



Achieving Optimum Bond Strength With Plasma Treatment

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abstract

The goal of this work was to improve adhesion to Tefzel using plasma surface treatment. The plasmas used were $O_2 + SF_6$, O_2 , and NH_3 . Joints made from the adherends using several commercially available epoxy adhesives were tested using a double lap shear configuration. Bond strengths for the treated adherends were measured to be as much as thirty times greater than for the untreated materials. ESCA analysis of the O_2 plasma treated Tefzel indicated a surface oxidation increase of about 7-8% over the untreated material, with the oxide being primarily in the form of an ester.

conference

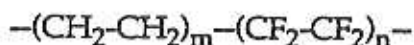
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INTRODUCTION

The goal of this study was to determine a plasma surface treatment method whereby fluorinated thermoplastics could be effectively bonded adhesively to other materials as well as to themselves. Fluorinated thermoplastics rank among the most difficult materials to adhesively bond. Their extremely inert surface chemistries coupled with comparatively low critical surface tensions present an obstacle to the development of composite structures with these materials. Added to these are mold release agents, thin oil films, or persistent low molecular weight fractions which bloom to the surface after processing, that can destroy a bond due to the presence of the weak boundary layer they present between adherend and adhesive. For the purpose of this initial work, Tefzel 200 was used, Tefzel being a registered trademark of E.I. Du Pont de Nemours. Tefzel 200 is a random copolymer of ethylene and tetrafluoroethylene as shown below.



Other than plasma treatments, the most effective method for improving bond strengths to fluorinated thermoplastics has been to etch the surface of the material with what is commonly called the sodium etch. Essentially, this consists of a brief submersion of the component to be bonded in a solution of sodium and naphthalene in tetrahydrofuran or other suitable solvent. This process is known to modify the fluoropolymer surface by

oxidation reactions concomitant with removal of fluorine from the polymer backbone.

There are many definitions of the term "plasma" depending on one's particular discipline. It has often been referred to as the fourth state of matter; the generation of plasma being analogous to the transitions that occur when energy is supplied to a material causing solids to melt and liquids to become gases. Sufficient additional energy supplied to a gas creates a plasma. In the case of cold gas plasma, typical of that used in this work, the process is excitation of a gas at reduced pressure by radio frequency energy. While on an atomic scale, plasma generation cannot be construed as a room-temperature equilibrium process, the plasma being composed of a large concentration of highly excited atomic, molecular, ionic and radical species, the bulk of the material remains near room temperature. The plasma contains free electrons as well as other metastable particles, which upon collision with the surfaces of polymers placed in the plasma environment break covalent chemical bonds thus creating free radicals on the polymer surface. These free radicals will then undergo additional reactions depending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that gas-radical reactions form a surface potentially very different from the starting bulk polymer. Since the process is conducted in a reactor under very controlled conditions, the end result is very reproducible.

There are three distinct plasma surface treatment processes which can change the chemical nature of a polymer surface: activation (oxidation or cross linking), deposition, and grafting¹. All three processes utilize the energies available in the gas plasma to initiate the reactions. In the case of activation the species in the plasma create free radicals on the surface which become satisfied by reacting with other species in the gas to form chemical groups, or moieties, not typical of the polymer being treated. For example, treatment of polyethylene in an oxygen plasma will yield carbonyl, hydroxyl, hydroperoxide, and carboxylic acid functional groups. These groups are very effective in reacting with a variety of adhesives, inks, or paints to form covalent bonds thereby establishing a surface which is readily bondable and very stable. If the gas that is chosen for the plasma is more complex, such as methane or ethane, the energetic species in the plasma causes the methane to break down into a variety of free radical species including the methylene radical whereby the methane polymerizes or rearranges to give a polyhydrocarbon polymer of high density and low permeability. The third process, plasma induced grafting, is a hybridization of plasma and conventional chemistry. In this technique a noble gas plasma such as helium or argon is employed which creates free radicals on the polymer surface being treated. However, after plasma treatment, but before the treated part is introduced to the atmosphere, an unsaturated monomer is brought into contact with the surface. The free radicals on the treated surface cause the unsaturated monomers to react with the surface resulting in the graft. A typical example is the grafting of acrylic acid to polyethylene to provide acid functionality. The acid can subsequently be saponified and hydrolyzed to provide a high water content gel on the surface. Other monomers which are

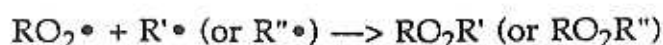
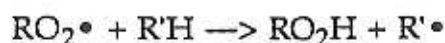
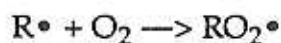
facilely employed are allyl alcohol and allyl amine to give surfaces predominant in hydroxyl or amine groups respectively.

While most, if not all, plasma equipment consists of similar components, the design of the reactor chamber, the distribution of power, the excitation frequency, and the gas dynamics can all be critical parameters influencing the efficiency and properties of plasma reactions. There has been an extensive amount of work published that shows a direct correlation between excitation frequency and plasma reactivity. Manufacturers of plasma equipment employing radio frequency excitation use either low frequencies, i.e. less than 400 KHz, or the higher frequencies at 13.56 or 27.12 MHz as specified by the FCC. For applications involving the treatment of plastics 13.56 MHz is the preferred frequency. Also important is whether the material being treated is in a primary or secondary plasma. Older equipment using large cylindrical barrels typically are secondary plasma systems. The plasma is created either between closely spaced, paired electrodes which may function as shelves or in the annulus between the vessels outer wall and a ring electrode when employed. Treatment of materials placed within the working volume depend on the diffusion of activated species created in the primary plasma, i.e., within the RF field. Diffusion of these activated species is very dependent on pressure; the higher the pressure, the shorter the mean free path. The mean free path is the distance active species can most likely travel before undergoing collisions which deactivate radicals or neutralize ions. Therefore, when using a secondary plasma the concentration of active species varies either across the diameter of a barrel system or between electrode pairs as the case may be. Thus, by the physical laws of nature the treatment within the working volume of a secondary plasma system cannot be uniform. By contrast when working within the RF field, or primary plasma, the gas is constantly being excited. Thus, polymeric articles being treated are immersed in a constant concentration of active species. Further, since diffusion is not a mechanistic limitation, significantly higher operating pressures may be used. This allows higher process gas flow rates assuring that off gassing species from the polymer are sufficiently diluted providing the full benefits of the desired process gas. In addition, the primary plasma is rich in ultraviolet radiation which is often an important initiation step in polymer reactions. Since UV radiation is line of sight, uniform treatment of multiple parts can only be obtained when working within the primary plasma. Otherwise any part in the shadow of another will receive different radiation and therefore the effectiveness of the treatment is expected to vary.

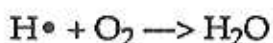
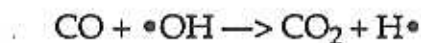
Use of plasma treatments to improve adhesion is relatively well known²⁻⁸. The work of Hansen, Schonhorn, and others in the mid 1960's represents some of the first work on glow discharge interactions with polymers leading to improved adhesion with these materials⁵⁻⁸. Their work involved the exposure of several dozen types of polymer materials to glow-discharge oxygen or inert gas plasmas. They found that exposing polyethylene and polytetrafluoroethylene to inert gas plasmas initially resulted in removal of hydrogen from the first and flourine from the second.

With longer exposure times of polyethylene to the plasma, cross linking occurred in the surface region; and with extremely long exposure times the surface molecules become highly conjugated. Indirect evidence indicated that similar processes occurred with the polytetrafluoroethylene. There was much evidence to indicate that the extensive cross linking by inert gas plasmas, which resulted in a surface layer having high cohesive strength, played the predominant role in increasing the adhesive joint strength. Changes in the critical surface tension of wetting did not seem to affect the adhesive joint strength. The effects of oxygen plasmas on various polymer surfaces on the other hand indicated the predominant formation of an oxide surface layer which presumably masked the cross linking effect. These results together with those of Reneker and Bolz⁹ and Lerner¹⁰ indicate that in addition to oxidation and/or cross linking, the removal of inert, chemically non-bound material from the polymer surface, which provides a weak boundary layer if left alone, are to primary factors which affect adhesion to the surface.

More recently considerable work has been done by Yasuda, Golub, Cormia, and others on the oxidation and etching effects of oxygen, nitrogen, or argon plasmas on various fluoropolymers¹¹⁻¹⁵. Yasuda, et. al.,¹¹, for example treated a number of polymer types including polytetrafluoroethylene using argon and nitrogen plasmas and studied the effects using electron spectroscopy for chemical analysis (ESCA). They found that the argon plasma treatment tended to cause oxygen incorporation into the surface and nitrogen plasma treatment resulted in incorporation of both nitrogen and oxygen. Polymers which already contained oxygen or nitrogen functionalities incorporated oxygen and nitrogen to a noticeably smaller extent. The more recent work of Golub, et. al.,^{12,14,15} on effects of oxygen plasma and atomic oxygen on various fluoropolymers indicated these materials undergo continuous erosion and oxidation and that the surface attains a steady-state chemical composition. Further, the materials were noted to reach time-dependent oxygen saturation levels and etch rates which depend upon the F/C ratio and the degree of crosslinking. That is, as either of these increase, the etch rate and oxygen saturation levels decrease and the time to oxygen saturation increases. A comparison of the surface oxygen concentrations after exposure of various polymer materials to oxygen plasma and low earth orbit, where the O₂/O ratio is about 0.1 at an altitude of 225 km, indicated a considerably larger uptake of oxygen in the plasma¹³. In a low pressure oxygen plasma atmosphere where the O₂/O ratio is reported to be about 10, the following oxidation reaction scheme has been proposed:

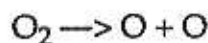


Where the RO_2H , RO_2R' , and RO_2R'' indicate the formation of acids and esters. Not indicated in the above reaction scheme are the possible formation of alcohols, ethers, peroxides, and hydroperoxides. The following reactions have been proposed to explain the presence of various gases within the plasma atmosphere:



Three plasma treatments were used in the work reported here: (1) $O_2 + SF_6$ (oxygen and sulfurhexafluoride) ; (2) O_2 ; and (3) NH_3 (ammonia). The first plasma treatment was studied because sulfur hexafluoride supposedly decomposes to SF_x and fluorine radicals in the plasma. The fluorine radicals improve the oxidation efficiency by stripping protons from the polymer surface to form HF. The resulting surface radicals are then readily attacked by oxygen. This process augments the removal of protons leaving radicals in the polymer backbone. With these arguments in mind, we expected the first plasma treatment to yield a more thorough oxidation of the surface and thus stronger adhesive bonds.

The second plasma treatment was studied for comparison with the first as well as the results of others. Oxygen dissociates into atoms in the plasma:



As indicated above the O_2/O ratio is approximately 10 in discharge plasmas. This means that about 5 % of the oxygen molecules are dissociated.

The third plasma treatment involved the use of ammonia in order to determine the possibility of directly grafting $-NH_2$ onto the surface. Epoxies are commonly cured using amines, the result being a secondary or tertiary amino alcohol. With this in mind, it was expected that if the amine graft to the surface was successful, then the result would be a surface which could react directly with the epoxide moiety in the adhesive. Consequently, the adhesive interface would be replaced by a planer region consisting of covalent bonds, thus providing the ultimate adhesive bond.

EXPERIMENTAL

TEFZEL SURFACE TREATMENT

PLASMA SURFACE TREATMENT

Tefzel tensile test specimens (TTS) were obtained from E.I. Du Pont de Nemours. Each of these were cut through at the midpoint of the neck in

anticipation of constructing double lap shear test specimens and then washed with methylethylketone (MEK). The specimens were shipped to Plasma Science, Inc. for plasma surface treatment in their PS 0500 system. This is a microprocessor controlled, 13.56 MHz, 600 watt primary plasma unit. The process parameters are given below in Table 1. After plasma treatment, the specimens were shipped back to Texas Research Institute Austin, Inc. for double lap shear testing. No special effort was made to protect the specimen parts from contact with the air, although the parts were handled using cotton gloves.

SODIUM ETCH

This surface treatment consisted of submersion of the part in a solution of sodium and naphthalene in tetrahydrofuran. For the purpose of this work, the etchant used was Tetra-Etch, obtained from W.L. Gore and Associates, Inc. The parts were first washed in MEK, allowed to air dry, and then dipped in the etch solution for 45 seconds. Afterward, they were washed with soap and water, then rinsed in MEK, and then allowed to air dry. Double lap shear specimens were constructed from the etched parts within 5-10 minutes after the etch cycle.

REVIEW OF COMMERCIAL ADHESIVES

The adhesives chosen for the double lap shear tests were: (1) Thermoset DC-80, (2) Magnolia Plastics Magnobond™ 6375, (3) Magnolia Plastics 6175-NM, (4) Emerson & Cuming Uniset™ D-276, (5) B.F. Goodrich A-1353-B, (6) B.F. Goodrich E1112, (7) B.F. Goodrich EXP 188, and (8) Key Polymers C7-55. The pertinent properties of these adhesives are listed in Table 2.

Table 1
Plasma Surface Treatment Process Parameters

Process	Gas Mixture	Flow Rates (L/sec.)	Chamber Pressure (Torr)	Power (watts)	Process Time (min.)
P1	90% O ₂ 10% SF ₆	0.015 0.0017	0.34	304	10
P2	100% O ₂	0.0085	0.24	544	15
P3	100% NH ₃	0.034	0.50	542	15

Table 2
Commercial Adhesives Tested on Plasma Treated Tefzel

Adhesive	Type	Cure Schedule (°C/Hours)
Thermoset™DC-80	Two Comp. Epoxy	25/24 121/0.1
Magnobond™6375 ¹ 6175-NM ¹	Two Comp. Epoxy One Comp. Epoxy Low Temp., Quick Cure	25/24 125/.88
Uniset™D-276 ²	One Comp. Epoxy Thixotropic Low Temp., Quick Cure	120/0.3
A1353B ³	One Comp. Epoxy Similar to D-276	120/0.5
E1112 ³	One Comp. Epoxy	120/1.0
EXP 188 ³	One Comp. Epoxy Experimental	120/1.0
C7-55 ⁴	One Comp. Epoxy	120/1.0

¹ Magnolia Plastics

² Emerson & Cuming

³ B.F. Goodrich

⁴ Key Polymers

TESTING OF ADHESIVE STRENGTH

BONDING TEFZEL TO TEFZEL

Shown in Fig. 1 is a schematic of the double lap shear test specimen during construction. The specimens were made by applying the adhesive to both sides of the bondline. The total adhesively bonded area in each specimen was one square inch, the lap size being 0.5 by 1.0 in. As each was made the specimens were placed in a clamp designed to hold 15 double lap shear specimens. This held the adherends in position as well as exerted a constant force on all specimens so that a repeatable bondline thickness was achieved. The single component adhesives were cured by placing the clamp assembly in an oven at 120-125 °C (250-260 °F) for two hours. The two component epoxies were mixed in the ratios specified by the manufacturer and blended for ten minutes. After the lap shear specimens were assembled, the two component adhesives were allowed to cure at room temperature for 24 hours. After curing, all specimens were evaluated using a United TM-10E instrument at a rate of strain of 0.51 cm/min. The instantaneous stress was plotted on a strip chart recorder from which the maximum stress (i.e., the adhesive bond breaking shear stress) was obtained.

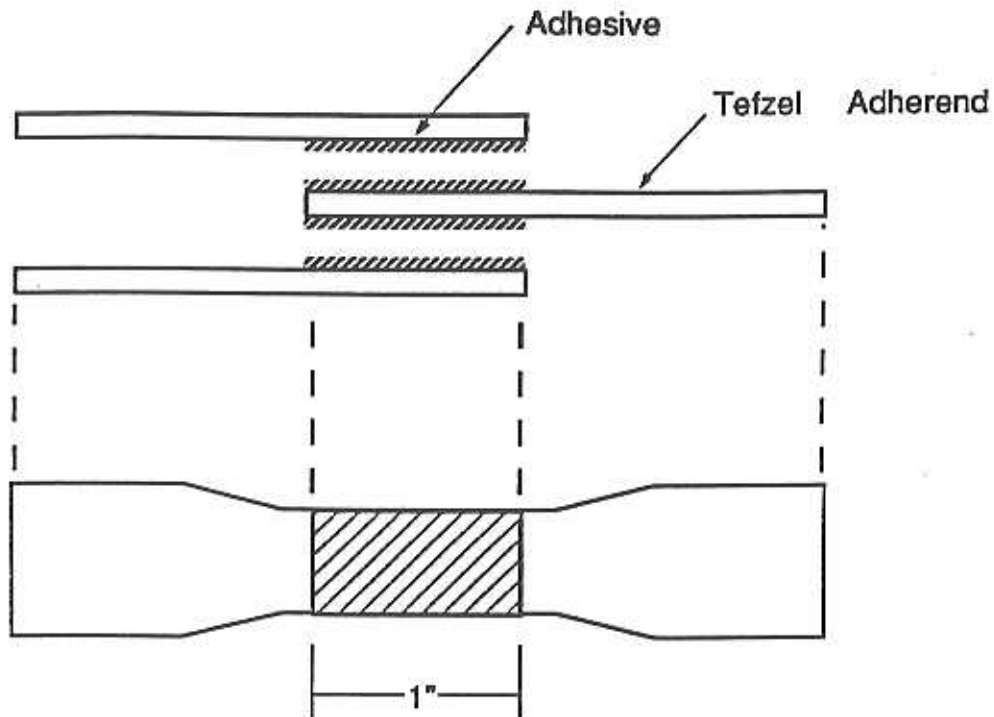


Figure 1. Schematic of the double lap shear test specimen.

BONDING TEFLON TO EPOXY-COATED STEEL

To determine the bond strength of Tefzel adhesively bonded to epoxy-coated steel, a slightly different tensile test configuration was used. In this case the middle piece was a 12.7 mm wide, 3.175 mm thick, 130 mm long epoxy-coated soft steel bar. The epoxy paint thickness was approximately 0.127 mm. The outer adherends of the double lap shear specimens were plasma-treated Tefzel.

SURFACE ANALYSIS

Surface analysis of the untreated (i.e., only solvent wiped with MEK) and plasma treated surfaces were performed using ESCA. The principle of ESCA is the excitation and ejection of core electrons in an atom or molecule using X-rays into vacuum. The kinetic energy with which the electron leaves the atom is sensitive to the chemical environment in which the atom resides and the energy of the incident X-ray photon. Thus, ESCA is a surface sensitive technique capable of obtaining elemental and chemical information from the top 100 Å of a surface. These ESCA measurements can detect elements with atomic numbers greater than helium, with a sensitivity of roughly one atom percent. The spectra reported here were taken and analyzed by Surface Science Laboratories using a Surface Science Instruments model SX-101 Microbeam ESCA Spectrometer. The X-rays were Al K α monochromatized using a quartz crystal. This work involved analysis only of the untreated Tefzel and the oxygen plasma treated material.

Survey scans (0-1000 eV) were measured from the treated and untreated Tefzel surfaces to determine what elements were present, and their approximate abundances. High resolution spectra were then taken from the spectral regions of the major elements. The survey spectra and high resolution spectra were taken with energy resolutions of 1.0 eV/channel and 0.16 eV/channel, respectively. The high resolution data were curve-fitted to resolve the presence of multiple components. The area from which the spectra were acquired was 600 by 1000 μm . An external source of electrons was used to irradiate the sample to compensate for "charging" on the insulating surface.

RESULTS

ADHESIVE BOND STRENGTH MEASUREMENTS

The results of the double lap shear tests are given in Tables 3 and 4. Each bond strength value in the tables represents an average of five measurements with the exception of the value for the untreated material. In this latter case, the value represents an average of only two measurements, since all other specimens delaminated before the test was performed. It is notable that when no surface treatment was used, approximately 70% of the specimens debonded adhesively during removal from the cure clamp or installation in the test machine. It was clear during these experiments that the adhesive could be flaked from the failed surface by rubbing with a fingernail. The results indicated an average factor of 21 increase in the bond strength (over no treatment) when the ammonia plasma was used, an average factor of 24 increase when the oxygen plasma was used, and an average factor of 27 increase when the oxygen/sulfur hexafluoride plasmas were used. The sodium-etched surface showed an increase in bond strength over the untreated material by only an average factor of 11. All treated specimens failed cohesively in the adhesive during the double lap shear tests. The adhesive remaining on the failed surface was not easily removed, even by scraping with a knife edge.

In comparing the results using B.F. Goodrich A-1353-B single component epoxy with plasma treated adherends (O_2/SF_6 and NH_3) and sodium etched adherends, the ammonia treatment gave approximately a factor of two increase in the bond strength, and the oxygen/sulfur hexafluoride a factor of three, over the sodium etch treatment. We also obtained results using the Key Polymers C7-55 single component epoxy with oxygen/sulfur hexafluoride plasma treated adherends and sodium etched adherends. In comparing the sodium etch results, it is seen that the bond strengths obtained with the two adhesives are nearly equal, but the spread in the data was greater with the Key Polymers adhesive. With the plasma treated surface, the bond strengths were about 0.25 MPa (megapascal) less than those obtained with the B.F. Goodrich epoxy.

The Emerson and Cuming Uniset D-276 single component epoxy was used to bond Tefzel to the epoxy coated steel. Comparing the results for this adhesive in Tables 3 (P2) and 4, it is obvious that there was a substantial increase in the bond strength when bonding to the epoxy coating as compared to Tefzel. Increases on the order of 20 to 60 % in the bond strengths were measured, although the spread in the data reflected by the values of the first standard deviation also increased considerably. Again, all failure modes were cohesive in the adhesive.

SURFACE ANALYSIS

Though previous workers^{7,10} successfully used attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to observe changes in the surface molecular structure which arose during the plasma treatment, we were unable to see these effects using the same technique. In the ATR-FTIR technique, the infrared beam penetrates the sample to a minimum depth ranging from 100 to 1000 Å over the infrared spectral range, when a germanium crystal is used. In addition, this volume must be chemically altered by approximately 10 to 20% or more in order to observe changes in the ATR-FTIR spectrum. If we effected chemical changes only at the surface covering only about 8 to 10 % of the surface, then these changes would be difficult to observe using the ATR-FTIR technique. This result is consistent with the comments by Hansen, et. al.,⁵ that fluorinated thermoplastics are relatively stable in atomic oxygen: the etching process is slow compared to that of other polymer materials and the primary oxidation products, which are volatile, are more readily attacked than the base polymer.

Survey ESCA spectra of Tefzel surfaces taken before and after oxygen plasma treatment are shown in Figures 2 and 3. High resolution spectra of the C_{1s}, O_{1s}, and F_{1s} regions before and after plasma treatment are shown in Figure 4. Analyses of the spectra were performed based on previously reported work¹³⁻¹⁶. Binding energies were referenced to the binding energy of the F_{1s} signal at 688.4 eV. Atomic percentages were calculated from the high resolution data. Peak assignments were based on the binding energies of reference compounds. Based on the analysis of these spectra, there was 3.2 % oxygen, 7.2 % hydrocarbon-like carbon (probably a contaminant), 49.4 % fluorine, and a small component of CF₃ prior to the oxygen plasma treatment. This last feature is curious, since there should be no perfluoromethylene moiety present in Tefzel (the molecular structure is described above). After treatment, the surface oxygen increased to 9.8 %, primarily in the form of an ester, the hydrocarbon-like carbon dropped to 2.9 %, the fluorine concentration dropped to 41.6 %, and the CF₃ disappeared entirely. It is notable that if ether or alcohol type C-O bonds formed during the oxidation process, these peaks would be obscured by the C-CF₂ peak.

Table 3.
Double Lap Shear Results for Tefzel-to-Tefzel Adhesively Bonded Joints

Surface Treatment ¹	Adhesive	Shear Strength (MPa)	Std. Dev. (63%)
P1	A-1353-B	2.31	0.11
P1	DC-80	2.28	0.19
P1	EXP 188	2.20	0.10
P1	C7-55	2.06	0.06
P1	D-276	2.02	0.10
P1	E1112	1.93	0.09
P1	6175-NM	1.92	0.05
P1	6375	1.49	0.12
P2	DC-80	1.83	0.13
P2	D-276	1.94	0.11
P2	6175-NM	1.82	0.16
P2	6375	1.47	0.02
P3	A-1353-B	1.72	0.00
P3	D-276	1.40	0.10
TE	A-1353-B	0.78	0.13
TE	C7-55	0.79	0.26
NO	D-276	0.07	0.01

¹P1=O₂+SF₆; P2=O₂; P3=NH₃; TE=Tetra-Etch; NO=No Treatment

Table 4.
Double Lap Shear Results for Tefzel-to-Steel¹ D-276 Adhesively Bonded Joints
Oxygen Plasma Treatment

Cure Schedule	Shear Strength (MPa)	Std. Dev. (63%)
20 min. at 120 °C	2.35	0.49
30 min. warm-up followed by 25 min. at 120 °C	3.07	0.20
15 min. warm-up followed by 45 min. at 120 °C	3.04	0.18

¹Steel surface coated with epoxy paint.

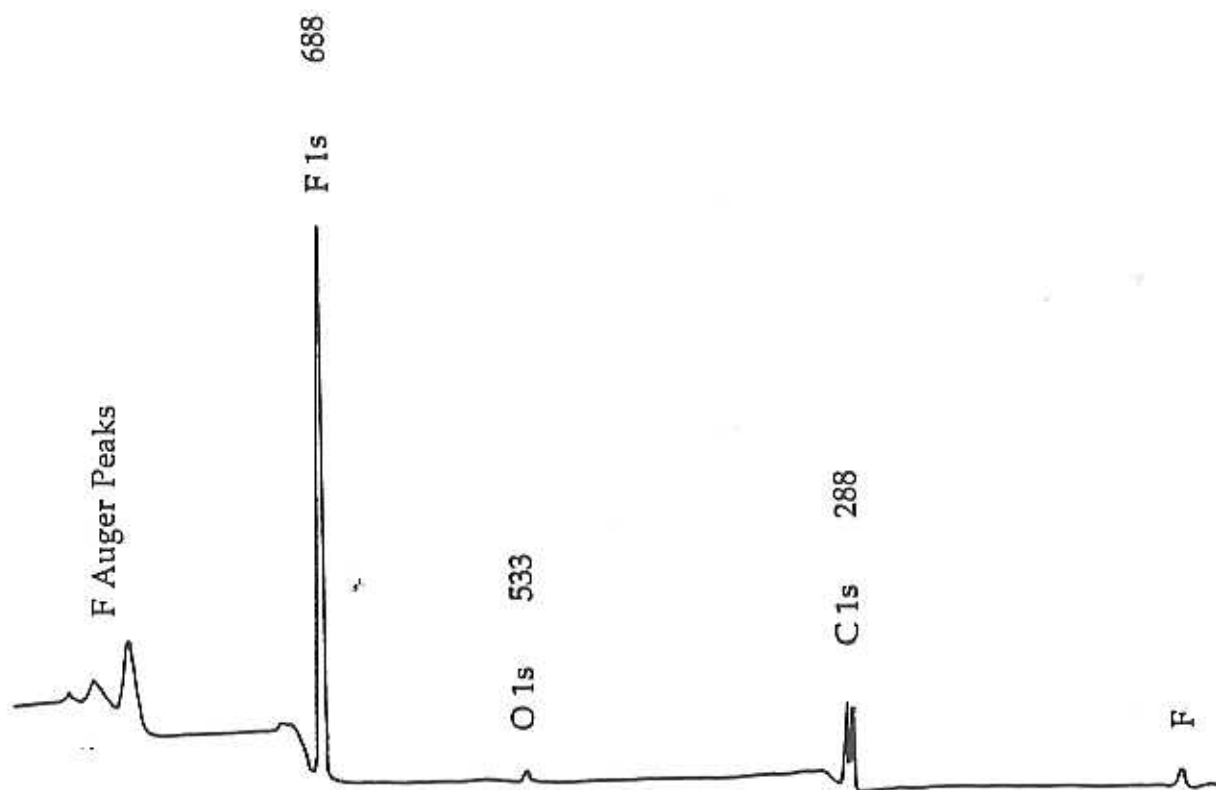


Figure 2. ESCA spectrum of Tefzel before plasma treatment. The pertinent peaks are labeled with the assignment and binding energy.

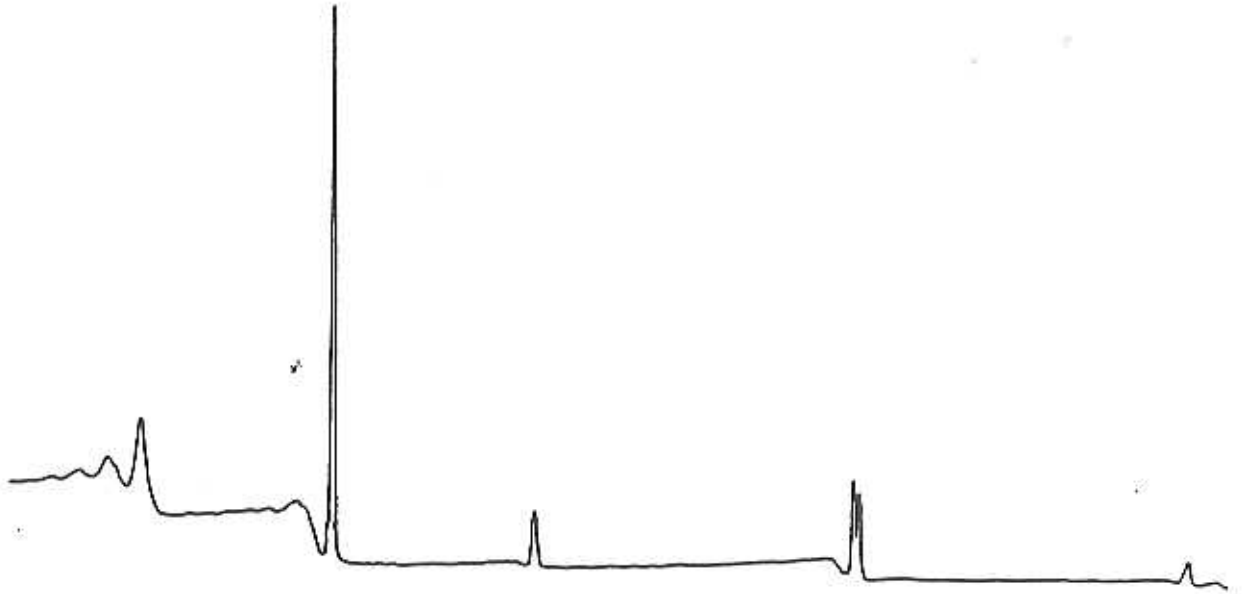


Figure 3. ESCA spectrum of Tefzel after oxygen plasma treatment.
The peak assignments are the same as those given in Fig. 2.



Figure 4. High resolution ESCA spectra in the C_{1s}, O_{1s}, and F_{1s} regions
a) before and b) after oxygen plasma treatment.

Table 5
ESCA Surface Chemical Analysis of Untreated and Oxygen Plasma Treated Tefzel

Element	Energy (eV)	Chemical Environment	Atomic Percent	
			Untreated	Treated
C 1s	284.6	\underline{C} -R ^a	7.2	
	285.2			2.9
C 1s	288.8	O= \underline{C} -OR ^a	0.0	3.3
C 1s	286.5	\underline{C} -CF ₂	49.7	
	286.2			19.0
C 1s	291.1	\underline{C} F ₂	22.5	20.2
C 1s	293.9	\underline{C} F ₃	1.1	0.0
O 1s	533.7		2.1	
O 1s	532.1	C- \underline{O}	1.9	
	533.6			9.8
O 1s	533.9	FC- \underline{O}	1.3	
	533.6			9.8
F 1s	688.4	\underline{C} F ₂	49.4	41.6

^aR=Hydrocarbon

CONCLUSIONS

Increases in bond strength were observed when using SF₆ + O₂ compared to O₂, but the change was only about 15%. This low an increase is likely due to the fact that even in the neat O₂ plasma atmosphere, there was a sufficient fluorine radical concentration, arising from the polymer surface, to improve the efficiency of the oxidation process.

The average increase of about 45 % in bond strength measured for Tefzel to epoxy coated steel as compared to Tefzel bonded to itself merits comment. Here we were essentially bonding Tefzel to epoxy using an elevated temperature curing epoxy adhesive. The chemical and well as physical compatibilities of the coating and adhesive probably made the largest contributions to increasing the adhesive bond strengths measured in these systems.

The results of the ESCA analysis indicated that the apparent concentration of carbon increased by 3 %, the concentration of oxygen increased by nearly 7 %, and the fluorine concentration decreased by 7 %. The F/C ratio decreased from 1.1 to 0.9. Based on the CH and CF bond energies, it is probable that the polymer is oxidized primarily at the CH sites. Fluorine atoms were not necessarily removed from the surface in large concentrations, rather the increase in oxygen caused the surface concentration of fluorine to be decreased. In order to form an ester, it is necessary to insert an oxygen

atom in the carbon backbone. A likely place for this to happen is the C-CF₂ bond, since it is weakened as a result of electron withdrawal by the vicinal, highly electronegative fluorines. Judging from the structure of Tefzel, the only other place to insert oxygen in the carbon backbone would be between the carbons of the ethylene linkage.

The expected improvements in bond strength with the NH₃ plasma treatment were not observed. This could be due the fact that the surface was not sufficiently aminated to obtain bond strengths comparable to the oxidized surface. As the results stand now, it is not possible to determine whether grafting occurred or if the surface was simply etched. More work is required, particularly ESCA surface analysis. It may also be necessary to explore other plasma treatment parameters such as process time and pressure as well as gas composition.

The improvements in bond strength were not as good as those obtained by previous workers. Ross² for example measured double lap shear strengths approaching 27 MPa with failure in the polymer adherend after a ten minute oxygen plasma treatment. The comparison may not be entirely fair however, since the center adherend was Halar (high molecular weight, 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene), the outer adherends were solvent washed and sanded steel, and the adhesive was EC-2214, a 120 °C curing contact pressure epoxy paste. Part of the difference is undoubtedly due to the difference in test geometries. Ross used a one-inch wide overlap, while that used in the work reported here was only a one-half-inch wide overlap. Some of the disparity is also believed to arise from differences in the plasma gas densities used in the current work compared to those used by the earlier workers so that the degrees of oxidation, volatilization and ablation were less. Several other possible differences in the plasma as enumerated in the introduction may have led to reduced oxidation of the surface.

Rose and Liston⁴ reported increases on the order of 160% in the surface energies with plasma treatment of various fluorocarbon thermoplastics and elastomers, corresponding to decreases on the order of 41 % for the water contact angle. Similar decreases in the contact angle were observed in our current work, but the data were rather widely spread and so we prefer to continue the work before reporting values and stating claims regarding the results.

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