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**SEMI-ANNUAL REPORT**

**SURFACE CHARACTERIZATION IN COMPOSITE AND  
TITANIUM BONDING**

BY

**T. A. DeVILBISS AND J. P. WIGHTMAN**

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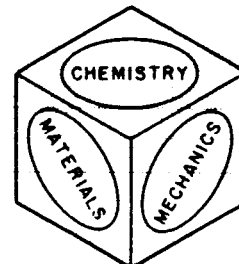
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AND TITANIUM BONDING

BY

T. A. DeVILBISS AND J. P. WIGHTMAN

PREPARED FOR  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA - Langley Research Center

Materials Division

Hampton, VA 23665

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from

Chemistry Department

Virginia Polytechnic Institute and State University

Blacksburg, VA 24061

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\*This report covers the period April 1, 1986 to September 30, 1986.

This Semi-Annual Report consists of preprints of the following two papers:

- (1) "SEM/XPS Analysis of Fractured Adhesively Bonded Graphite Fiber Surface Resin-Rich Graphite Fiber Composites".

This paper describes the failure surface analysis of adhesively bonded carbon fiber composites. The emphasis was on the bonding of composites where the surface was intentionally made resin-rich. This paper has been submitted for publication in Composites.

The following related paper was published earlier: "SEM/XPS Analysis of Fractured Adhesively Bonded Fibre-Reinforced Polyimide Composites", T. A. DeVilbiss, D. L. Messick, D. J. Progar and J. P. Wightman, Composites, 16, 207-219 (1985).

- (2) "Surface Characteristics of Carbon Fibers".

This paper describes the surface analysis of both commercially available and pretreated carbon fibers. The interaction of the fibers with polysulfone is described. This paper was presented at the International Conference on Composite Interfaces, Cleveland, OH, May, 1986. This paper will appear in the proceedings of the conference.

SEM/XPS ANALYSIS OF FRACTURED ADHESIVELY BONDED GRAPHITE FIBER SURFACE  
RESIN-RICH GRAPHITE FIBER COMPOSITES

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INTRODUCTION

Previous work<sup>1</sup> studying the lap shear strengths of polyimide/graphite fiber composites showed that grit blasting was an effective surface treatment to prepare these composites for adhesive bonding. The resulting lap shear strengths were reasonable. The failure mode of most of these bonded composites was seen to occur mostly within the bonded composite. It was therefore thought that by fabricating a composite with a surface rich in resin, the extent of composite failure could be reduced. This modification should result in a bonded composite that would give higher lap shear strengths.

The conclusion from the previous study<sup>1</sup> on "resin-poor" samples was that the lap shear strength of the bonded composites decreased with thermal aging. Scanning electron microscopy showed a significant amount of failure within the composite due to fiber-matrix debonding. X-ray photoelectron spectroscopy showed that the fluorine signal observed on the fracture surfaces of the failed lap shear joints increased with longer aging times. The locus of failure moved from within the composite to failure at the original bonding interface. It was not concluded whether the fluorine was the cause of the failure or whether it was just a symptom.

## EXPERIMENTAL

### Composites

Approximately 2.54 mm thick 14 ply Celion 6000/LaRC-160 polyimide composites with a  $(0,0,0,+30,-30,+30,-30)_s$  layup were fabricated at the Langley Research Center. During fabrication, an adjustment was made to allow the resin to accumulate at the composite surface. The composite prepared in this manner is identified as a surface resin-rich composite. Figure 1 shows the vacuum bag layup and the staging conditions for the prepreg compaction step. Figure 2 shows the vacuum bag layup and the curing conditions used to prepare the resin-rich composites. The surfaces of the composites were prepared for bonding either by wiping with methanol (AR) or by grit blasting (GB) with 120 size aluminum oxide grit and washing with methanol. The composites were then heated in a forced-air oven at 100°C overnight before priming. The surface treated composites were primed with BR 34B-18 (American Cyanamid). A supported aluminum filled polyimide adhesive (FM 34B-18) was placed between the composite panels and cured according to the cure cycle described previously<sup>1</sup>.

The bonded specimens were isothermally aged in a forced air oven controlled to within  $\pm 1\%$  at 177°C and 232°C for 500 and 1000 hours. The lap shear tests were conducted on an Instron Universal Testing instrument according to ASTM D-1002 at a cross head-speed of 1.27 mm min.<sup>-1</sup>. Elevated temperature tests were performed in an R I Controls clamshell quartz-lamp furnace after a 10 min. soak with the temperatures controlled to within  $\pm 3^\circ\text{C}$  for all tests.

### Scanning Electron Microscopy (SEM)

SEM photomicrographs were obtained using a Polaroid camera attached to an

Advanced Metals Research model 1000 scanning electron microscope. Specimens were cut on a diamond wheel saw to approximately 10 X 10 mm. A thin film of gold was evaporated onto the samples to enhance the conductivity.

#### X-Ray Photoelectron Spectroscopy (XPS)

XPS studies were conducted with a Perkin-Elmer PHI-5300 electron spectrometer. A magnesium K $\alpha$  x-ray source was used at 250 mwatts power. The samples were prepared for XPS examination by punching a 9 mm disk from the sample of interest. The sample was mounted on the specimen holder with double stick tape.

### RESULTS AND DISCUSSION

#### Pretreated Surfaces

SEM photomicrographs of the resin-rich samples are shown in Figure 3. It can be seen that the surface is smooth. SEM photomicrographs of the composite samples from the previous work<sup>1</sup> showed peaks and valleys due to resin-rich and resin-poor regions created by the release cloth weave. XPS analysis of the resin-rich sample shows 77. % carbon, 17. % oxygen, 3.1 % nitrogen, 1.4 % fluorine, 0.5 % sodium, and 0.4 % copper. The grit blasted (GB) sample was not available for analysis.

#### Lap Shear Strengths

Lap shear strengths of the bonded composites before and after thermal aging are listed in Table I. The predominant failure modes of the adhesive bond are also listed in Table I. Figure 4 shows the lap shear strengths for the unaged bonded composite specimens and indicates no apparent effect of the surface pretreatment on lap shear strengths. A significant decrease in lap shear strength with increasing test temperature is evident. Figures 5 and 6

show the lap shear strengths for aged specimens. The lap shear strengths decrease with thermal aging. The strength loss is greater at the higher temperatures and the longer aging times.

#### Scanning Electron Microscopy

SEM photomicrographs of the surfaces of the failed resin-rich lap shear specimens are shown in Figures 7-9. The SEM photomicrographs for the failed lap shear specimens of Reference 1 were presented in that publication and will not be repeated here. Figure 7 is typical of the type of failure seen in the majority of the failed resin-rich specimens. It can be seen that in addition to the adhesive failing within the bondline, there is a considerable amount of bare fiber showing. The observation of bare fiber indicates that failure may be caused from within the composite. Figure 8 shows a typical adhesive type failure. It can be seen that much of the original surface is exposed. In addition, there is some adhesive left on the failure surface.

#### X-Ray Photoelectron Spectroscopy

The XPS results are tabulated in Table II. Carbon, oxygen, and nitrogen are present in the matrix resin, the fibers, and the adhesive. Fluorine results from the mold release material used in composite manufacture. Aluminum is the filler material in the adhesive. The source of magnesium is uncertain. There is very little difference in the atomic percentages of elements detected on the failed surfaces. This indicates that failure occurred in about the same place within the adhesive bond for each sample tested. The only sample that showed a difference was the as-received (AR) sample which was aged 1000 hrs. at 232° C and tested at room temperature.

This sample showed about 0.6% fluorine. The presence of fluorine observed on the composite surface before bonding confirms the assignment of interfacial failure as indicated in Table I.

#### SUMMARY

The surface resin-rich samples did not appear to give a significant increase in the lap shear strength over the surface resin-poor samples previously tested. Lap shear strengths decreased with increasing aging time and temperature. Visual examinations indicated that the resin-rich samples failed mostly by cohesive failure within the adhesive. However, SEM examination indicates that these samples also had a significant amount of fiber/matrix debonding. Samples thermally aged at 232° C for 1000 hrs. failed adhesively possibly indicated by the high fluorine content on the failed surfaces.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- 1 DeVilbiss T. A., Messick D. L., Progar D. J., and Wightman J. P., "SEM/XPS analysis of fractured adhesively bonded graphite fibre-reinforced polyimide composites", Composites, 16, No. 3, (July 1985) pp 207-219.



## AUTHORS

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TABLE I

## LAP SHEAR STRENGTHS (LSS) AND PREDOMINANT FAILURE MODE OF BONDED COMPOSITES

TREATMENT	TEST TEMPERATURE °C	RESIN-POOR		RESIN-RICH	
		LSS (MPa)	FAILURE MODE	LSS (MPa)	FAILURE MODE
AR	RT	18	A,R	21.	C
AR	177	16.	A,C	16.	C
AR	232	13	A,C	14.	C
AR, 500 hrs, 177°C	RT	17.	A	18.	A,C
AR, 500 hrs, 177°C	177	16.	A,C	14.	C
AR, 1000 hrs, 177°C	RT	14.	A	14.	A,C
AR, 1000 hrs, 177°C	177	13.	A	12.	A
AR, 500 hrs, 232°C	RT	8.4	A	13.	M
AR, 500 hrs, 232°C	232	9.1	A	12.	A,C
AR, 1000 hrs, 232°C	RT	7.1	A	8.6	A
AR, 1000 hrs, 232°C	232	6.6	A	9.3	A
GB	RT	20.	CO	21.	C
GB	177	16.	C	15.	C
GB	232	14.	C	13.	C
GB, 500 hrs, 177°C	RT	15.	CO	20.	C
GB, 500 hrs, 177°C	177	16.	CO,C	15.	C
GB, 1000 hrs, 177°C	RT	13.	CO	18.	M
GB, 1000 hrs, 177°C	177	14.	CO,C	15.	C
GB 500 hrs, 232° C	RT	11.	CO	13.	M
GB 500 hrs, 232° C	232	11.	CO,C	12.	C
GB 1000 hrs, 232° C	RT	9.4	C,CO	11.	M
GB 1000 hrs, 232° C	232	9.0	C	12.	M

C - Cohesive failure of the adhesive

CO - Failure within the composite exposing bare fibers

A - Adhesive failure (interfacial failure)

R - Surface resin (matrix polymer) separation from fibers

M - Mixed failure modes

TABLE II  
XPS ANALYSIS OF FRACTURED LAP SHEAR RESIN-RICH SPECIMENS

<u>TREATMENT</u>	<u>TEST TEMPERATURE, °C</u>		<u>ATOMIC CONCENTRATION (%)</u>				<u>Mg</u>
	<u>C</u>		<u>O</u>	<u>N</u>	<u>F</u>	<u>Al</u>	
AR	RT	79.	14.	5.0	0.1	NS	0.5
GB	RT	80.	14.	4.5	NS*	0.3	0.6
AR	232	72.	23.	5.2	0.1	NS	NS
AR, 1000 hrs, 232°C	RT	76.	19.	5.0	0.6	NS	NS
GB, 1000 hrs, 232°C	232	81.	14.	4.7	NSP**	NS	NS

\*NS - not scanned

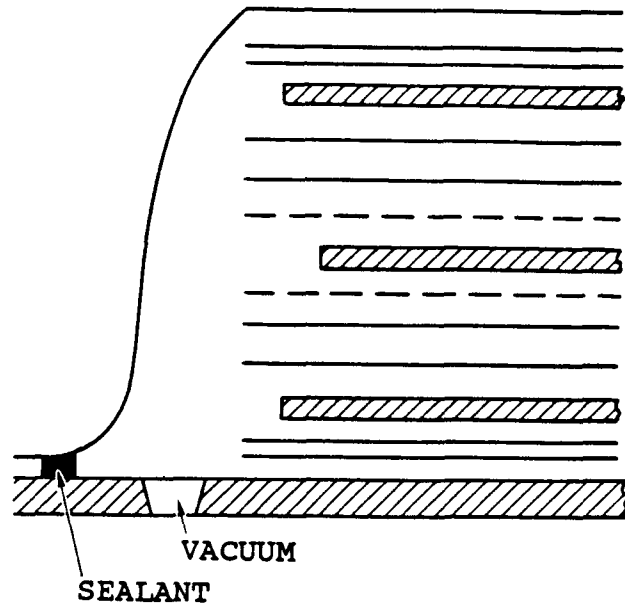
\*\*NSP - no significant peak

## Figure Legend

- | <u>No.</u> | <u>Title</u>  |
|------------|---|
| 1.         | Typical (a) vacuum bag layup and (b) staging conditions for fabrication of Celion 6000/LaRC-160 composite.  |
| 2.         | Typical (a) vacuum bag layup and (b) curing conditions for Celion 6000/LaRC-160 composites.   |
| 3.         | SEM photomicrograph of as received resin-rich composite.  |
| 4.         | Average lap shear strengths for unaged bonded composites.   |
| 5.         | Lap shear strength test results for bonded composite specimens aged for 500 hrs at 177 and 232°C.   |
| 6.         | Lap shear strength test results for bonded composite specimens aged for 1000 hrs at 177 and 232°C.  |
| 7.         | SEM photomicrograph of failed, resin-rich composite bonded as received, no aging, tested at room temperature. The appearance is typical of photomicrographs where cohesive failure was indicated (20X). |
| 8.         | SEM photomicrographs of failed resin-rich composite bonded as received, aged 1000 hrs. at 232°C, tested at 232°C. The appearance is typical of adhesive type failure (20X).                             |

(a) VACUUM BAG LAYUP

Kapton Vacuum Bag  
2 Layers 162 Glass Cloth  
Steel Caul Plate  
Kapton Film  
TFE Coated 140 Glass Cloth  
TFE Coated 104 Glass Cloth  
Composite Prepreg  
TFE Coated 140 Glass Cloth  
TFE Coated 104 Glass Cloth  
Kapton Film  
Steel Caul Plate  
2 Layers 162 Glass Cloth  
Staging Plate

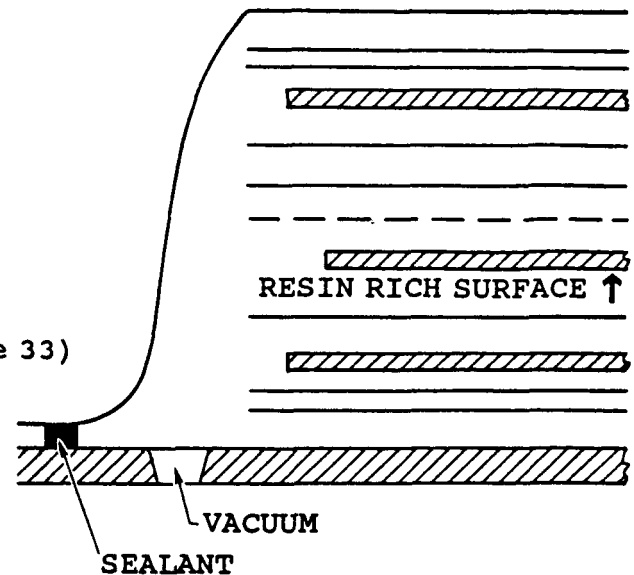


(b) STAGING CONDITIONS

1. Pull a partial vacuum (i.e. 12.7 mm Hg on vacuum gage)
2. Heat at 3° C/min. (5° F/min.) to 107° C (225° F)
3. After 15 min. at 107° (225° F), increase vacuum (i.e. 1.27 mm Hg on vacuum gage)
4. After 30 min. at 107° C (225° F), increase to full vacuum
5. After 60 min. at 107° C (225° F), apply 0.34 MPa (50 psi) pressure and continue heating at 3° C/min. (5° F/min.) to 232° C (450 F)
6. Hold at 232° C (450° F) for 60 min. Start cooling.
7. Remove vacuum and pressure on reaching 193° C (280° F).
8. Cool to room temperature

(a) VACUUM BAG LAYUP

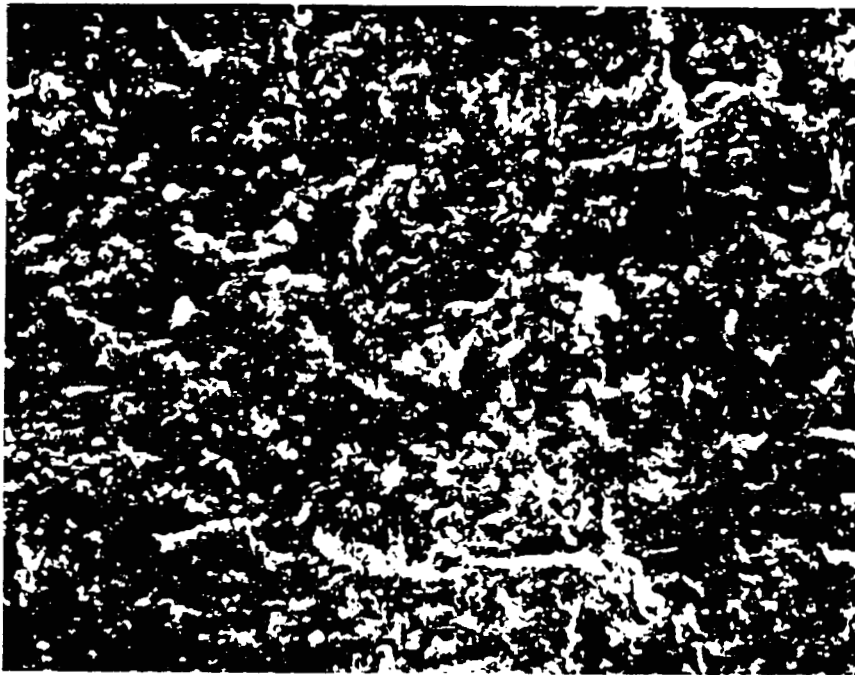
Kapton Vacuum Bag  
2 Layers 162 Glass Cloth  
Steel Caul Plate  
Kapton Film  
TFE Coated 140 Glass Cloth  
TFE Coated 104 Glass Cloth  
Staged Composite  
Kapton Film (Coated with Freekote 33)  
Steel Caul Plate  
2 Layers 162 Glass Cloth  
Steel Plate

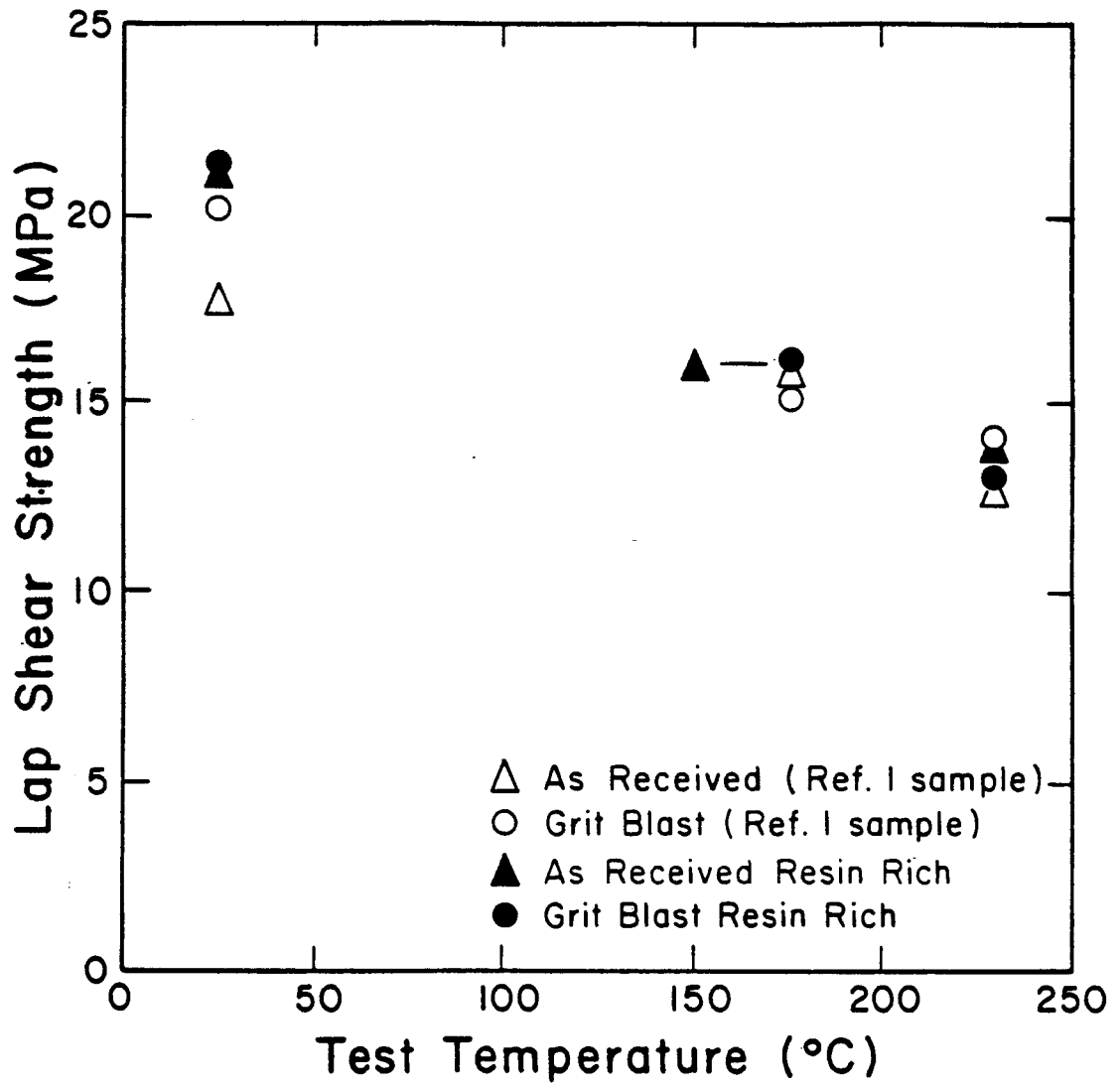


(b) CURING CONDITIONS

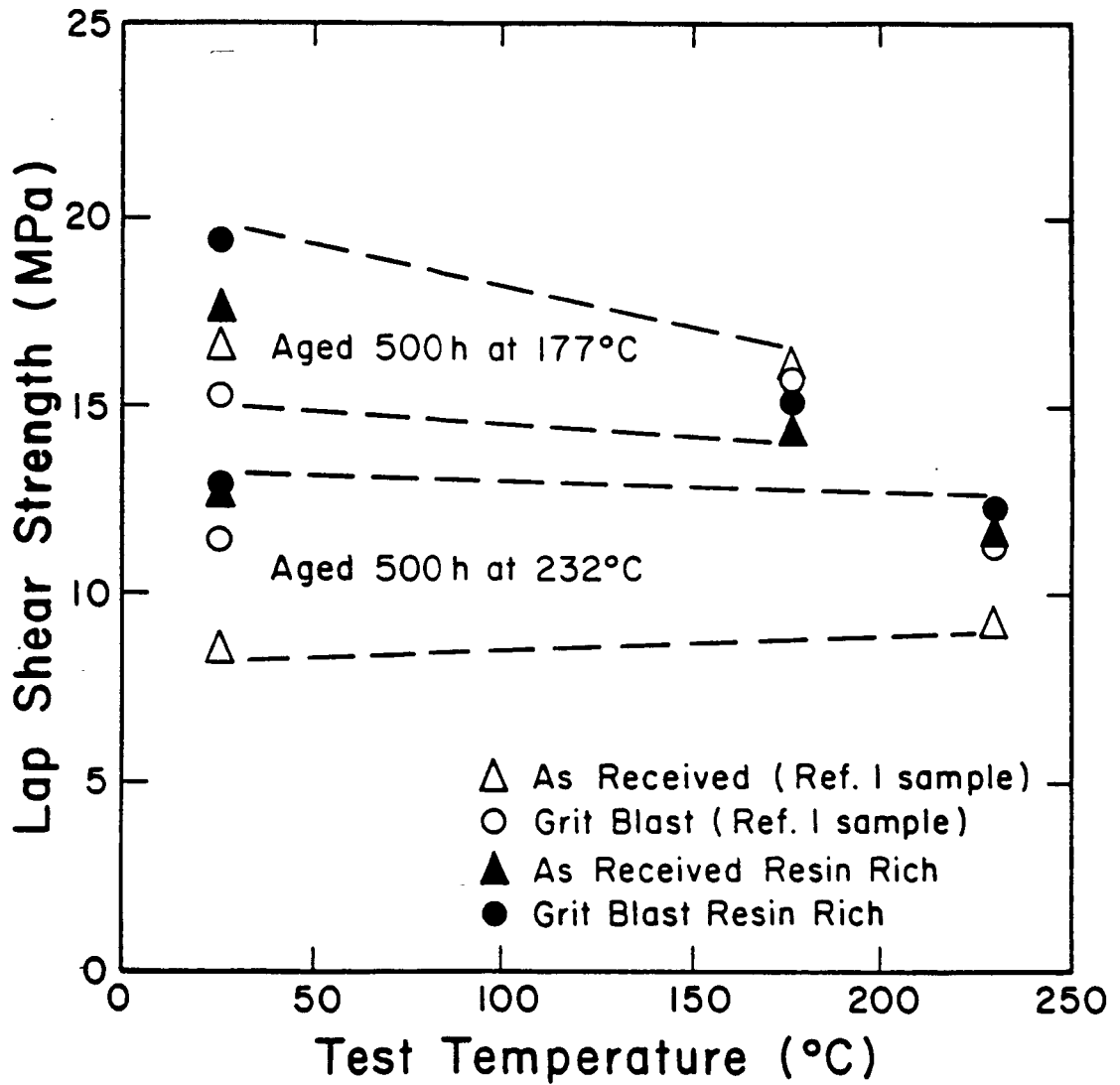
1. Full vacuum from start
2. Heat at  $5.5^{\circ}\text{C}/\text{min.}$  ( $10^{\circ}\text{F}/\text{min.}$ )
3. Apply  $0.34\text{ MPa}$  ( $50\text{ psi}$ ) upon reaching  $38^{\circ}\text{C}$  ( $100^{\circ}\text{F}$ )
4. Continue heating to  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ).
5. After 15 min. at  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ), apply  $2.1\text{ MPa}$  ( $300\text{ psi}$ )
6. Hold  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ) an additional 15 min.
7. Continue heating at  $5.5^{\circ}\text{C}/\text{min.}$  ( $10^{\circ}\text{F}/\text{min.}$ ) to  $332^{\circ}\text{C}$  ( $630^{\circ}\text{F}$ ), hold for 3 hr., Cool.
8. Remove vacuum and pressure on reaching  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ).
9. Cool to room temperature.

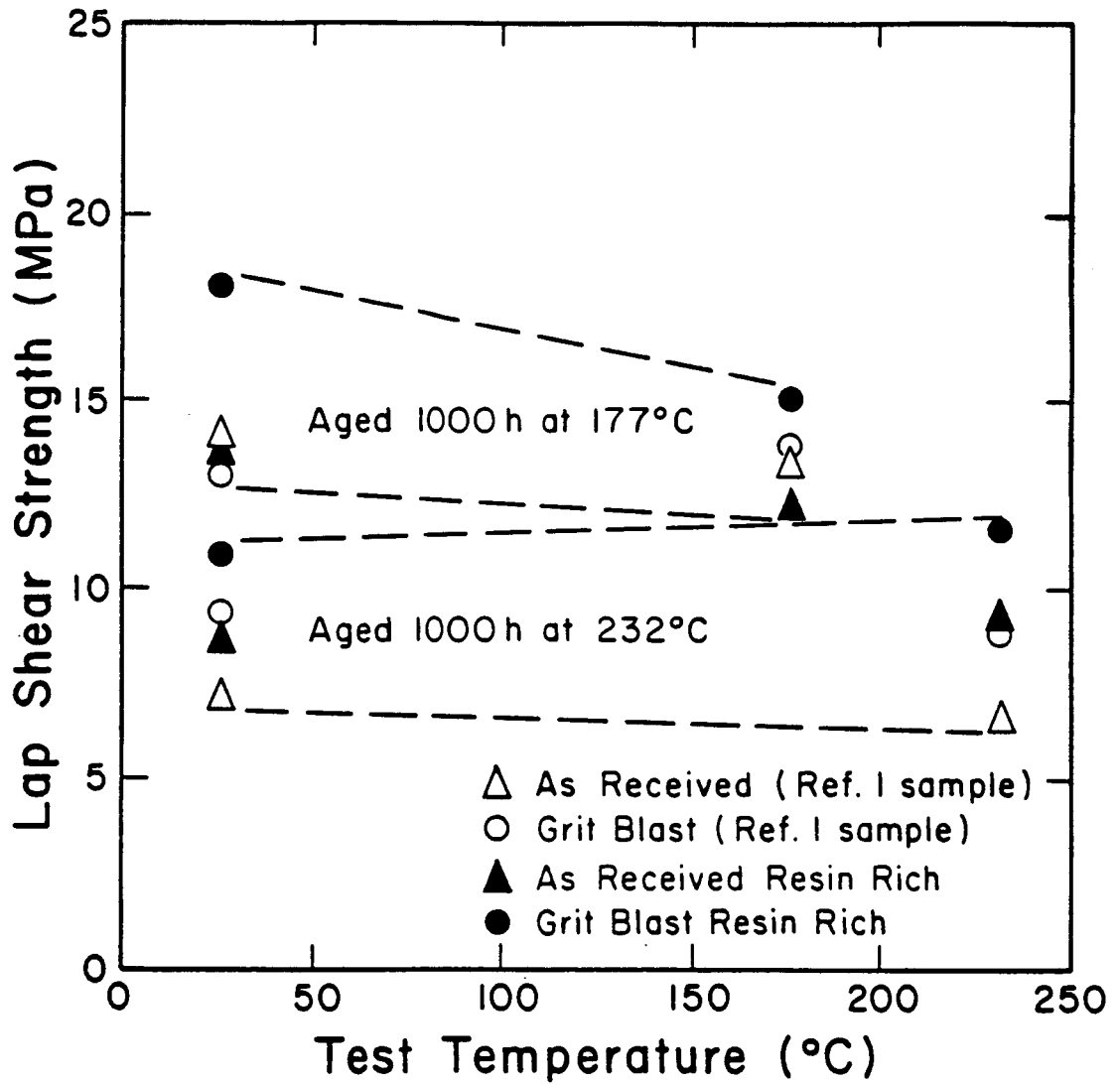
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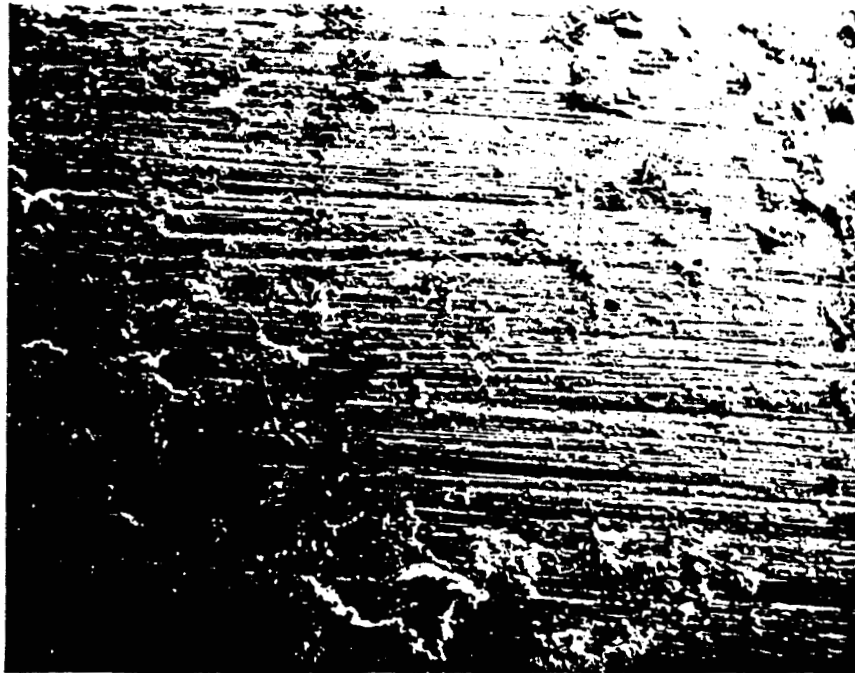




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## SURFACE CHARACTERISTICS OF CARBON FIBERS

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### INTRODUCTION

The use of carbon fibers as a reinforcing material in thermosetting matrices has found wide use. With the use of reactive epoxy resins, it is reasonable to assume that chemical reactions could occur between the epoxy and the carbon fiber. Most thermosetting matrix composites tend to be brittle. Thermoplastic matrix materials on the other hand tend to be more ductile. Their use may allow the manufacture of composites having high fracture toughness. However, since they do not undergo further polymerization upon composite formation, they are less likely to form chemical bonds between fiber and matrix. This work is aimed at understanding the physical structure and chemical composition of carbon fiber surfaces in order to promote adhesion to thermoplastic matrices.

### EXPERIMENTAL

#### Carbon Fibers

The fibers used in this study included Hercules AU-4 (a low modulus carbon fiber with no surface treatment), Hercules AS-4 (same as AU-4 but having undergone a proprietary surface treatment), Celanese Celion 6000 and Union Carbide T-300. Two types of T-300 fiber were studied; one had been surface treated and the other no surface treatment.

### Surface Treatments

The surface treatments used in this study included anodization of AU-4 in  $\text{H}_2\text{SO}_4$ , NaOH,  $\text{NH}_4\text{HCO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{H}_2\text{O}$ , and boiling AS-4 in 70% nitric acid for 3 hours. The electrolyte concentrations, voltages, current densities, and treatment times are listed in Table I. The fibers were rinsed in distilled water and dried in an oven at  $100^\circ\text{C}$  for 12 hours after anodization.

### Surface Analysis

The surfaces of the fibers were analyzed by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS spectra were recorded on a Perkin Elmer PHI 5300 electron spectrometer with a magnesium  $\text{K}\alpha$  x-ray source operated at 250 mwatts. SEM photomicrographs were obtained on a Philips 420 scanning transmission electron microscope.

### Surface Derivatization

In order to obtain a better understanding of the functionality of the carbon fiber surface, a derivatization scheme developed by Everhart and Reilley (1) was used. In this technique, a series of reagents containing fluorine or some other elemental tag is used. The reagents are chosen so that they will react only with specific functional groups on the surface of interest. By scanning for the elemental tag using XPS, the presence of that functional group can be identified on the surface. A schematic diagram of the derivatization process and the reagents used are outlined in Figure 1.

### Surface Molecular Structure Determination

In order to understand more about the molecular structure of the carbon fiber surface after anodization, ultraviolet absorption spectra of the anodization bath were obtained on a Perkin Elmer 3300 UV/VIS spectrophotometer. Mass spectra of the carbon fiber surfaces were obtained on a Vacuum Generators VG/SIMS LAB secondary ion mass spectrometer using neutral

argon ions as the bombarding source. Positive and negative mass fragments emitted from the surface were detected with a quadrupole mass spectrometer. Mass fragments from 0-200 atomic mass units (AMU) were detected.

#### Surface Energy Analysis

The wetting force of the carbon fibers were measured in five liquids of varying polar and dispersive components using a Perkin Elmer TGA-2 microbalance. The fibers were attached to a wire hook with a cyanoacrylate adhesive. The fibers were then dried in an oven at 100° C for 4 hours. The hook was then placed in the microbalance and the liquid was raised up to wet the fiber. The contact angle was calculated from the fiber diameter, the liquid surface energy, and the wetting force as described by Hammer and Drzal (2). Six fibers were measured for each liquid and surface treatment. The liquids used included water, ethylene glycol, formamide, methylene iodide, and bromonaphthalene. Polar and dispersive components of the fiber surface energy were determined by assuming a geometric mean interaction between the dispersive surface energy on the fiber and the liquid, and between polar groups on the fiber and the liquid, to account for the work of adhesion. This technique has been described by Hammer and Drzal (2).

#### Breaking Strength

The breaking strength of the fibers (length = 2.5 cm) were measured. The fibers were attached with a cyanoacrylate adhesive across a paper tab. The paper tab was then mounted in a table model Instron with a 50 g capacity load cell. Electrical alligator clips were used as the machine clamps. The paper was then burned away with a nichrome wire attached to a 10 V power supply. The fiber was then pulled in tension with a crosshead speed of 5 mm per minute. Twenty to thirty fibers were broken for each fiber surface of interest. The breaking strength was also measured as a function of length.

The fibers were mounted in paper tabs similar to the ones described above except that they had either 12.5 or 6 mm holes.

#### Fiber Critical Length

To measure the interaction of the matrix with the fiber, a fiber critical length test was performed as described by Wadsworth and Spilling (3). In this test, an annealed (600°F, 30 min oven cool) A1100 aluminum coupon (2.5 cm x 15 cm) was coated with a 5 g/100 ml solution of UDEL P1700 polysulfone in methylene chloride. Fibers were then individually placed on the coated coupon spaced about 7 mm apart. The fibers were then coated with the polysulfone solution. After the solvent was allowed to evaporate, the coupon-fiber-polymer system was annealed at 250°C in a vacuum oven for 12 hours. The coupons were cooled in the oven. After cooling, the coupons were pulled in tension to 30% strain in an Instron testing machine. The broken fiber lengths were measured on a microscope with a micrometer stage.

#### Adsorption From Solution

In order to obtain an understanding of the interaction between polymers and carbon surfaces, an adsorption from solution experiment was performed. Graphite powder of about  $10 \text{ m}^2/\text{g}$  was used. It was determined that the surface area of carbon fibers was too low ( $0.5 \text{ m}^2/\text{gm}$ ) to give a significant concentration change. Solutions of UDEL P1700 polysulfone (ranging from  $3 \times 10^{-2}$  to  $1 \times 10^{-2} \text{ g}/100 \text{ ml}$ ) in methylene chloride or chloroform were prepared. To a 10 ml aliquot of the solution, 0.5 g of the graphite powder was added. The system was shaken overnight and then centrifuged. Aliquots of the centrifuged solution were diluted 10:1. The change in concentration of the polysulfone directly proportional to the amount of polysulfone adsorbed, was detected using a Perkin Elmer ultraviolet spectrometer set at 265 nm.

## RESULTS AND DISCUSSION

The carbon 1s photopeaks and atomic concentrations of elements detected by XPS on the surface of carbon fibers as received from the manufacturer are shown in Figure 2. The surface treated fibers contain about 20% total oxygen and nitrogen content. It can be seen that the Hercules surface treatment adds more nitrogen to the fiber surface than the other commercial treatments.

SEM photomicrographs of the commercially available fibers are shown in Figure 3. It can be seen that the Hercules fibers have a fairly smooth surface when compared to the Celion 6000 and Union Carbide T-300 fibers.

The derivatization results for the AS-4 and Celion 6000 fibers are shown in Tables II and III respectively. The main feature to observe in these tables is the appearance of the fluorine signal from the elemental tag. It can be seen that the fluorine signal increases for the PFB reaction on the AS-4 fibers. This indicates there might be amine groups on the AS-4 surface. The Celion 6000 fiber is observed to have amine and carbonyl groups on its surface.

The carbon 1s photopeaks as well as the atomic concentrations of elements detected by XPS for the surface treated fibers are shown in Figure 4. It can be seen that these treatments add from 17 to 30% total oxygen and nitrogen to the fiber surface. The NaOH treatment added only 17% oxygen. The treatments in ammonium salts as well as the nitric acid boil added both oxygen and nitrogen to the fiber surface.

The SEM photomicrographs of the surface treated fiber are shown in Figure 5. It can be seen that the 0.05 M sulfuric acid appears to flake off layers of the fiber surface. The 0.05M NaOH treatment etches into the fiber surface. At higher concentrations of NaOH, the treatment appears to attack the surface more uniformly. The nitric acid boil causes large etch pits.



The ultraviolet absorption spectra of the sulfuric acid and NaOH anodization baths are shown in Figure 6. The NaOH bath has an absorption into the visible region. The sulfuric acid bath absorption drops off quickly in the visible region. This indicates that the molecular species created by NaOH are more aromatic than the molecular species created by the sulfuric acid.

In order to determine if the same molecular species could be detected on the fiber surfaces, the fast atom bombardment mass spectra (FABMS) of these fiber surfaces are shown in Figure 7. The upper spectra show the mass fragments from 0 to 100 atomic mass units (AMU) emitted from the fiber surface. The pattern for both fibers show a cracking pattern typical of aliphatic compounds. The lower spectra show the mass fragments of 100 to 200 AMU emitted from the fiber surface. These higher mass fragments can be assigned to aromatic compounds. It should be pointed out here that the NaOH spectrum in the 100-200 AMU region is ten times less intense than the sulfuric acid treated fibers. This indicates that the fibers anodized in sulfuric acid may be more aromatic than the NaOH treated fibers.

The polar and dispersive components of the surface energy of the fibers studied are listed in Table IV. There was a lot of variability in these measurements. Therefore, the differences observed may not be significant. Some interesting observations however are that the Union Carbide fibers have a low polar component, and the sulfuric acid anodized fibers have a high dispersive component. This high dispersive component would be predicted if the surface were aromatic as indicated by the FABMS results.

The breaking strengths of the fibers at 2.54 cm length are listed in Table V. It can be seen that the surface treatment caused about a 20% loss in

the strength of the fiber. The treatments used here (0.5M NaOH or H<sub>2</sub>SO<sub>4</sub> larger at 6V for 2 min) are thus probably too severe. The breaking strengths of the Hercules and Union Carbide fibers at different lengths are shown in Figure 8. It can be seen that the strength of the Hercules fibers increases with decreasing length. The Union Carbide fiber strengths were less dependent on length. This could be due either to surface effects (from the surface treatment or precursor) or from the structure of the carbon in the fiber.

The fiber critical lengths of the AS-4, AU-4, NaOH anodized, and H<sub>2</sub>SO<sub>4</sub> anodized fibers are shown in Table VI. The treated fibers show a much shorter fiber length. It is not certain at this point whether this is due to an improved fiber matrix adhesion or due to a decrease in the fiber strength.

The results from the adsorption experiment are shown in Figure 9. Although the results are scattered, it appears that more polysulfone is being adsorbed on the graphite powder surface from methylene chloride than from chloroform. No conclusions can be drawn from this experiment as yet. However, it is felt that the adsorption properties of fiber sizings may have a great effect on the dynamical properties of the resulting composite.

#### ACKNOWLEDGEMENTS

The support of NASA-LaRC of the research under Grant NAG-1-343 is acknowledged. Enabling funds for the purchase of the surface analyzer equipment came from the National Science Foundation and Virginia Tech.

#### REFERENCES

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- 2) Hammer, G. E. and Drzal, L. T., "Graphite Fiber Surface Analysis by X-Ray Photoelectron Spectroscopy and Polar/Dispersive Free Energy Analysis", Appl. Surf. Sci., 4, 340 (1980).
- 3) Wadsworth, N. J. and Spilling, I., "Load Transfer from Broken Fibers in Composite Materials", Brit. J. Appl. Phys. (J. Phys. D) ser. 2, 1, 1049 (1968).

TABLE I  
ANODIZATION CONDITIONS

Electrolyte	Concentration	Voltage (Volts)	Current (amps/ <sup>2</sup> )	Time (minutes)
NaOH	0.05M	4.0	1.45	30
	0.10M	4.0	1.93	30
	0.25M	4.0	2.90	30
	0.50M	4.0	4.83	30
	1.00M	4.0	7.74	30
	0.50M	6.0	11.60	2
H <sub>2</sub> SO <sub>4</sub>	0.05M	4.0	2.90	30
	0.10M	4.0	3.87	30
	0.25M	4.0	7.74	30
	0.50M	4.0	11.12	30
	1.00M	4.0	10.64	30
	0.50M	6.0	14.49	2
NH <sub>4</sub> HCO <sub>3</sub>	5%	2.4	0.48	30
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	5%	4.0	3.86	30
H <sub>2</sub> O		4.0	0.48	30

TABLE II  
 DERIVATIZATION RESULTS FOR HERCULES AS-4 FIBERS

Treatment	Functional Group	Atomic Percentages				
		C	O	N	F	Hg
CONTROL		84.9	11.0	4.1	0	-
PFB	NH,NH <sub>2</sub>	77.7	13.8	3.3	5.2	-
TFE	COH	86.5	8.4	3.8	1.3	-
TFAA	COOH, COH	85.9	9.4	3.4	1.4	-
PFPH	C=O	82.9	11.7	4.4	0	-
Hg	C=C	80.7	14.6	2.9	0	1.8

TABLE III  
 DERIVATIZATION RESULTS FOR CELION 6000 FIBERS

Treatment	Functional Group	Atomic Percentages				
		C	O	N	F	Hg
CONTROL		84.2	14.1	1.6	0	-
PFG	NH, NH <sub>2</sub>	81.6	13.9	1.3	3.1	-
TFE	COH	82.1	13.7	1.9	1.0	-
TFAA	COOH, COH	81.6	15.1	1.9	1.5	-
PFPH	C=O	84.5	12.4	2.0	1.2	-
Hg	C=C	81.5	13.6	1.5	0.4	1.4

TABLE IV  
SURFACE ENERGY ANALYSIS

Fiber	$\gamma_p$	$\gamma_d$
Celion 6000	18.1	29.6
AS-4	22.0	29.4
AU-4	18.2	28.1
NaOH Anodized	21.0	28.8
H <sub>2</sub> SO <sub>4</sub> Anodized	22.4	33.7
HNO <sub>3</sub> Boiled	18.1	29.6
T-300 No Shear	9.5	32.9
T-300 Shear	11.1	35.8

TABLE V  
BREAKING STRENGTH OF CARBON FIBERS

Fiber*	S (GPa)	$\sigma$
Celion 6000	2.48	0.51
AS-4	2.87	0.87
AU-4	2.71	0.79
NaOH Anodized	2.21	0.78
H <sub>2</sub> SO <sub>4</sub>	2.12	0.95
T-300 No Shear	2.20	0.39
T-300 Shear	2.24	0.38

\*2.54 cm length

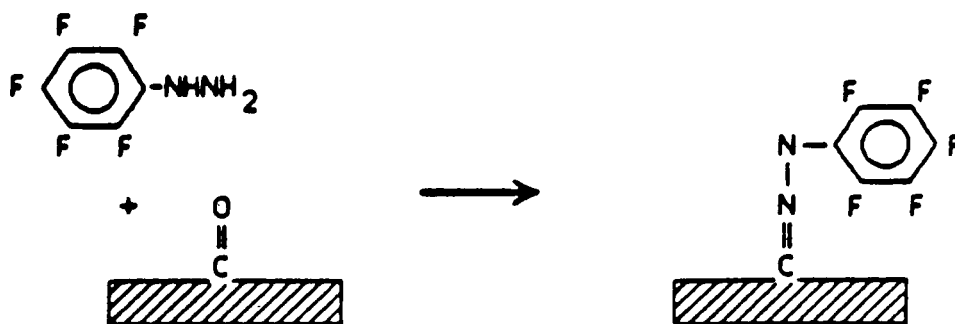


TABLE VI

FIBER CRITICAL LENGTHS OF FIBERS CAST IN 5% UDEL P1700

<u>Fiber</u>	<u>Fiber Length (mm)</u>	<u><math>\sigma</math></u>
AS-4	0.45	0.12
AU-4	0.42	0.11
H <sub>2</sub> SO <sub>4</sub> Anodized	0.27	0.07
NaOH Anodized	0.34	0.08

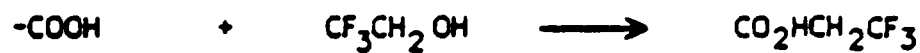
Figure.1 DERIVATIZATION SCHEME



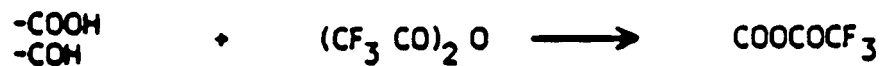
PENTAFLUOROBENZALDEHYDE (PFB)



TRIFLUOROETHANOL (TFE)



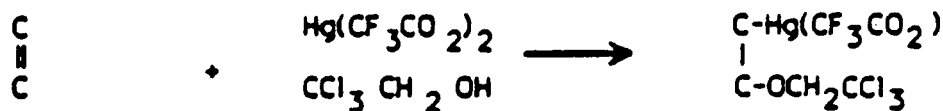
TRIFLUOROACETIC ANHYDRIDE



PENTAFLUOROPHENYLHYDRAZINE (PFPH)



MERCURIC TRIFLUOROACETATE (HgTFA)



# Figure 2 XPS ANALYSIS OF COMMERCIALY AVAILABLE CARBON FIBERS

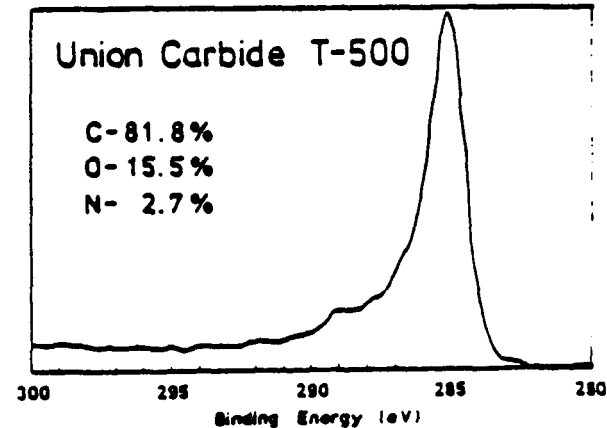
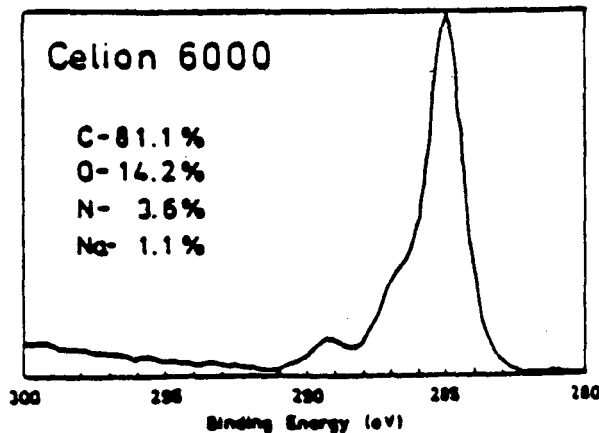
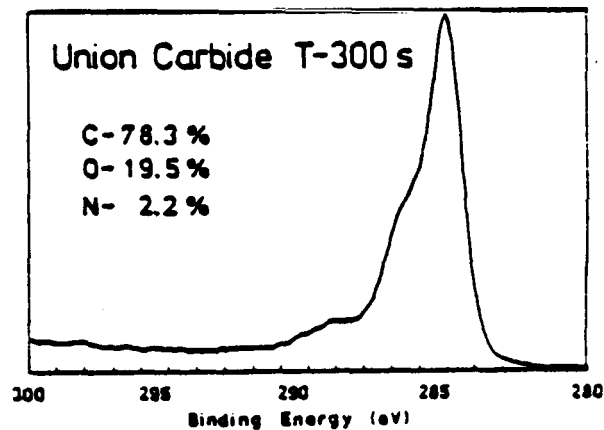
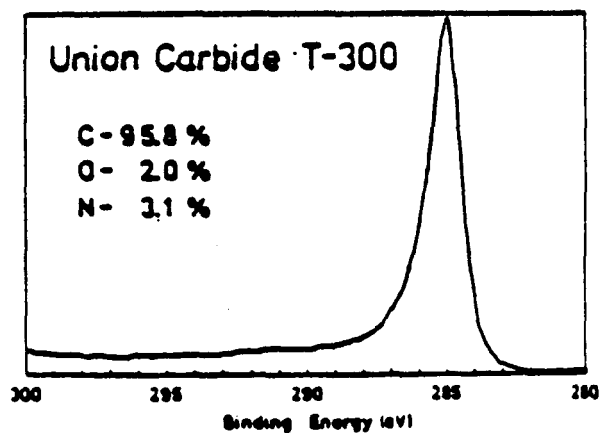
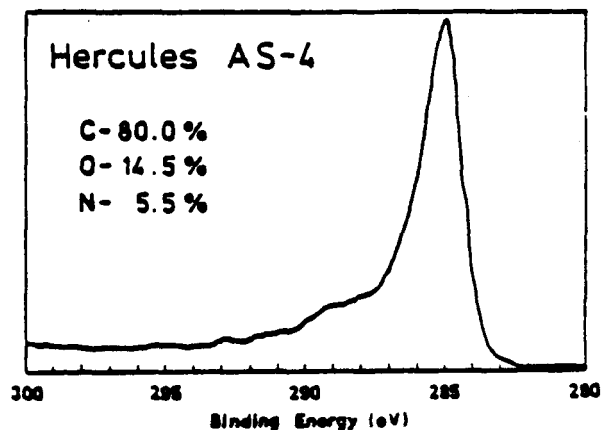
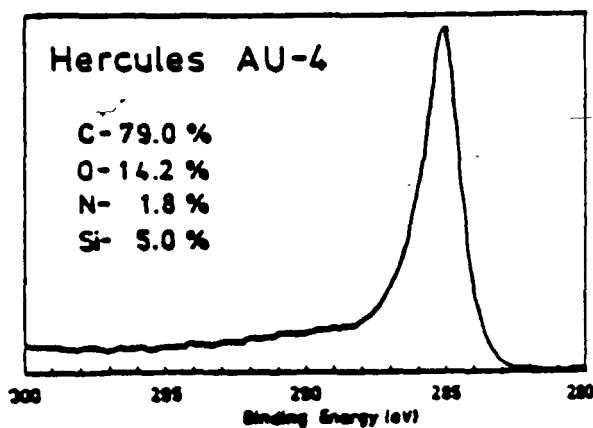
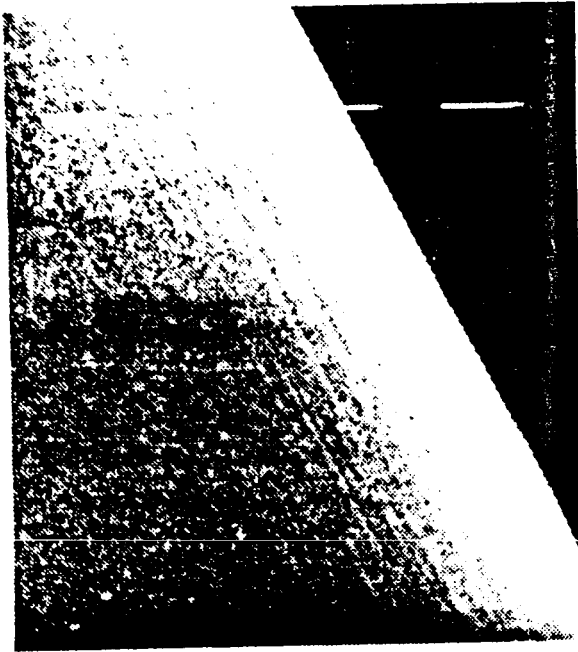


Figure 3: SEM Photomicrographs of Commercially Available Carbon Fibers (25,000 X)

AU-4



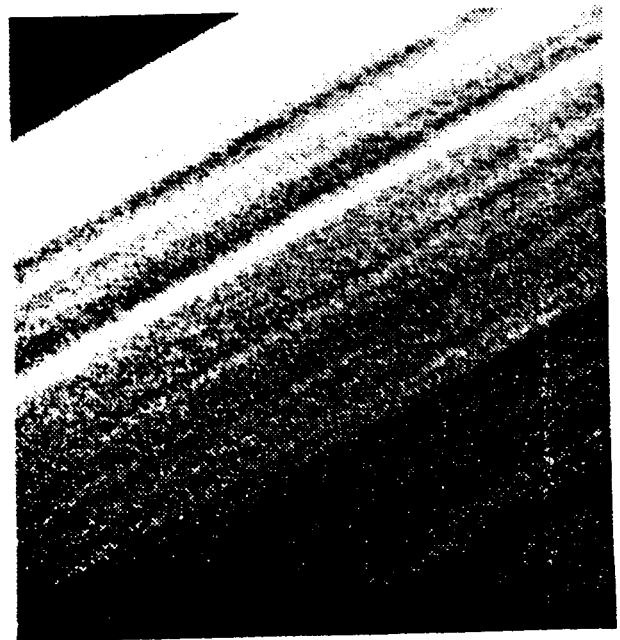
AS-4



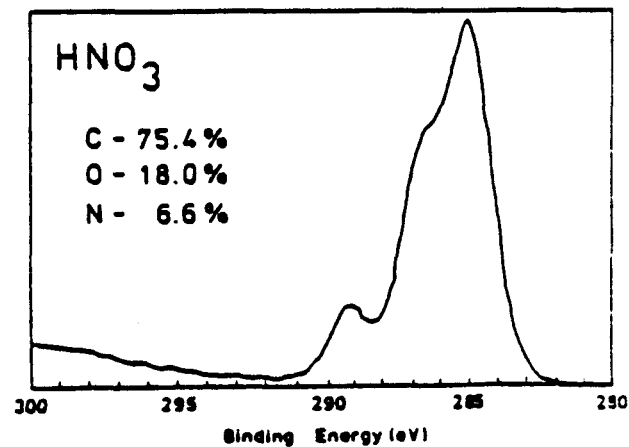
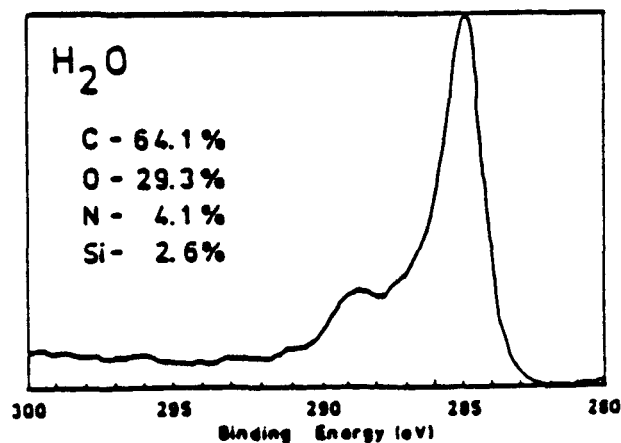
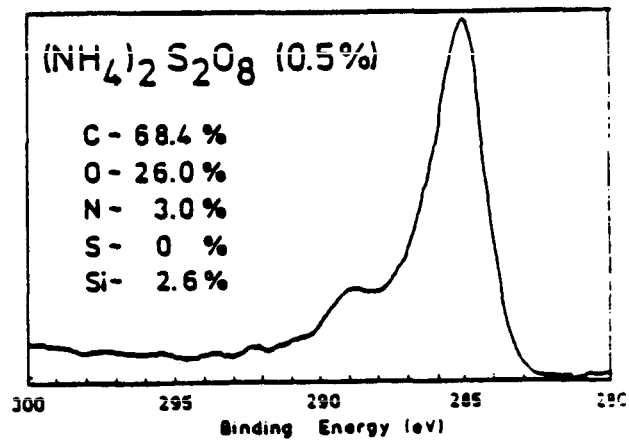
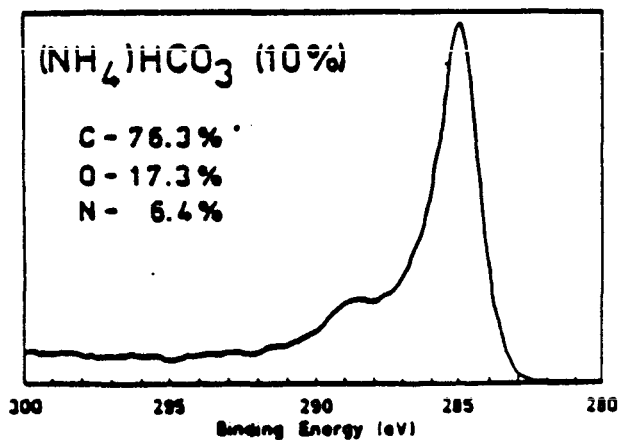
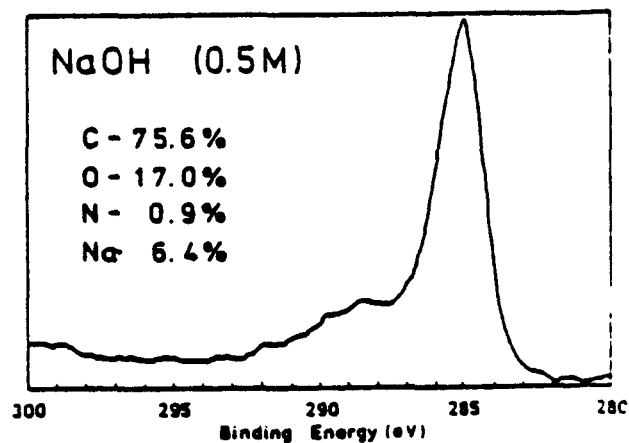
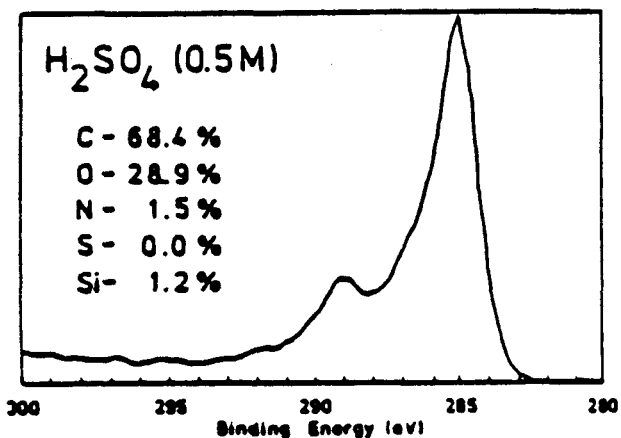
Union Carbide T-300



Celion 6000



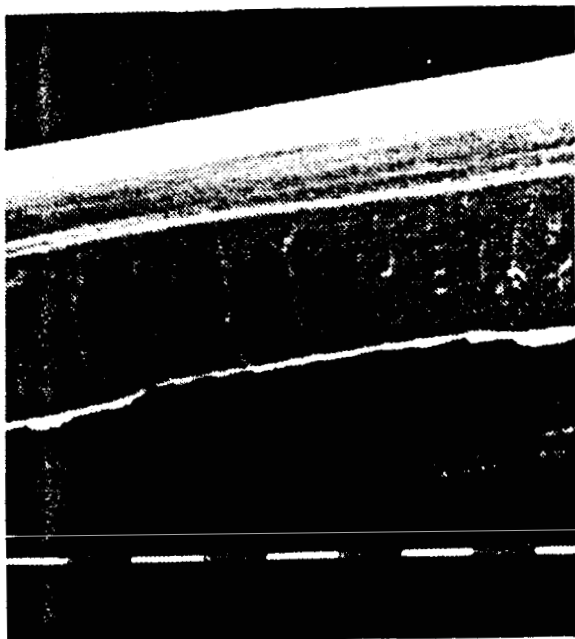
# Figure 4 XPS ANALYSIS OF SURFACE TREATED CARBON FIBERS



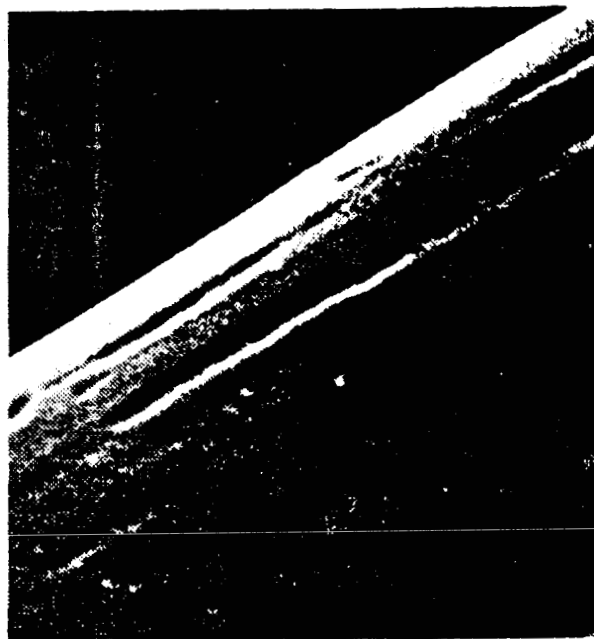
ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 5: SEM Photomicrographs of Surface  
Treated Carbon Fibers

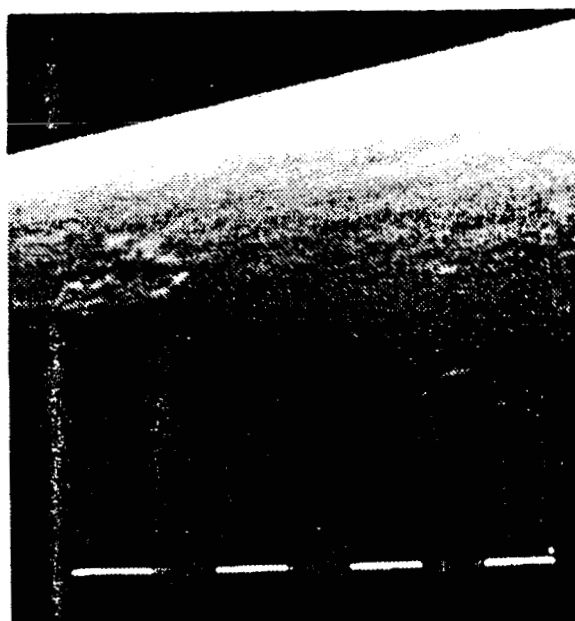
0.05M  $H_2SO_4$  anodized



0.05M NaOH anodized



0.5M NaOH anodized



$HNO_3$  boiled

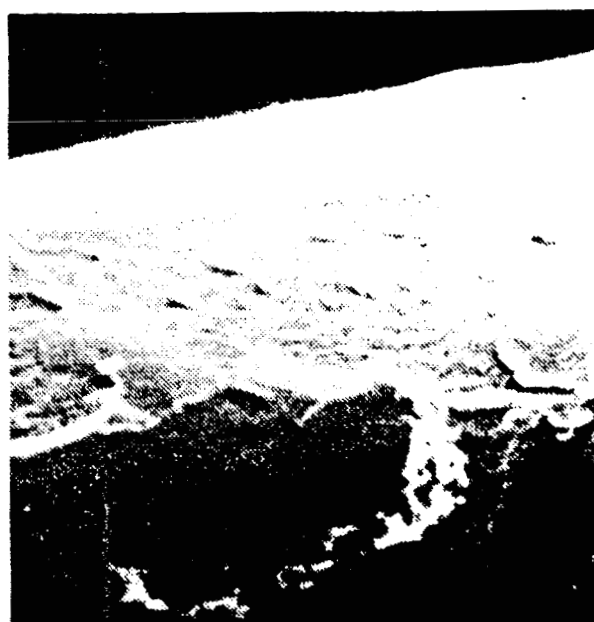


Figure 6: UV Absorption Spectra of Anodization Bath

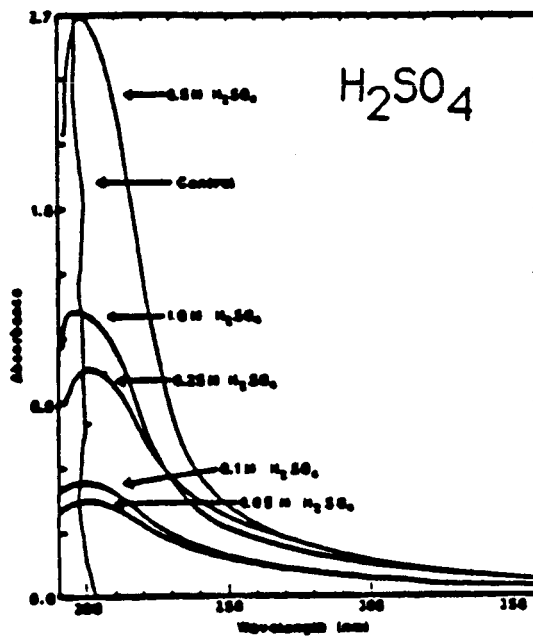
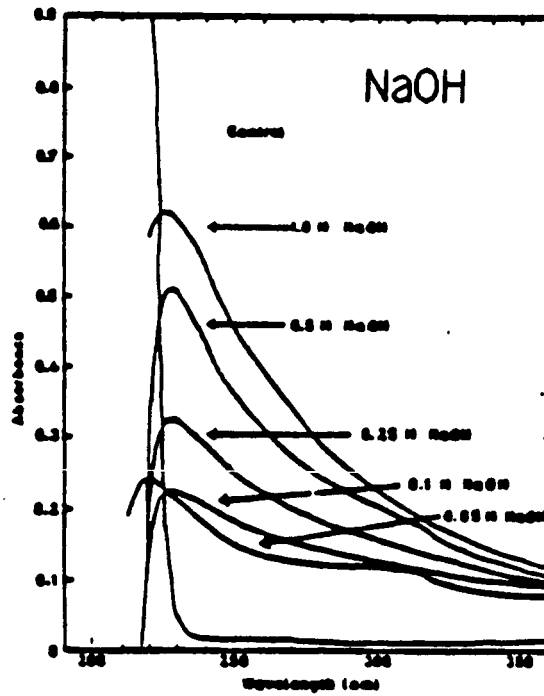


Figure 7: FABMS Spectra of Surface Treated Carbon Fibers

