra yarns and the uniformity of coverage for dip-coated yarns and fabrics. Of particular interest is the observation by SEM that plasma gases etch the surface of the polyethylene, producing varying effects on the fiber surface friction. While difficult to measure spectroscopically, the presence of coatings that affect fiber friction are confirmed by SEM.

Key Words: Scanning electron microscopy, ultrahigh strength polyethylene fiber, plasma treatment, fiber friction testing, polymer surface grafting.

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Introduction

High strength, high modulus fibers such as aramids (i.e., Kevlar®) and the more recent ultrahigh strength poly(ethylene) (i.e., Spectra®) are important materials for ballistic protection. These high strength fibers are oriented polymers that achieve over 90% of the theoretical modulus of an extended carbon chain [17]. This leaves little room for vast improvements in fibrous material properties and ballistic protection, although many fiber properties such as stress, strain and modulus are still being optimized with respect to ballistic performance.

One approach for improving the ballistic resistance of woven fabrics is through the modification of interfiber friction. It is not known whether high friction or low friction between the fibers in a weave will improve ballistic resistance. Recent studies conducted at DuPont (Chitrangrad B, private communication, 1990) suggest that for Kevlar, fabric panels of less than seven layers show increased ballistic resistance for high friction fibers. Also, researchers in the Netherlands reported in a patent application that ballistic performance could be improved for Spectra and Kevlar yarns through increased friction [5]. Kevlar and Spectra are inherently low-friction fibers, due to their high crystallinity. Numerous investigators have been modifying these surfaces recently [2, 6, 8-16, 18]. We have found that Spectra friction can be increased by 150% through polymer coating or grafting onto the fiber.

Surface modifications to fibers are difficult to measure, due to the small cross-section of the fibers (about 50 μm in diameter) and due to non-uniform treatment of the yarn bundle. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to quantitatively measure the presence of surface treatments on the Spectra yarns, but were unsuccessful in this application. SEM was found to be the only effective method of characterizing fiber surface modifications. SEM was used to verify the extent and uniformity of surface treatments for: **1)** Spectra yarns treated with plasma gases of CO_2, NH_3 or acrylic acid; **2)** Spectra yarns that had been plasma treated, followed by a reaction with a diisocyanate; **3)**

Spectra yarns that were further reacted through the surface isocyanate with a low molecular weight poly(propylene glycol); and **4)** Spectra yarns and fabrics that had been dip-coated with frictional dressing and adhesive compounds.

Materials and Methods

Materials

The samples studied were of two forms, yarns and fabrics. These included Spectra 900 yarn, consisting of about 150 filaments with an untwisted configuration and Spectra 1000 fabric, in a plain weave 6.5 oz/yd and 650 denier. Yarn and fabric were produced by Allied Signal, Inc., Fibers Division, Petersburg, VA.

Polymers and reagents used to modify the yarn surfaces were: poly(propylene glycol), PPG, supplied by Mobay Corporation, Polyurethane Division, Pittsburgh, PA, in molecular weights of 1012, 2007, and 2976 amu; toluene 2,4-diisocyanate (TDI), used as received; acrylic acid, distilled before use; lithium aluminum hydride (LiAlH$_4$); dibutyl tin dilaurate (DBTDL); and thionyl chloride (SOCl$_2$), used as received (all reagents were supplied by Aldrich).

The following adhesives were used as topical coatings to increase fiber surface friction of untreated yarns and fabrics: Krylon® Belt Dressing, Borden Inc., Columbus, OH; 3M Super 77® Spray Adhesive, 3M Adhesives, Coatings and Sealers Division, St.Paul, MN; 3M Scotch-Grip® Contact Cement, 3M Adhesives, Coatings, and Sealers Division.

Sample Pretreatment

In some cases, Spectra yarns and fabrics were used as received with spin finishes present or as fabric off the loom. At other times, pretreatment of the samples was accomplished by one of two different methods: **1)** acetone extraction in Soxhlet extractor or **2)** scouring of the samples with a 1% aqueous solution of trisodium phosphate (Na$_3$PO$_4$) at 60 °C as recommended by Holmes and Schwartz [6] to remove finishes, followed by acetone extraction.

Surface Treatments

Spectra 900 yarn was wrapped onto a reel constructed of glass rods held between poly(propylene) ends in such a manner that the yarn was untwisted and spread onto the rods, thereby exposing a large number of the fibers to the acetone wash and the plasma gasses. Unexposed portions of yarn existed at contact points with the glass rods of the reel and between the fibers themselves. The reel was inserted into a plasma chamber designed and operated by Advanced Surface Technology of Billerica, MA. Under high vacuum, the spooled yarn was exposed to a plasma gas of either carbon dioxide, or ammonia, or in one case, acrylic acid for 10-20 minutes, a time determined to be sufficient for surface reaction for polyethylene fibers. Carbon dioxide plasma produces carboxyl, peroxy, ether and hydroxyl groups at the surface of the substrate [1], while ammonia plasma aminates the surface [6].
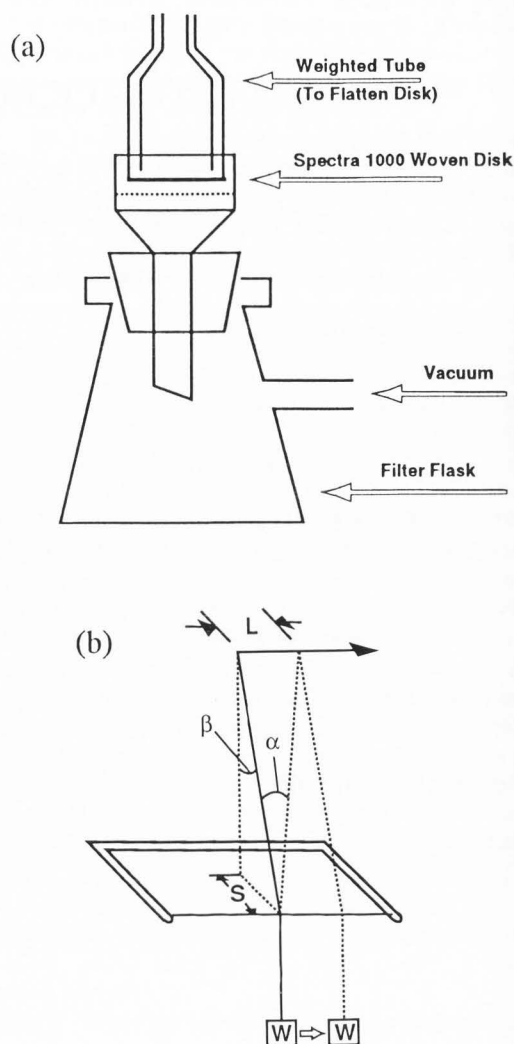
Figure 1. a) Drawing of vacuum apparatus for application of solutions to Spectra 1000 disks; b) Schematic of the modified Howell friction test.

Following CO$_2$ treatment, Spectra 900 yarn with functionalized surface was refluxed in neat, excess thionyl chloride (SOCl$_2$) to convert acid terminals to the appropriate acid chloride, then reacted with lithium aluminum hydride (LiAlH$_4$) in dimethyl formamide solvent for conversion to hydroxyl groups. The yarn was then reacted with 5% 2,4-toluene diisocyanate(TDI) and a catalytic amount of dibutyl tin dilaurate (DBTDL) in toluene under dry nitrogen for one hour. This should produce a fiber surface with isocyanate functional groups covalently attached through urethane linkages in the case of the CO$_2$ treated yarns. In addition to the SOCl$_2$/ LiAlH$_4$ pretreatment of the carboxylated surface, a direct reaction between TDI and the CO$_2$ plasma-treated surface was conducted. A continuous stream of gas bubbles was produced at the yarn surface during the TDI/ DBTDL reaction with the CO$_2$-treated surface, indicating that the reaction involved the addition of isocyanate

to surface carboxylic acid, followed by decarboxylation to the urethane moiety:

$$OCN-R-NCO + HOOC-R' \rightarrow$$
$$OCN-R-NH-C(O)-O-C(O)-R' \rightarrow$$
$$OCN-R-NH-C(O)-R' + CO_2 \quad (1)$$
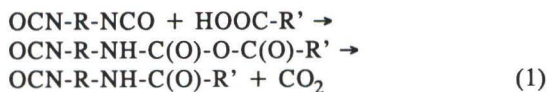
Following NH_3 treatment, the aminated surface of the yarn was similarly reacted directly with TDI/DBTDL to produce urea linked isocyanate pendent groups. Poly(propylene glycol), PPG, was grafted onto the plasma/TDI treated yarns by immersing the yarn into a bath of 5% PPG with 2 drops dibutyl tin dilaurate in toluene, followed by refluxing for one hour. The grafted yarns were extracted in acetone for four hours at 56 °C to remove any unreacted or agglomerated homopolymer. Many yarns treated in this way exhibited noticeable weight gain, although gains were found to be variable and generally too difficult to measure reliably. Estimates of coating thickness based on weight gains for yarns were technically difficult and were found to be unrealistic, considering the SEM evidence of non-uniformity of coverage in a yarn bundle.

Topical treatments were applied to Spectra 900 yarns by continuous application of 100%, 50%, and 10% solutions of adhesive in toluene. These adhesives included the Krylon Belt Dressing, the 3M Adhesive, and the 3M Contact Cement.

Spectra 1000 fabric was cut into 2-1/4 inch (5.72 mm) diameter discs and fit into a Buchner funnel (Fig. 1a). Adhesives of appropriate dilution were poured onto the fabric and drawn through by vacuum. After reversing the disc in the funnel, adhesive was drawn through a second time. Adhesive treated discs were vacuum oven dried for three hours at 80 °C. The various surface treatments applied to yarns and fabrics are summarized in Table 1.

Surface Characterization

Chemical analysis of the treated surface included measurements with a Perkin Elmer 1740 FTIR Microscope. This showed a hint of surface nitrogen at 2300 cm^{-1} for the ammonia plasma treated yarn. In another test, Diffuse Reflectance FTIR of the yarns showed no presence of plasma treatment or post reaction products with TDI or PPG. Generally, FTIR is not sensitive enough to measure the surface changes of plasma treatments or even post-treatments.

X-ray photoelectron spectroscopy (XPS) has been shown to measure quantitatively the amount of oxygen present at the surface after a carbon dioxide plasma treatment and the amount of surface nitrogen present from an ammonia treatment [3]. However, if the surface treatment is too thick (greater than 10 nm), this technique produces only chemical information about the coating layer instead of concentration information at the interface. Because our post-plasma grafting and our topical coatings were well over 100 nm thick, XPS measurements could be used only to measure the plasma-induced chemical changes on the yarns, and could not give us any indication of how much TDI or polymer was

Table 1. Surface Treatments

Spectra 900 Yarn

Control with spin finish present
Acetone washed or extracted
Scrubbed with 1% Na_3PO_4
Acetone Washed/CO_2 Plasma
Acetone Washed/NH_3 Plasma
Acetone Washed/Acrylic Acid Plasma
Acetone Washed/CO_2 Plasma/$SOCl_2$/$LiAlH_4$/TDI
Acetone Washed/NH_3 Plasma/TDI
Acetone Washed/CO_2 Plasma/$SOCl_2$/$LiAlH_4$/TDI/ PPG (2007 amu)/Acetone Extracted
Acetone Extracted/CO_2 Plasma/$SOCL_2$/$LiAlH_4$/TDI/ PPG (2976 amu)/Acetone Extracted
Acetone Washed/NH_3 Plasma/TDI/PPG(2007amu) or PPG (1012 amu)/Acetone Extracted
Acetone Extracted/10% Krylon Belt Dressing
Acetone Extracted/50% Krylon Belt Dressing
Acetone Extracted/100% Krylon Belt Dressing
Acetone Extracted/50% 3M Adhesive
Acetone Extracted/50% 3M Contact Cement

Spectra 1000 Fabric

Control off-loom
Scrubbed with 1% Na_3PO_4
Acetone Washed/Vacuum Coated with 10% Krylon
Acetone Washed/Vacuum Coated with 50% Krylon
Acetone Washed/Vacuum Coated with 100% Krylon
Acetone Washed/Vacuum Coated with 50% 3M Adhesive
Acetone Washed/Vacuum Coated with 50% 3M Contact Cement

Table 2. XPS of Plasma Treated Spectra 900 Surfaces

| Sample | Atomic Concentration (%) | | | | | | |
	O	N	C	Ca	Cl	P	Si
Control	19.5	---	73.9	---	---	---	6.6
NH_3-Treated	21.0	4.9	69.4	0.7	1.4	0.9	2.3
CO_2-Treated	18.0	1.1	77.1	---	---	---	3.8
PAA-Treated	24.9	---	63.8	---	---	---	11.3

ultimately added to the surface, and whether the polymer was chemically bound or simply adsorbed.

XPS of the plasma treated surfaces was performed by Advanced Surface Technology Inc. of Billerica, MA on a Perkin Elmer Model 5400 ESCA spectrometer. This instrument uses a magnesium anode operated at 400 watts. Base pressure of this instrument was 2×10^{-10} torr. All specimens were examined initially with low resolution survey scans to determine which elements were present. High resolution multiplex data were taken to determine the binding energy of the elements detected in the survey scans. The quantification of the elements detected are summarized in Table 2. The approximate sampling depth for these experiments was 5.5 nm relative to carbon electrons.
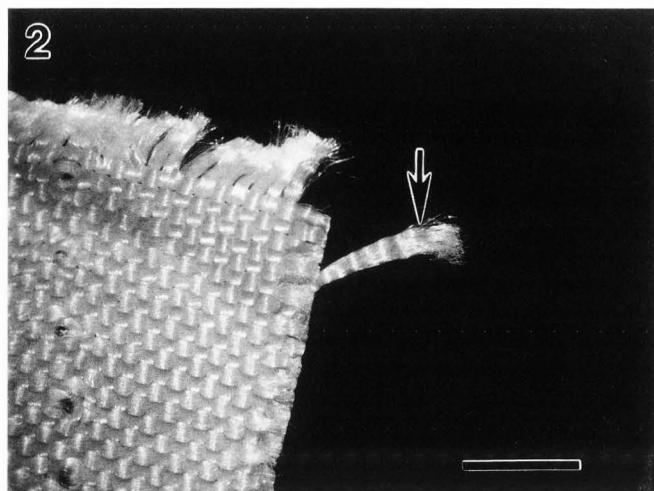
Figure 2. Photomicrograph showing a yarn (arrow) being teased from a swatch of Spectra 1000 woven cloth. Bar = 5 mm.

The XPS data shown here are inconclusive regarding the extent of surface modification. Since very small sample areas are examined by XPS, surface treatment irregularities appear to have influenced the results. The ammonia treated surface shows an increased oxygen, decreased carbon and the appearance of nitrogen compared to the control. We expect to see nitrogen, and the increased oxygen is likely due to reaction of plasma produced free radicals after the treatment. The CO_2 treated surface shows no evidence of plasma modification, since the oxygen level has decreased from the control to the treated condition. This XPS scan may have been performed on an untreated section of fiber. Despite this negative XPS result, our post reactions with this yarn indicated vigorous reaction with TDI and the yarn surface, confirming the presence of carboxyl groups from the plasma treatment. The acrylic acid plasma treated yarn exhibited a significant increase in oxygen content over the control, indicating the presence of polymerized acrylic acid at the surface examined by XPS.

Experiments were undertaken by SEM that verified the extent and uniformity of surface treatments for samples described in Table 1. As discussed below, SEM was used to identify surface pitting (the presence of small pits on the otherwise unaffected surface), etching (the appearance of extensive surface erosion with little original surface left), and surface coating features such as agglomeration, material strands, and coverage of the normal fiber features seen in the control.

Individual yarns (Fig. 2) or fibers were teased from Spectra 1000 fabric or 900 yarn. Yarns or fibers were prepared for SEM examination by the methods of Cohen *et al*. [4]. Samples were cut to approximately 1.5 cm in length and then placed onto double-sided adhesive carbon tape that had been affixed to an SEM stub. After

Figure 3. Spectra 1000 untreated control showing the typical extrusion-produced striations (arrows) and kinks (K). Bar = 10 μm.
Figure 4. Spectra 1000 scrubbed with 1% tri-sodium phosphate at 60 °C and extracted with acetone. Extensive surface pitting can be seen (arrows). Bar = 5 μm.
Figure 5. Spectra 1000 dipped into 10% Krylon Belt Dressing solution. A thin layer of the belt dressing (D) has coated much of each fiber and has agglomerated (A) in various areas. Bar = 10 μm.
Figure 6. Spectra 1000 coated with 10% Krylon Belt Dressing solution under vacuum. The dressing (D) seemed to be more evenly spread compared with the dip coating in Fig. 5, and there was far less agglomeration (A). Bar = 10 μm.
Figure 7. Spectra 1000 vacuum coated with a 10% solution of 3M Adhesive. Some fibers were heavily coated with the adhesive (A), whereas others were lightly coated (arrows), indicating an uneven treatment. Bar = 10 μm.
Figure 8. Spectra 1000 vacuum coated with a 10% solution of 3M Scotch Contact Cement. There is a thin coating of cement (C) covering most of the fibers as well as strands (arrows) of dried cement found throughout the sample. Bar = 10 μm.

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sputter coating with gold-palladium in a Hummer X sputter coater (Anatech, Alexandria, VA), each sample was examined in a Zeiss CSM 950 SEM operating at 5 kV using a working distance of 17 mm.

Photomicrographs were taken with Polaroid Type 52 film. All surface treatments were found to be nonuniform throughout the yarns for both Spectra 900 and Spectra 1000. Not all the fibers within the bundles were surface modified, and along the length of fibers, the extent of modification varied, as seen by regions of agglomeration, regions of thin coating, and regions of untreated surface.

An overview of the Spectra 1000 fabric (Fig. 2) was taken at lower magnification using a Zeiss Ultraphot optical microscope in reflected light with a 2.5-5X Luminar lens. The film used was Polaroid Type 55.

Interfiber friction was measured using a modified Howell [7] static friction measurement, as shown in Fig. 1b. In this arrangement, two yarns are crossed and the coefficient of friction, μ, is found by triangulation of forces,

$$\mu = (W\ g\ \sin\alpha) / (W\ g\ \sin\beta), \text{ which reduces to } \mu = L/S \tag{2}$$

In this relationship, μ is the friction coefficient, W is the weight applied to the vertical fiber, g is gravity, α and β are the angles, and L and S are the distances shown in Fig. 1b. S represents the "drag angle" between the vertical yarn and the horizontal yarn, and L is the length of displacement of the vertical yarn with respect to the horizontal yarn. During the test, a minimum of 20 friction values of μ were taken and averaged for a final measure of friction coefficient, shown in Table 3.
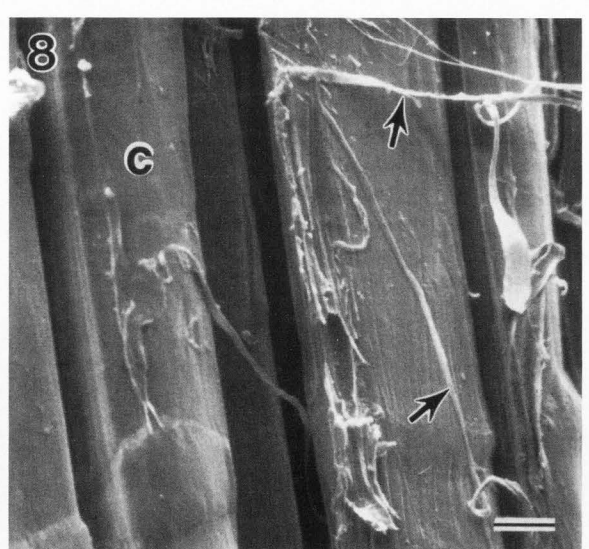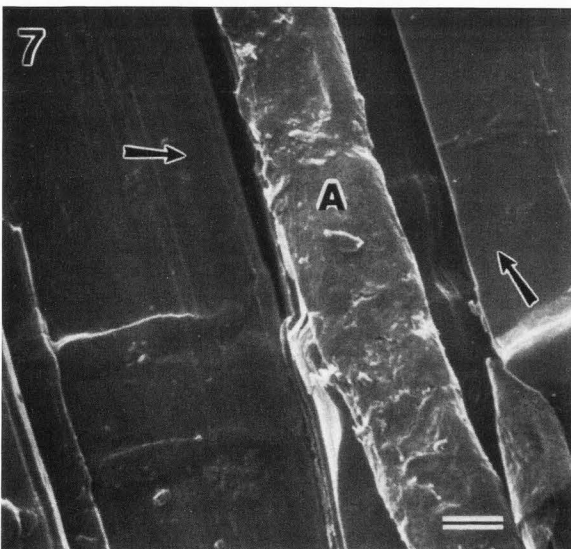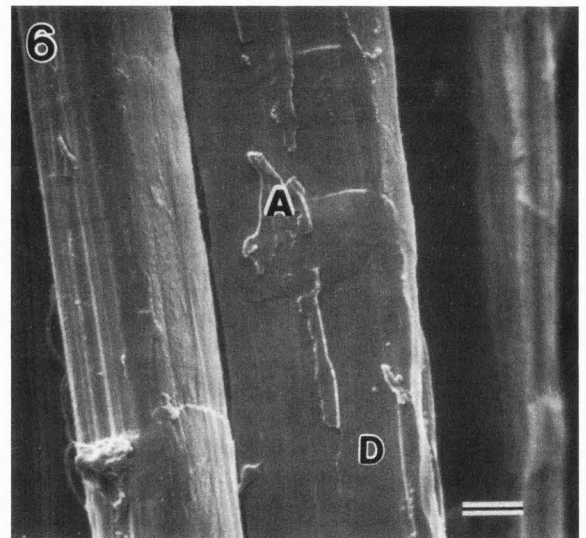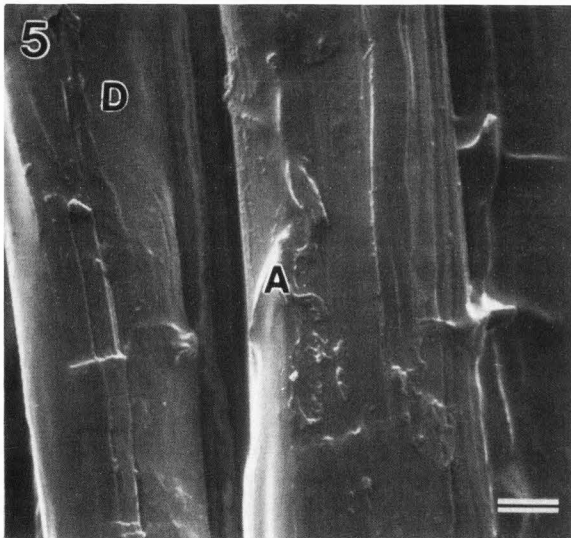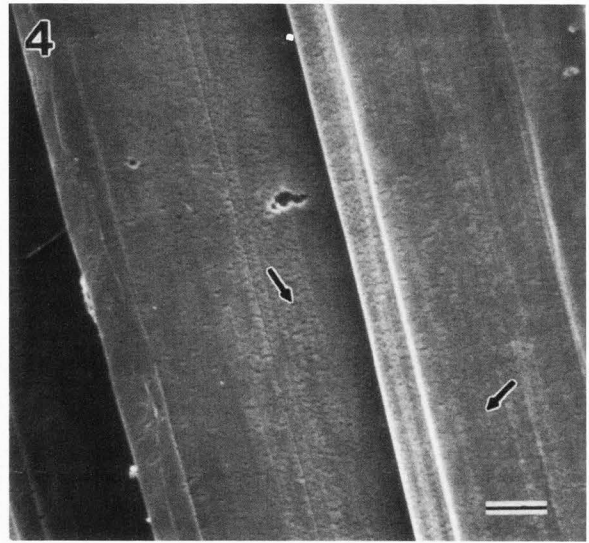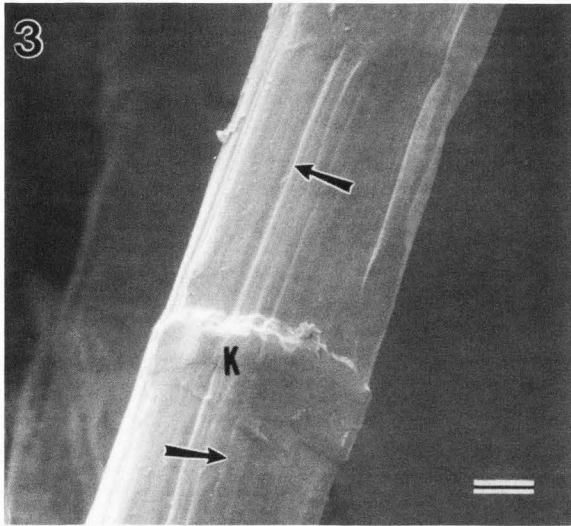
Table 3. Interfiber Friction

Fiber	Howell Friction (μ)
Kevlar 29 control	0.08 ± 0.05
Spectra 900 control	0.13 ± 0.01
Spectra 900/NH_3 Plasma	0.16 ± 0.03
Spectra 900/NH_3/TDI/PPG (1012 amu)	0.29 ± 0.03
Spectra 900/CO_2 Plasma	0.20 ± 0.04
Spectra 900/CO_2/TDI/PPG (2007 amu)	0.20 ± 0.03
Spectra 900/CO_2/TDI/PPG (2976 amu)	0.23 ± 0.06
Spectra 900/Acrylic Acid Plasma	0.17 ± 0.04
Spectra 900/10% Krylon	0.20 ± 0.07
Spectra 900/50% Krylon	0.22 ± 0.10
Spectra 900/100% Krylon	0.48 ± 0.30
Spectra 900/50% 3M Adhesive	0.11 ± 0.04
Spectra 900/50% 3M Contact Cement	0.15 ± 0.04

Results and Discussion

Friction testing was performed on Spectra 900 yarns only; this test could not be performed on the Spectra 1000 fabrics, due to the short yarn lengths available from the treated samples. The friction of unmodified Spectra 900 compared well with friction measured for another highly crystalline, high tensile yarn, Kevlar 29. It is interesting to note that Kevlar friction appears to be as low as that of polyethylene fibers.

Friction data in Table 3 indicate that NH_3 plasma treatment did not dramatically increase the frictional properties of the yarns. However, further reaction with PPG did significantly improve the friction of the ammonia plasma treated Spectra 900 yarn. Additionally, the lower molecular weight PPG (1012 amu) seemed to provide more friction than the PPG (2007 amu) or PPG (2976 amu). Unlike the aminated surface, the CO_2 plasma treated surface was rendered frictional after plasma exposure, and subsequent grafting onto the surface did not further increase the friction coefficient. Plasma vapor treatment using acrylic acid should have produced a grafted poly(acrylic acid, PAA) onto the surface of Spectra, but a highly frictional surface did not result from this treatment. This result may have been due to a highly cross-linked plasma polymerized acrylic acid and/or incomplete coverage of the yarn surfaces during plasma treatment.

Topical treatments altered the frictional nature of Spectra to a great extent. The most successful treatment appeared to be the 100% Krylon Belt Dressing, achieving a coefficient of friction of 0.48 Friction coefficient values approaching 0.5 are difficult to measure by the modified Howell method due to the limited travel distance, L, in our design. It requires a large L to overcome the frictional forces between very frictional fibers, a criterion necessary to measure μ. This difficulty is the cause of the large variability of the measurement of μ for the thickly coated highly frictional Spectra 900/100% Krylon.

Figure 9. Spectra 900 scrubbed with 1% tri-sodium phosphate at 60 °C and extracted with acetone. Some surface pitting can be seen (arrows). Bar = 10 μm.

Figure 10. Spectra 900 treated with CO_2 plasma. Extensive etching (arrows) of the surfaces of most of the fibers can be seen. Bar = 10 μm.

Figure 11. Spectra 900 treated with CO_2 plasma and further reacted with TDI and PPG (2007 amu). Extensive surface etching (arrows) of most of the fibers can be seen, but no surface coating from the PPG reaction is evident. Bar = 10 μm.

Figure 12. Spectra 900 treated with CO_2 plasma, reacted with $SOCl_2$, $LiAlH_4$, then with TDI and PPG (2976 amu). In addition to surface etching (arrows) on some of the fibers, there is an uneven surface coating (C) on most of the fibers. Bar = 10 μm.

Figure 13. Spectra 900 treated with NH_3 plasma, run number 1. There is some surface etching (arrows) and a very thin surface coating (C). Bar = 10 μm.

Figure 14. Spectra 900 treated with NH_3 plasma, run number 2. Some surface etching (arrows) and a very thin surface coating (C) can be seen. Bar = 10 μm.


SEM observations of the surface treated yarns of Spectra 900 and fabrics of Spectra 1000 verified the friction results in terms of the extent of surface modification. A slight increase in surface friction could be measured for the CO_2 plasma treated fiber (the NH_3 plasma treated fiber showed negligible friction change), perhaps due to the etching seen by SEM on the fiber surface. Grafting post-reactions increased friction, and corresponding SEM evidence of added surface coating of the fibers confirmed the source of this increase: the surface grafted PPG. Increasing concentrations of Krylon Belt Dressing applied to the yarns corresponded to increased coefficients of friction, while SEM of these yarns indicated the presence of both thin and thick coatings on the individual fibers within the yarn bundles.

Fibers taken from Spectra 1000 untreated control yarns (Fig. 3) exhibit the typical kinks and striations produced during the manufacturer's extrusion process. Spectra 900 untreated control fibers are similar in appearance to the Spectra 1000 fibers. Yarns taken from treated fabrics showed nonuniform surface coverage due to crossover points in the fabrics. Spectra 900 yarns also showed incomplete coverage at contact points between the yarns and the spool and from fiber contact along the yarn length.

The Spectra 1000 fabric sample treated with 1% Na_3PO_4 at 60 °C and extracted with acetone shows pitting of the surfaces of all the fibers examined (Fig. 4).

When the fabric was either dipped into a 10% Krylon belt dressing solution (Fig. 5) or coated with the same solution under vacuum (Fig. 6), the fibers were covered with a thin layer of the dressing, with some agglomeration of material.
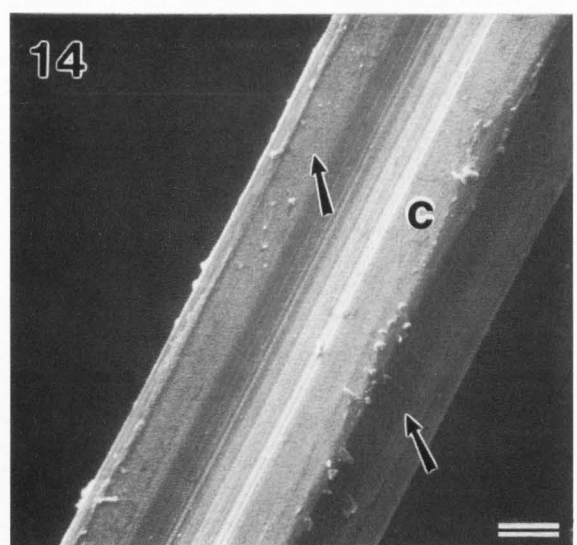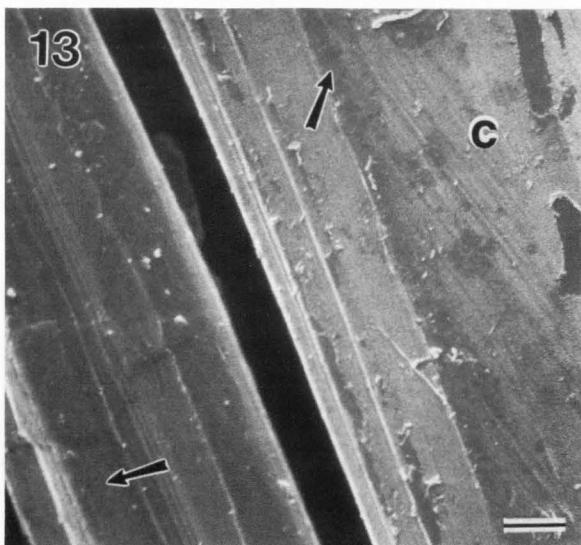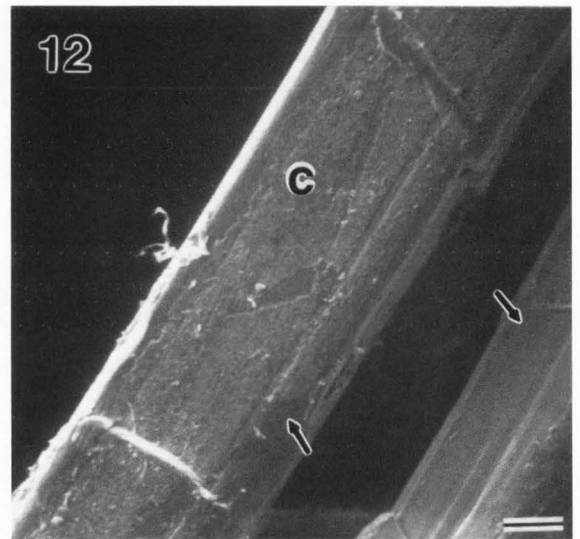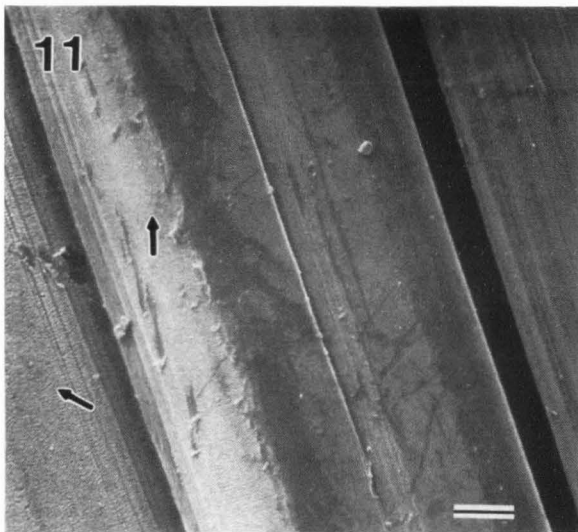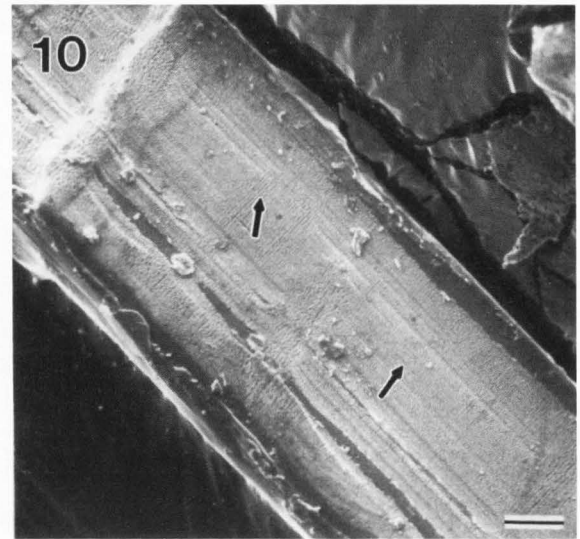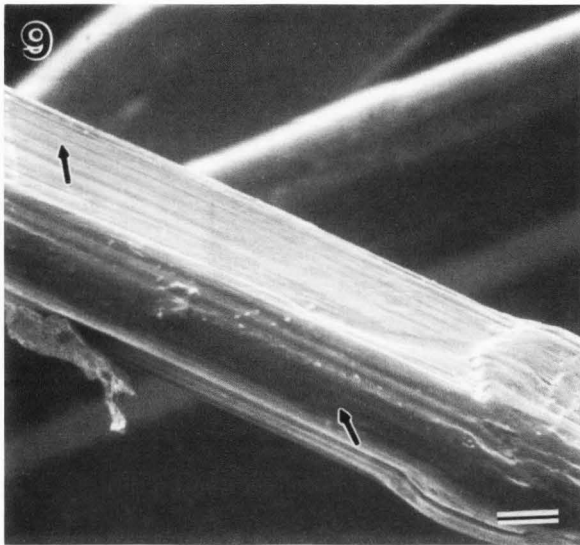
Vacuum coating with a 10% solution of 3M adhesive (Fig. 7) produced a relatively thick coating on some of the fabric fibers, but a much thinner coating on others, possibly due to concentration variations in the applied solution. The application of a 10% solution of Scotch contact cement under vacuum (Fig. 8), on the other hand, produced a thinner coating of material than in Fig. 7. However, a large number of strands of dried contact cement covered most of the fibers, again due to concentration variations.

The Spectra 900 yarn sample, which had been scrubbed with 1% Na_3PO_4 at 60 °C and extracted with acetone (Fig. 9) did not appear to have the degree of surface pitting seen in the similarly treated Spectra 1000 sample (Fig. 4). Except for the small degree of pitting and some agglomerated material, Fig. 9 looked very much like a Spectra 900 control sample with the kinks and striations similar to those seen in the Spectra 1000 control (Fig. 3). It appears that Spectra 1000 is more susceptible to surface chemical degradation than Spectra 900.

It was determined that fabric samples would not benefit from a plasma treatment, due to the ineffective penetration of the treatment into the crossover points. Only the yarn samples of Spectra 900 were treated with plasma gasses. The sample treated with CO_2 plasma (Fig. 10) showed a surface that had undergone a significant amount of etching, as did the sample treated with CO_2 plasma and further reacted with 2,4-toluene diisocyanate (TDI) and PPG (2007 amu) (Fig. 11). In the sample treated with CO_2 plasma, $SOCl_2$, $LiAlH_4$, TDI and finally with PPG (2976 amu) (Fig. 12) there appears to have been some surface pitting, but there is also a thin, uneven coating as in the CO_2/TDI/PPG (2007 amu) treated sample (Fig. 11).

NH_3 plasma treatments were attempted twice to check reproducibility of the surface modification. In the first run (Fig. 13) and the second run (Fig. 14) of the NH_3 plasma treatment, the fibers do exhibit some surface etching; thin surface coating appears somewhat more pronounced in the first run.

There is virtually no etching of the surface in the sample treated with acrylic acid plasma (Fig. 15); however, there is a small amount of agglomerated material. The minor extent of surface modification verifies the modest friction gain and suggests that the plasma polymerized monomer gas did not adhere to much of the available fiber surface.

The sample treated with NH_3 plasma, TDI and PPG (2007 amu) in Fig. 16 shows a fairly uniform surface coating with some agglomeration of material. Another similarly treated sample (Fig. 17) has a significantly greater amount of agglomerated material on its surface. There is a greater amount of agglomerated material on the surface of Spectra 900 yarns (Fig. 18) treated with CO_2 plasma, TDI and PPG (2007 amu) than other samples. In the Na_3PO_4-scoured samples, surfaces of some of the individual Spectra 1000 yarns show unmarred surfaces (Fig. 19A), although some particles can

Figure 15. Spectra 900 treated with acrylic acid plasma. There is virtually no surface etching, but there is a small amount of agglomerated material (arrows) on most of the fibers. Bar = 10 μm.

Figure 16. Spectra 900 treated with NH_3 plasma, TDI and PPG (2007 amu) shows some agglomeration (arrows) on a uniformly coated surface. Bar = 10 μm.

Figure 17. Spectra 900 treated with NH_3 plasma, TDI and PPG (2007 amu). There is a significant amount of agglomerated material (arrows). Bar = 10 μm.

Figure 18. Spectra 900 treated with CO_2 plasma, TDI and PPG (2007 amu). The amount of agglomerated material (arrows) is greater than the other fibers shown in Fig. 11. Bar = 10 μm.

Figure 19. Spectra 1000 extracted with acetone and scoured with 1% Na_3PO_4. **A)** These fibers appear clean and unmarred. **B)** Fibers from another portion of the same yarn seen in (A) have some agglomerated material (arrows). This illustrates the uneven treatment in scouring of the fabrics: yarns covered at crossover points in the weave remain untreated. Bar = 20 μm.

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be seen. Other portions of the yarn, however, have somewhat more agglomerated material on the surface (Fig. 19B).

The 10% Krylon Belt Dressing treated samples exhibit the same non-uniform surface characteristics as many of the other surface treated samples. Specifically, some portions of each yarn have relatively small amounts of surface coating (Fig. 20A), while other areas of the same yarn have a greater amount of coating (Fig. 20B). In Figure 21A, a portion of the yarn treated with a 50% Krylon Belt Dressing solution appears to be relatively free of the coating, whereas the amount of coating on other areas of the same yarn is appreciably greater (Fig. 21B). Very little coating can be seen on one portion of yarn treated with 100% Krylon (Fig. 22A); however, on another portion of the same yarn, so much Krylon is present, that some of the yarn's fibers appear to have been inundated by it (Fig. 22B). Apparently, as the concentration of the Krylon solution is increased, the non-uniformities in the coating thicknesses become increasingly pronounced.

Spectra 900, coated with 50% Krylon Belt Dressing, shows evidence of coating disruption after friction testing (Fig. 23). Surface cracking seen in this photomicrograph may be the result of tearing or wrinkling of the Krylon layer during friction measurements.

Conclusions

Surface modifications could not be accomplished with complete uniformity on Spectra 900 yarns treated with plasma and Spectra 1000 yarns treated with adhesive and dressing solutions.
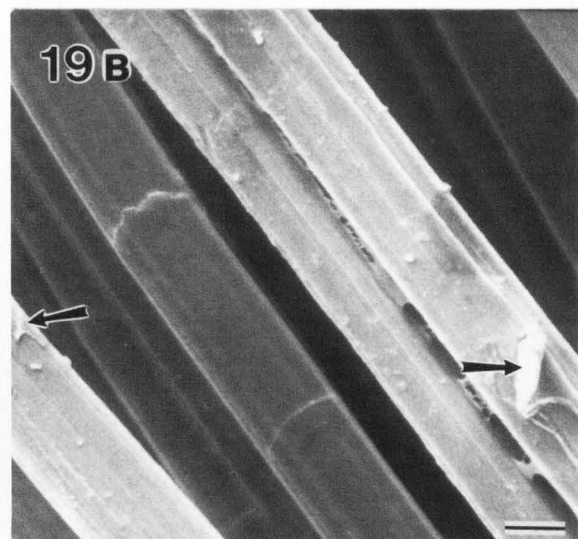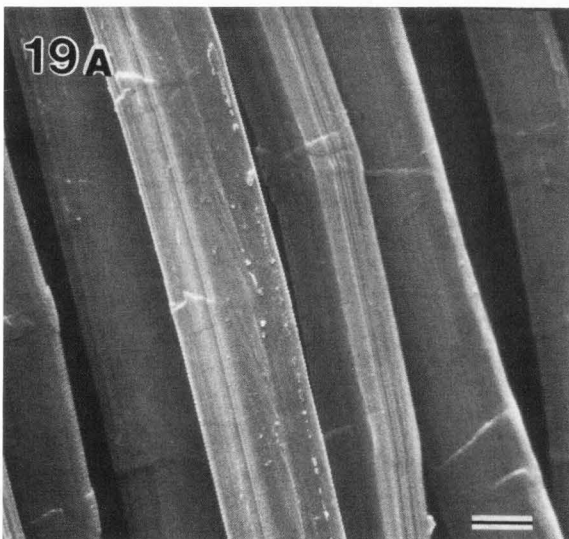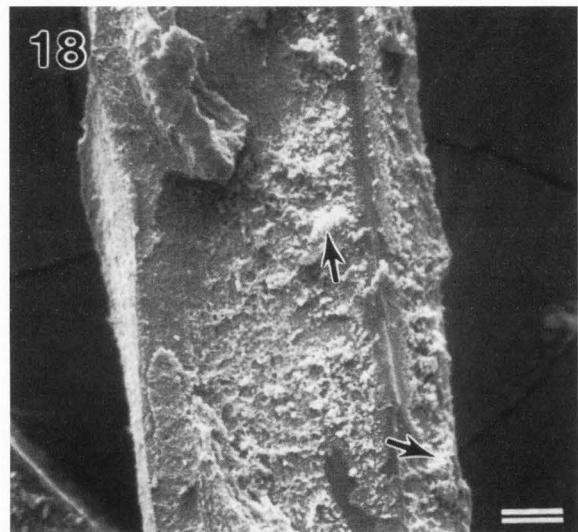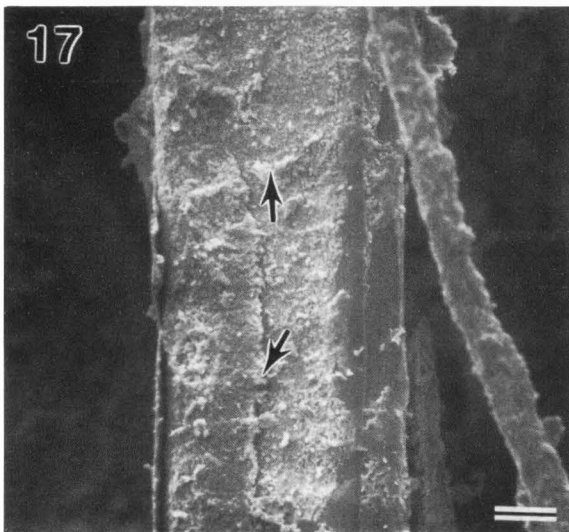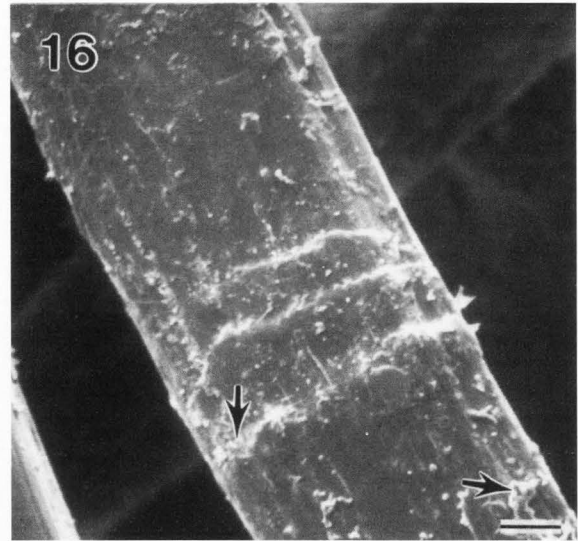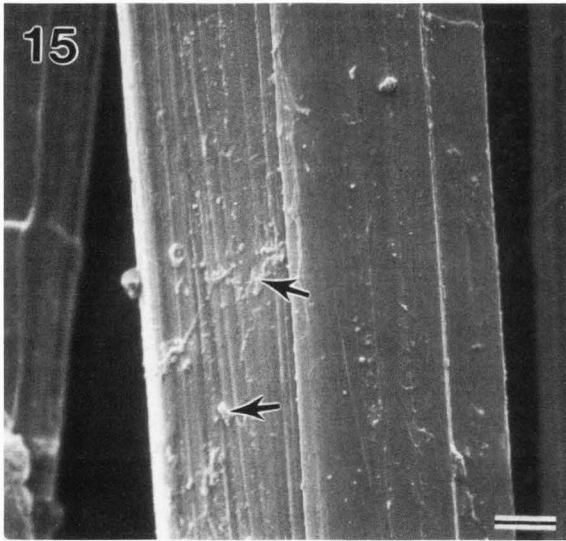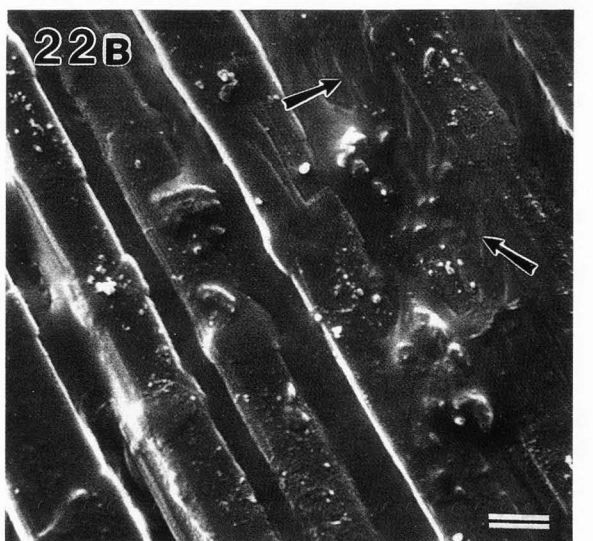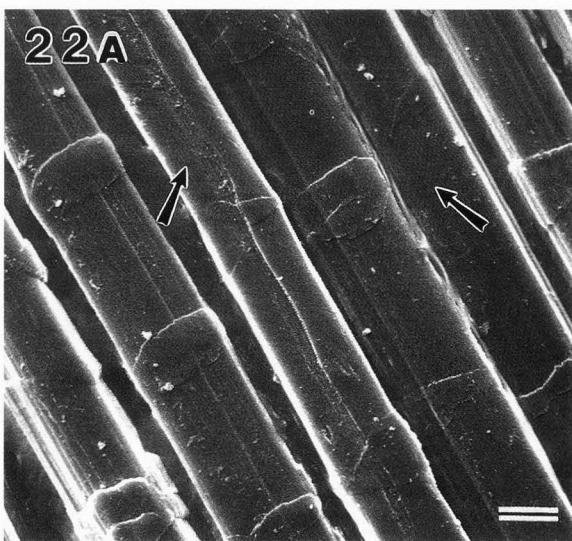
Figure 20. Spectra 1000 treated with 10% Krylon Belt Dressing. **A)** The fibers appear to have a thin coating (C) due to the protection of crossover yarns. **B)** These fibers had a thicker coating (arrows) of belt dressing than in A). Bar = 20 μm.
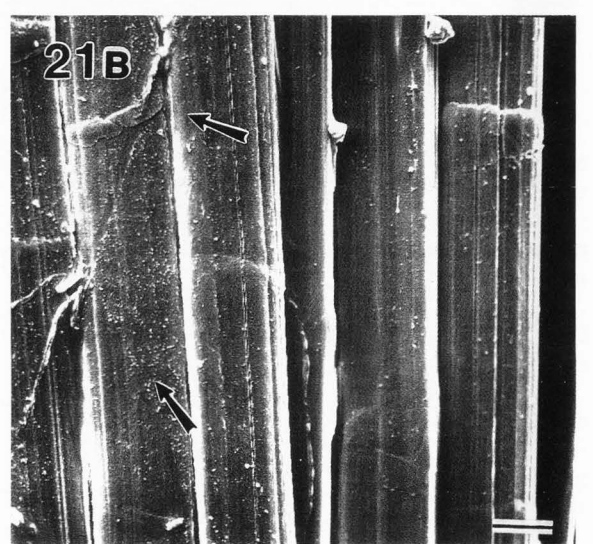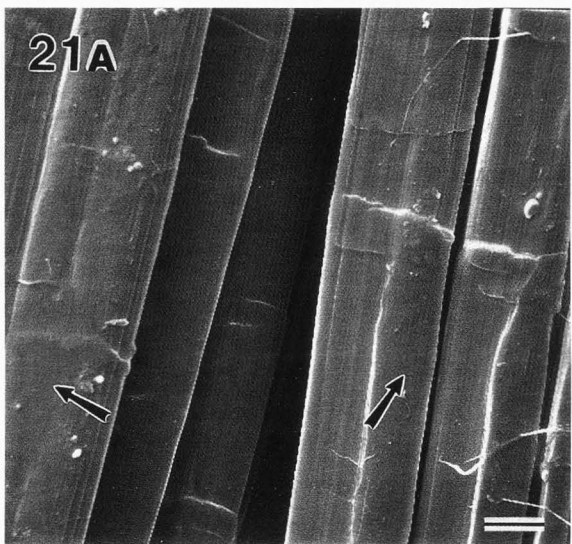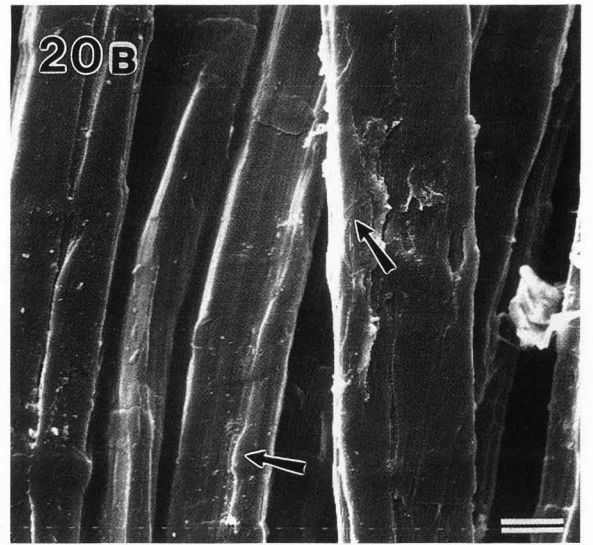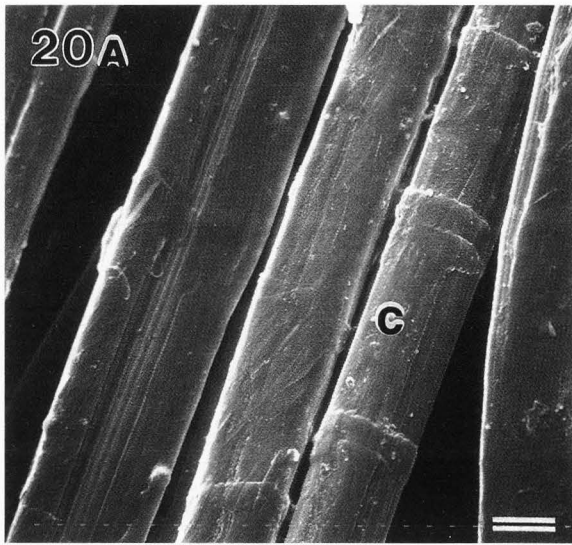
Figure 21. Spectra 1000 treated with 50% Krylon Belt Dressing. **A)** There appears to be a thin coating (arrows) on this portion of the sample. **B)** Another portion of the same sample has a slightly thicker coating (arrows). The uneven treatment is apparently caused by the construction of the weave. Bar = 20 μm.

Figure 22. Spectra 1000 treated with 100% Krylon Belt Dressing. **A)** This portion of the yarn has only a thin layer of Belt Dressing (arrows). **B)** The fibers on this portion of yarn were completely covered by belt dressing (arrows). Bar = 20 μm.

Spectra 900 yarns having the most agglomerated material on the surface were those treated with: **A)** NH$_3$ plasma, TDI and PPG (2007 amu), and **B)** CO$_2$ plasma, TDI and PPG (2007 amu). Treatment with just CO$_2$ plasma caused significant surface etching in the Spectra 900 yarns and contributed to a surface friction value nearly equal to the frictional level of the polymer grafted surface.

Among the Spectra 1000 yarns treated with Krylon Belt Dressing, those treated with a 100% solution were the most thoroughly covered, although significant coverage defects were seen in fabrics treated with all solution concentrations of 10, 50 and 100%. Spectra 1000 yarns that were covered by portions of other yarns (at fabric weave crossover points) were not penetrated by the belt dressing solution. Spectra 900 yarns were also not uniformly treated by plasma exposure, due to the crossover points of the yarn on the spool. In general, this was due to the contact points between fibers which could not be avoided in either the yarns or the fabrics. However, the observed non-uniformities were not extensive enough to prevent the overall effect of increasing a fiber's frictional properties with a variety of treatments. The Spectra 900 yarns that had the most agglomerated material on their surfaces also had the highest friction coefficients, and those Spectra 900 yarns that exhibited the most surface etching also had high friction coefficients.

The highest friction coefficients of the treated Spectra 900 yarns were found in those samples treated with 50% and 100% Krylon Belt Dressing solutions and in those yarns reacted with NH$_3$/TDI/PPG (1012 amu).
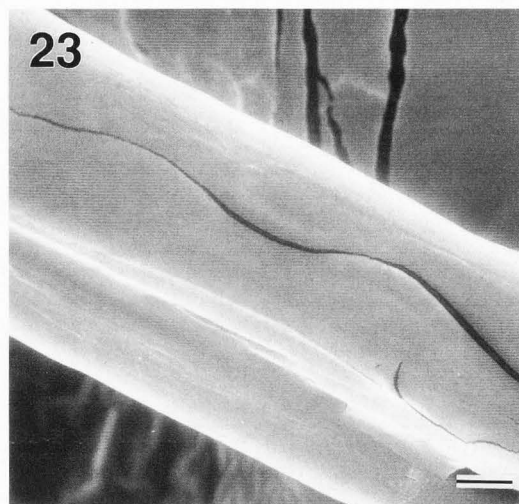
Figure 23. Spectra 900 yarn treated with 50% Krylon Belt Dressing after friction testing. Surface cracking of the coating is apparent for this specimen, but absent from similarly coated samples that were not tested. Bar = 10 μm.

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Discussion with Reviewers

B.A. Wood: Figure 4, 10 and 11 show profuse micro-cracking in a direction perpendicular to the fiber axis. You have described these features as pitting or etching; how can they be distinguished from cracking of the specimen coating resulting from unwanted specimen-beam interactions?

Authors: Every effort was made to minimize beam damage. After the fibers were brought into focus, the image was stored. Since the voltage used (5 kV) was relatively low and the fibers were viewed for only several seconds before image storage and subsequent photography, we are confident that the surface characteristics seen in the photomicrographs were the result of plasma or cleaning treatments, not the result of unwanted specimen-beam interaction.

L.S. Penn: Does the surface etching seen in this work decrease fiber tensile strength, and would such a decrease be expected to reduce ballistic performance of the fabric, thereby counteracting the expected improved ballistic performance brought about by increased fiber-to-fiber friction?

Authors: Surface etching caused by plasma treatments does decrease fiber tensile strength. This paper is a report of work in progress, and at this time, we are measuring fiber tensile strength for treated and untreated samples.

We are also currently conducting ballistic testing of the scoured/treated and scoured/untreated Spectra 1000 fabrics. Preliminary data suggest that the Krylon treated (frictional) fabrics have a lower ballistic penetration resistance than untreated fabric, although both have been scoured, and therefore "pitted."

N.H. Ladizesky: It is seen in this work that treatment with 1% Na_3PO_4 at 60 °C and extraction with acetone on Spectra 1000 fabric produces substantial surface pitting, while the same treatment applied to Spectra 900 yarn results in a lower degree of pitting. In my view, the "missing" parameter is the mechanical energy stored in the fibers during weaving, resulting in a stressed surface with higher susceptibility to attack. A similar situation was recently reported with melt spun and drawn polyethylene fibers, whereupon the woven material without any treatment showed pits, while these were absent on untreated yarns [8].

Authors: This is an excellent explanation of the pitting seen in our samples, and although Spectra is a more highly crystalline, higher strength yarn than the melt spun example, it seems likely that weaving does produce damage susceptible surfaces in the yarns.

J.L. Mead: Long plasma exposure times have been found to degrade the properties of Kevlar fibers [1]. Is this of concern for these fibers? Could you have used shorter plasma times, not see as much pitting of the surface, and still obtain the desired results in surface modification?

Authors: Plasma treatments were conducted by another laboratory; it was determined that the 10 minute exposure time was needed for the Spectra fibers, based on extensive experience with past treatments of Spectra. We are currently evaluating the tensile properties of the fibers. Ballistic testing is also in progress at this time, and no conclusions are available yet.

P.W. Yip: You show that as the concentration of the Krylon solution increases, the non-uniformities of the coating thickness becomes more pronounced. Could it be that as the concentration of the Krylon solution becomes higher, the viscosity of the solution also gets higher, thus harder to spread, penetrate and wet the different fibers in the yarn?

Authors: This is a good explanation of the non-uniformities seen by SEM. The Krylon Belt Dressing is a solution of a rosin-containing compound in 50% petroleum distillates. We dilute this mixture further with 90% and 50% acetone by volume. All solution viscosities are low enough to be aerosol sprayed. We think that the 100% Krylon coated yarns show the most agglomeration due to the high concentration of rosin present.

P.W. Yip: What is the difference between Fig. 11 and Fig. 18?

Authors: The same yarn sample was examined in both photographs. However, different fibers from the same bundle are shown in each case. This comparison shows the non-uniformity of the coating, where the fibers in Fig. 11 show only etching and no PPG (2007 amu) coating. The fiber in Fig. 18 exhibits a significant coating layer that completely covers evidence of the plasma etching.