

Surface Property Modification of Aromatic Polyamides by Microwave Plasmas

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Synopsis

Various microwave plasma treatments were applied to Kevlar in the form of multifilament fabric and single fiber. Plasma-modified fabrics were used to construct two-ply laminates using a triazine resin adhesive. Very significant increases in the bond strength of laminates may be attributed to the plasma treatments; the effectiveness of plasma treatment is best utilized by reducing to a minimum the time interval between plasma exposure and contact of treated substrate with impregnating (adhesive) fluid. Mechanical properties of single Kevlar fibers seem to deteriorate somewhat on plasma exposure, but the cohesive strength of multifilament cloth is enhanced by the same treatments.

INTRODUCTION

The use of "cold" high-frequency plasmas for the surface modification of substrates is a subject of increasing fundamental and applied interest.^{1,2} In our laboratories, that interest has focused principally on a large-volume microwave plasma apparatus (LMP),³ which has been used for purposes ranging from basic studies of plasma polymerization^{4,5} to applications-oriented surface modification, by plasma-formed polymers, of metals⁶ and minerals,⁷ among other substrates.

In the work being reported, LMP treatments have been performed on substrates of aromatic polyamides, notably du Pont Kevlar. The outstanding mechanical properties of Kevlar fibers and of structures based on Kevlar have been well documented, along with some of their shortcomings.^{8,9} The latter aspects have led to procedures such as the surface photoaddition of halo-olefins,¹⁰ intended to increase the polymer's flame and acid resistance. Our concern is with the apparent difficulty of bonding Kevlar with adhesives of the epoxy and triazine type. A comparative study of bond strength has been carried out using, for the most part, laminates based on control Kevlar multifilament cloth and similar structures in which the Kevlar had first been subjected to plasma treatment. The effect of plasma treatment on the inherent mechanical properties of the polyamide is noted more briefly. This article amplifies on results that are the subject of a current patent application.¹¹

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EXPERIMENTAL

Materials. The polyamide substrate was a multifilament cloth originating with Clark-Schwebel Co. and produced from Kevlar-29 fiber. In some instances, single fibers used in our experiments were withdrawn from the cloth. The adhesive (resin) involved in this work was Mobay Chemical Corp. triazine A, in which methyl ethyl ketone was the solvent and zinc octoate the dryer catalyst (at 8% by weight of resin).

Plasma Treatments. All plasma treatments were carried out with LMP apparatus described in detail elsewhere.^{3,4,7,8} The apparatus, operating at a frequency of 2.45 GHz, generated "cold," thermodynamically nonequilibrium plasmas, which may be classified according to the type of vapor and procedure employed:

- (1) Chemically inert plasma, using Ar gas.
- (2) "Grafting" plasmas in which the substrate was first activated in an Ar plasma, then immediately exposed to a polymerizable vapor (e.g., allyl amine, AM) in the absence of plasma.
- (3) Nonpolymerizable reactive-gas plasmas, using N₂, NH₃, and air.
- (4) Polymerizable reactive gas plasmas, in which AM, propane epoxy (PE), and hexamethyldisiloxane (HMDSO) were used.

Each of the above four categories of treatment was applied to Kevlar strips cut to 2.5 × 15 cm dimensions or to single fibers some 15 cm in length. The principal variables in plasma treatment were gas pressure, nominal microwave power, and exposure time. Gas pressures used were in the range 0.2–1.0 torr, power intensities were in the range 100–700 W, and exposure times ranged from 5 to 60 s, in all cases in pulsed exposures of 5 s duration.

The importance of substrate temperature on plasma processes has been discussed in detail.⁵ Throughout this work, Kevlar substrates were maintained at a temperature not exceeding 100°C.

Sample Preparation. In the majority of cases, two-ply laminates of the type Kevlar/triazine resin/Kevlar were employed in this work. To prepare these laminates, plasma-treated Kevlar specimens were contacted immediately upon removal from the LMP reactor with triazine resin. A micrometer-adjusted doctor blade was used to ensure uniform thickness profiles of resin-impregnated cloth. In most cases, wet thickness was controlled to give a total substrate/resin weight ratio of about 60/40. Ratios varying from 80/20 to 50/50 were involved less frequently. In some instances, resin impregnation of Kevlar occurred some time after the plasma treatment. This procedure was followed in order to detect effects of time-dependent changes in the surface properties of plasma-modified Kevlar, a subject discussed further in later sections of this report. In all cases, the wet surfaces of impregnated cloth were contacted to form two-ply laminates, and these were cured by first heating in an air oven for 15 min at 125°C and then by compression molding at 175°C and 1500 psi.

Test Procedures. Bond strength of laminates was evaluated by peel tests, in which the separated ends of laminates were clamped in the jaws of an Instron table model tester, and the specimens were peeled at 180° and a jaw separation rate of 1 cm/min. Because peel strength was found to depend on details of laminate preparation steps, such as the substrate/resin ratio, cooling procedure following compression molding, etc., we have chosen to base interpretation of LMP treatment effects on comparative rather than absolute peel strength data.

Accordingly, in all tests, control laminates using untreated Kevlar were produced under fabrication conditions as closely similar as possible to those used to prepare the LMP-treated structures. The peel strength ratio r , to be used below as a criterion of LMP treatment effectiveness, is defined by

$$r = (UPS)_p / (UPS)_c$$

where UPS designates ultimate peel strength (i.e., at failure of the laminate), and the subscripts p and c identify plasma-treated and control samples, respectively.

Chemical and physical effects of plasma treatment on Kevlar surfaces were studied by electron spin resonance (ESR) and infrared spectroscopy. ESR data were obtained with a JEOL-JES-ME X-band spectrometer. A Perkin-Elmer model 467 infrared spectrophotometer was used in the frustrated multiple internal reflection (FMIR) mode, using a KRS-5 crystal. Surfaces of Kevlar cloth and of peeled laminates were examined by scanning electron microscopy (SEM), using a Cambridge Stereoscan instrument.

RESULTS AND DISCUSSION

Peel Strength of Laminates

Nine different plasma environments, representing categories 1–4 identified above, were chosen for surface conditioning Kevlar cloth. In each experimental sequence, operating variables were set at values specified in Table I, which also shows that peel strength and effectiveness ratios r are average quantities obtained from as many as nine repeats of the same nominal plasma treatment.

The data presented in Table I show that with a few exceptions, to be considered below, plasma treatments are capable of strongly enhancing the bond strength of Kevlar/resin laminates. Inert gas plasmas of type 1 appear to influence bond strength only mildly. These are in essence similar to the familiar CASING technique¹² and cannot be expected to modify chemically the Kevlar substrate in a very substantial manner. As is shown subsequently, Ar plasma can actually weaken the tensile strength of individual Kevlar fibers, hence the ~10% increase in peel strength of the two-ply structure is considered to be due to significantly enhanced bonding at the plasma-treated Kevlar/resin interface. This supposition is borne out qualitatively in that failures in control laminates were always adhesive, while in many of the structures using LMP-treated Kevlar the failure mode was cohesive (tearing of the laminate or fracture in the resin layer).

Plasmas of types 2–4, all capable of producing significant physical and/or chemical modification in the polymer substrate, result in bond strength which is frequently more than 50% above the performance of control laminates, as shown in column II, Table I. In sequence 9a, using HMDSO, well over twice the peel strength is developed in the Kevlar/resin laminate. The plasma polymerization of this organosilicone monomer has been studied extensively^{4,5}; evidently, in the present context, it appears to be a particularly promising “coupling” agent for the Kevlar/triazine system.

Experimental sequences 6 and 9 in Table I illustrate the effect of the time interval between plasma treatment and contact with the impregnating adhesive resin on bond strength in the two-ply laminates. The point is further illustrated

TABLE I
Summary of Bond Strength Performance of Kevlar Laminates

No.	Category	Plasma	P, torr	Conditions		S	UPS treated, g/in.	UPS control, g/in.	r
				P(W) ^b	t ₁ , (s) ^c				
1	1	Argon (Ar)	0.8	100	30	4	720	650	1.10
2	2	Ar + Allylamine graft	0.8	200	30	2	1050	700	1.50
3 ^a	2	Triazine + Ar	0.37	300	35	3	470	380	1.24
4	3	NH ₃	0.5	350	30	3	730	550	1.33
5	3	Air	0.5-0.7	400	30	4	700	350-500	1.40-1.84
6a	3	N ₂	0.5	500	30	2	1100	600	1.83
6b	3	N ₂	0.5	200	35	1	625	390	1.60
6c	3	N ₂	0.6	300	30	9	800	625	1.28
7	4	Allylamine	0.2	500	30	7	650	800	0.81
8	4	Propane epoxy	0.25	400	45	2	625	465	1.34
9a	4	HMDSO	0.2	500	30	3	1320	600	2.20
9b	4	HMDSO	0.2	700	30	2	625	620	1.01
9c	4	HMDSO	0.2	700	30	2	425	620	0.69

^a Kevlar was triazine dipped, then exposed to Ar plasma. Lamination done immediately following plasma treatment.

^b Nominal power (power absorbed by plasma was somewhat less).

^c t₁ = Duration of plasma treatment.

^d t₂ = Elapsed time after treatment, when sample was impregnated. Normally impregnation followed treatment within a few minutes.

in Figure 1, where the r factor is plotted against that time interval. Plasmas of both types 3 and 4 produce bond strength enhancement which decreases significantly with the time interval. The decrease seems more pronounced in the HMDSO set than in N_2 . In each case, it is presumably attributable to surface radical recombination and/or surface oxidation by atmospheric oxygen, as suggested by ESR data discussed below.

Finally, in this part of the discussion, we note that the choice of variables for the LMP treatments described in this work was based primarily on convenience of operation. Thus, the reported peel strength enhancements for any of the sequences described in column 3 of Table I are typical but not necessarily optimum performance levels. On the other hand, the fabrication procedures were developed to maximize the peel strength of untreated Kevlar laminates. The reported results therefore may be viewed also as indication of strong enhancement, by plasma processes, of absolute bond strength attainable in Kevlar/resin structures of this type.

Mechanical Properties of Plasma-Treated Kevlar

As has already been noted above, bond strength enhancement due to plasma treatment of Kevlar must be viewed in the light of evidence, given in Table II, that Ar plasmas modify the stress/strain behavior of single fibers as well as of multifiber fabric. Clearly, the load at break for both types of specimens decreases appreciably with the duration of plasma exposure. At the same time, however, the elongation at break is increased in the fabric, though not in the single fiber, remaining for the latter in the range 2–3%, in agreement with the results of Kopopasek and Hearle.⁸ In Table II, we have reported the work requirement for failure (column headed Area parameter), estimated by integrating under the stress-strain curve. For single fibers, this is reduced by Ar plasma exposure, but a slight increase is observed for the multifilament fabric. Previously cited work⁸ shows that in Kevlar structures interfilament cohesion tends to be weak, an artifact of the characteristic morphology of single Kevlar fibers.⁸ We suggest

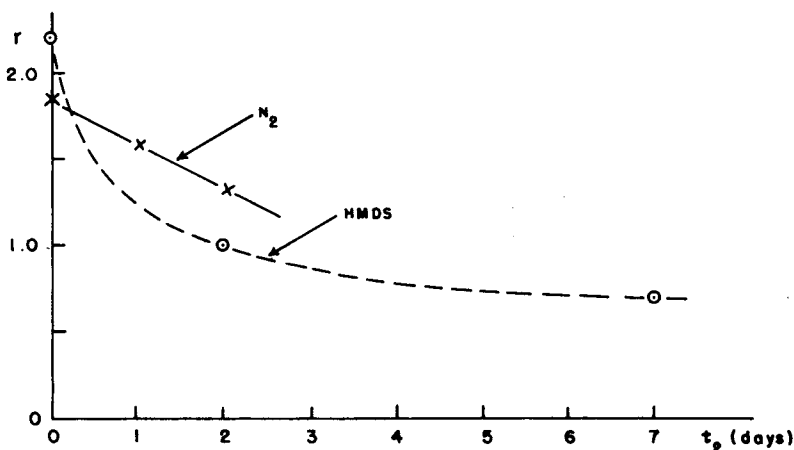


Fig. 1. Variation of peel strength ratio with interval between plasma treatment and exposure to adhesive.

TABLE II
Effect of Ar Plasma Treatment on Kevlar Tensile Properties

Sample	Multifiber fabric		Single fiber	
	Load at break, kg	Area parameter, cm ²	Load at break, kg	Area parameter, cm ²
Control	52 ± 7	6.10	1.64 ± 0.2	2.15
Ar treatment(s)				
60 s	30 ± 5	6.15	—	—
30 s	41 ± 6	6.45	1.05 ± 0.1	1.20
15 s	—	—	1.50 ± 0.2	1.85

that Ar plasma treatment enhances interfiber cohesion, with the net result of a more balanced state of mechanical properties. The apparent enhancement of interfiber cohesion undoubtedly contributes to the improved performance of two-ply laminates, discussed above.

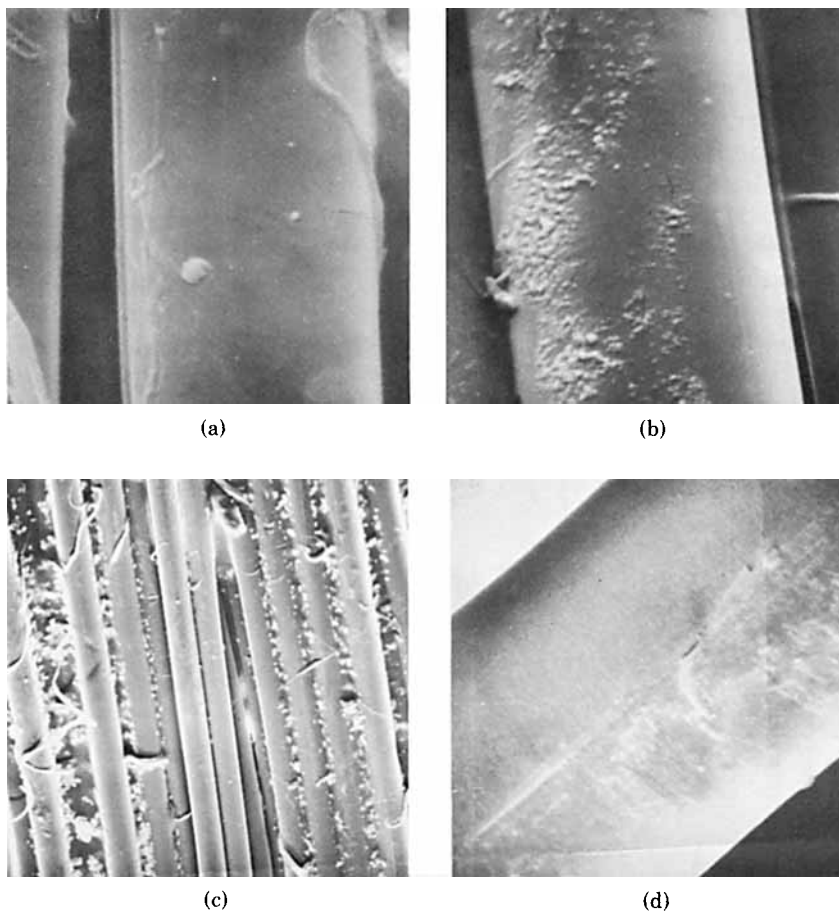


Fig. 2. Scanning electromicrographs of Kevlar: (a) Untreated fiber (5000 \times); (b) 30 s air plasma (5000 \times); (c) 30 s air plasma—cloth sample (500 \times); (d) HMDSO plasma (7000 \times).

Analytical Results

Electron microscopy clearly reveals the existence of surface modifications arising from plasma treatment, typical SEM data being shown in Figure 2. The control single fiber [Fig. 2(a)] shows an essentially smooth surface, with some irregularities similar to those reported by Konopasek and Hoarle.⁸ Figure 2(b) shows surface roughening due to an air plasma (type 3), and possibly attributable to surface oxidation of the Kevlar. A similar effect is observed in a multifiber Kevlar sample following air-plasma treatment, as shown by the lower magnification (500 \times) datum in Figure 2(c). Finally, a type 4 plasma, in this case HMDSO treatment, produces a fiber [Fig. 2(d)] on which a thin layer of plasma polymer may be discerned.

The presence of HMDSO plasma-polymer on Kevlar, suggested above and resulting in very significant enhancement of bond strength in Kevlar/resin structures, is further documented by FMIR infrared spectra. Figures 3(a) and 3(b) compare spectra for untreated control Kevlar and for HMDSO plasma-treated Kevlar, respectively. They are seen to differ appreciably, the following features being particularly notable:

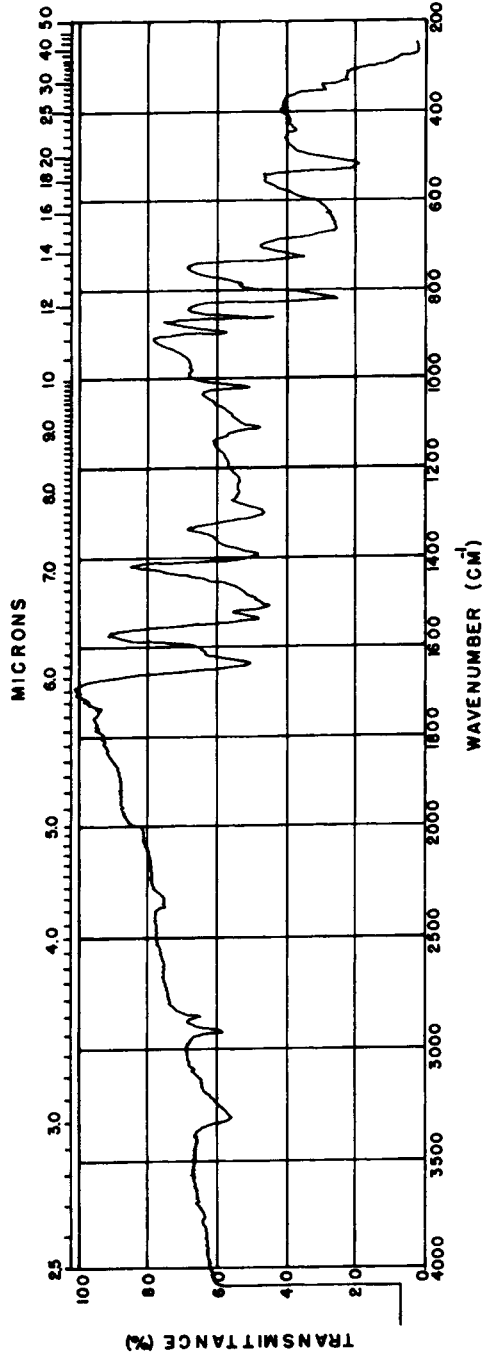
(1) The 3300 cm^{-1} absorption of Kevlar, due to $\nu(\text{N-H})$ vibrations, clearly seen in Figure 3(a), is not visible in Figure 3(b).

(2) Strong absorption bands only seen in Figure 3(b) at 1260, 1020, and 800 cm^{-1} may be assigned to vibrations of Si-CH₃, Si-O-Si, and Si-C groups, respectively. The spectrum of Figure 3(b), in fact, shows numerous similarities to spectra of plasma-polymerized organosilicone films on metal and glass substrates discussed in greater detail elsewhere.^{4,5} There can be little doubt, therefore, that an essentially identical plasma-polymer is also deposited on Kevlar.

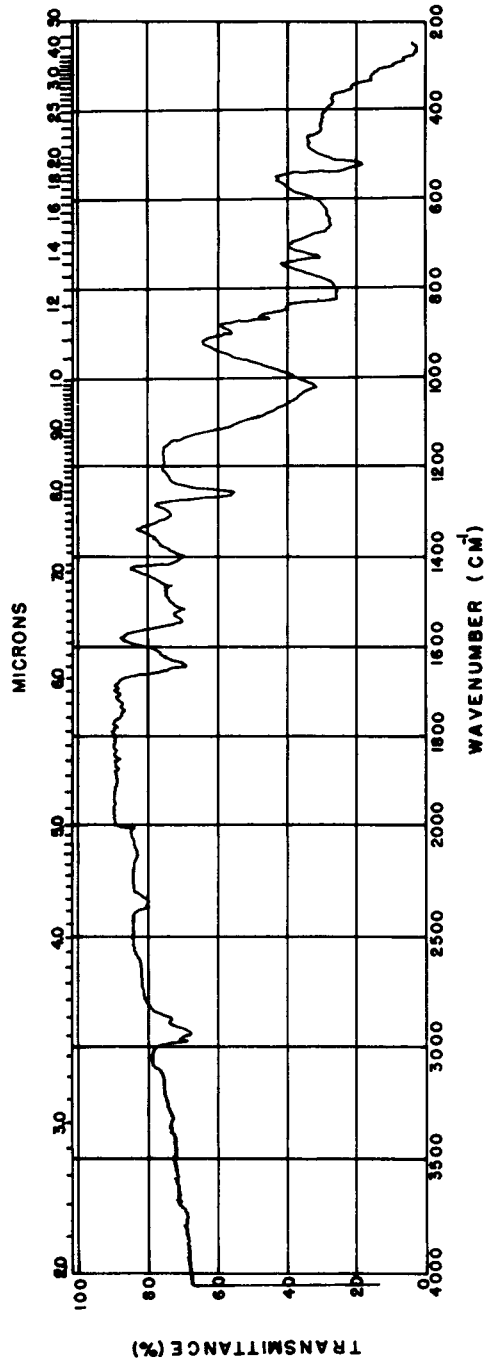
Finally, ESR spectra are presented in Figure 4 in order to amplify on the time-dependent decay of plasma treatment effectiveness, notably where plasmas of type 3 are concerned. The comparison of Figure 4 involves untreated Kevlar and substrates subjected to N₂ and CO₂ plasmas (the latter gas was not used in evaluations of bonding properties). Clearly, the indicated plasma treatments result in ESR spectra which differ significantly from the "control" spectrum when the ESR evaluation follows immediately a given plasma treatment. The effect may be assigned to the presence of a variety of radical species on the plasma-exposed Kevlar surface. ESR spectra obtained after the samples had been exposed to the atmosphere for 24 hr show a tendency to revert back to the "control" spectrum. This tendency is consistent with the recombination or oxidation of surface radicals, as suggested earlier in this report.

CONCLUSIONS

We conclude that the surface structure of aromatic polyamides, exemplified by Kevlar, is significantly modified by "cold" microwave plasmas. Each of four plasma types is capable of enhancing the bond strength of Kevlar/triazine structures, as shown by increases in the peel strength of two-ply laminates. While the ultimate tensile strength of Kevlar fibers may in some cases be somewhat decreased by certain plasma treatments, these treatments also enhance



(a)
Fig. 3. (a) FMIR-infrared spectrum for untreated Kevlar. (b) FMIR-infrared spectrum for Kevlar, following 90 s HMDSO plasma.



(b)
Fig. 3. (Continued from previous page.)

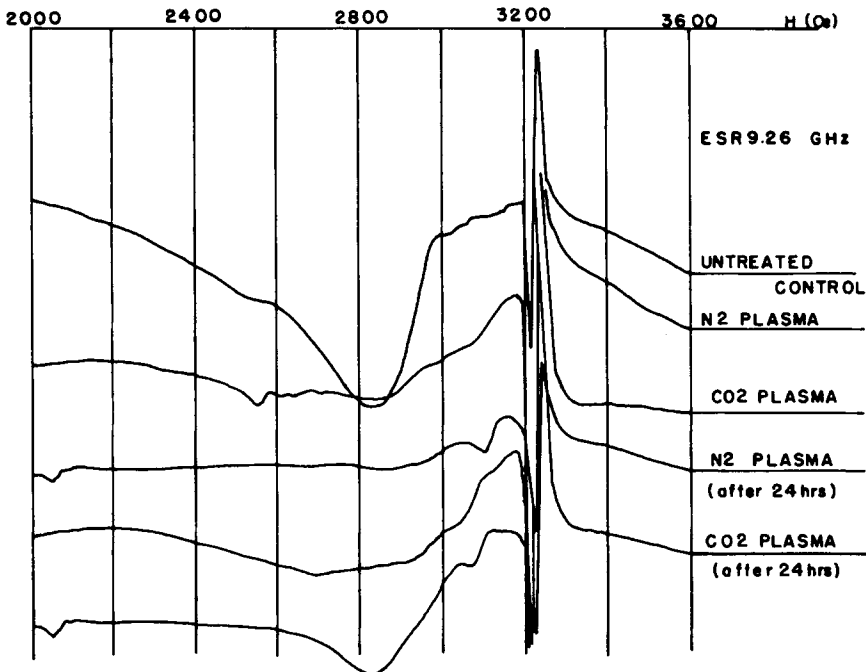


Fig. 4. X-Band ESR spectra of untreated and plasma-treated Kevlar. Plasma treatments in N_2 and CO_2 were 30 s duration. Region near 3200 Oe corresponds to $g = 2$.

cohesive bonding between individual fibers, thereby influencing positively the mechanical property balance of multifilament structures.

This work was supported in part by grants from the Natural Sciences and Engineering Research Council, Canada. The assistance, in experimental portions, of Drs. J. Dib and A. M. Wrobel is gratefully acknowledged, as are useful discussions held with E. Sacher.

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Received September 18, 1980

Accepted December 24, 1980