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SEMI ANNUAL REPORT

FRACTURE SURFACE ANALYSIS IN COMPOSITE
AND TITANIUM BONDING

BY

T. A. DEVILBISS AND J. P. WIGHTMAN

(NASA-CR-176309) FRACTURE SURFACE ANALYSIS
IN COMPOSITE AND TITANIUM BONDING (Virginia
Polytechnic Inst. and State Univ.) 39 P
HC A03/MF A01 CSCL 11D

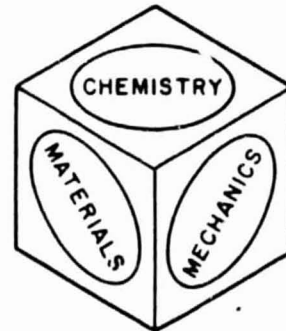
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G3/24 27654

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September, 1985

I. INTRODUCTION

In order to understand the mechanical properties of fiber-reinforced composite materials, it is necessary to understand the mechanical properties of the matrix materials and of the reinforcing fibers. Another factor that can affect the mechanical properties of a composite material is the interaction between the fiber and the matrix. In general, composites with strong fiber matrix bonding will give higher modulus, lower toughness composites. Composites with weak bonding will have a lower modulus and more ductility.

The situation becomes a bit more complex when all the possibilities are considered. Some things which should be taken into consideration are the following: the properties of the surface layer on the fiber, the interactive forces between polymer and matrix, the surface roughness and porosity of the fiber, and, the morphology of the matrix polymer at the fiber surface.

In practice, the surface of the fibers are treated to enhance the mechanical properties of a composite. These treatments include anodization, acid etching, high temperature oxidation, and plasma oxidation to name a few. The work presented here is aimed at understanding the chemical nature of carbon fiber surfaces. Our overall goal is to be able to predict the surface properties of carbon fibers treated in various ways, and then to relate surface properties to fiber matrix bonding.

II. METHODS AND MATERIALS

Fibers

The fibers used in this study included Hercules AU-4 (a low modulus carbon fiber without any surface treatment after carbonization), Hercules AS-4

(a low modulus carbon fiber with a proprietary surface treatment), Celanese Celion 6000 (a low modulus carbon fiber with a proprietary surface treatment), Union Carbide T-300 and T-500. T-300 is a low modulus fiber; T-500 is an intermediate modulus fiber. Three types of T-300 were studied and two of them had undergone no surface treatment, but had been manufactured under different (but unknown) conditions. One of these fiber samples had been given a lot number of YT-060683-1 and will be designated T-300 YT, the other did not have a lot number, but will be designated T-300 SM (SM being the initials of the person preparing the fiber for our observation). The third T-300 fiber had undergone a proprietary surface treatment. The T-500 had also undergone a proprietary surface treatment.

Surface Treatments

The surface treatments used in this study were acid etching, and anodization. Acid etching was performed by wrapping about 2 meters of AS-4 fibers around a 15mm diameter by 50mm glass cylinder then placing this in 70% boiling nitric acid for 3 hours. The acid etched fibers were then analysed by XPS, derivatization, and contact angles as described below.

Anodization was carried out on AU-4 fibers. Approximately 1100 mm (43.3") of fibers were wrapped around a glass frame as shown in Figure 1. A piece of 0.15mm (0.006") copper was used for the electrical contact. The electrolytes used were sodium hydroxide, sulphuric acid, ammonium carbonate, and distilled water. The anodization conditions are summarized in Table I. In this work, the voltage was set and the current measured. The amount of current per unit surface area was calculated by dividing the current by the estimated geometrical surface area.

The anodization bath was analyzed by UV spectroscopy after anodization. The original solution was used as a reference. After anodization, the fibers

were rinsed in distilled water, placed in a glass vial and dried at 100° C for 24 hours. The fibers were then analysed by XPS.

X-Ray Photoelectron Spectroscopy

The fiber surfaces were chemically analyzed by X-ray photoelectron spectroscopy using a Perkin Elmer PHI 5300 electron spectrometer. A Mg K α X-ray source was used at 250 mwatts of power. This spectrometer operates in a fixed analyzer transmission (FAT) mode. Several of the spectra were recorded on a Kratos XSAM 800 electron spectrometer with Mg K α X-ray source (250 mwatt power) in a fixed retarding ration (FRR) mode. All spectra were recorded with the angle between the plane of the fibers and the electron analyser at 90° unless otherwise noted. Percentages of elements present were calculated by determining the area under each peak. These areas were adjusted by a sensitivity factor characteristic of each element.

In order to better understand the functional nature of the carbon fiber surface, the carbon 1s peaks were curve fit by assuming the shape and size of deconvoluted peaks contained in the total peak. In order to help in choosing the peak shape, graphite powder was used as a standard to determine the full width at half maximum, and the gaussian-laurentzian character of the carbon peak.

The AS-4 and the T-300 SM fibers were also analysed with the fibers oriented at different angles relative to the electron analyser. By performing this angular dependent study, it is possible to obtain some idea of the depth profile of the various atomic species present on the fiber surface. The angles measured were 10°, 30°, and 90°.

A derivatization scheme developed by Everhart and Reilley [1] was also used. In this technique, a series of reagents containing fluorine or some other elemental tag are 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 is shown in Figure 2. The reagents used are outlined in Table II.

Contact Angles

The contact angles of various liquids on the surface of carbon fibers were measured by the technique described by Drzal [2]. In this method, the wetting force of the fiber penetrating the liquid is measured using an electrobalance. This is related to the contact angle by equation [1].

$$F = \gamma_L \pi d \cos \theta \quad [1]$$

where F is the wetting force, γ_L is the surface energy of liquid, d is the diameter of fiber, and θ is the contact angle.

All wetting force measurements were made on a Perkin Elmer TGS-2 Thermogravimetric system. The diameter of the fibers were measured on a Unitron Model 3452 measuring microscope at 600X magnification. By using liquids of known polar and dispersive components, the polar and dispersive components of the surface energy of the fiber could be estimated. This was done by assuming that the polar and dispersive components add to equal the total surface energy of the liquid and the solid as given by equations [2a] and [2b].

$$\gamma_L^T = \gamma_L^D + \gamma_L^P \quad [2a]$$

$$\gamma_S^T = \gamma_S^D + \gamma_S^P \quad [2b]$$

The equation for the work of adhesion (W_A) is shown in equation [3].

$$W_A = \gamma_L (1 + \cos \theta) \quad [3]$$

If we use the assumption given in equation [4] that the work of adhesion

$$W_A = 2 \left[(\gamma_S^P \gamma_L^P)^{1/2} + (\gamma_S^D \gamma_L^D)^{1/2} \right] \quad [4]$$

can also be equated to twice the geometric mean of the product of the

dispersive components of the solid and liquid plus the geometric mean of the respective polar compounds, equation [5] is obtained.

$$\gamma_L (1 + \cos \theta) / (2\gamma_L^D)^{1/2} = (\gamma_S^D)^{1/2} + (\gamma_S^P)^{1/2} (\gamma_L^P / \gamma_L^D)^{1/2} \quad [5]$$

By plotting the left hand side of Eqn. [5] as a function of $(\gamma_L^P / \gamma_L^D)^{1/2}$ and assuming a linear relation, the polar and dispersive components of the solid surface can be obtained from the slope and intercept squared, respectively. The liquids used in this study and their surface energy characteristics are shown in Table III.

Scanning Transmission Electron Microscopy

Electron Micrographs of the fibers were obtained with a Phillips Model 420 scanning transmission electron microscope (STEM). The fibers were mounted on a copper mount with silver paint. The fibers were not coated before examination.

III. RESULTS AND DISCUSSION

Scanning Transmission Electron Microscopy (STEM)

STEM photomicrographs of the commercially available and some of the surface treated fibers are shown in Figures 3-9. The AS-4 and AU-4 fibers appear to be smooth with a few ridges on the AU-4 fiber. The other fibers have large ridges. There were no other observable differences between the surfaces of these fibers.

XPS-Curve Fit Carbon 1s Peaks

A typical curve-fit carbon 1s photoelectron peak is shown in Figure 13. The one shown here is for the AS-4 fiber. It can be seen that there are several peaks at different binding energies. This has been shown to be due to the carbon being in different binding states. The higher the binding energy of the carbon, the greater its oxidation state. The main peak at the lowest binding energy is typically assigned to carbon bonded to carbon. The next

peak going up in binding energy generally occurs at 1-1.6 eV from the main peak. This is normally assigned to carbon singly bonded to oxygen, nitrogen, and sulfur. The next peak at 2-3.5 eV from the main peak is due to carbon doubly bonded to oxygen, nitrogen, and sulfur. Peaks at higher binding energies are due to carbon in higher oxidation states.

Derivatization

The AS-4, Celion 6000, and AS-4 boiled in nitric acid 3 hrs. fibers were chosen for the derivatization study. The XPS results for these 3 fibers are shown in Table IV. The terms ' ΔBE ' and 'FWHM' refer to shift in binding energy and full width at half maximum, resp. The derivatization results for these fibers are shown in Tables V-VII.

From Table IV it can be seen that the Hercules AS-4 fiber has a relatively low oxygen content, but a high nitrogen content. Boiling in nitric acid increases the oxygen content but decreases the nitrogen content. The derivatization results for these two fibers indicate that the AS-4 fibers are high in amines on their surface whereas nitric acid removes these amine groups and creates carbonyl groups. This is also confirmed by looking at the carbon 1s curve fit peaks. The AS-4 peak shows a large shoulder at +1.30 eV from the main carbon peak. This shoulder can be assigned to amine and alcohol groups. The nitric acid treated sample shows a smaller peak at +0.98 eV, but a larger peak at +1.08 eV. This peak can be assigned to carbonyls and other higher oxidation states of carbon. The Celion 6000 fiber has a moderate oxygen level and a low nitrogen level. The carbon 1s peak for this fiber shows major peaks at +1.66 eV and +4.30 eV from the main carbon peak. The +1.66 eV peak can be assigned to the amines and alcohols which are also seen in the derivatization. The +4.30 peak can be assigned to carbonyls which were also seen in the derivatization reaction.

Contact Angles

In an effort to relate functional groups to contact angles, the same fibers that were studied by derivatization were also studied by contact angle analysis. The contact angles of the liquids used on these fibers are shown in Table VIII. Figure 14 shows the plot of Eqn. [5] used to obtain the polar and dispersive components of the total surface energy.

All the fibers had about the same dispersive component. However, the nitric acid treated sample had a polar component much lower than the AS-4 or Celion 6000 fiber.

Angular Dependent XPS

As the angle decreases, the escape depth of the ejected electrons becomes shorter. Therefore, the electrons ejected at smaller angles are more representative of the surface layer. The XPS results of AS-4 and T-300 SM fibers obtained at various angles are shown in Table IX. It can be seen that the oxygen content of both fibers increases as the angle decreases. This indicates that there is more oxygen at the surface of these fibers than in the bulk. The nitrogen content of the AS-4 fiber increases with decreasing angle while the nitrogen content of the T-300 SM fiber decreases with decreasing angle. This shows that the AS-4 fiber surface is nitrogen rich, while the T-300 SM fiber is not. This result for the AS-4 fiber supports the derivatization results where amine groups were indicated as functional groups on the surface.

Commercially Available Fibers

The atomic percentages of elements detected, and the percentages of the individual peaks within the carbon peak for the commercially available fibers are listed in Table X.

The AS-4 and Celion 6000 fiber have a higher nitrogen content than the other fibers. The surface treated fibers have higher oxygen contents than the untreated fibers. The treated fibers also have a higher percentage of carbon in a higher oxidation state as seen by the curve fit carbon peaks.

Shear treatment of the T-300 fiber increases the oxygen content of the fiber. Analysis of the carbon 1s peak shows a large shoulder at +1.53 eV, and a smaller one at +3.67 eV. This indicates a large increase in alcohol groups with a slight increase in higher oxidation states of carbon. There may also be some amines formed. However, the nitrogen content would indicate that there are not many.

The shear treated T-500 fiber also had a high oxygen content. However, it was not as high as the shear treated T-300. This may be due to the higher crystal order of the T-500, the higher crystalline regions being less accessible to oxidation. The carbon 1s peak is similar to that of the shear treated T-300, except that it shows less alcohol groups (+1.50 eV) and slightly more carbon in higher oxidation states. The untreated Union Carbide T-300 SM fiber had a very low oxygen and nitrogen content. Its carbon 1s peak is essentially featureless.

The other untreated fiber (T-300 YT) had a much higher oxygen content. Its carbon 1s peak was also featureless. It is not certain why the oxygen content of this fiber is so high, or why there are not features in the carbon peak. (Note: SEM analysis indicates a patchy layer that may be sizing or oil and it may be that the fiber was mislabeled or contaminated).

Anodization

The UV absorption spectra of the NaOH anodization baths after anodization are shown in Figure 15. It was necessary to dilute the solution 10:1 with water in order to obtain a good spectra. The control used was 1M NaOH with

distilled water as the reference. The UV absorption spectra of the H_2SO_4 anodization bath is shown in Figure 16. It was not necessary to dilute this solution to obtain a spectra. The control used was 1M H_2SO_4 with distilled water as with reference. In both electrolytes, the reference used was the original solution before anodization.

Comparison of these spectra shows that the NaOH bath has more absorbance in the longer wavelength region. This indicates that this bath contains more conjugated molecules than the H_2SO_4 bath. A proposed model is that as the fibers are being anodized, the edges of the graphite layers are undergoing chemical reactions. As the anodization proceeds, the layers are removed from the fiber surface and go into the anodization solution. Therefore, it is expected that the surface of the anodized fiber will be similar to the material found in the anodization bath. More work is needed to verify this suggestion. However, if this is true, it is expected that the NaOH anodized fibers will have more dispersive contribution to its surface energy than the H_2SO_4 anodized fibers. This is expected since the NaOH anodization bath has more conjugated molecules. This conjugation should give a higher electron density which would make the fiber surface more polarizable.

The XPS results for the AU-4 fibers anodized in NaOH are shown in Table XI. The XPS results for the AU-4 fibers anodized in H_2SO_4 , $(NH_4)_2CO_3$, and H_2O are shown in Table XII. NaOH anodization tends to increase the peak at +1-1.5 typical of carbon singly bonded to oxygen, while H_2SO_4 anodization tends to increase the oxygen content more and to increase the peaks at +2.1-2.5 eV and +3.5-4.0 eV typical of carbon doubly bonded to oxygen and higher oxidation states. The $(NH_4)_2CO_3$ anodized fibers had a much higher nitrogen content. The peak at +1.28 eV was also increased. This would be due to amine groups, or carbon singly bonded to nitrogen. The H_2O anodized fibers showed an

increase in oxygen, and an increase in the carbon peak at +3.92 eV. Thus H₂O anodization creates functional groups of carbon in higher bonding sites.

STEM photomicrographs of some of the anodized fibers are shown in Figures 11-13. The 0.05M NaOH appears to attack specific areas on the fiber surface and create large cavities. The 0.05M H₂SO₄ appears to cause layers of the graphite to be removed. 0.5M NaOH attacks the fiber surface more uniformly. The treatments used here were rather severe and caused considerable damage. Further work will include anodization for shorter times.

REFERENCES

- 1) Everhart, D. S., and Reilley, C. N., "Chemical Derivatization in Electron Spectroscopy for Chemical Analysis of Surface Functional Groups Introduction on Low-Density Polyethylene Film", Anal. Chem., 53, 665, (1981).
- 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).

TABLE I

ANODIZATION CONDITIONS

<u>Electrolyte</u>	<u>Concentration</u>	<u>Voltage</u> <u>(volts)</u>	<u>Current</u> <u>(amps/m²)</u>	<u>Time</u> <u>(minutes)</u>
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
H ₂ SO ₄	0.05M	4.0	2.90	30
	0.1M	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
(NH ₄) ₂ CO ₃	5.0%	2.4	0.48	30
H ₂ O		4.0	0.097	30

TABLE II
 REAGENTS USED IN DERIVATIZATION SCHEME

PEN. FLUOROBENZALDEHYDE (PFB)				
-NH, NH ₂	+	OCHC ₆ F ₅	----->	N-CH ₆ F ₅
TRIFLUOROETHANOL (TFE)				
-COOH	+	CF ₃ CH ₂ OH	----->	CO ₂ HCH ₂ CF ₃
TRIFLUOROACETIC ANHYDRIDE (TFAA)				
-COOH				CO ₂ HCH ₂ CF ₃
	+	(CF ₃ CO) ₂ O	----->	
-COH				COOCOFC ₃
PENTAFLUOROPHENYLHYDRAZINE (PFPH)				
-C=O	+	C ₆ F ₅ NHNH ₂	----->	C-NHNHC ₆ F ₅
MERCURIC TRIFLUOROACETATE (HgTFA)				
-C		HgCF ₃ CO ₂) ₂	----->	C-Hg(CF ₃ CO ₂)
	+			
-C		CCl ₃ CH ₂ OH		C-OCH ₂ CCl ₃

TABLE III
SURFACE ENERGIES OF LIQUIDS USED

Item	Water	Ethylene Glycol	Form- amide	Diiodo- Methane	Bromo- Napthalene
Total surface energy (ergs/cm ²)	72.8	48.3	58.3	50.8	44.6
Dispersive surface energy (ergs/cm ²)	21.8	29.3	32.3	48.5	44.6
Polar surface energy (ergs/cm ²)	51.0	19.0	26.0	2.4	0.0

TABLE IV

XPS RESULTS OF CARBON FIBERS STUDIED BY DERIVATIZATION

AS-4	<u>C</u>	<u>O</u>	<u>N</u>			
	80.0%	14.5%	5.5%			
<u>C 1s Analysis</u>	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	65.1		1.39			
C2	21.4	+1.30	1.65			
C3	8.1	+3.03	1.56			
C4	5.4	+4.34	1.71			
AS-4 HNO ₃ 3Hrs.	<u>C</u>	<u>O</u>	<u>N</u>			
	75.4%	18.0%	6.6%			
<u>C 1s Analysis</u>	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	42.1		1.4			
C2	19.5	+0.98	1.33			
C3	29.54	+2.08	1.54			
C4	9.83	+4.38	1.51			
Celion 6000	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	81.1%	14.2%	3.6%		1.0%	
<u>C 1s Analysis</u>	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	71.1		1.41			
C2	23.3	+1.66	1.86			
C3	5.6	+4.30	1.42			

TABLE V
 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 ₂	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 VI
 DERIVATIZATION RESULTS FOR CELION 6000 FIBERS

Treatment	Functional Group	Atomic Percentages				
		C	O	N	F	Hg
CONTROL		84.2	14.1	1.6	0	-
PFB	NH, NH ₂	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 VII
 DERIVATIZATION RESULTS FOR HERCULES AS-4 FIBERS BOILED IN NITRIC ACID
 FOR 3 HRS.

Treatment	Functional Group	Atomic Percentages				
		C	O	N	F	Hg
CONTROL		75.4	18.0	6.7	0	-
PFB	NH, NH ₂	71.5	24.4	1.9	2.2	-
TFE	COH	72.9	23.5	1.9	1.6	-
TFAA	COOH, COH	74.1	23.2	2.1	0.5	-
PFPH	C=O	71.0	24.0	2.6	2.4	-
Hg	C=C	73.5	23.4	0.3	0	-

TABLE VIII

CONTACT ANGLES OF CARBON FIBERS IN VARIOUS LIQUIDS

<u>Fiber</u>	<u>Water</u>	<u>Ethylene Glycol</u>	<u>Formamide</u>	<u>Diiodo- Methane</u>	<u>Bromo- Naphthalene</u>
AS-4	48.9	29.7	22.6	44.7	39.7
Celion 6000	51.0	33.4	47.2	44.2	33.6
HNO ₃ (3 hrs.)	70.3	47.7	38.6	48.2	40.0

TABLE IX

ANGULAR DEPENDENT XPS RESULTS OF AS-4 AND T-300 SM FIBERS

AS-4 90 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	80.0%	14.5%	5.5%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	65.1		1.39
C2	21.4	+1.30	1.65
C3	8.1	+3.03	1.56
C4	5.4	+4.34	1.71
AS-4 30 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	79.46%	17.7%	3.0%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	63.3		1.45
C2	19.2	+1.28	1.52
C3	9.1	+2.69	1.93
C4	8.4	+4.22	1.91
AS-4 10 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	74.0%	19.7%	6.3%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	58.3		1.40
C2	16.5	+1.31	1.38
C3	8.6	+2.63	1.52
C4	10.8	+4.12	1.84

TABLE IX (Continued)

T-300 SM 90 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	95.7%	2.0%	2.1%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	77.7		1.32
C2	19.1	+1.31	1.77
C3	3.2	+3.41	2.00
T-300 SM 30 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	93.6%	4.8%	1.5%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	79.5		1.36
C2	16.2	+1.41	1.58
C3	3.6	+3.24	2.18
C4	0.6	+5.76	1.15
T-300 SM 10 Degrees	<u>C</u>	<u>O</u>	<u>N</u>
	92.0%	6.9%	1.1%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	70.2		1.35
C2	20.5	+1.38	1.45
C3	6.4	+2.94	1.53
C4	2.9	+4.98	1.45

TABLE X

XPS RESULTS-ATOMIC PERCENTAGES AND CARBON 1S CURVES FIT RESULTS
FOR COMMERCIALY AVAILABLE CARBON FIBERS

AS-4	<u>C</u>	<u>O</u>	<u>N</u>			
	80.0%	14.5%	5.3%			
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	65.1		1.39			
C2	21.4	+1.30	1.65			
C3	8.1	+3.03	1.56			
C4	5.4	+4.34	1.71			
AU-4	<u>C</u>	<u>O</u>	<u>N</u>			
	82.6%	13.4%	2.2%			
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	78.3		1.45			
C2	16.1	1.40	1.44			
C3	5.6	3.38	2.94			
Celion 6000	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	81.1%	14.2%	3.6%		1.0%	
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	71.1		1.41			
C2	23.3	+1.66	1.86			
C3	5.6	+4.30	1.42			

TABLE X (Continued)

T-300 SM	<u>C</u>	<u>O</u>	<u>N</u>
	95.7%	2.0%	2.1%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	77.7		1.32
C2	19.1	+1.31	1.77
C3	3.2	+3.41	2.00
T-300 YT	<u>C</u>	<u>O</u>	<u>N</u>
	89.6%	9.2%	1.2%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	80.4		1.36
C2	14.1	+1.45	1.45
C3	5.5	+3.22	2.00
T-300 Shear	<u>C</u>	<u>O</u>	<u>N</u>
	78.3%	19.5%	2.2%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	66.4		1.47
C2	24.7	+1.53	1.56
C3	8.9	+3.67	2.61
T-500 Shear	<u>C</u>	<u>O</u>	<u>N</u>
	81.8%	15.5%	2.7%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>
C1	72.1		1.40
C2	17.6	+1.50	1.50
C3	4.1	+2.86	1.14
C4	6.2	+4.00	1.58

TABLE XI

RESULTS FOR NaOH ANODIZED AU-4 CARBON FIBERS

AU-4	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	81.6%	13.4%	2.2%			1.8%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	78.65		1.45			
C2	16.1	1.40	1.44			
C3	5.3	3.38	2.94			
AU-4 0.05M NaOH 4V-30m	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	79.5%	13.2%	3.4%			3.9%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	65.5		1.37			
C2	20.7	+1.37	1.70			
C3	6.2	+3.18	1.22			
C4	7.6	+4.47	2.00			
AU-4 0.25M NaOH 4V-30m	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	78.7%	15.9%	1.2%			4.2%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	44.9		1.36			
C2	36.8	+1.05	1.50			
C3	8.5	+1.62	1.49			
C4	9.8	+4.46	2.11			

TABLE XI (Continued)

AU-4 1 M NaOH 4V-30m

	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	78.6%	13.3%	1.2%			6.8%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	41.8		1.61			
C2	41.0	+0.98	1.26			
C3	5.1	+1.38	1.35			
C4	7.4	+3.66	1.35			
C5	4.7	+5.57	1.83			

TABLE XII

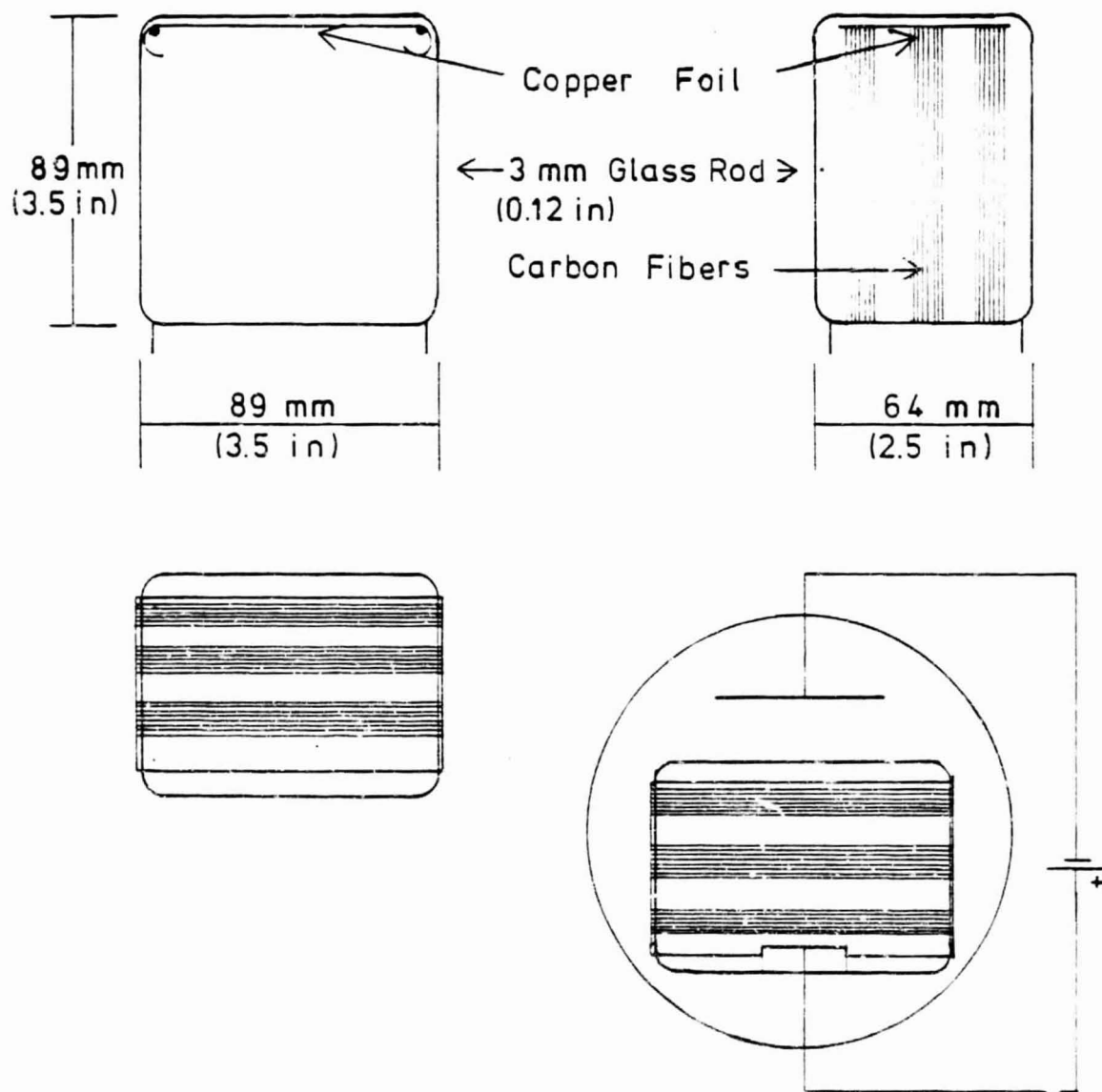
XPS RESULTS FOR AU-4 FIBERS ANODIZED IN H_2SO_4 , $(NH_4)_2CO_3$, AND H_2O

AU-4	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	82.6%	13.4%	2.2%			1.8%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	78.3		1.45			
C2	16.1	1.40	1.44			
C3	5.6	3.38	2.94			
AU-4 0.05 M H_2SO_4	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	61.9%	32.3%	2.3%	0.4%		3.1%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	57.1		1.43			
C2	18.0	+1.19	1.36			
C3	10.4	+2.46	1.52			
C4	14.5	+4.22	1.77			
AU-4 0.5 M H_2SO_4	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	68.4%	28.9%	1.5%			1.2%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	57.2		1.51			
C2	18.6	+1.22	1.62			
C3	6.8	+2.44	1.16			
C4	17.4	+4.05	1.98			

TABLE XII (Continued)

AU-4 1.0 M H ₂ SO ₄	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	60.6%	35.2%	2.2%			2.0%
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	62.1		1.48			
C2	14.4	+1.24	1.41			
C3	11.6	+2.13	1.50			
C4	11.9	+4.14	1.76			
AU-4(NH ₄) ₂ CO ₃	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	76.3%	17.3%	6.4%			
C 1s Analysis	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	58.5		1.40			
C2	21.3	+1.28	1.59			
C3	5.9	+2.56	1.26			
C4	9.63	+3.75	1.63			
C5	4.62	+5.03	1.76			
AU-4 H ₂ O	<u>C</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>Na</u>	<u>Si</u>
	64.5%	29.4%	3.5%			2.6%
	<u>%</u>	<u>Δ BE</u>	<u>FWHM</u>			
C1	54.9		1.35			
C2	19.6	+1.15	1.54			
C3	10.5	+2.39	1.39			
C4	14.8	+3.92	1.81			

Figure #1. Anodization Apparatus



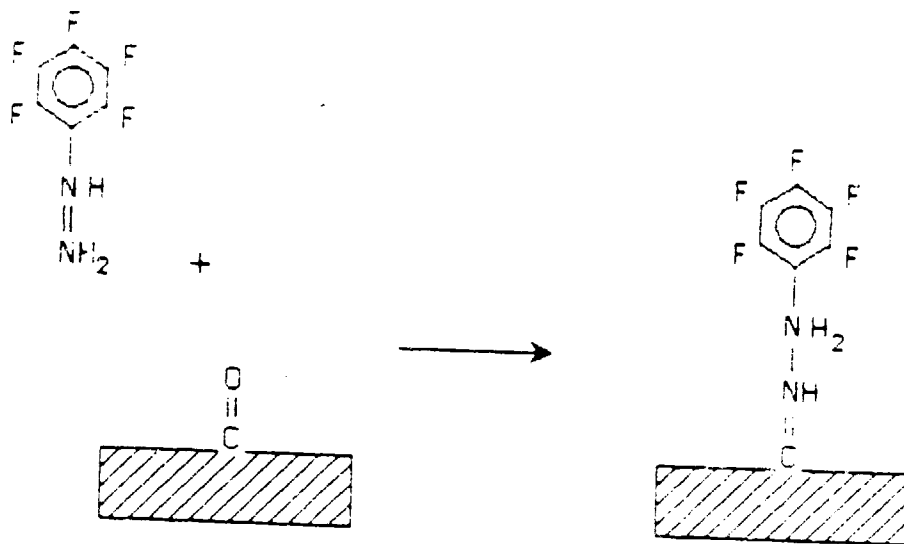


Figure #2. Typical Derivatization Reaction

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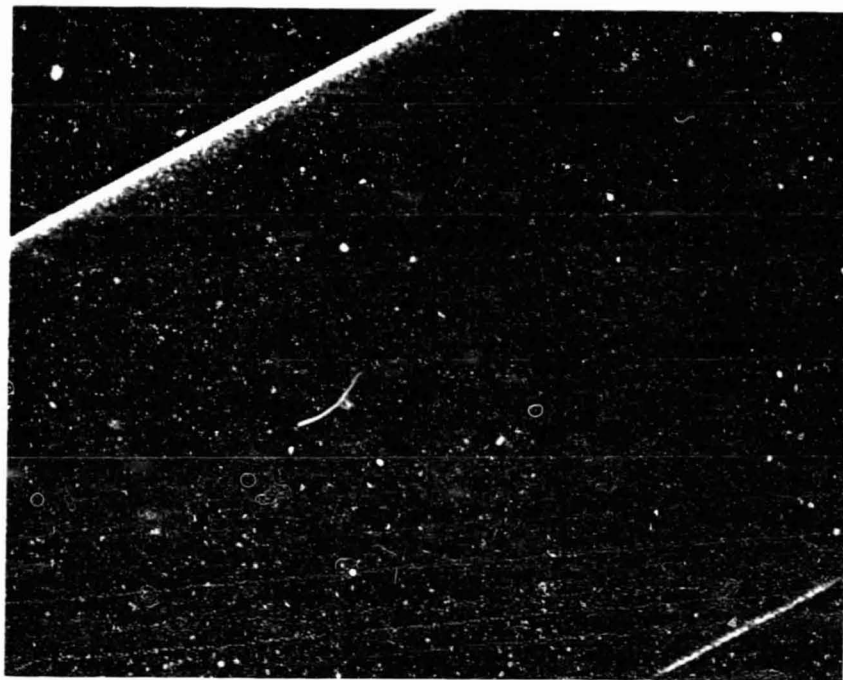


Figure #3. STEM Photomicrograph of Hercules AS-4 Carbon Fiber (12500X)

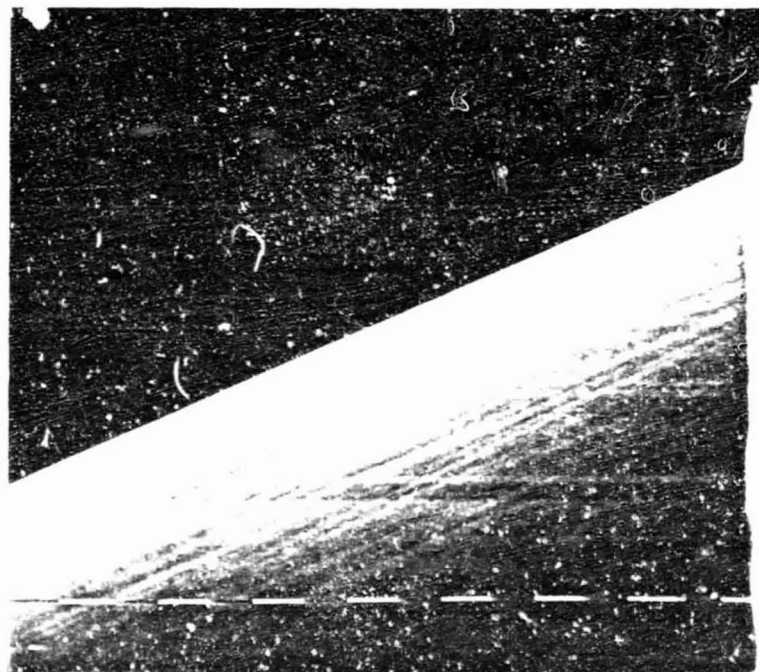


Figure #4. STEM Photomicrograph of Hercules AU-4 Carbon Fiber (12500X)

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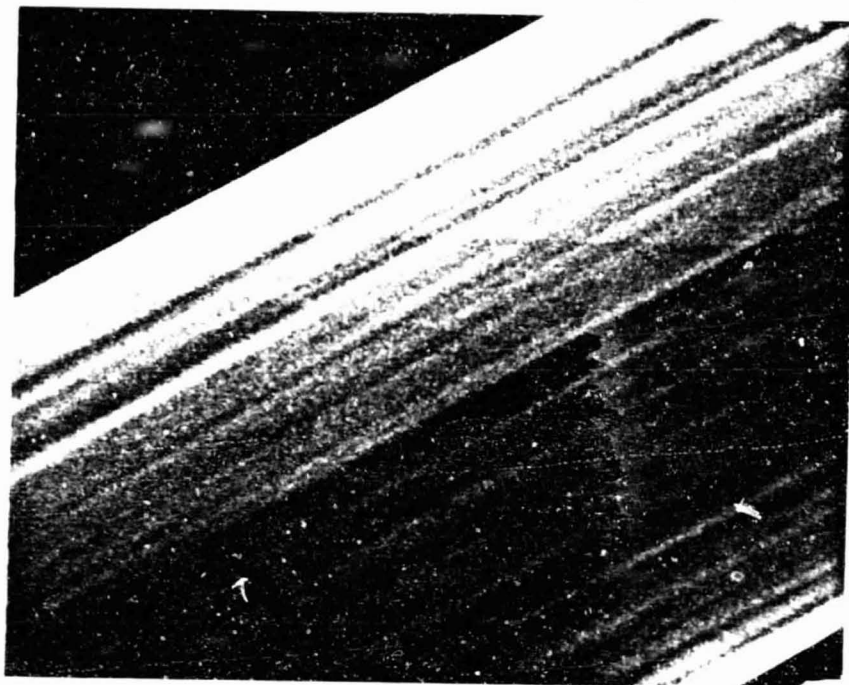


Figure #5. STEM Photomicrograph of Celion 6000 Carbon Fiber (12500X)

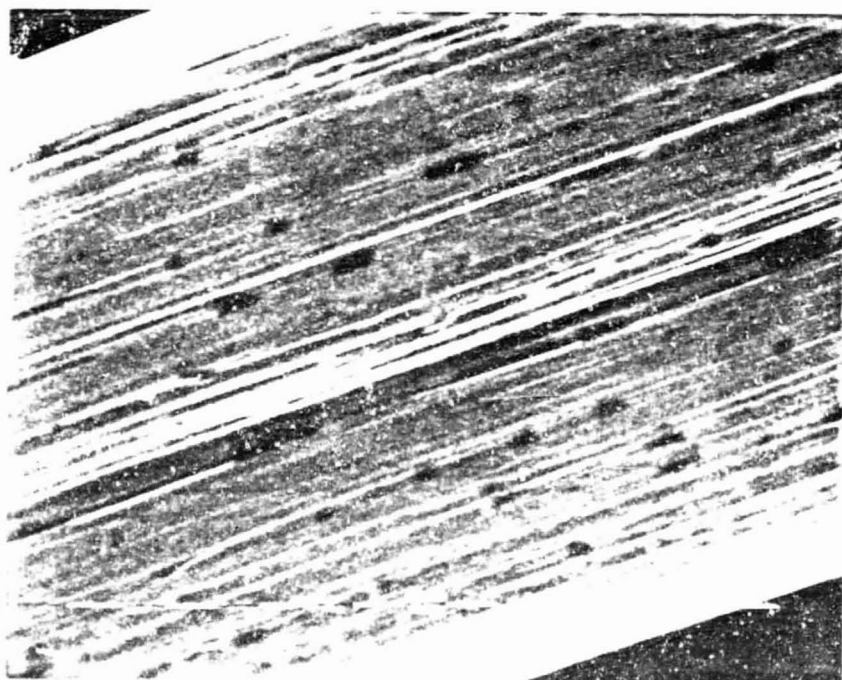


Figure #6. STEM Photomicrograph of Union Carbide T-300 YT Carbon Fiber (12500X)

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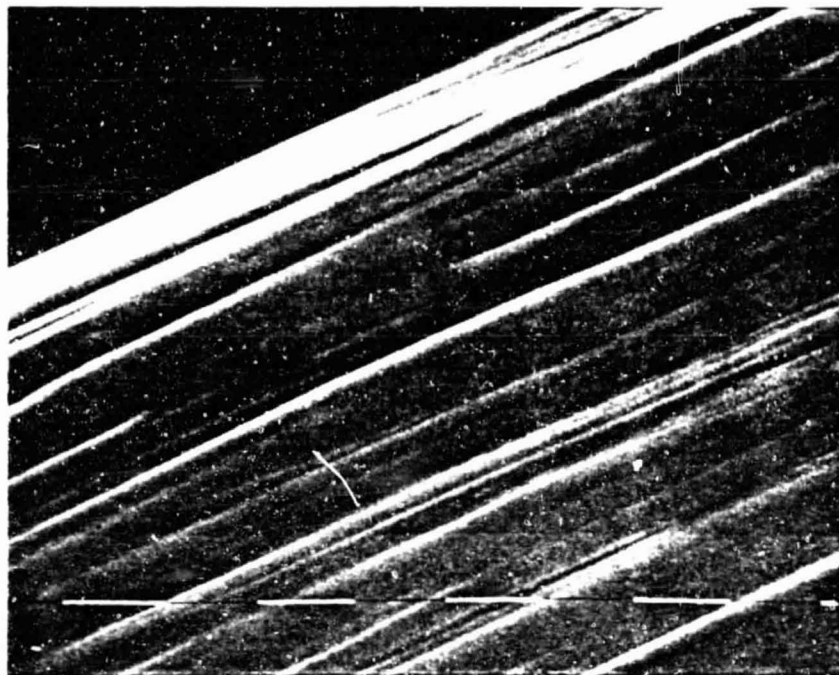


Figure #7. STEM Photomicrograph of Union Carbide T-300 SM Carbon Figer (25,000X)

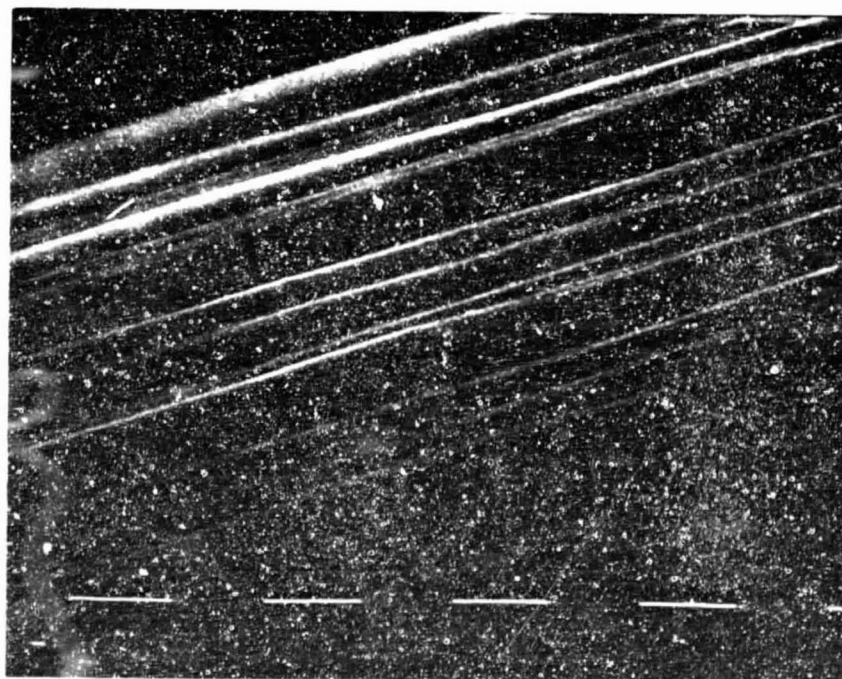


Figure #8. STEM Photomicrograph of Union Carbide T-300 Shear Carbon Fiber (25,000X)

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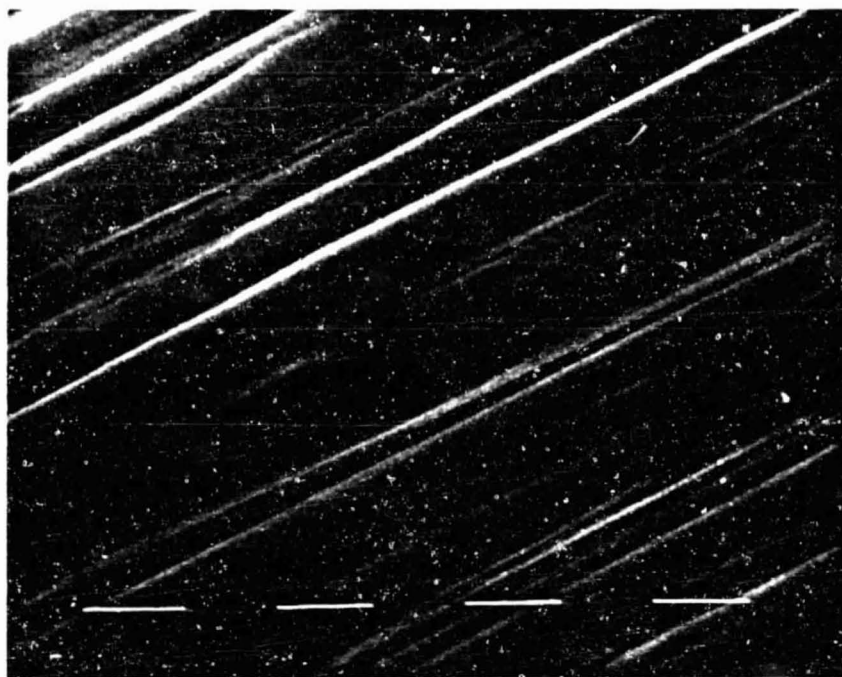


Figure #9. STEM Photomicrograph of Union Carbide T-500 Carbon Fiber (25,000X)

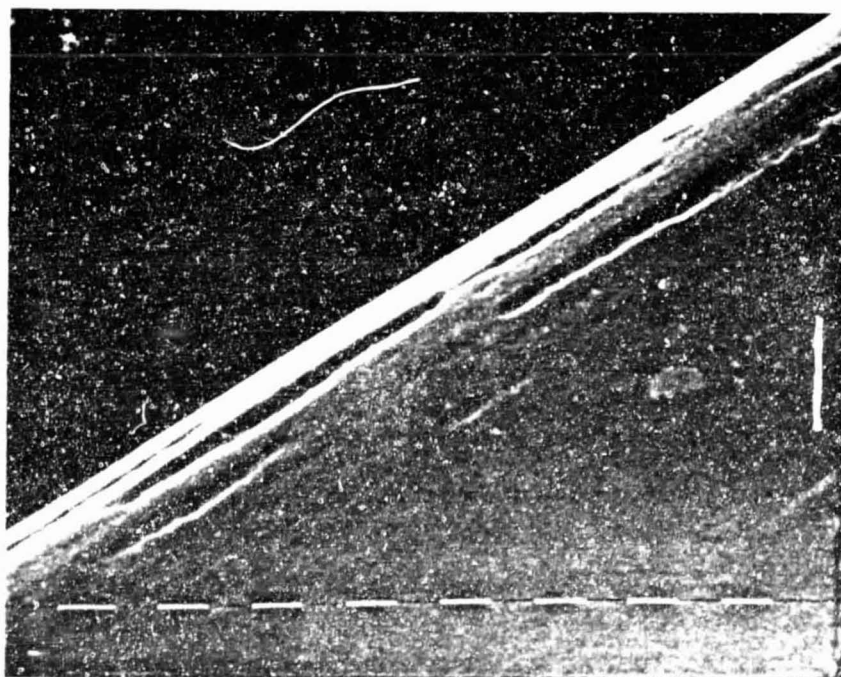


Figure #10. STEM Photomicrograph of Hercules AU-4 Carbon Fiber Anodized in 0.05M NaOH (12,500X)

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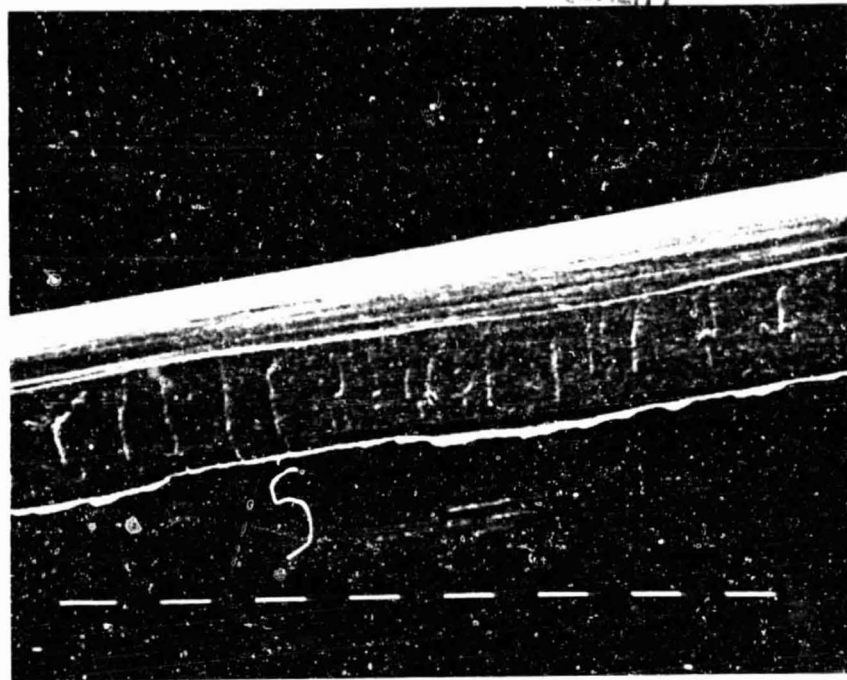


Figure #11. STEM Photomicrograph of Hercules AU-4 Carbon Fiber Anodized in 0.05M H_2SO_4 (12,500X)

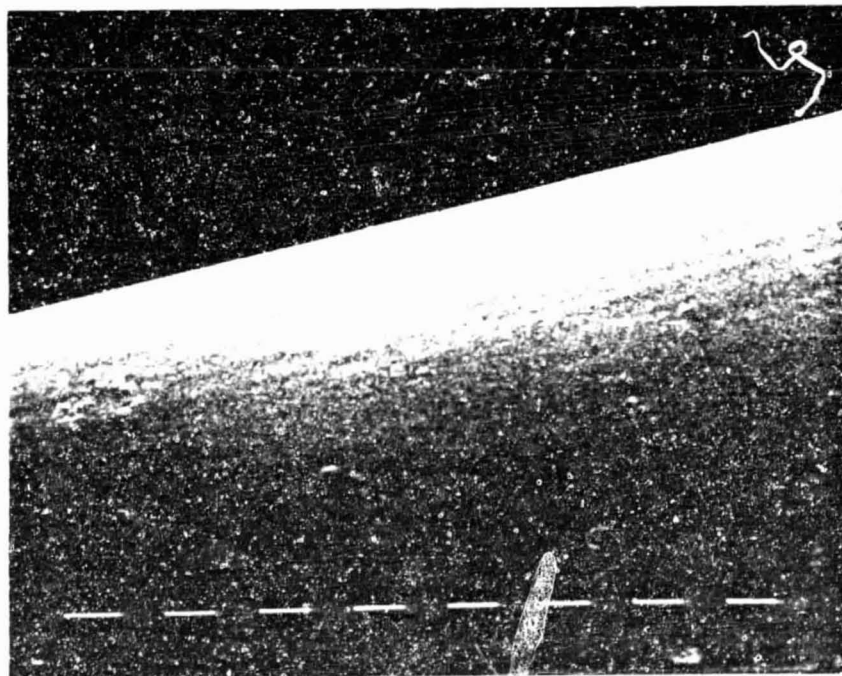


Figure #12. STEM Photomicrograph of Hercules AU-4 Carbon Fiber Anodized in 0.5M NaOH (12,500X)

Figure #13. Curve Fit Carbon 1s Photopeak of Hercules As-4 Fibers.

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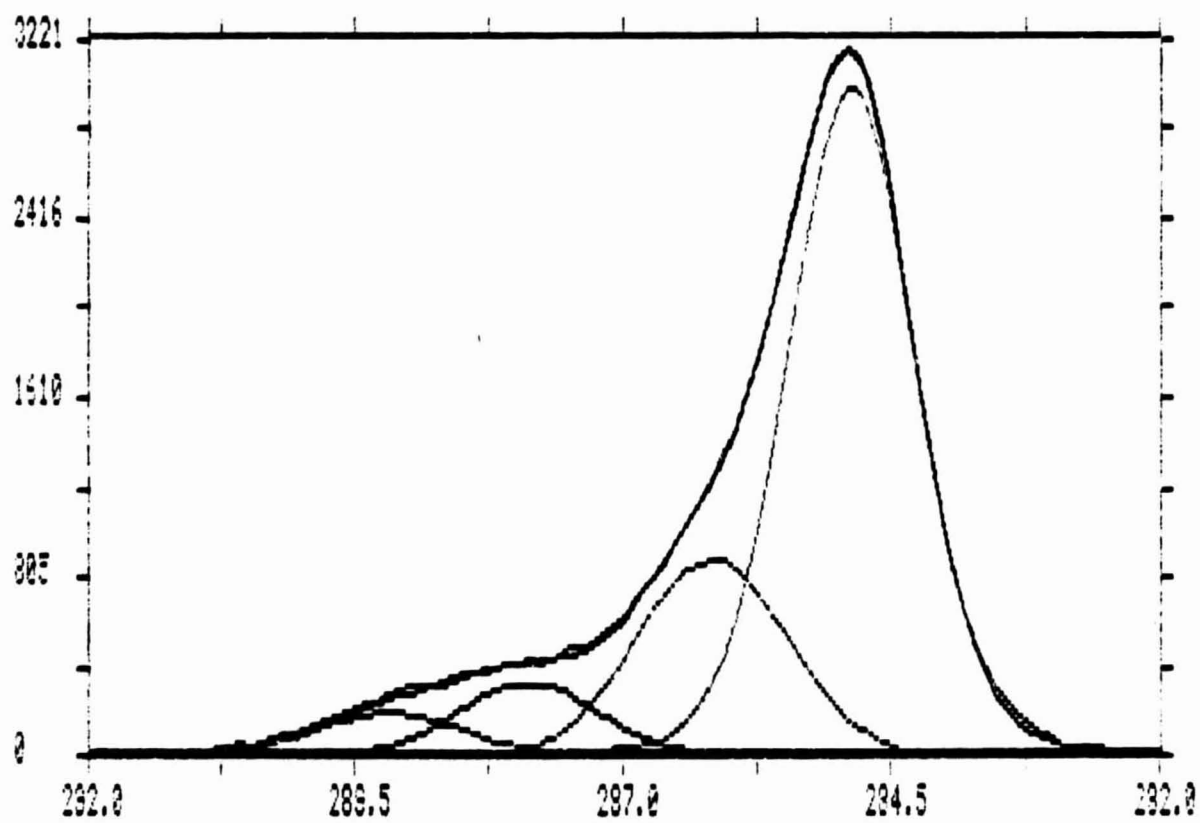
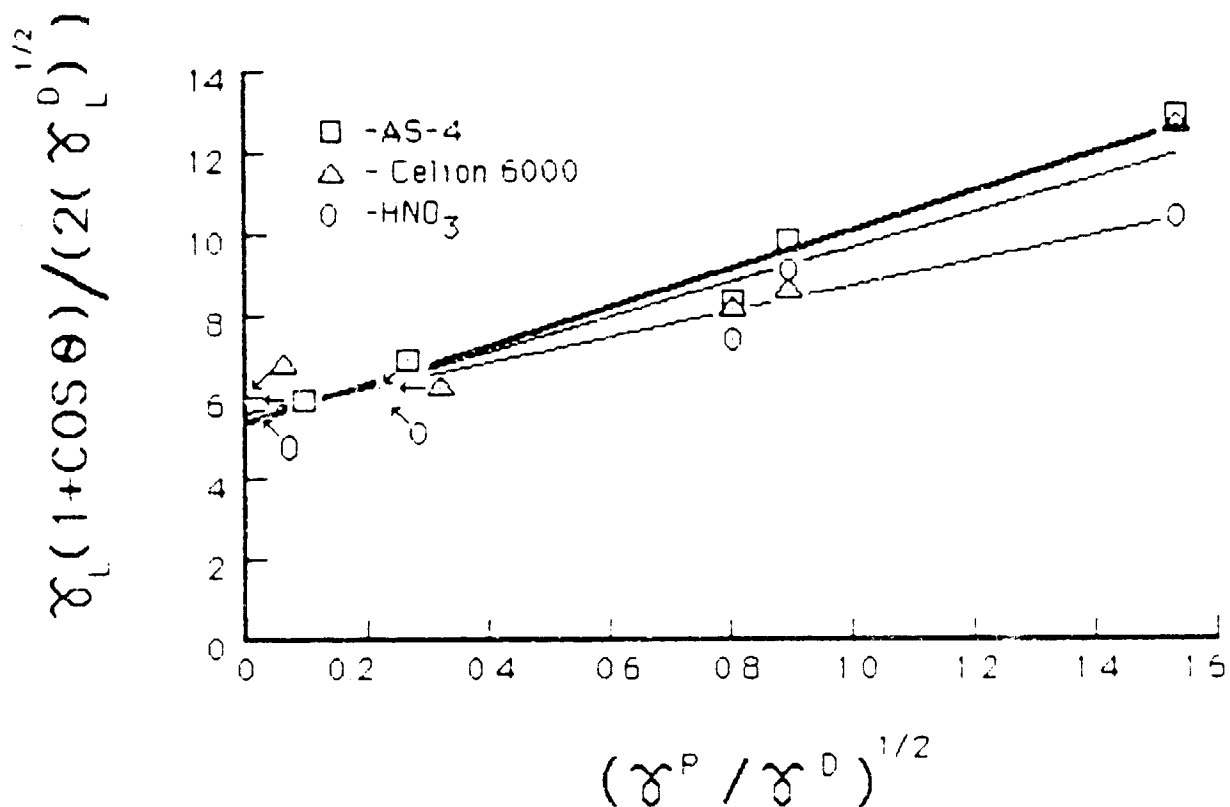


Figure #14. Work of Adhesion Versus $(\gamma_L^P / \gamma_L^D)^{1/2}$



FIBER

γ^D

γ^P

HERCULES AS-4

29.4

22.0

CELION 6000

29.6

18.1

NITRIC ACID TREATED

31.8

9.8

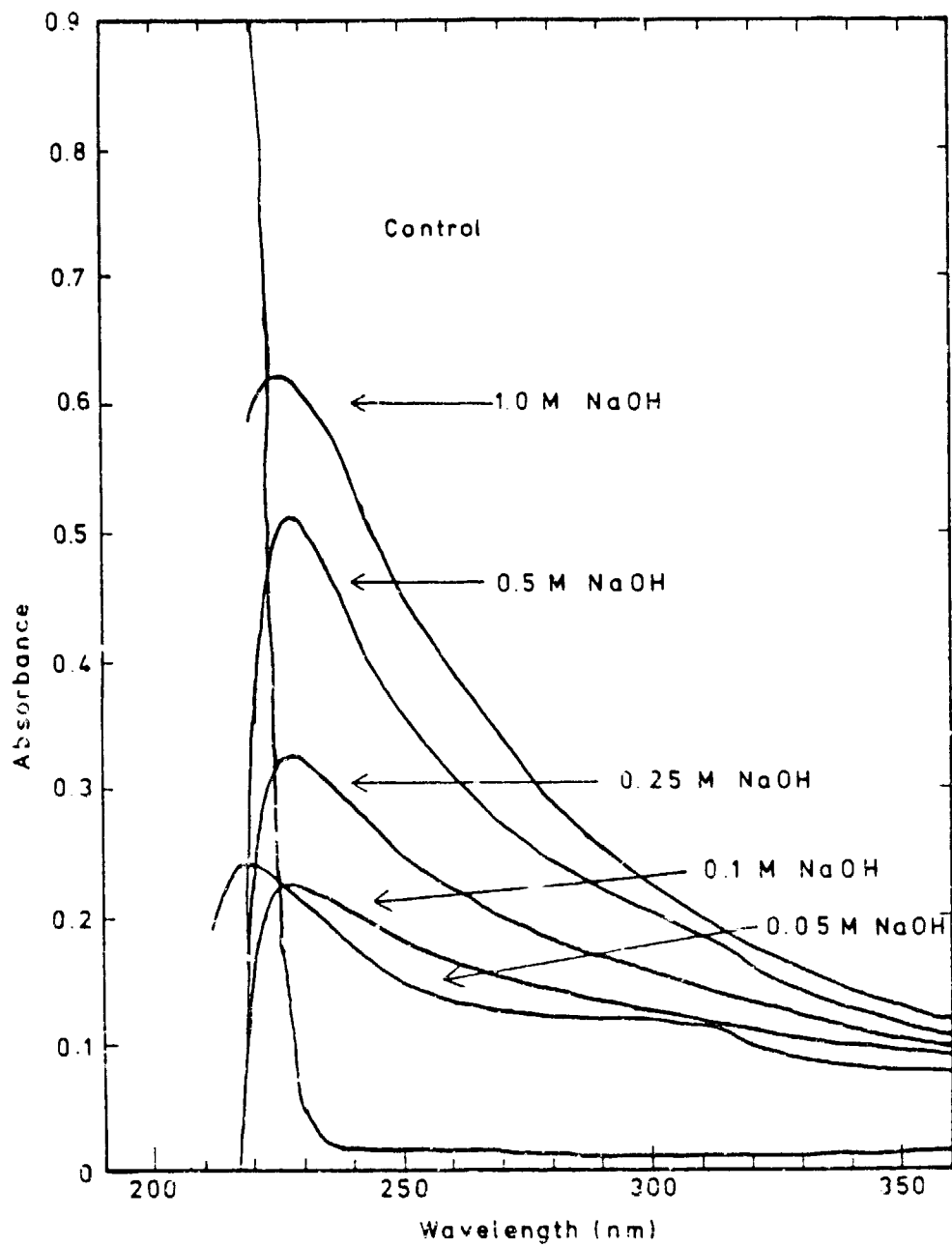


Figure #15. UV Spectra of Anodization Bath after Anodization of Hercules AU-4 Fibers in NaOH.

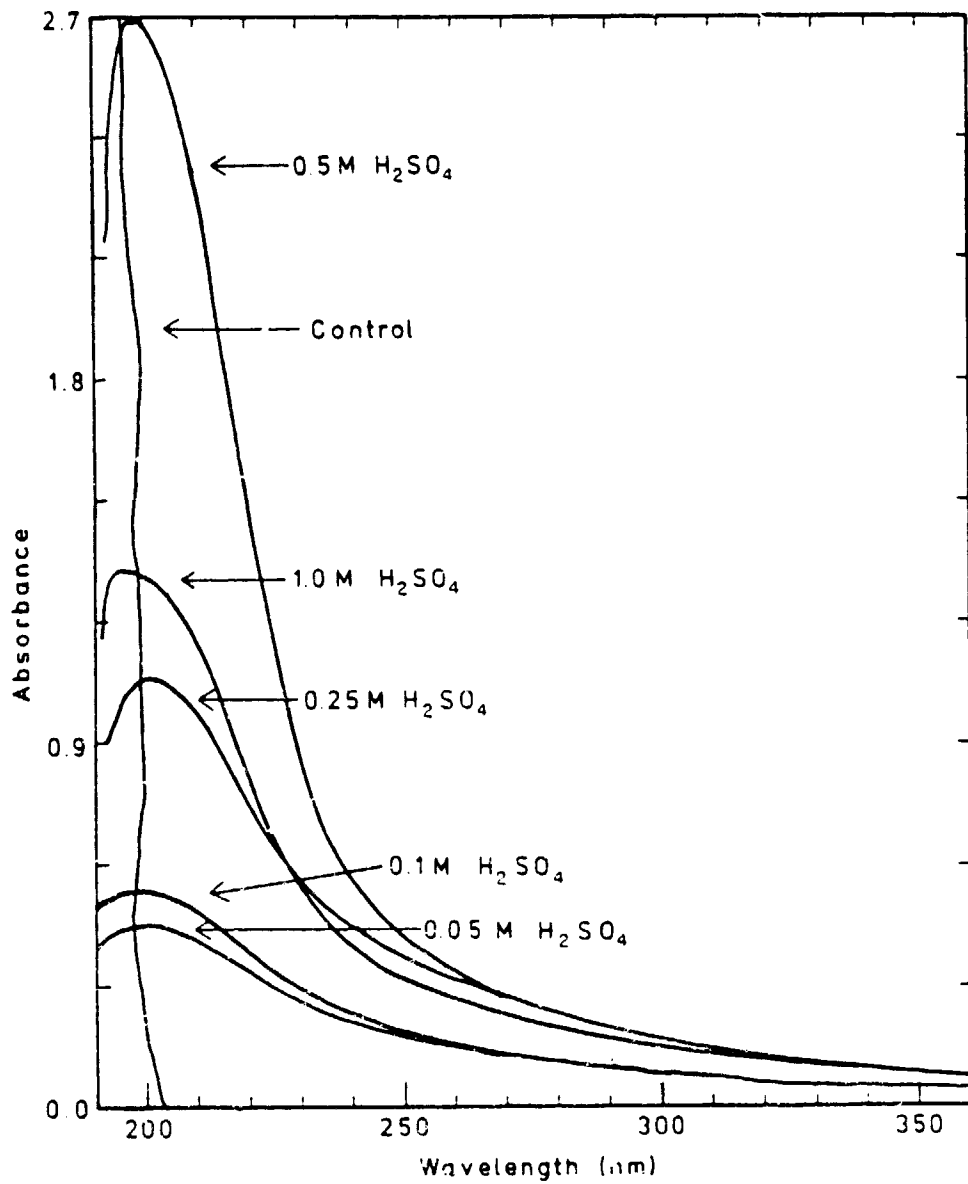


Figure #16. UV Spectra of Anodization Baths after Anodization of Hercules AU-4 Fibers in H₂SO₄.