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FINAL TECHNICAL REPORT

SURFACE ANALYSIS IN COMPOSITE BONDING

by

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I. INTRODUCTION

Langley Research Center (LaRC) has been actively engaged in advancing composites and composite structures technology for the past decade. Several large LaRC composite application programs such as CASTS, SCR, and ACEE, have had a significant impact in extending the use of composites in aircraft and spacecraft structures. The use of composite materials in aircraft and spacecraft structures. The use of composite materials has many advantages over metallic structures; for example, composite structures almost always result in significant weight savings, cost savings, and a reduction in the total number of components when compared to metallic designs. Efficient joining methods are of primary importance for the increased use of composite materials on aircraft structures. The joining techniques for composites are limited to mechanical fasteners and adhesive bonding, the latter being the preferred technique.

Studies utilizing epoxy matrix composites and epoxy adhesives have been widely reported in the literature; however, there is a lack of information on studies using high temperature composites and adhesives. The development of efficient joining procedures for high temperature composites, i.e., graphite/polyimide, is very important for the fabrication of advanced aerospace structures. The long term objective of this study is to establish the effect of composite surface treatments on the strength and durability of high temperature adhesive bonded graphite polyimide structures.

Crane et al. (1) studied the effect of peel ply, chemical, and mechanical surface treatments on the wettability and bondability of a cured epoxy/graphite composite with Narmo 329-1C epoxy adhesive. Their results indicate no obvious correlation between surface energetics and bond strength. Of the surface treatments studied, the sanded surface gave improved bond strength compared to the untreated sample.

Pater and Scola (2) using Fourier transform infrared spectroscopy, studied surface contamination from the transfer of various release agents to the composite surface during fabrication of a series of Kevlar, glass, and graphite/epoxy composites. The type of mold, mold surface treatments, release agent used, and reinforcing fibers were the factors found to influence the amount of release agent transfer. Adhesive bonding to the composite was not addressed in the report.

The effect of the degree of abrasion obtained by alumina grit blasting of epoxy composite surfaces on the strengths of epoxy bonded joints was studied by Stone (3). Incomplete abrasion of composite surfaces resulted in reduced joint strength for some adhesives, as well as a high proportion of composite/primer interface failure, probably due to polytetrafluoroethylene residues from the release cloths during fabrication.

Parker and Waghorne (4) also studied carbon fiber-reinforced composite laminates that were molded against release cloths, metal plates coated with release agents, and sheets of silicone rubber. X-ray photoelectron spectroscopy (XPS or ESCA) was used to investigate the chemical composition of the surfaces and indicated contamination by release agents during fabrication which resulted in reduced strengths for epoxy adhesive-bonded joints. Abrasion by various methods reduced, but did not eliminate, the contamination.

There is a continuing need to establish the role of the interfacial region in determining the bond strength and durability of composite bonds. Preliminary studies (5,6) on the characterization of a variety of graphite fibers including Celion 6000 using both scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) have been reported. Donnet has emphasized recently (7) the importance of the surface characterization of fibers in attempting to understand the properties of composites. However, the emphasis in the present work is on composite bonding, that is, the adhesive bonding between composites in contrast to fiber-matrix interaction. The primary objective of the research is the characterization of pretreated composite surfaces before adhesive bonding and of fractured composite surfaces following lap shear strength measurements.

II. EXPERIMENTAL

A. Samples. The composites were made by Rockwell International from Celion 6000 graphite fibers with a NR 150B2 polyimide finish in a polyimide (LARC-160) matrix. Prepreg was supplied to Rockwell International by Fiberite. Details of the fabrication process have been reported (8). Properties of the composites are given in Table I.

The as-received sample designated Sample No. 1 delaminated on punching and hence a virgin internal surface was produced and designated Sample No. 1D. The composites were pretreated at NASA-LARC in the twelve different ways listed in the second column of Table II. Details of each pretreatment are given below. Sample No. 2 was lightly (2-3 quick passes) blasted using 120 grit alumina and air pressure of 90 psi with the nozzle held approximately 8-10 inches from the sample. Sample No. 3 was blasted using 100 grit alumina and air pressure of 15 psi. Sample No. 4 was lightly (one pass) blasted with 88-140μ diameter glass beads in a Dry Horner® with the nozzle held about 12 inches from the surface. Sample No. 5 was handsanded manually using 600 SiC sandpaper. Sample No. 6 was handsanded manually in a criss-cross pattern with 180 SiC sandpaper. Ethanolic KOH solution at room temperature was spread on Sample No. 7 and soaked for 2-3 minutes. Additional ethanolic KOH solution was spread and soaked for 2-3 minutes. Sample was then rinsed with distilled water and blow dried. Hydrazine hydrate at room temperature was spread on Sample No. 8, soaked for 15 minutes, rinsed with distilled water and blow dried. A 50/50 (by volume) solution of concd. H_2SO_4 and 30% H_2O_2 at room temperature was spread on Sample No. 9, soaked for 30 minutes, rinsed with distilled water and blow dried. Samples Nos. 10-12 were irradiated at different fluxes using a Flashblast® model FB-200 to obtain 14, 24 and 40 J/cm^2. Sample No. 12 following irradiation was washed with methanol to remove residue and the washed sample was coded Sample No. 12W.

After pretreatment, the composite panels were adhesively bonded using LARC-160. Details of the bonding procedure have been reported (9). Lap shear strengths of the bonded composites before (control) and after thermal aging at 450°F (232°C) are listed in Table V. The thermal aging test conditions and the pretreatment are also listed in Table V.

B. X-ray Photoelectron Spectroscopy (XPS). XPS studies of the pretreated composites prior to bonding and of the fractured composites following lap shear tests were obtained with a Physical Electronics SAM 550 spectrometer using a Mg x-ray anode. Punched samples were mounted to the XPS stage with double-sided tape. A wide scan of binding energies (0 to 1000 eV) was performed on pretreated Sample Nos. 1 and 10 initially. Subsequent narrow scans were completed for the elements C, N, O, S, F, Al, Si, and K on all samples. A wide scan of binding energies (0 to 1000 eV) was performed on fractured Sample Nos. 3F-9F and 13F-15F. Subsequent narrow scans were completed for the elements C, N, O, and F on all samples. The atomic fraction of each of the elements present in the top 5 nm of the surface was calculated. In a separate experiment, XPS depth profiling was done on pretreated Sample No. 1 using a Physical Electronics ESCA/SAM spectrometer. The argon ion sputering rate was about 2 nm/min.

C. Contact Angles. Five different liquids of varying surface tensions were used for contact angle determinations. The liquids and respective surface tensions (in mJ/m^2) are noted below: water (72.8), formamide (58.3), methylene iodide (50.8), bromonaphthalene (44.6), n-hexadecane (27.6). A droplet of each liquid approximately 5 mm in diameter was placed on each composite sheet. Contact angles were measured with a Gaertner Scientific goniometer within 30 seconds after the introduction of the droplet. A second replication was completed for each liquid on each composite. Means were calculated using the University IBM 1360 computer system which was also used to construct plots of measured contact angle (θ) as a function of surface tension (γ). Critical surface tensions for each composite were obtained by extrapolation of cos θ vs γ plots using the Zisman approach (10).

III. RESULTS AND DISCUSSION

Results are presented separately for the pretreated composites and for the fractured composites following lap shear tests. It is pointed out that a thorough scanning electron microscopy (SEM) study of both pretreated and fractured composites has been carried out (11) and selected results have been reported (8).

A. Pretreated Composites

1. X-ray Photoelectron Spectroscopy (XPS). An extensive XPS study was done on the composite samples before and following different pretreatments. Wide scan XPS spectra were obtained on Samples Nos. 1, 1D, 7, 8, and 9. The major photopeaks were assigned to fluorine, oxygen, nitrogen and carbon. The presence of large amounts of fluorine on the surface of some of the samples even after pretreatment is a striking result and emphasizes the importance of surface analysis in determining trace concentrations of elements on bonding surfaces which may be detrimental to bond properties. In addition, trace amounts of calcium and sodium were noted on Sample No. 7, and Sample Nos. 1 and 7, respectively.

Narrow scan XPS spectra were obtained on all samples and in addition to scanning for fluorine, oxygen, nitrogen, and carbon, scans were also made for potassium, sulfur, aluminum, and silicon. These latter elements were suspected surface impurities based on the known pretreatments. Potassium was not detected on any sample; sulfur appeared as a trace impurity but it may be associated with the sample holder.

The quantitative results of the XPS analysis are given in Tables II and III. The binding energies (B.E.) in eV and the atomic fractions (A.F.) for the F 1s, O 1s, N 1s and C 1s photopeaks are listed in Table II. Half of the samples contained high concentrations of surface fluorine even following pretreatment and in every case, a high binding energy photopeak around 292 eV was observed in the C 1s spectrum. This is a characteristic of carbon-fluorine bonding (11). Of particular interest is the fact that the as-received composite (Sample No. 1) has a large fluorine signal. However, the fluorine photopeak is some 100 times smaller for a freshly exposed surface (Sample No. 1D) produced on delamination of the same sample. It is concluded that the fluorine signal results from fluoropolymers transferred to the composite surface from Teflon coated glass fabric used in the fabrication process.

The atomic fraction ratios are listed in Table III. There are large differences in the F/C ratio for the various samples. The mechanically pretreated composites generally have lower F/C ratios than the chemically pretreated composites. The longer Flashblast treated samples show a much reduced fluorine signal. Further, the values of the O/C ratio are fairly constant except for the Flashblast pretreated Sample Nos. 11, 12 and 12W. A parallel trend is noted in the N/C ratio. It appears as though the Flashblast pretreatment carbonizes the surface region resulting in the removal of oxygen and nitrogen possibly as gaseous species, for example, CO and HCN.

2. XPS-Depth Profiling Analysis: The XPS results for a wide scan of pretreated

Sample No. 1 prior to argon ion sputtering are listed in the first line in Table IV. Again carbon, fluorine, oxygen, and nitrogen are the main elements present in the surface. Trace amounts of silicon and sulfur are also noted. The depth profiling results are also listed in Table IV. The composition of carbon and fluorine as a function of sputter time is shown in Figure 1. It is apparent that the fluorine is localized on the very outer surface of the sample. After only 30 seconds of argpn ion sputtering, the fluorine signal decreased by a factor of ten from 42. to 4.6 while the photopeak at 293 eV for carbon associated with fluorine decreased from 17.0 to zero and the photopeak at 284.6 eV for carbon associated with the polyimide matrix increased from 29.4 to 82.8. Minor variations in the distribution of the other elements are noted in the results listed in Table IV.

In summary, the surface fluorine is associated with the external composite surfaces only which suggests the inclusion of fluorine during composite fabrication. The order of removal of the surface fluorine species by treatment is, Flashblast > mechanical > chemical, with Flashblast being the most effective.

3. Critical Surface Tension. The critical surface tension (γ_c) of each pretreated composite sample is listed in Table III. A correlation is seen between the surface fluorine concentration as measured by XPS and the value of the critical surface tension obtained from the contact angle measurements. The results of these two independent techniques are plotted in Figure 2. Indeed, the higher the surface fluorine concentration, the lower the critical surface tension. The observed lower γ_c values are in agreement with critical surface tensions reported for fluoropolymers (10).

B. Fractured Composites

1. XPS Analysis of Fractured Surfaces: The results of XPS analysis of fractured

surface following lap shear tests before and after thermal aging are collected in Table VI. The average binding energy of the F 1s, O 1s, and N 1s photopeaks over the samples is constant. The most intense C 1s photopeak occurs at 284.6 eV. A higher binding energy C 1s photopeak is noted at 292.0 eV in some samples which is assigned to C-F bonding (12). There is a third C 1s photopeak at 287.8 eV in all but one sample which is assigned to C-O bonding. The average calculated values for the O/C (=0.16 ± 0.02) and the N/C (=0.048 ± 0.007) atomic fraction ratios are remarkably constant over all samples. On the other hand, values of the F/C atomic fraction ratios vary more than thirty-fold (0.005 to 0.16). There are no significant concentrations of other residuals/contaminants on the fractured composites either before or after thermal aging.

The F/C ratios are re-listed in the last column in Table V along with the lap shear strengths and thermal aging conditions. The values of the fluorine to carbon ratio $(F/C)_0$ for the pretreated composite prior to bonding are also listed in Table V.

The XPS results and lap shear strengths are summarized in Figure 3. Variations in values of the $(F/C)_0$ ratio for the different pretreated composite surfaces have been discussed above. The lap shear strength of the control samples does not depend on the pretreatment. In particular, the lap shear strength of bonded composites does not correlate with the $(F/C)_0$ value; that is, large differences in the $(F/C)_0$ values for the pretreated composite do not effect the lap shear strength of the control bonded composition samples. One might have expected that large quantities of fluoropolymer on the bonding surface would lead to a diminished lap shear strength. This is not the case.

The (F/C) values for the fractured control surfaces are consistently lower and with less deviation than the $(F/C)_0$ values even when the initial $(F/C)_0$ values are quite high. The average value of F/C is only 0.028 ± 0.012 whereas the average value of $(F/C)_0$ is 0.21 ± 0.12.

Thermal aging at 450°F for 1000 hrs reduces the lap shear strength in all cases by about 50%. The concentration of fluorine on the fracture surface after thermal aging is invariably higher than on the fracture surface of the control sample. Further, the fluorine concentration on the fracture surface after thermal aging is proportional to the fluorine concentration $(F/C)_0$ on the pretreated composite surface before bonding. The appearance of significant concentrations of fluorine on the fracture surface of the thermally aged samples compared to the control surface suggests migration of fluorine-containing molecules into the fracture interphase during thermal aging. The effect, if any, of this fluorine containing material on the reduced lap shear strength of thermally aged samples is not established.

In summary, as depicted in Figure 4, the pretreated unbonded composite surfaces contain a variable fluorine concentration. Migration of the fluorine species may occur during bonding. The control samples have high lap shear strengths and a minimal surface fluorine concentration. The thermally aged samples have a reduced lap shear strength and an increased surface fluorine concentration proportional to the fluorine concentration on the prebonded surface.

IV. SUMMARY

This research focused initially on XPS analysis and contact angle measurements on graphite fiber composites pretreated in a number of different ways including mechanical, chemical and light irradiation. A significant fluorine signal was observed by XPS on the as-received Celion 6000/LARC-160 composite surface prior to pretreatment. Only a trace fluorine signal is noted on a delaminated surface of the same as-received sample. This result indicates that fluorine is introduced probably by contact with the Teflon coated glass fabric during the fabrication step. Chemical pretreatment was the least effective method of removing surface fluorine while the Flashblast® process reduced the fluorine signal to trace levels. Critical surface tensions of the pretreated composites were determined from measured contact angles. Low critical surface tensions were characteristic of composite surfaces having high surface fluorine concentration as determined by XPS.

The XPS analysis of fractured lap shear samples followed the XPS analysis of the pretreated composites. The lap shear strength of the control samples was independent of the type of pretreatment and in turn the surface fluorine concentration. In contrast, the lap shear strength of thermally aged bonded composites was about one-half that of the control samples. There was a significant increase in the surface fluorine concentration on the fracture surfaces of the thermally aged samples. The effect, if any, of this fluorine on the lap shear strength of thermally aged composites was not established. The XPS results and contact angle measurements produced information on the surface contamination as a result of fabrication techniques which may provide answers to the strength and durability of adhesively bonded composites. These techniques have been shown to be capable of providing valuable information with respect to surface analysis of pretreated composites prior to adhesive bonding and following lap shear fracture .

V. ACKNOWLEDGEMENTS

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TABLE I

PROPERTIES OF CELION 6000/LARC-160 COMPOSITE

Panel No.	T_g(°C)	Average Thickness(mm)	Specific Gravity	V_F %	Void %
1	344 (651°F)	2.2 (0.086 in)	1.57	59	0.1
2	332 (629°F)	2.0 (0.079 in)	1.58	61	<1.0

[a] $(0,0,0,+30,-30,+30,-30)_s$ ply orientation.

TABLE II

XPS ANALYSIS OF PRETREATED COMPOSITE SURFACES

Sample No.	Sample Pretreatment	Photopeak				
		F 1s	O 1s	N 1s	C 1s	
1	As-received	689.0	531.8	399.8	(284.6)	B.E.(eV)
		0.19	0.11	0.030	0.66	A.F.
1D	Delaminated	688.8	532.4	400.2	(284.6)	
		0.002	0.11	0.020	0.86	
2	120 Al_2O_3 Grit Blast	689.0	531.4	399.8	(284.6)	
		0.13	0.11	0.020	0.73	
3	Boeing Grit Blast	689.0	532.0	400.0	(284.6)	
		0.060	0.15	0.023	0.75	
4	Glass Bead Blast	689.2	531.8	400.0	(284.6)	
		0.12	0.12	0.024	0.73	
5	600 SiC Handsand	689.4	532.2	400.2	(284.6)	
		0.025	0.13	0.020	0.80	
6	180 SiC Handsand	689.0	531.8	400.0	(284.6)	
		0.027	0.12	0.032	0.81	
7	Ethanolic KOH	689.2	531.8	399.8	(284.6)	
		0.26	0.10	0.012	0.63	
8	$NH_2NH_2 \cdot H_2O$	689.2	531.8	399.6	(284.6)	
		0.20	0.10	0.041	0.64	
9	Concd. H_2SO_4	689.2	532.0	400.0	(284.6)	
	+ 30% H_2O_2	0.19	0.12	0.020	0.66	
10	Flashblast® #1	689.4	532.0	400.2	(284.6)	
		0.14	0.080	0.026	0.74	
11	Flashblast® #2	-	532.6	-	(284.6)	
		NSP	0.053	NSP	0.93	
12	Flashblast® #3	689.2	532.4	400.0	(284.6)	
		0.006	0.078	0.010	0.89	
12W	Flashblast® #3	-	532.4	400.0	(284.6)	
	(after MeOH wash)	NSP	0.071	0.021	0.89	

NSP - no significant peak

TABLE III

XPS ATOMIC RATIOS AND CRITICAL SURFACE TENSIONS OF PRETREATED COMPOSITE SURFACES

Sample No.	Atomic Fraction Ratio			Critical Surface Tension (mJ/m^2)
	F/C	O/C	N/C	
1	0.29	0.17	0.045	23.
1D	0.0023	0.13	0.023	--
2	0.18	0.15	0.027	31
3	0.08	0.20	0.031	37
4	0.16	0.16	0.032	33.
5	0.031	0.16	0.025	35.
6	0.033	0.15	0.040	40.
7	0.41	0.16	0.019	23.
8	0.31	0.16	0.064	28.
9	0.29	0.18	0.030	31.
10	0.19	0.11	0.035	37.
11	<0.001	0.057	<0.001	40.
12	0.0067	0.088	0.011	40.5
12W	<0.001	0.080	0.023	--

TABLE IV

ESCA PROFILE OF SAMPLE NO. 1

SP Time (Min.)	Wt%									
	Na	F-s	F-b	O	N	Ca	C-s	C-b	Si	S
0.0	0.0	42.2	0.0	7.9	2.0	0.0	17.0	29.4	1.0	0.6
0.5	1.3	4.6	3.4	2.9	3.2	1.0	0.0	82.8	0.4	0.5
1.0	0.7	3.0	1.5	3.0	3.0	1.0	0.0	87.9	0.0	0.0
1.5	0.5	2.8	1.5	3.1	3.1	0.0	0.0	89.1	0.0	0.0
2.0	0.6	2.5	0.9	2.6	3.1	0.0	0.0	90.2	0.0	0.0
3.0	0.5	1.9	1.2	2.6	2.7	0.0	0.0	91.1	0.0	0.0
5.0	0.0	1.9	1.3	2.1	3.2	0.0	0.0	91.6	0.0	0.0
7.0	0.6	0.0	1.3	2.7	2.6	0.0	0.0	92.8	0.0	0.0
10.0	0.5	0.0	0.7	2.2	2.8	0.0	0.0	93.9	0.0	0.0
15.0	0.8	0.0	0.0	1.9	3.0	0.0	0.0	94.6	0.0	0.0

TABLE V

LAP SHEAR STRENGTHS OF THERMALLY AGED ADHESIVELY BONDED COMPOSITES

			Exposure		Test	LSS	
Sample No.	Pretreatment	$(F/C)_o$	Temp. (°F)	Time (hrs)	Temp. (°F)	(psi)	F/C
1FB	As Received	0.29	Control	--	RT	3045	0.026
2FB	As Received	0.29	450	1000	RT	1245	0.15
3FB	As Received	0.29	450	1000	450	1160	0.13
4FB	600 SiC Hansanded	0.031	Control	--	RT	2940	0.020
5FB	60 SiC Handsanded	0.031	450	1000	RT	1445	0.034
6FA	120 Al_2O_3 Grit Blasted	0.18	Control	--	RT	2950	--
6FB	120 Al_2O_3 Grit Blasted	0.18	Control	--	RT	2950	--
7FA	120 Al_2O_3 Grit Blasted	0.18	450	1000	RT	1355	0.005
7FB	120 Al_2O_3 Grit Blasted	0.18	450	1000	RT	1355	0.015
8FB	Boeing Grit Blasted	0.08	Control	--	RT	2545	--
9FB	Boeing Grit Blasted	0.08	450	1000	RT	1445	0.022
10FA	$NH_2NH_2 \bullet H_2O$	0.31	Control	--	RT	3080	0.018
10FB	$NH_2NH_2 \bullet H_2O$	0.31	Control	--	RT	3080	0.011
11FA	$NH_2NH_2 \bullet H_2O$	0.31	450	1000	RT	1220	0.079
11FB	$NH_2NH_2 \bullet H_2O$	0.31	450	1000	RT	1220	0.090
12FB	Ethanolic KOH	0.41	Control	--	RT	2610	0.054
13F	Ethanolic KOH	0.41	450	1000	RT	975	0.16
14FB	Flashblast© #3	<0.001	Control	---	RT	2935	--
15FB	Flashblast© #3	<0.001	450	1000	RT	1280	--

A - polymer rich (less fibers)
B - polymer poor (more fibers)

TABLE VI

XPS ANALYSIS OF FRACTURED COMPOSITE SURFACES

Sample No.	Binding Energy (eV)				Atomic Fraction Ratio		
	F 1s	O 1s	N 1s	C 1s	F/C	O/C	N/C
1FB	689.6	532.2	400.4	284.6 288.0	0.025	0.13	0.044
2FB	689.4	531.8	400.0	284.6 288.4 292.2	0.15	0.16	0.034
3FB	689.4	531.6	400.0	284.6 288.0 292.2	0.13	0.18	0.053
4FB	689.4	531.8	400.2	284.6 288.6	0.020	0.15	0.055
5FB	689.6	531.8	400.0	284.6 288.4	0.034	0.16	0.050
6FA	NSP	532.0	400.2	284.6 288.4	--	0.15	0.048
6FB	NSP	532.0	400.6	284.6 288.6	--	0.12	0.050
7FA	NSP	532.0	400.2	284.6 288.4	0.005	0.17	0.038
7FB	689.8	532.0	400.0	284.6 288.6	0.015	0.16	0.052
8FB	NSP	532.0	400.4	284.6	--	0.10	0.038
9FB	688.8	531.6	400.0	284.6 288.0	0.022	0.23	0.067
10FA	689.6	532.0	400.2	284.6 288.4	0.018	0.18	0.056
10FB	689.8	532.0	400.2	284.6 288.6	0.011	0.14	0.044
11FA	689.4	531.8	400.0	284.6 288.4 292.0	0.079	0.18	0.052
11PB	689.6	531.8	400.0	284.6 288.4 292.2	0.090	0.16	0.048
12FB	690.0	532.0	400.2	284.6 288.6 292.4	0.054	0.14	0.046
13F	689.4	531.6	399.8	284.6 288.0 292.0	0.16	0.18	0.057
14FB	NSP	532.0	400.2	284.6 288.6	--	0.13	0.030
15FB	NSP	531.8	400.2	284.6 288.6	--	0.17	0.053

A - polymer rich (less fibers)
B - polymer poor (more fibers)

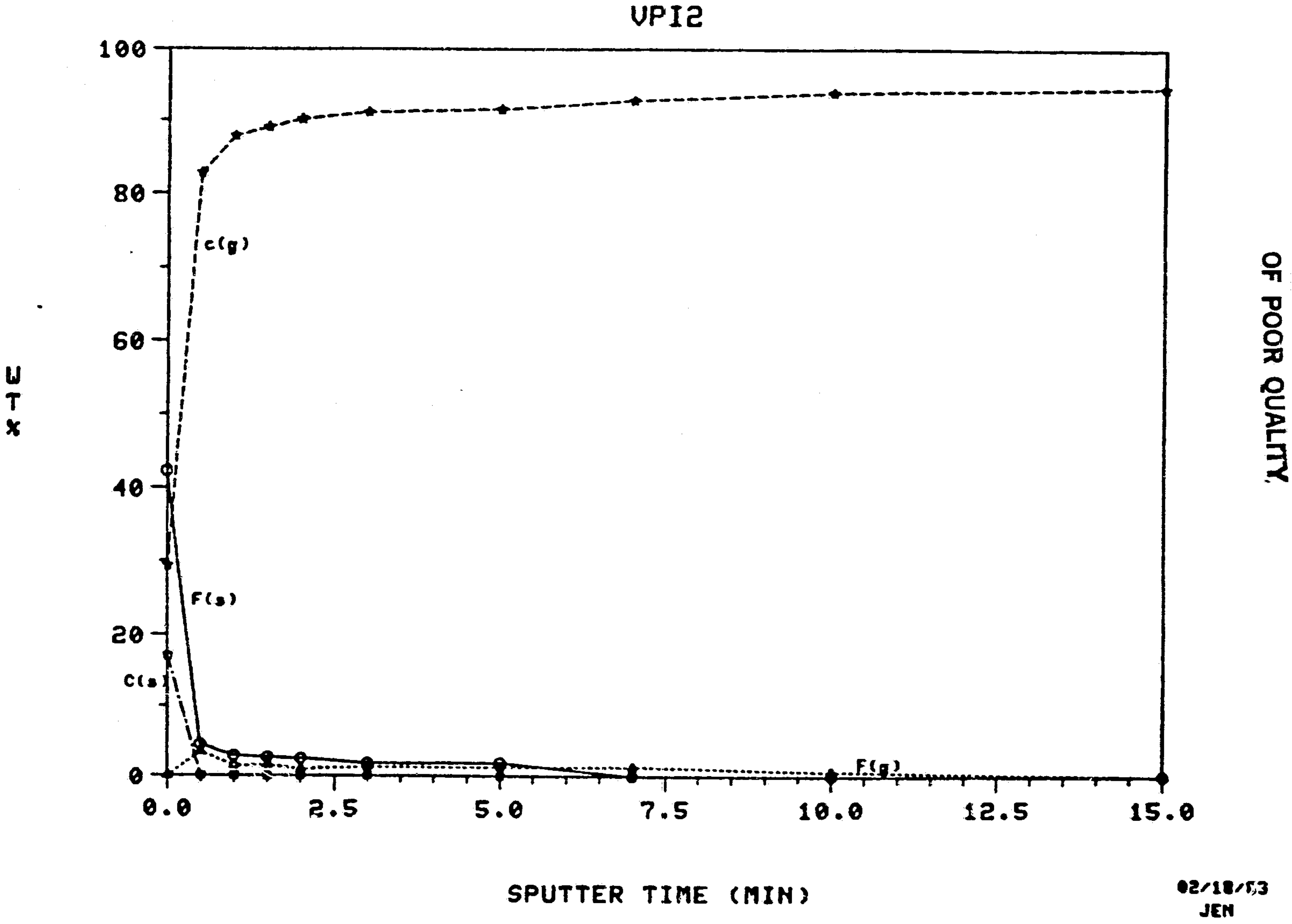

Figure 1. XPS depth profile analysis of as-received composite.

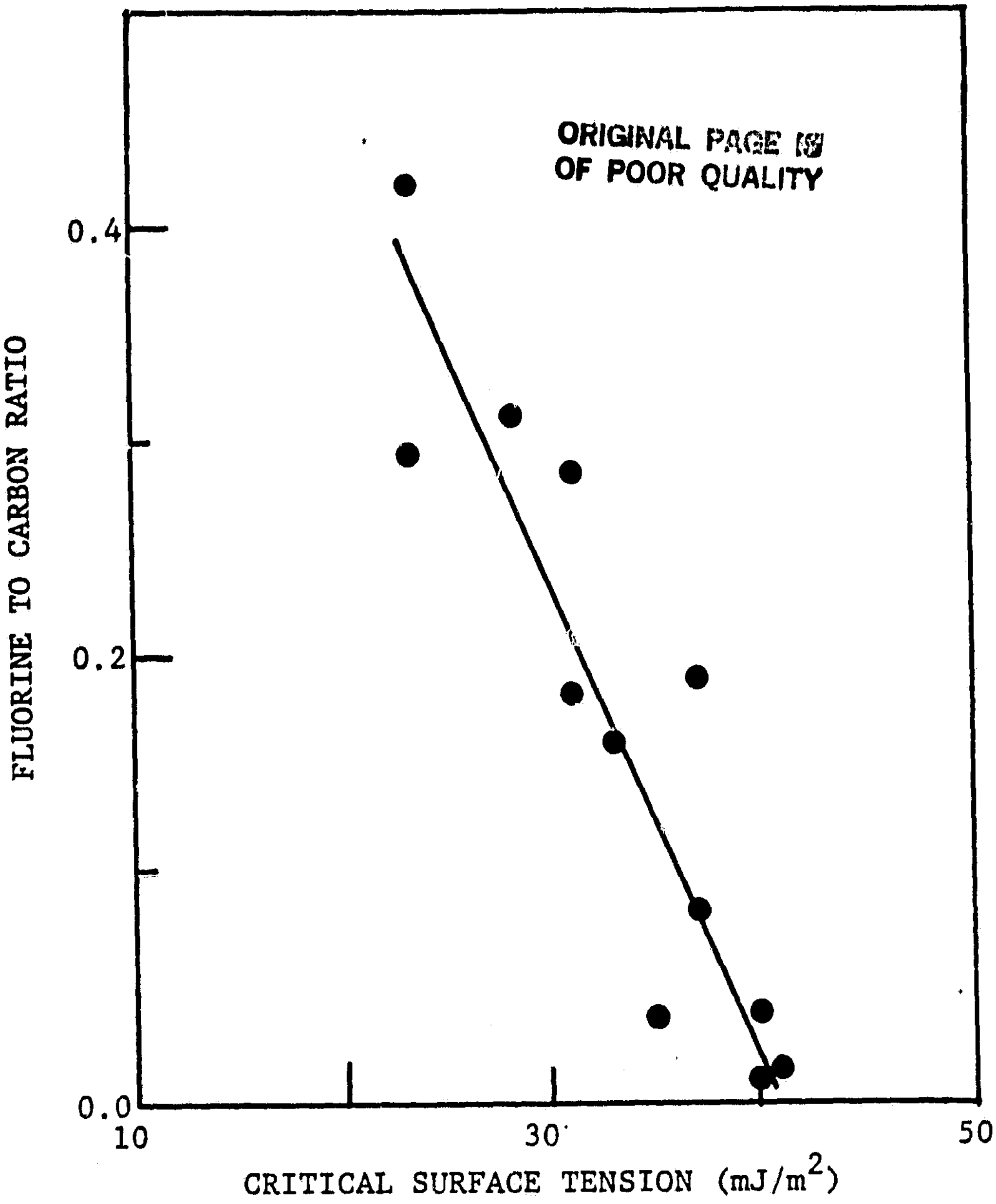

Figure 2. XPS fluorine to carbon ratio as a function of the critical surface tension of pretreated composites.

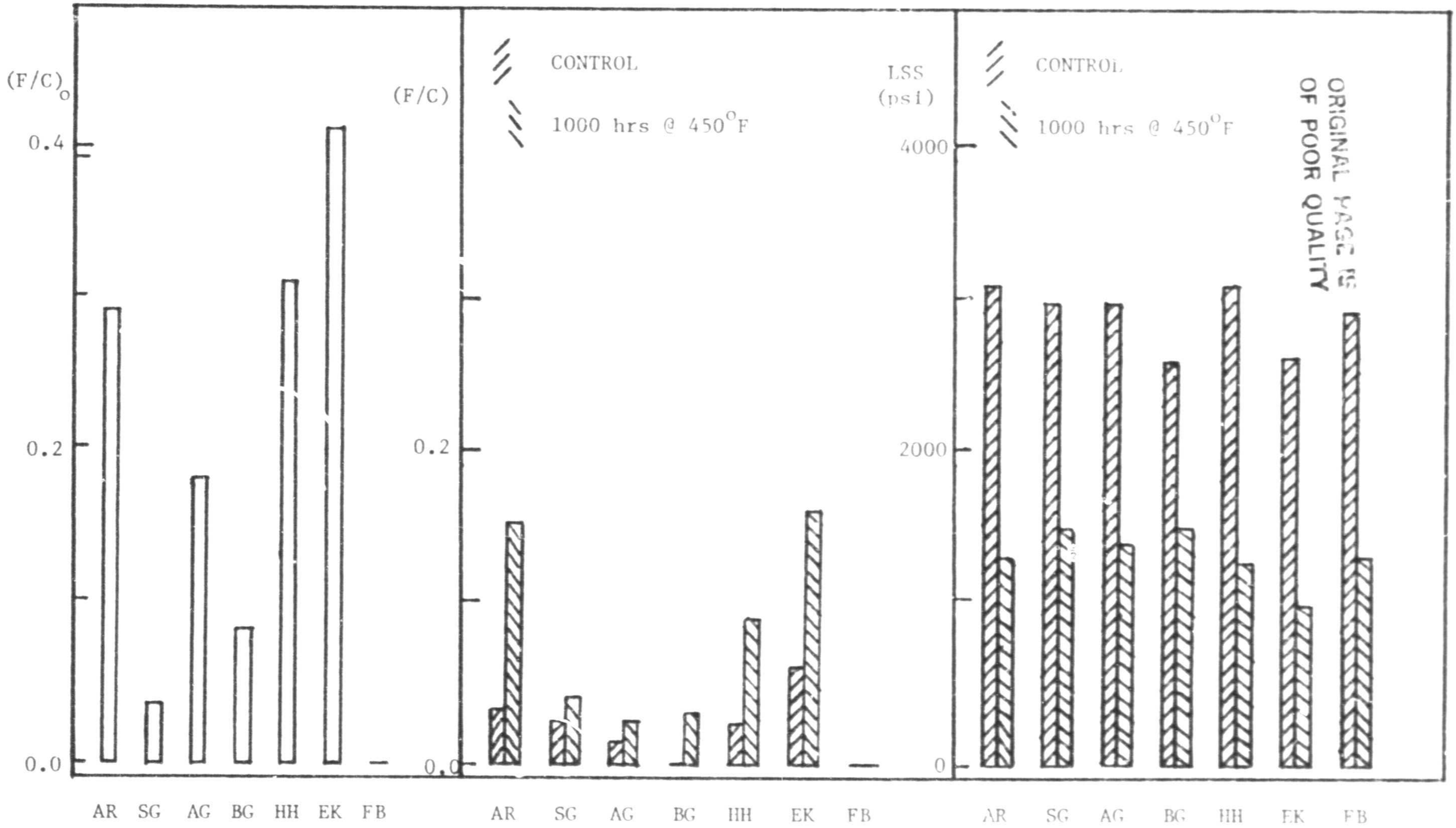

Figure 3. Values of $(F/C)_o$ for pretreated composites, (F/C) for fractured composites before and after thermal aging and lap shear strengths of bonded composites for different pretreatments: AR - as received; SG - SiC grit blast; AG - Al_2O_3 grit blast; BG - Boeing grit blast; HH - hydrazine hydrate; EK - ethanolic KOH; FB - Flashblast.

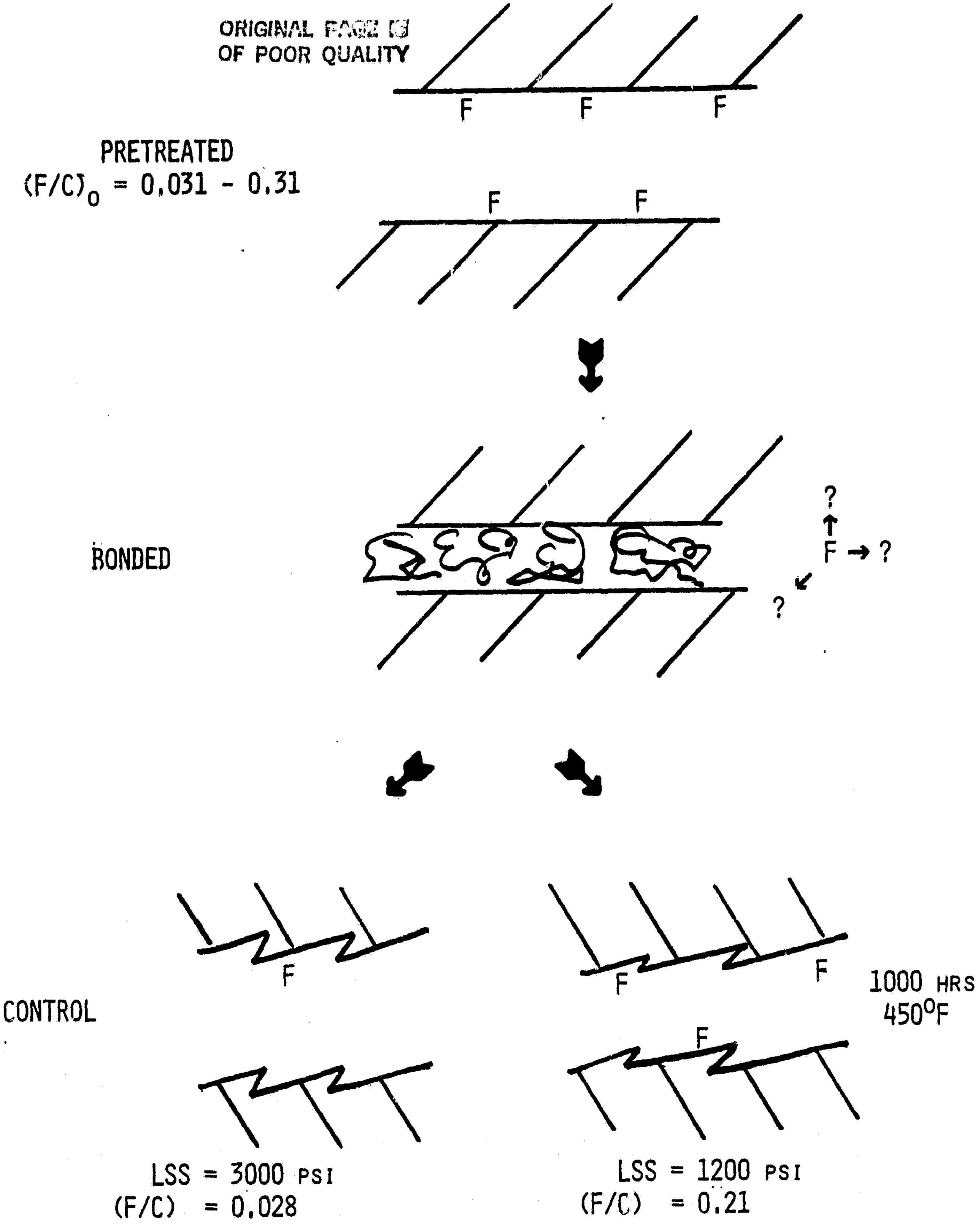

Figure 4. Schematic diagram illustrating variations in surface fluorine concentration on pretreated and on fractured composites before and after thermal aging.