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Continuous Plasma Treatment and Resin Impregnation of a High-Strength Fiber Material

By J. S. Tira

Published September 1983

Final Report

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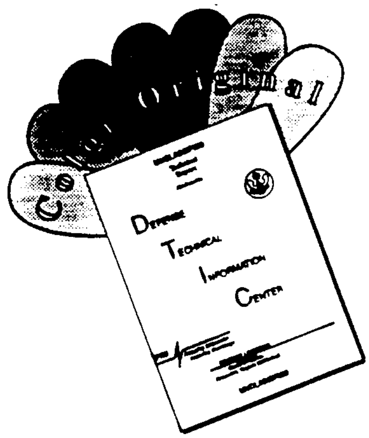

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CONTINUOUS PLASMA TREATMENT AND RESIN IMPREGNATION OF A HIGH-STRENGTH FIBER MATERIAL

By J. S. Tira

Published September 1983

Final Report
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Technical Communications
Bendix Kansas City Division

CONTINUOUS PLASMA TREATMENT AND RESIN IMPREGNATION OF A HIGH-STRENGTH FIBER MATERIAL

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A system was developed for the continuous plasma treatment of fibrous, reinforcing materials used in composites. Data are presented on the removal of moisture from Kevlar 49 Aramid by the use of argon and zero air plasma. Adhesion test results with plasma-treated, unidirectional Kevlar 49/epoxy laminates showed an improvement in adhesion ranging from 1.4 to 3.7 times, as reported by the plasma treatment effectiveness parameter. Limited tensile testing of resin-impregnated yarn showed no catastropic failure from plasma treatment.

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SUMMARY

A system was developed for the continuous plasma treatment of fibrous, reinforcing materials used in composites. It was demonstrated that moisture could be removed from Kevlar 49 fibers by passing them through the continuous plasma. Adhesion test results with plasma-treated, unidirectional Kevlar 49/epoxy laminates showed an improvement in adhesion ranging from 1.4 to 3.7 times, as reported by the plasma treatment effectiveness parameter. Limited tensile testing of plasma-treated, resin-impregnated yarn showed no catastropic failure as a result of plasma exposure.

DISCUSSION

SCOPE AND PURPOSE

Kevlar 49 Aramid is an organic fiber (aromatic polyamide) with high tensile strength. It has become popular for a variety of applications ranging from body armor to aircraft structural parts. However, it is well known that the adhesion of a resin binder to the Kevlar filaments is poor because of poor wettability of the Kevlar surface. This condition may be the result of three distinct conditions: absorbed moisture on the surface, sizing or contamination, and low surface energy.

Plasma treatment is a common method of improving surface adhesion,[1] and has been used to improve wettability of fibers. Briefly, the technique consists of reacting an ionized gas with the surface in a controlled environment to remove absorbed water, dissociate surface sizing and contaminant, and create bonding sites.

In order to make plasma treatment practical for a large quantity of Kevlar fiber, yarn, or roving, it was decided that a continuous plasma operation was necessary. Additionally, because of the characteristic of Kevlar to absorb moisture, it was decided to have the resin- or binder-impregnating operation performed as soon after plasma treatment as practical. Once the continuous plasma and impregnating were determined operational, 180° peel or adhesion specimens were prepared and tested to evaluate resin adhesion to Kevlar reinforcement.

ACTIVITY

Moisture Analysis of Kevlar 49 Yarn

Previously reported work has shown that ashed samples of Kevlar 49 contain sodium sulfate (Na_2SO_4), a known desiccant.[2] When present on the fiber, sodium sulfate may contribute to water absorption.

The moisture content of one lot of off-the-shelf Kevlar 49 was determined by heating samples at different temperatures in a Du Pont 902 Moisture Analyzer and determining the moisture removed. As the test temperature increased, a larger moisture content value was reported until a moisture content of 2.86 weight percent was obtained.

Other samples of Kevlar 49 were conditioned in dry flowing nitrogen gas at 50°C for various times ranging from 1 to 6 hours. As the exposure time increased, the moisture content decreased. After exposure to the 50°C temperature in flowing nitrogen gas for 6 hours, the moisture content had been reduced to 0.20 weight percent.

Another test was performed to demonstrate how the Kevlar 49 absorbed moisture in a 50 percent relative humidity (RH). After 5 hours, the moisture content had increased to 1.15 weight percent. These data and other intermediate time and temperature data on the effects of moisture on Kevlar 49 are reported in Table 1.

Moisture Analysis of Plasma-Treated Kevlar 49 Yarn

The next point of interest was to determine whether moisture could be removed from Kevlar 49 yarn by plasma treatment. Samples of yarn were subjected to argon and nitrogen plasma at different operational conditions using an International Plasma Corporation plasma system, Model 1105B-1640ST. Samples were immediately analyzed after treatment using the Du Pont Moisture Analyzer. The results are reported in Table 2. Using a constant time period in the chamber, but increasing the power level, the moisture content decreased with increasing power.

Design and Layout of a Continuous Plasma System

A continuous system was designed to operate the plasma system while continuously moving Kevlar 49 yarn through the chamber; resin impregnate the treated yarn immediately after it comes out of the plasma chamber and before it is exposed to any potentially contaminating or moisture laden environment; and wrap plasma-treated and resin-impregnated Kevlar 49 on a suitable fixture for making test specimens.

Figure 1 is a schematic of the plasma system with controlled environmental chambers at both ends. The resin impregnation tank is located inside the exit chamber. The plasma system generates radio-frequency gaseous plasma and is comprised of the following:

1. A source of RF electrical power,

2. A means of coupling the RF power into the treatment chamber,

3. A system of gas handling components to control the flow of reactant plasma gases, and

4. A glass reactor chamber approximately 101.6 cm long and 15.2 cm in diameter. The plasma chamber is shielded by a metal case and screen.

Table 1. Moisture Analysis of Kevlar 49 Yarn

Analysis	Moisture Content (Weight Percent)
Removable Moisture Content at Test Temperature (°C)	
25	0.9
50	1.77
120	2.85
200	2.86
Removable Moisture Content Remaining Versus Conditioning Time at 50°C in Flowing Dry Nitrogen for Exposure Time (h)	
1	0.57
2	0.30
3	0.24
4	0.19
5	0.22
6	0.20
Moisture Content Increase with Time (h) in 50 Percent RH*	
1	0.72
2	0.87
3	0.90
4	1.16
5	1.15

*After 17 h in dry nitrogen, followed by various times in a 50 percent RH environment.

Environmental Chambers

Two environmental chambers were constructed of Plexiglas (Rohm and Haas Co., Philadelphia) using solvent bonding and mechanical screws. One chamber is located at the entrance of the plasma reactor and contains the spool of untreated Kevlar 49 yarn or roving. The environmental chamber on the exit side is larger, containing the epoxy-impregnating tank resin for the continuous impregnating operation. Both chambers are supported on benches. Access ports have been cut into each chamber to allow easy access for working inside.

Figures 2 and 3 are photographs of the two environmental chambers. Each chamber is equipped with an adjustable pressure regulator

Table 2. Moisture Content Remaining After Plasma Treating Kevlar 49 Yarn Using the Static Plasma Process

Power (W)	Time (min)	Pressure (N/m^2)	Moisture Content (Weight Percent)
After Argon Plasma Exposure			
5	15	26.6	1.13
20	15	26.6	0.72
50	15	26.6	0.60
After Nitrogen Plasma Exposure			
50	10	66.4	0.88
75	10	66.4	0.54
100	10	66.4	0.43
125	10	66.4	0.38
150	10	66.4	0.36
175	10	66.4	0.41

for the in-coming gas, a pressure relief valve which will open if an excessive gas pressure builds up in the chamber, and a vacuum relief valve in case an excessive vacuum occurs within the chamber. The two relief valves were installed as a safety precaution. Both environmental chambers have a slight positive pressure using the same gas used in the plasma reactor chamber.

Fiber Pass-Throughs

In order to pass the Kevlar 49 fiber into and out of the reactor chamber and keep a reduced pressure in the chamber, some type of pass-through was needed. This was accomplished using tungsten carbide wire drawing dies. They are available in different orifice sizes which made it advantageous for running different denier sizes of Kevlar 49 yarn and roving. The tungsten carbide die is a very hard, highly polished surface fluted on one side. The dies were made interchangeable by placing an O-ring around the perimeter, which creates a snug fit in the environmental chamber wall. By varying the orifice size with the Kevlar denier size, the amount of gas bleed-in to the plasma reactor chamber can be controlled. Figures 4 and 5 show Kevlar 49 yarn entering and leaving the plasma reactor chamber through these orifices.

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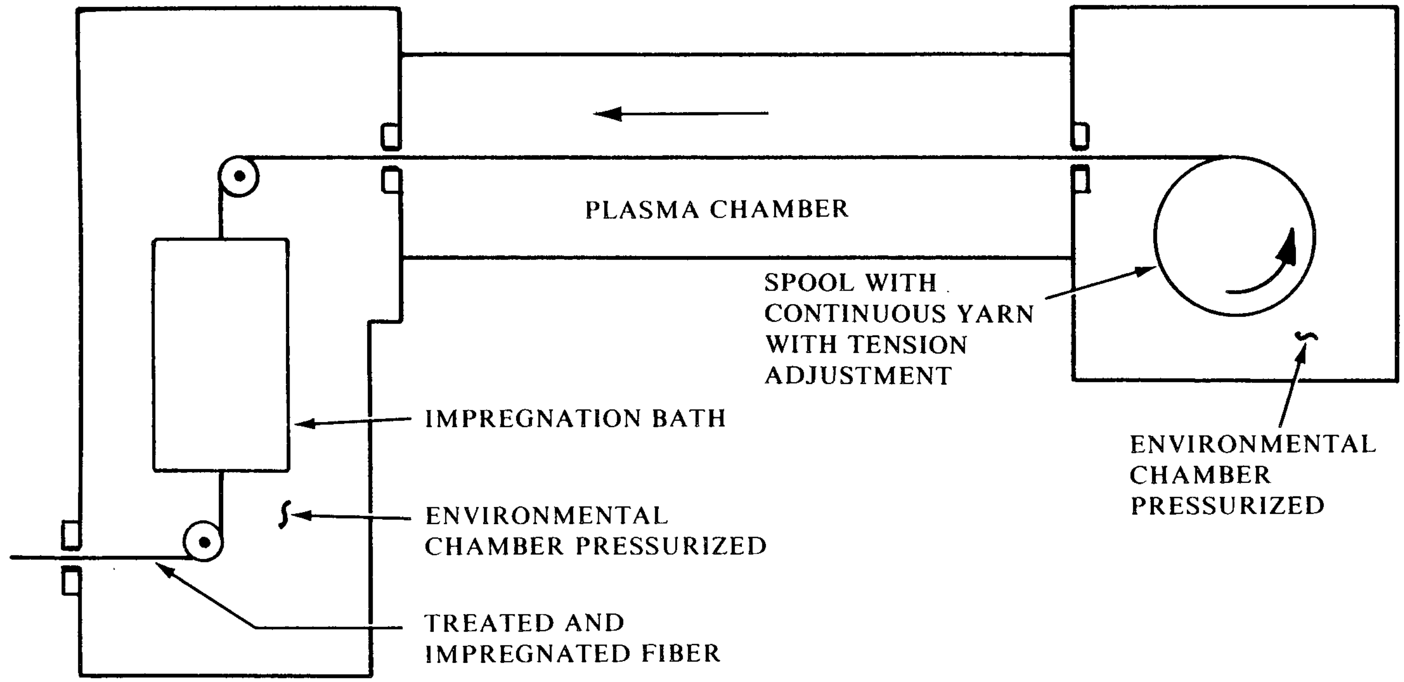

Figure 1. Schematic of Continuous Plasma System

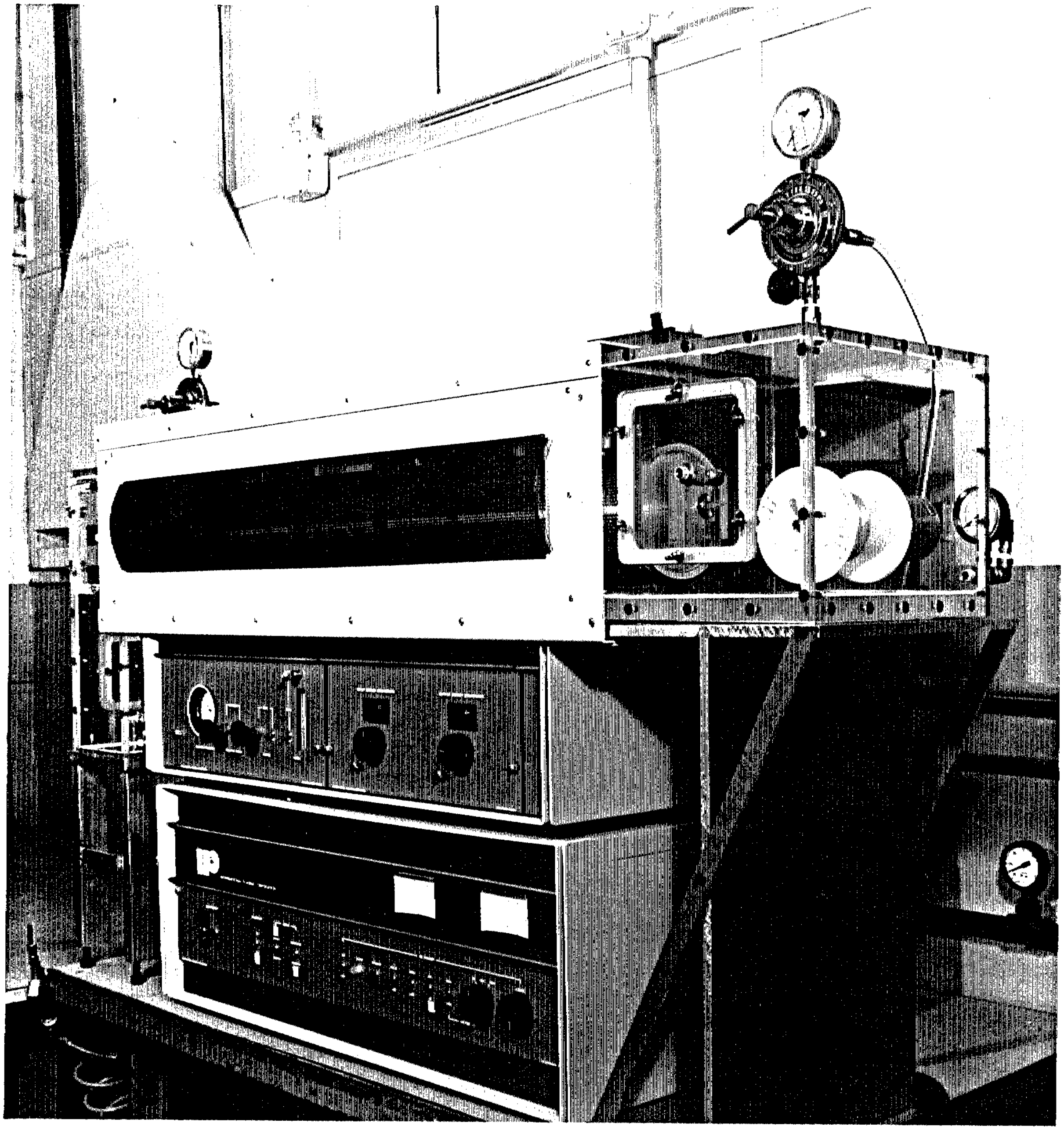

Figure 2. Environmental Chamber on Entrance Side of Plasma Reactor

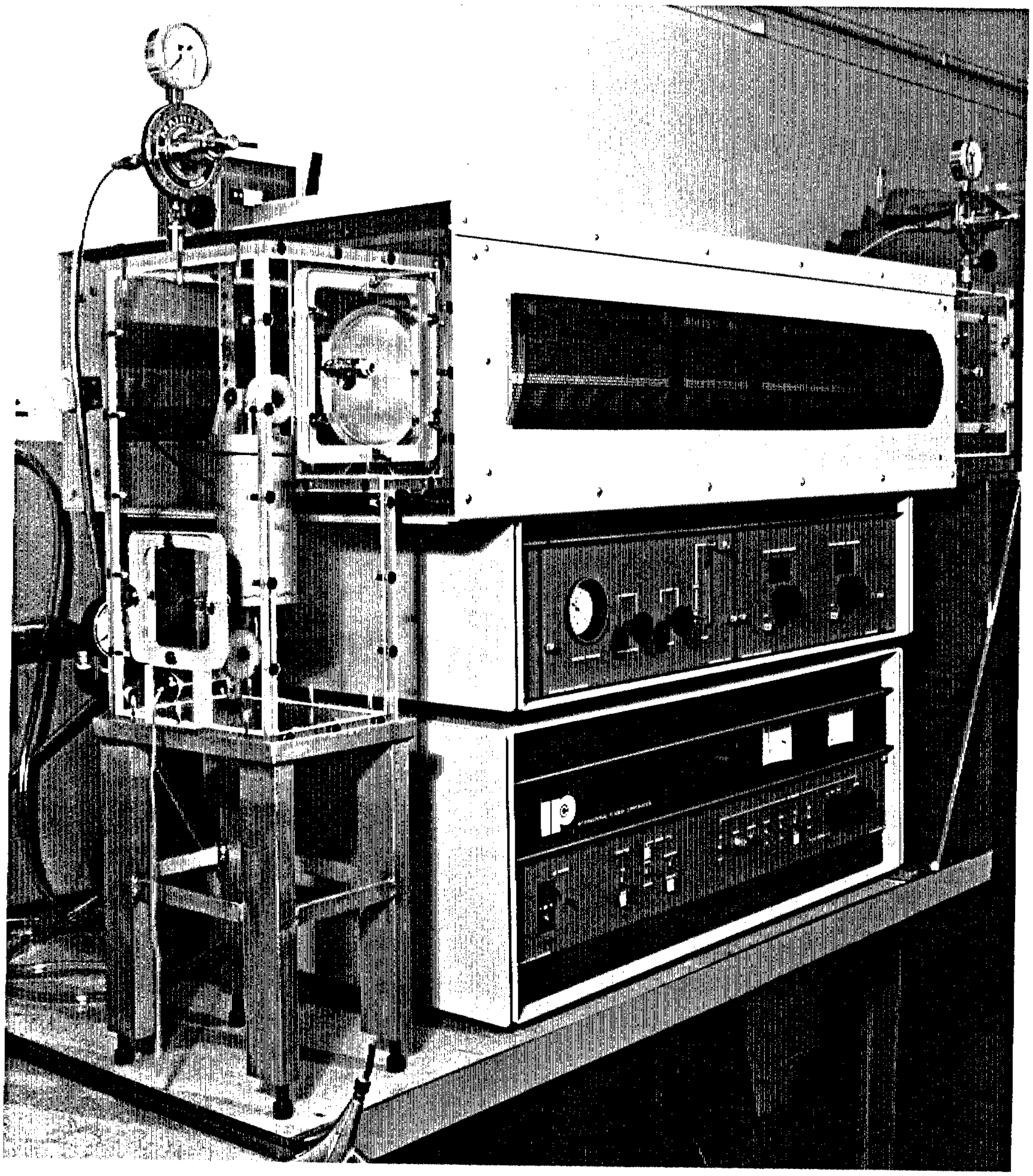

Figure 3. Environmental Chamber on Exit Side of Plasma Reactor

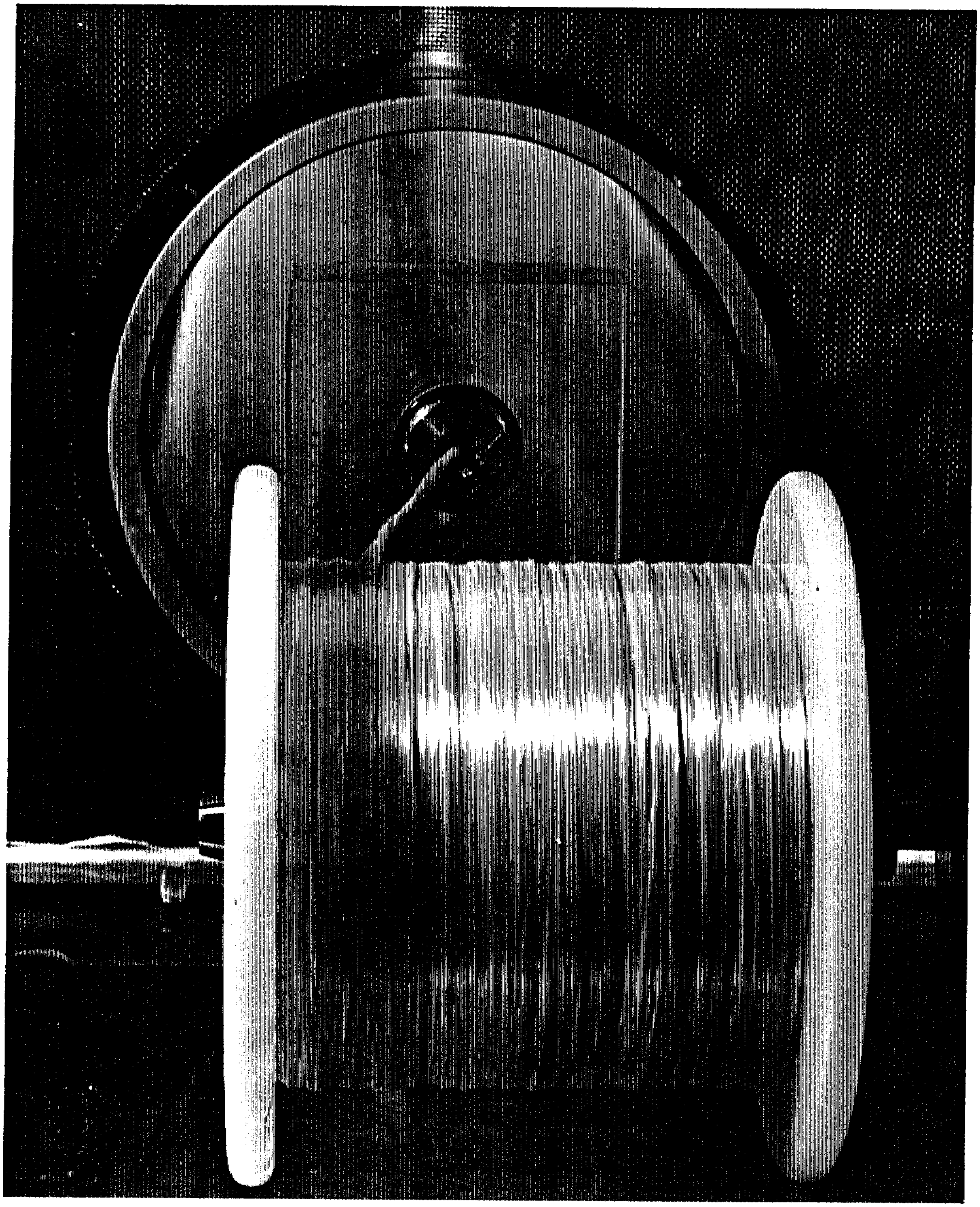

Figure 4. Kevlar Yarn Entering Plasma Reactor Chamber Through an Orifice

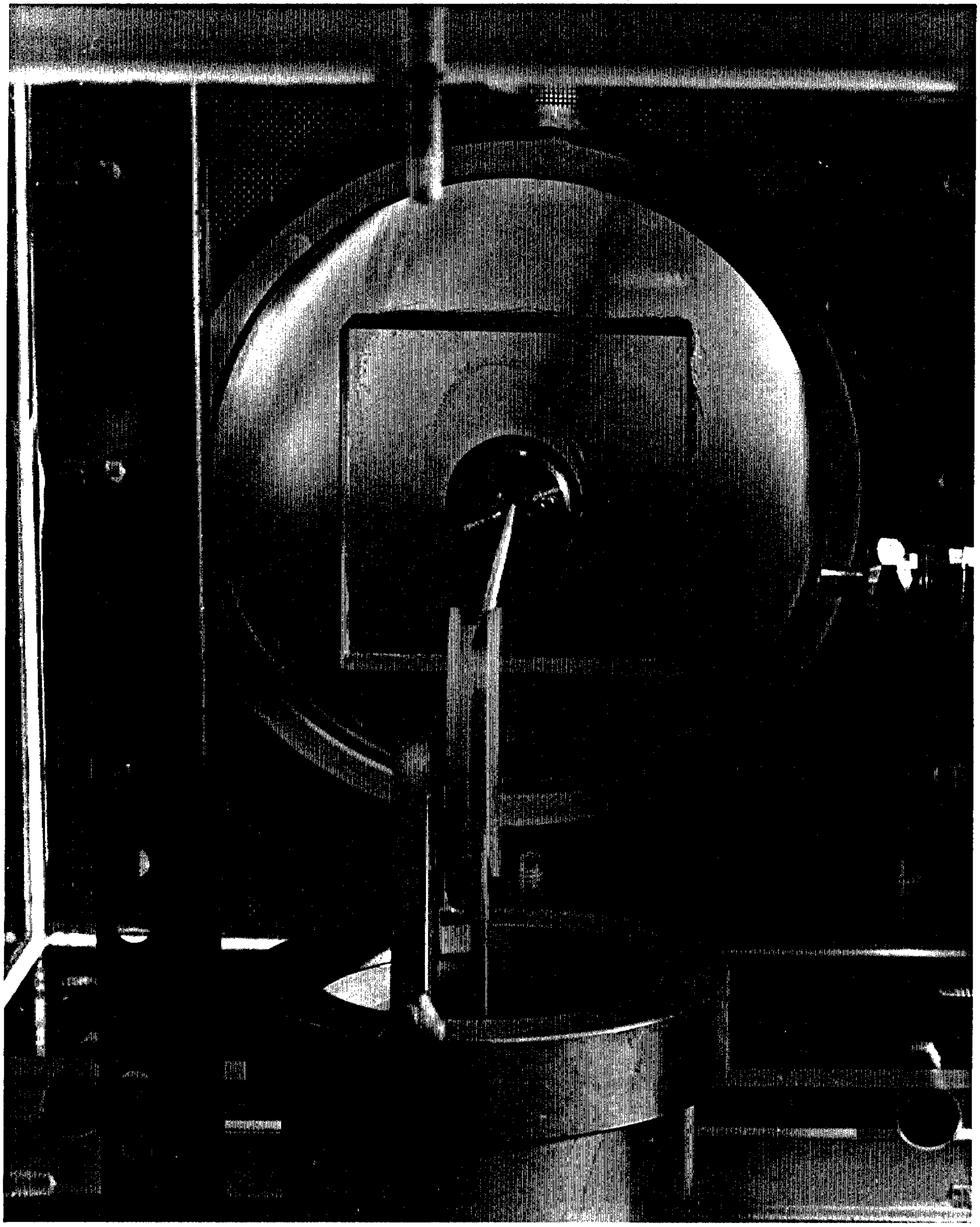

Figure 5. Kevlar Yarn Leaving Plasma Reactor Chamber Through an Orifice

Quartz Windows

When the plasma system is operating, the vacuum drawn in the reactor chamber pulls the two environmental chambers against a rubber gasket at both ends of the reactor. This exposes two Plexiglas faces directly to the plasma environment once a plasma is struck. After a period of time the Plexiglas surfaces became etched and very small cracks appeared internally. In order to stop this reaction, a quartz window was attached to each environmental chamber to interface with the plasma reactor chamber and to avoid a catastrophic failure of the environmental chambers.

Resin-Impregnating Bath

After coming out of the plasma chamber, the cleaned and activated Kevlar 49 yarn goes around a nylon pulley and into an epoxy resin-impregnating bath where it is wetted with resin between the filaments. Any excess resin is wiped off the Kevlar by a silicone squeegee as it comes out the bottom of the resin container.

Figure 6 shows the Kevlar yarn coming out of the plasma reactor chamber, through the impregnating bath, and out the environmentally controlled chamber as a resin-impregnated, continuous yarn ready for making parts or specimens.

Figures 7 and 8 show the continuous plasma system in operation. Kevlar 49 roving, which has been plasma-treated and resin-impregnated, is being wrapped on a variable speed mandrel to make fiber tensile test specimens.

Operating Procedure

The operation of the continuous plasma system works on the principle that the two environmental chambers are pressurized with the pre-selected gas which will be used in the plasma reactor chamber. This gas will bleed through the two orifices into the reactor chamber. A vacuum pump removes the air in the reactor chamber, and it is replaced by the selected gas. The radio frequency (RF) power is turned on and a plasma is developed. The selected power level is then tuned. Figure 9 presents the operating procedure for pressurizing the environmental chambers and obtaining a plasma.

Tensile Strength of Plasma-Treated Kevlar 49 Yarn

Tensile testing was performed on plasma-treated and resin-impregnated Kevlar 49 yarn, type 968, denier 380 to determine whether plasma treatment degraded the yarn. The resin used to impregnate the yarn was Dow Chemical DER 332, a DGEBA epoxy with Jeffamine T403 hardener, an aliphatic polyether triamine (100/45 parts by weight). Specimens were wrapped on the mandrel shown in Figure 8.

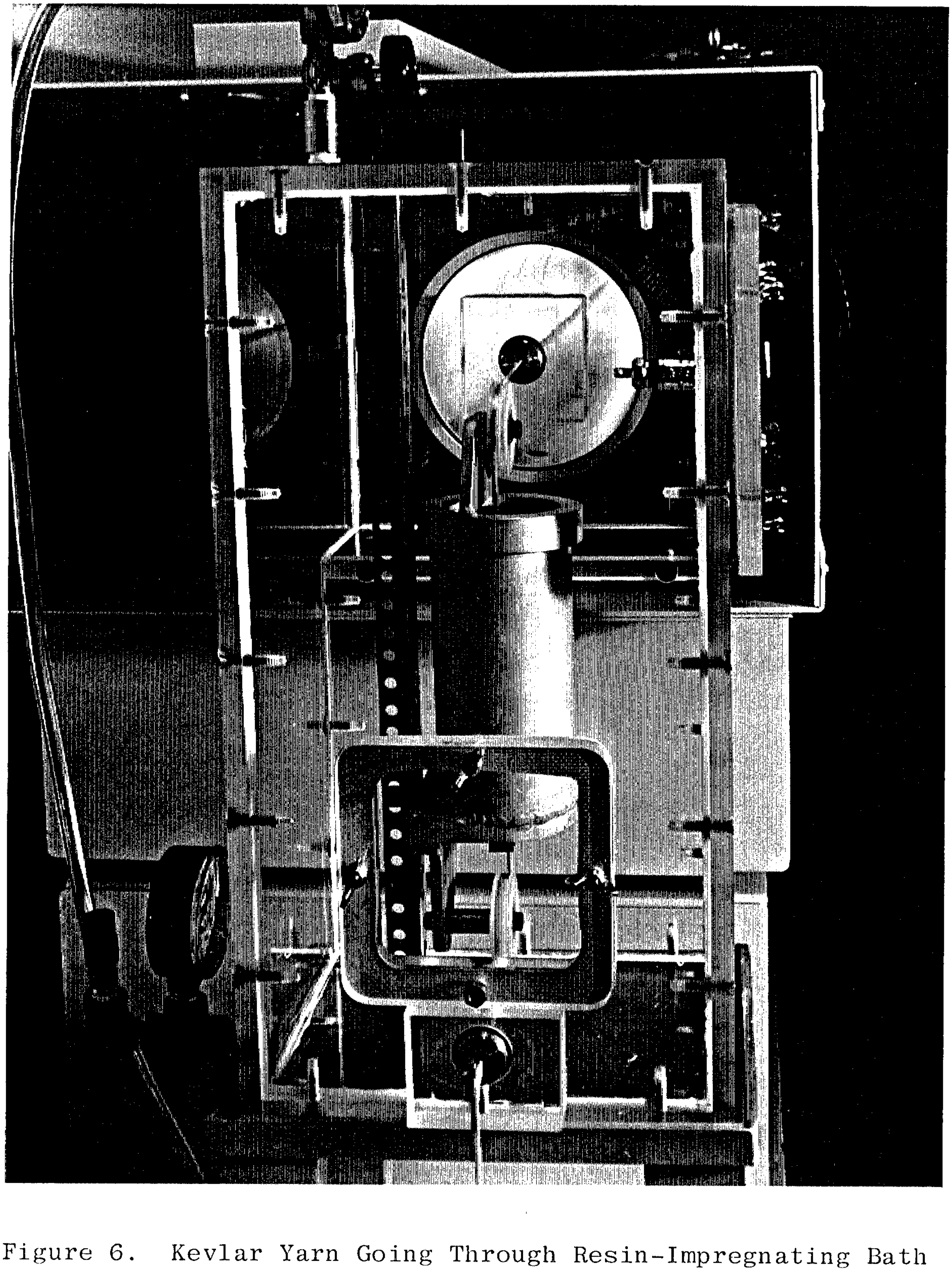

Figure 6. Kevlar Yarn Going Through Resin-Impregnating Bath

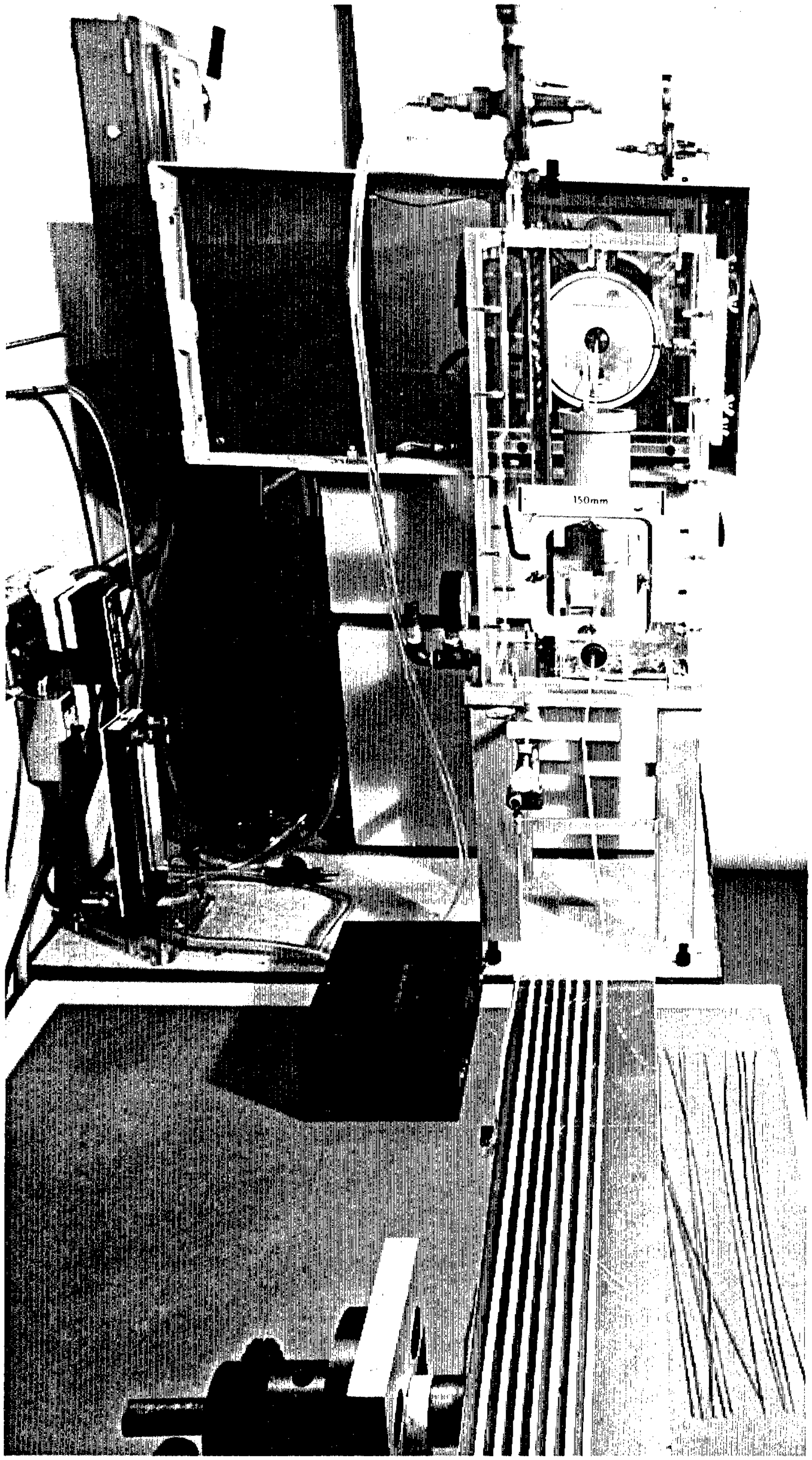

Figure 7. Exit End View of Continuous Plasma System

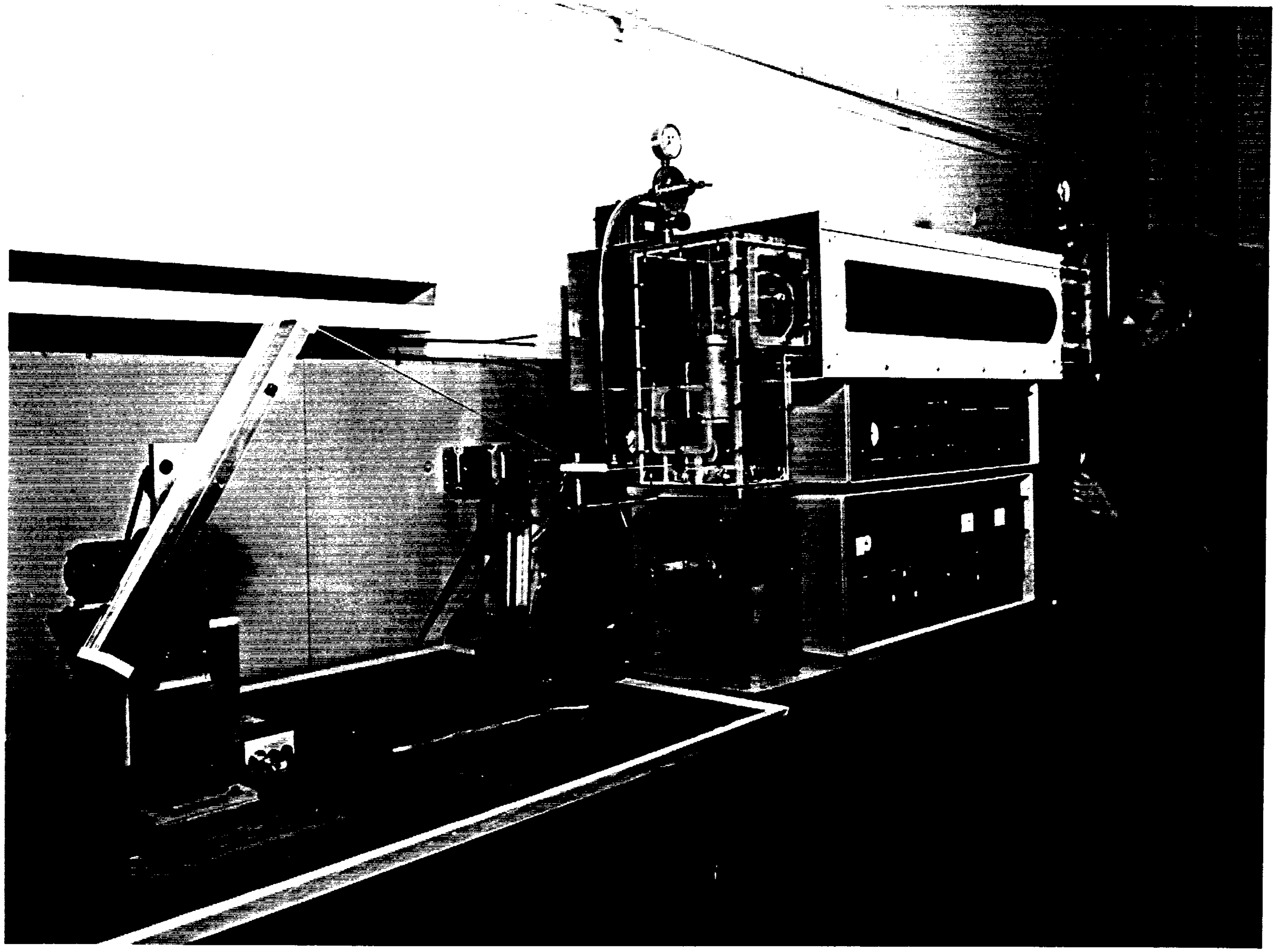

Figure 8. Continuous Plasma System in Operation

PROCEDURE FOR PRESSURIZING ENVIRONMENTAL CHAMBERS

1. Open main valve on gas bottle and set regulator at approximately 35.6 N.
2. Set regulator on top of each Environmental Chamber at zero (0).
3. Slowly open each regulator valve on the Environmental Chambers (checking the pressure gages in each chamber) until a pressure of 6.9×10^3 N/m^2 or less is achieved.

   CAUTION: DO NOT EXCEED 2.1×10^4 N/m^2 IN EITHER CHAMBER; OTHERWISE, THE PRESSURE RELIEF VALVE WILL RELEASE.

PROCEDURE FOR OPERATING PLASMA SYSTEM

1. Turn main power switch to ON.
2. Set reactor switch to OFF.
3. Set mode switches to LOCAL and MANUAL.
4. Set RF power switch to OFF. Operation light should be ON.
5. Set power switch to CW.
6. Set high/low switch to LOW.
7. Set DC/RF switch to RF.
8. Set meter switch to FWD (forward)
9. Set meter (power) switch to selected power level. When ready light comes on, the plasma system is ready to operate.
10. Turn purge switch to OFF.
11. Turn Vacuum Pump main switch to ON.
12. Set pumping speed switch to HIGH. When reactor gage shows zero (0), a vacuum has been achieved in the reactor chamber.
13. When the pressure gage reads 93 N/m^{2}or less, the RF power switch may be turned ON. A plasma in the reactor chamber should be visible.
14. Set power switch to desired level.
15. Plasma system is now operational.

Figure 9. Operating Procedure - Continuous Plasma System

Twenty individual fiber specimens were wrapped on each mandrel (ten on each side). The specimens were cured on the mandrel at 80°C for two hours and then at 125°C for 3 hours. Each specimen was cut to a 47.0-cm length. The resin content was determined for each batch of specimens and varied between 21.0 and 32.0 percent. Testing was performed by the Ernest Orlando Lawrence Livermore National Laboratory (LLNL) using their fixturing and testing technique.[3]

Table 3 summarizes the plasma-operating conditions, along with the tensile strength results. Based on these results, no short-term reduction in strength was observed for those samples treated with zero air or argon plasma and compared to non-plasma-treated specimens. No attempt was made to evaluate long-term effects.

Adhesion in Kevlar/Epoxy Interface

Of particular interest was the effect of plasma treatment on the adhesion in Kevlar/epoxy laminates. Adhesion was evaluated using 25.4-mm-wide T-Peel specimens made with Kevlar 49 roving, type 968, 5-end, 1420 denier. The resin impregnate (Dow Chemical DER 332 with Jeffamine T-403 hardener) was the one described previously. Curing of the laminate was also identical.

Test specimens were prepared by wrapping resin-impregnated Kevlar roving on a mandrel similar to that shown in Figure 8. The Teflon end caps were removed from the aluminum mandrel and a 25.4-mm-wide by 0.76-mm-deep channel was cut into both faces. One layer of resin-impregnated roving was laid down to make a unidirectional laminate. Pieces of Teflon-coated fabric, 76.2 by 25.4 mm, were placed at each end of the mandrel on top of the first layer of roving. A second layer of impregnated roving was laid down. Upon removal from the winding machine, the mandrel was covered with two pressure plates to control laminate total thickness and to apply uniform pressure during cure. Figure 10 illustrates the laminate on the mandrel and the molded part after removal.

After the laminate was removed from the mandrel, it was cut into four identical test specimens, each 247.7-mm long by 25.4-mm wide. Figure 11 shows the four identical test specimens. Before testing, the pieces of Teflon release fabric were removed. Since the four test specimens were produced from the same wrapping and curing operation, they are believed to be identical.

Adhesion testing was performed according to ASTM-D-1876, Peel Resistance of Adhesives (T-Peel Test). Figure 12 shows a typical test specimen being peeled apart at 180° in the jaws of a tensile-testing machine.

Table 4 presents a summary of the adhesion results. The Kevlar had been continuously plasma treated and impregnated using the

Table 3. Tensile Strength of Plasma-Treated and Resin-Impregnated Kevlar 49 Yarn

Gas	Power (W)	Tensile Strength After Plasma Treatment (MN/m^2) 4 min	2 min
No Plasma	--	3322.4	3101.6
		3456.9	3315.5
		3184.4	2987.0
		3051.9	3347.2
		3468.6	3366.5
		$\bar{x}$ = 3296.8	$\bar{x}$ = 3223.7
Zero Air	50	3412.7	3227.8
		3192.6	3357.5
		3274.1	3514.2
		3171.9	3267.8
		2994.6	3251.3
		$\bar{x}$ = 3209.2	$\bar{x}$ = 3323.7
	100	3518.3	---
		3267.2	3248.5
		3259.6	3393.4
		3080.2	3078.1
		3235.4	3127.8
		$\bar{x}$ = 3272.0	$\bar{x}$ = 3212.0
	150	2826.9	3127.8
		3247.8	2722.7
		3038.1	2913.9
		3048.4	3223.0
		2998.7	2853.2
		$\bar{x}$ = 3031.9	$\bar{x}$ = 2968.1
Argon	50	2708.9	2962.2
		3056.0	3312.7
		3022.9	3015.3
		3110.5	3243.7
		2833.8	2821.4
		$\bar{x}$ = 2946.4	$\bar{x}$ = 3071.1
	100	2925.6	3327.2
		2972.5	3306.5
		2652.4	3075.3
		2980.8	3164.3
		3077.4	3265.8
		$\bar{x}$ = 2921.7	$\bar{x}$ = 3227.8

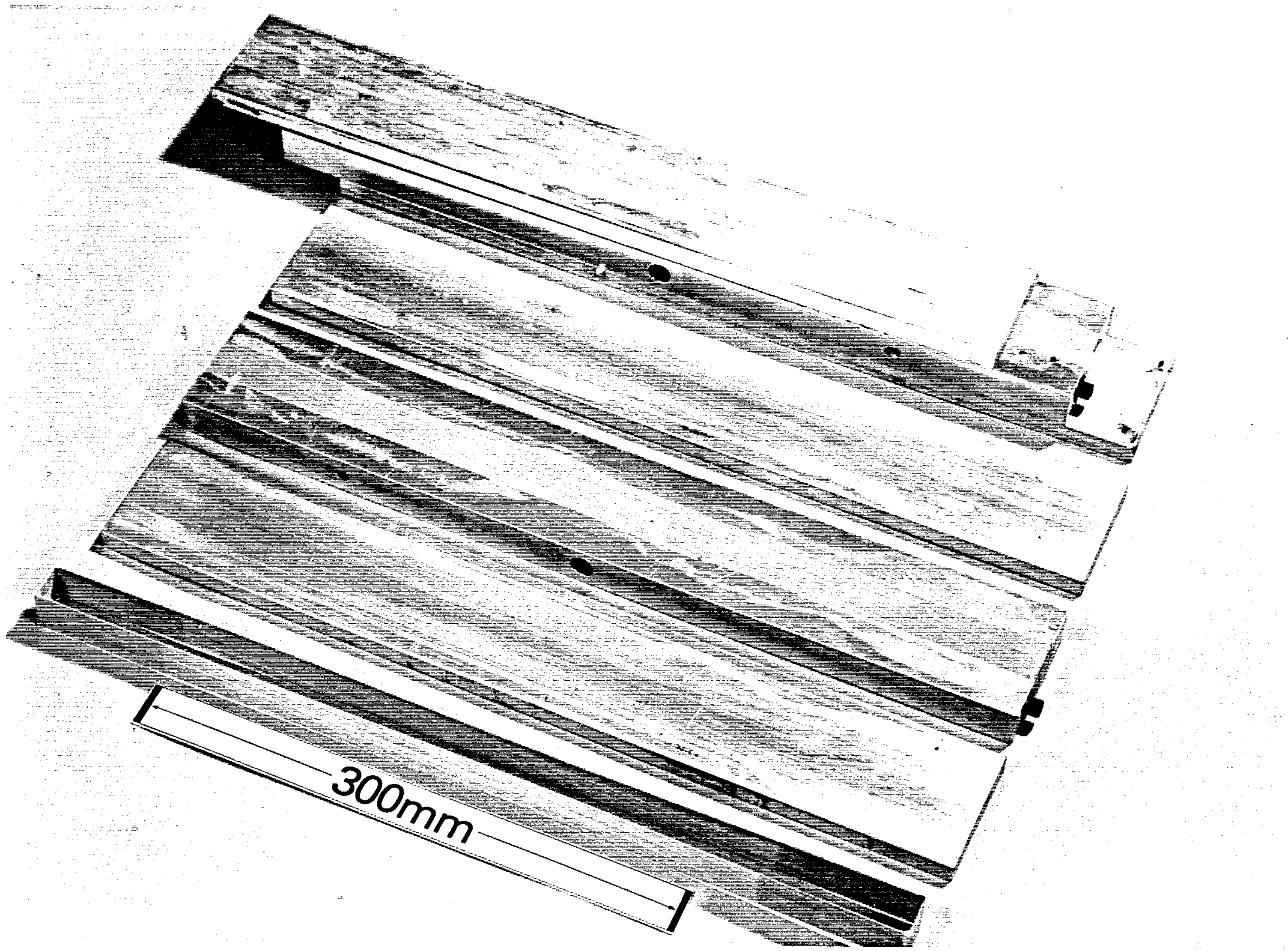

Figure 10. Aluminum Mandrel With Kevlar/Epoxy Laminate

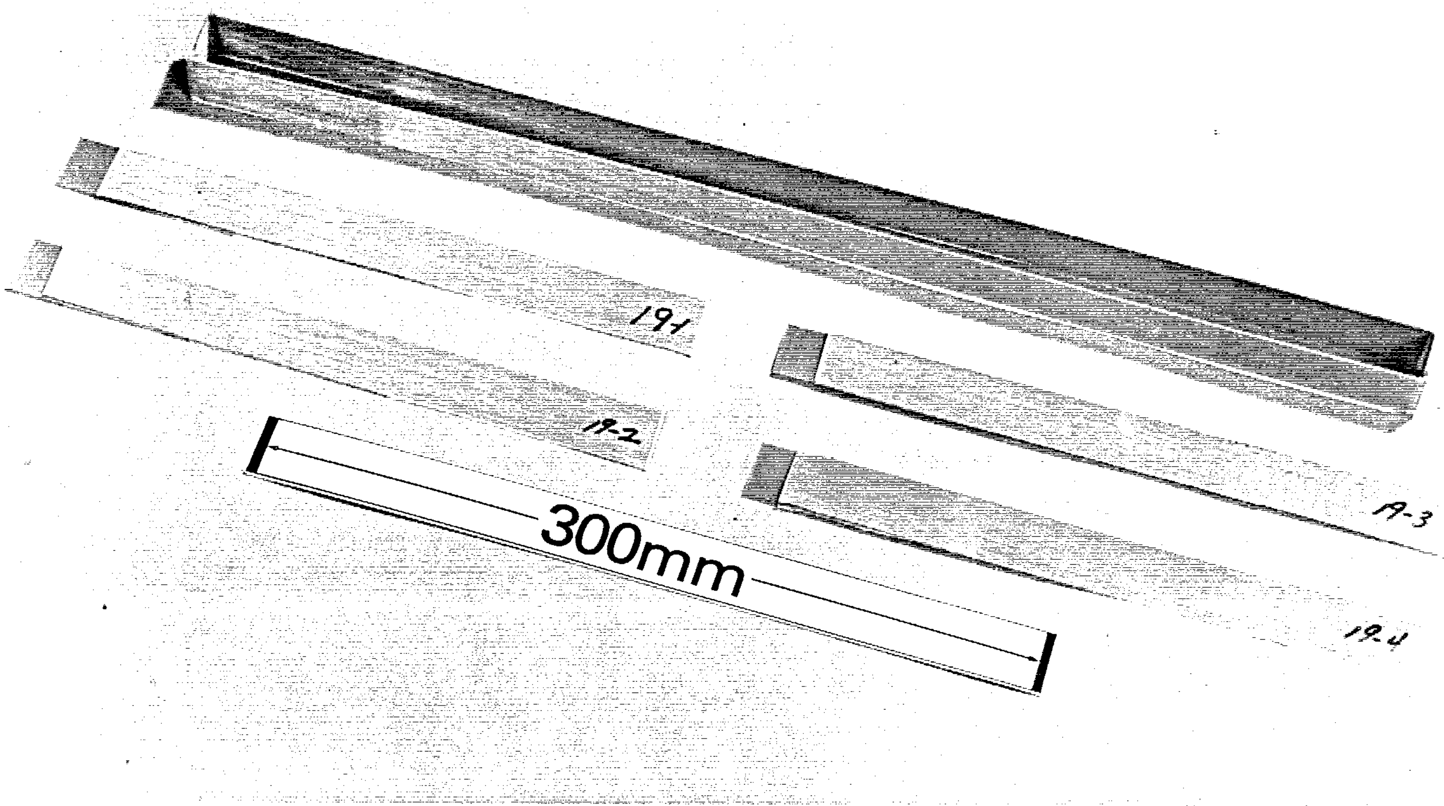

Figure 11. Kevlar/Epoxy Laminate in Various Stages of Preparation

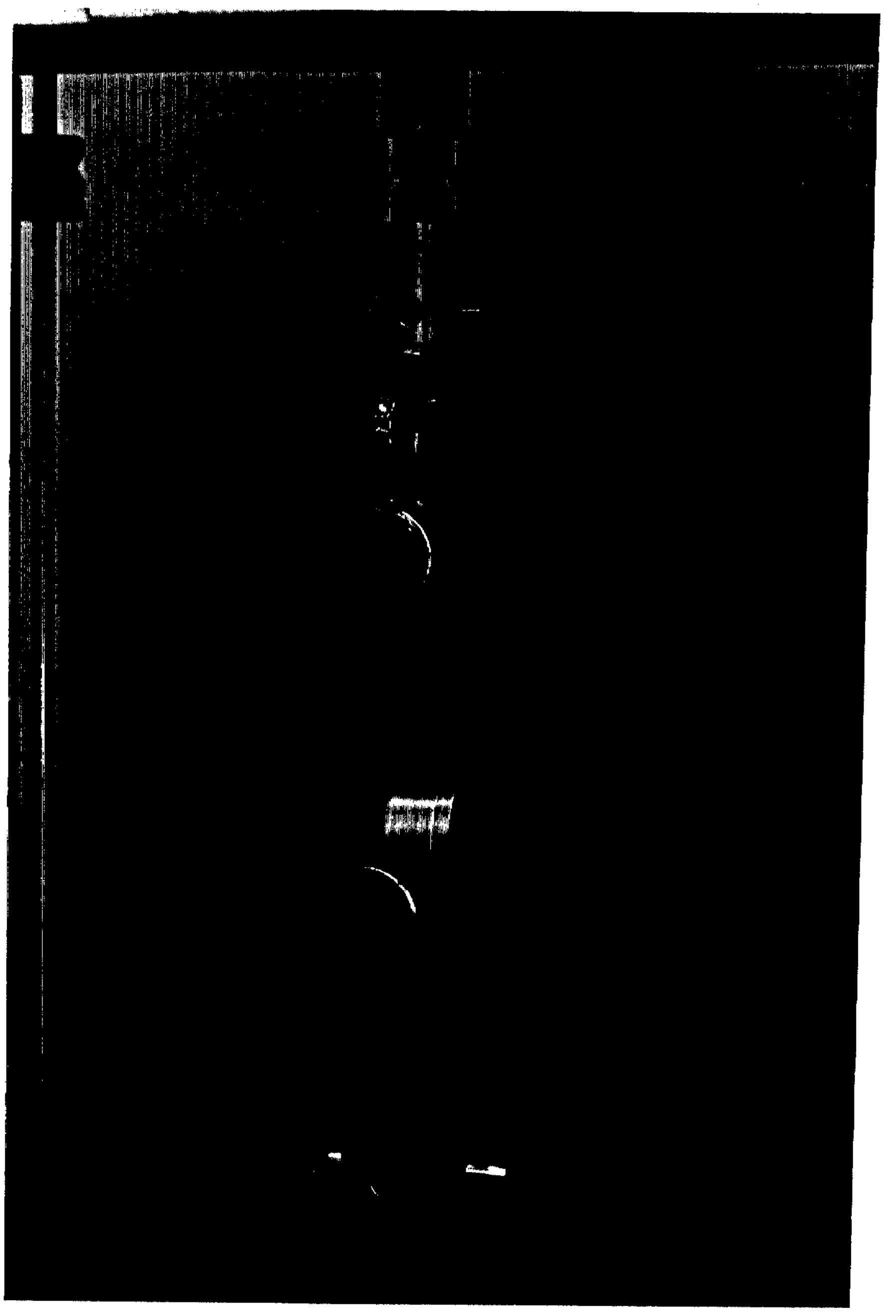

Figure 12. Adhesion Specimen in Testing Fixture

Table 4. Adhesion Performance of Kevlar Laminates

Plasma (Gas)	Power (W)	Pressure (N/m^2)	Mean Peel Strength (N/25.4 mm) After Treatment (min) 1	2.5	4
Argon	50	79.9 to 93.0	35.2	-	34.8
	125	93.0	-	35.2	-
	150	86.3	-	-	39.2
	200	93.0 to 99.6	32.1	-	36.5
No Plasma	-	-	16.3	-	15.0
Zero Air	50	106.3 to 119.6	31.2	-	37.8
	125	119.6 to 172.8	-	36.1	-
	200	119.6 to 172.8	31.2	-	35.6
No Plasma	-	-	17.6	-	10.1
Nitrogen	50	119.6	12.8	-	29.9
	125	119.6	-	30.4	-
	200	119.6	28.6	-	33.9
No Plasma	-	106.3	19.8	-	19.4

system developed during this project. Control laminates using untreated Kevlar were fabricated in an identical manner as treated Kevlar, except that no plasma was used.

Peel strength and adhesion are dependent upon many details of the laminate preparation, including resin viscosity, cure temperature, and molding pressure. Therefore, it was decided to base interpretation of plasma treatment effects on comparative rather than on absolute adhesion (peel strength) data. Accordingly, a peel strength ratio, R, was developed to evaluate the plasma treatment effectiveness.

$$R = (PSt)_p/(PSt)_c$$

Where

R = Peel strength ratio,

PSt = Peel strength (N/25.4 mm),

p = Plasma treated, and

c = Control (no plasma treatment).

An R value of 1 means there was no improvement in adhesion strength. An R value of 2 means there was a doubling of strength because of plasma treatment.

Table 5 is a summary of the treatment effectiveness. The use of plasma treatment with all three gases resulted in an improvement. Increased power with increased time did not necessarily increase adhesion with an accompanying increase in treatment effectiveness. A low power level for a short time accomplished the same as a high power level for a long time. This may be significant, because for large quantities of fiber, treatment time will be an important factor in considering productivity and cost.

ACCOMPLISHMENTS

It was demonstrated that plasma treatment can remove moisture in Kevlar 49 Aramid fiber. Data showed a decrease in moisture content with increasing plasma power level when holding time and pressure constant.

A system was developed for the continuous plasma treatment of Kevlar 49 fiber. In addition to the continuous plasma treatment, the treated fiber was immediately impregnated with an epoxy resin within an inert environment.

Adhesion test results with plasma-treated, unidirectional Kevlar 49 laminates showed an improvement in adhesion ranging from 1.4 to 3.7 times, as reported by the plasma treatment effectiveness parameter. No catastrophic degradation in tensile strength was observed from plasma treating the Kevlar 49 fiber in zero air or argon atmospheres. More thorough testing is needed.

FUTURE WORK

A long-term project is planned to further evaluate the use of continuous plasma treatment for treating reinforcing materials used in composites. Other materials to be investigated, in addition to Kevlar 49, are graphite, glass, and nylon. More sophisticated test specimen configurations will be investigated to evaluate the adhesion between the resin binder and the fibrous reinforcement. Additionally, it is hoped to modify the present continuous plasma system to make it more efficient and able to handle tape material in addition to yarn or roving goods.

Table 5. Plasma Treatment Effectiveness

Plasma Gas	Power (W)	Treatment Effectiveness (R)*	
		1 min	4 min
Argon	50	2.2	2.3
	150		2.6
	200	2.0	2.4
Zero Air	50	1.8	3.7
	200	1.8	3.5
Nitrogen	50		1.5
	200	1.4	1.8

*Treatment Effectiveness (R)=(PSt)p/(PSt)c

Where

R = Peel strength ratio,
PSt = Peel strength (N/25.4 mm),
p = Plasma treated, and
c = Control (no plasma treatment).

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