

Plasma Processes and Adhesive Bonding of Polytetrafluoroethylene

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The virtues of chemical inertness and low surface energy which make polytetrafluoroethylene (PTFE) a valuable engineering polymer also account for the difficulty in achieving structural adhesive bonds. While plasma surface treatment has proven to be the most effective means of maximizing strength and permanence of adhesive bonds with the most inert of engineering polymers, a simple plasma treatment has proven elusive for PTFE. The following studies evaluate two very different plasma processes, activation and deposition, as a means to achieve reliable and high-strength structural adhesive bonds. Sodium naphthalene-etched PTFE is used as a control. Presented are ESCA data which support a theory that improvement is limited by a weakened boundary layer of the PTFE.

BACKGROUND

Plasmas (electrically charged gases) make up 99% of our universe, but until the second half of the twentieth century plasmas were not of much commercial value. Since 1970, plasmas have found growing use in the modification of plastics to enhance adhesive bond strength and the permanency of decorative and functional coatings.

Plasmas occur over a wide range of temperatures and pressures, but all plasmas have approximately equal concentrations of positive and negative charge carriers, so the net space charge approaches zero. Within the plasma exist many species: ions, electrons and various neutral species at many different energy levels, as well as photons. These energetic particles collide with the surfaces of materials placed in the plasma chamber, causing molecular disruptions. This leads to drastic modifications of the structure and properties of surfaces.

The chemistry of the reaction determines the effect a plasma has on a polymer. The plasma process causes changes only to a depth of several molecular layers. In addition, plasma surface reactions change the molecular weight of the surface layer by scissioning (reducing molecular length), branching and cross-linking. The type of surface change depends on the composition of the surface and the gas used. This work reports on attempts to develop an effective plasma process to facilitate adhesive bonding of polytetrafluoroethylene (PTFE) without the need to employ corrosive materials, such as solutions of Tetra-Etch[®].

EXPERIMENTAL

Both plasma activation and plasma deposition were examined as a means of improving adhesion. The activation studies were conducted by using a Taguchi

experimental matrix design to investigate the four pertinent process variables (gas chemistry, power, gas flow rate and process time). The evaluation of plasma deposition was of limited scope (a full Taguchi matrix was not explored).

Materials

Polytetrafluoroethylene sheets 3.175 mm ($\frac{1}{8}$ inch) thick were purchased from Furon Corporation, who provided a certificate of analysis attesting to the content as 100% PTFE. All samples were cleaned in an isopropyl alcohol ultrasonic bath for 5 min prior to use.

Tetra-Etch[®], a commercial sodium etch solution, was purchased from its manufacturer, W. L. Gore & Associates, Inc., Flagstaff, Arizona. It was used in strict conformance to the manufacturer's recommended procedure. Tetra-Etch[®] is a solution of a sodium naphthalene complex (25%) in ethylene glycol dimethyl ether (75%).

Miller Stephenson 907 adhesive, a two-part epoxy adhesive system, was used in accordance with the manufacturer's recommendations for stoichiometry and cure schedule.

Sodium etch

The PTFE sheets were washed in an IPA ultrasonic bath prior to treatment in the sodium etchant solution. Etching was done for 10 s in Tetra-Etch[®] solution, followed by rinsing in boiling water, washing by IPA and air drying.

Plasma modification was done in a Plasma Science Model PS 0500 plasma system, a primary plasma with 13.56 MHz rf excitation, under the following conditions

NH₃ flow rate = 44 sccm†
 rf Input power = 1200 W
 Process time = 1.0 min
 Process pressure = 0.100 Torr

† Standard cubic centimeters per minute. A flow rate of 1 sccm = 4.46×10^{-5} mol min⁻¹.

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me sheets, in addition to the plasma modification treatment, were also exposed to a proprietary plasma polymerization process using a hydrocarbon gas. In order to promote adhesion between the hydrocarbon coating and an epoxy resin system, the deposited thin film was oxidized by a post-treatment in an O_2 plasma as follows:

O_2 flow rate = 100 sccm
 Input power = 230 W
 Process time = 0.10 min
 Process pressure = 0.100 Torr

This third sample will be referred to as the polymerized sample in subsequent discussion.

Testing methodology

A pneumatic adhesion tensile test instrument, PATTI® Model 2A, manufactured by SEMicro, Rockville, Maryland, was used to evaluate adhesion. Test procedures followed manufacturer's recommended procedures and conform to ASTM D4541. In this test method, an aluminum stub is bonded to the test surface and the force normal to the surface required to debond it from the surface is recorded. Bonding of the Al stub to the treated PTFE surface used a two-part epoxy adhesive, the Epoxy 907 Adhesive System (manufactured by Miller Stephenson Chemical Co., Inc. of Danbury, CT). The epoxy was air-cured for 24 h at room temperature prior to testing. Figure 1 is a schematic of the specimen configuration prior to tensile testing. After testing, ESCA analysis was performed at three locations: the modified surface outside of the bonded area, the PTFE

surface at the site of the bond failure, and the debonded surface of the bolt.

The ESCA measurements were performed using a Surface Science Instruments SSX-100 spectrometer with an Al K α x-ray source ($h\nu = 1486.6$ eV) in a 1×10^{-8} Torr vacuum. The energy scale was calibrated using the Au 4f_{7/2} and Cu 2p_{3/2} signals at 83.9 and 932.5 eV, respectively. Surface neutralization during the ESCA measurements was achieved using a flux of low-kinetic-energy electrons (2–7 eV) and an electrically grounded 90% transmission nickel screen positioned 1 mm above the sample surface.

Sensitivity factors for the Si 2p, Si 2s, C 1s, O 1s and F 1s signals were determined using high-molecular-weight dimethyl silicone and Teflon® plumber's tape. Sensitivity factors for other elements were determined by interpolation, assuming that the combined effect of escape depth and instrument transmission function is an exponential function of kinetic energy. For each of the calibrated signals, the ratio of the sensitivity factor to the photoionization cross-section was calculated. These standard 'correction factors' were used to estimate correction factors for other signals, assuming the exponential function of kinetic energy.

The spectral data were quantified by measuring the area under the signals and using the sensitivity factors to calculate relative abundances. The high-resolution data were peak-fitted using 80% Gaussian and 20% Lorentzian peak shapes to resolve the presence of multiple species. For a given element, the abundance of each species was estimated from its relative peak area.

RESULTS

Plasma activation is a process employing a gas not capable of polymerization. The intent of the plasma process is to replace a portion of the non-functionalized moieties on the polymer backbone with functional groups related to the process gas. In this specific case, ammonia was selected as the process gas with the intent of incorporating amino and/or amine groups on the fluoropolymer backbone. The ESCA data shown in Table 1 show that nitrogen has been incorporated into the surface of the PTFE as a result of the NH_3 plasma activation. Moreover, the high-resolution ESCA scans (Table 2) show that this nitrogen is in the form of amine (N_1) or amino (N_2) groups. The ESCA data in Tables 1 and 2 also show considerable incorporation of oxygen functionality, probably the result of oxygen in the air combining with free radicals on the surface of the PTFE.

The results of Table 3 indicate that extended treatment time appears to provide minimal benefits. Such rapid plateaus are surprising because in prior studies with other engineering resins,⁵ a strong dependence on process time, especially over the first 120 seconds, is normally noted.

Plasma polymerization is a process in which the process gas undergoes polymerization when excited to a plasma state. Since many free radicals are present, it is generally accepted that the initial molecular layer of the deposited film is likely to be grafted to the substrate.⁷

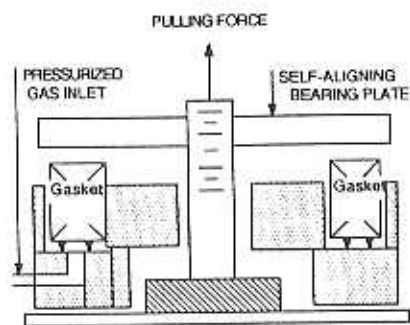
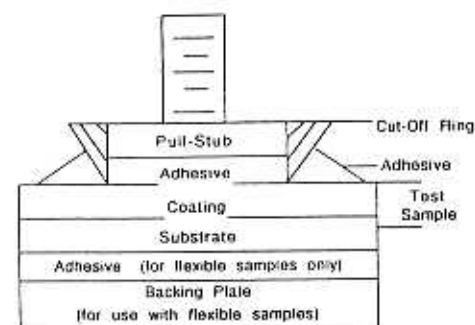


Figure 1. Cross-section schematic of pull-stub attached to coating (top) and piston attached to pull-stub (bottom).

Table 1. ESCA elemental composition data (at.%)

Sample description	C	S	Mg	Ca	N	O	F	Na	Si
PTFE virgin	33	—	—	—	—	—	67	—	—
Tetra-Etch®									
Treated surface	71	0.4	1.2	0.9	1.9	17	7.9	—	—
PTFE side	37	—	—	—	1.2	1.0	61	0.2	—
Bolt side	40	—	—	—	2.2	2.8	53	2.1	—
Plasma activation									
Treated surface	46	—	—	—	6.4	6.3	39	—	—
PTFE side	33	—	—	—	—	—	67	—	—
Bolt side	35	—	—	—	0.7	0.4	64	—	—
Plasma-polymerized									
Treated surface	69	0.2	—	—	4.2	24	—	0.6	1.6
PTFE side	33	—	—	—	0.9	1.3	64	—	—
Bolt side	40	—	—	—	0.7	3.7	54	—	0.8

The absence of fluorine (Table 4) and the type of carbon identified in the ESCA data (Table 5) support the contention that a film with a carbon backbone was deposited. The film was of sufficient thickness to mask the

fluorine in the PTFE bulk from ESCA detection (i.e. $>100 \text{ \AA}$).

The sodium-etched PTFE surface has a radically different composition from either of the two plasma-

Table 2. High-resolution ESCA nitrogen and oxygen identification*

Sample description	N ₁	N ₂	N ₃	O ₁	O ₂	O ₃
PTFE control						
Binding energy (eV)	—	—	—	—	—	—
Atomic per cent	—	—	—	—	—	—
Sodium etch surface						
Binding energy (eV)	NM	NM	NM	531.3	532.8	—
Atomic per cent	NM	NM	NM	6.0	11	—
Sodium etch, PTFE side						
Binding energy (eV)	NM	NM	NM	531.2	532.8	—
Atomic per cent	NM	NM	NM	0.6	0.6	—
Sodium etch, bolt side						
Binding energy (eV)	399.2	400.6	—	531.2	532.6	—
Atomic per cent	1.6	0.6	—	1.3	1.5	—
Plasma-polymerized surface						
Binding energy (eV)	399.7	401.1	—	531.3	532.5	—
Atomic per cent	2.3	1.9	—	7.7	17	—
Plasma-polymerized, PTFE side						
Binding energy (eV)	NM	NM	NM	531.3	532.6	—
Atomic per cent	NM	NM	NM	0.7	0.7	—
Plasma-polymerized, bolt side						
Binding energy (eV)	399.8	—	—	531.4	532.7	—
Atomic per cent	0.7	—	—	2.0	1.7	—
Ammonia plasma-activated						
Binding energy (eV)	400.0	—	401.5	—	532.3	533.8
Atomic per cent	4.3	—	2.1	—	4.3	2.0
Ammonia plasma-activated, PTFE side						
Binding energy (eV)	—	—	—	—	—	—
Atomic per cent	—	—	—	—	—	—
Ammonia plasma-activated, bolt side						
Binding energy (eV)	399.4	401.0	—	531.9	—	534.1
Atomic per cent	0.4	0.3	—	0.3	—	0.2

* Binding energies were corrected to the binding energy of the C 1s ($-(\text{CH}_2)_n-$) signal at 284.6 eV or the F 1s (CF_2) signal at 689.2 eV. Atomic percentages were calculated from the high-resolution data. Peak assignments were based on the binding energies of reference compounds. Peak assignments: N₁ is NR₂; N₂ is NR₃; N₃ is NR₄⁺; O₁ is C=O; O₂ is C—O, C=O; O₃ is C—O. NM, not measured.

Table 3. Effect of plasma process time on NH_3 plasma activation*

Process time (min)	Average pull strength ^b (psi)
0.08	245 ± 56
0.25	340 ± 51
0.50	318 ± 59
1.00	360 ± 23
2.00	329 ± 15
4.00	309 ± 20
8.00	279 ± 12
8.00	267 ± 26 ^c
16.00	251 ± 22
32.00	243 ± 29
Sodium-etched	1871 ± 50

* Plasma Science 0500 plasma system at 1200 W and 0.100 Torr. PATTI® tester; procedures conform to ASTM D4541; Miller Stephenson 907 adhesive (two-part epoxy).
^b Repeat of measurement at 8 min process time.

Table 4. High-resolution ESCA fluorine identification^a

Sample description	F ₁	F ₂	F ₃
PTFE control			
Binding energy (eV)	—	—	689.2
Atomic per cent	—	—	67
Sodium etch surface			
Binding energy (eV)	684.8	—	689.8
Atomic per cent	1.5	—	6.4
Sodium etch, PTFE side			
Binding energy (eV)	—	—	689.7
Atomic per cent	—	—	61
Sodium etch, bolt side			
Binding energy (eV)	684.9	—	689.3
Atomic per cent	1.4	—	52
Plasma-polymerized surface			
Binding energy (eV)	—	—	—
Atomic per cent	—	—	—
Plasma-polymerized, PTFE side			
Binding energy (eV)	—	—	689.5
Atomic per cent	—	—	64
Plasma-polymerized, bolt side			
Binding energy (eV)	—	—	689.0
Atomic per cent	—	—	54
Ammonia plasma-activated			
Binding energy (eV)	685.5	687.4	689.2
Atomic per cent	4.8	4.4	30
Ammonia plasma-activated, PTFE side			
Binding energy (eV)	—	—	689.5
Atomic per cent	—	—	67
Ammonia plasma-activated, bolt side			
Binding energy (eV)	—	—	689.4
Atomic per cent	—	—	64

^a Binding energies were corrected to the binding energy of the C 1s ($-(\text{CH}_2)_n-$) signal at 284.6 eV or the F 1s (CF_2) signal at 689.2 eV. Atomic percentages were calculated from the high-resolution data. Peak assignments were based on the binding energies of reference compounds. Peak assignments: F₁ is ionic F or C—F; F₂ is CF_2 ; F₃ is CF_x .

treated samples. The sodium dehalogenation establishes a surface nearly devoid of fluorine, as evidenced by the reduction in $-\text{CF}_2$ carbon from 31% to <3% and $-\text{CF}_2$ fluorine from 67% to 6.4%.

The PTFE side under both the plasma-activated and the plasma-polymerized PTFE surfaces exhibit high-resolution ESCA scans very similar to virgin PTFE. Analysis of the area of debond from the sodium-etched sample shows neither pure PTFE nor the sodium-etched surface prior to bonding. CF_2 carbon (Table 5, labeled as C₆) at the debonded area is 27% vs. 31% and 2.6%, respectively, for virgin and sodium-etched PTFE, and CF_x fluorine (labeled F₃ in Table 4) is 61% at the debonded surface as compared to 67% and 6.4%, respectively, for virgin and sodium-etched PTFE.

DISCUSSION

Chemical modification

The commonly accepted mechanisms for the modification of PTFE surfaces by sodium etchants are dehalogenation, leaving unsaturated sites (producing NaF), and the subsequent oxidation of these unsaturated sites to form carbonyl and other groups. This mechanism is supported by ESCA data, which show the absence of fluorine and the presence of oxygen when PTFE is modified by an Na/ NH_3 etch.¹ This oxidized surface is apparently unstable because exposure to heat and light may remove some of the layer to expose the underlying unmodified fluoropolymer.²

As seen in the high-resolution ESCA scans, the sodium etching process removes fluorine from the PTFE and results in the presence of a high atomic percentage of carbon peaks at 284.6 eV (C₁, due to C—R bonds, where R could be either H or C atoms). This is consistent with considerable cross-linking of the PTFE during the etching process, since C—R amounts to 48% of the surface composition of the etched sample. This cross-linking could account for the high adhesion strength of the sodium-etched samples. The sodium-etched samples appear to fail in adhesion at the transition zone between the etched surface and the virgin PTFE underneath.

Plasma modification

A number of researchers^{3,4} have reported both ammonia and nitrogen/hydrogen mixtures to be effective in making the PTFE surface hydrophilic, although the resulting epoxy adhesive bond strength was disappointing. One study⁶ used sophisticated analytical techniques to investigate PTFE modification by various plasmas. Their work showed that with ammonia plasma the surface was modified, as evidenced by the appearance of covalently bonded nitrogen. In contrast, air plasma caused degradation of the PTFE surface to form volatile products. Since the C—F bond is considerably more stable than C—C bonds, the predominance of chain scission vis-à-vis fluorine abstraction would be anticipated. Thus, the facile incorporation of nitrogen to the PTFE surface with ammonia plasma is surprising.

Table 5. High-resolution ESCA carbon identification^a

Sample description	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
PTFE control							
Binding energy (eV)	284.6	285.9	—	—	—	292.1	—
Atomic per cent	1.2	0.4	—	—	—	31	—
Sodium etch surface							
Binding energy (eV)	284.6	286.4	—	288.1	—	292.6	—
Atomic per cent	48	16	—	3.8	—	2.6	—
Sodium etch, PTFE side							
Binding energy (eV)	284.6	286.3	—	—	—	292.5	—
Atomic per cent	7.4	1.9	—	—	—	27	—
Sodium etch, bolt side							
Binding energy (eV)	284.6	286.0	287.7	—	—	292.2	—
Atomic per cent	12	4.4	0.6	—	—	23	—
Plasma-polymerized surface							
Binding energy (eV)	284.6	286.3	—	288.2	—	—	—
Atomic per cent	46	17	—	6.6	—	—	—
Plasma-polymerized, PTFE side							
Binding energy (eV)	284.6	286.3	—	—	—	292.4	—
Atomic per cent	1.7	1.1	—	—	—	31	—
Plasma-polymerized, bolt side							
Binding energy (eV)	284.6	285.9	—	—	—	291.9	—
Atomic per cent	12	2.4	—	—	—	26	—
Ammonia plasma-activated							
Binding energy (eV)	284.6	287.0	—	288.6	290.2	292.0	293.7
Atomic per cent	14	10	—	5.1	3.0	13	1.5
Ammonia plasma-activated, PTFE side							
Binding energy (eV)	284.6	286.3	—	—	—	292.4	—
Atomic per cent	0.4	0.2	—	—	—	32	—
Ammonia plasma-activated, bolt side							
Binding energy (eV)	284.6	286.0	—	—	—	292.3	—
Atomic per cent	1.8	0.8	—	—	—	32	—

^a Binding energies were corrected to the binding energy of the C 1s ($-(CH_2)_n-$) signal at 284.6 eV or the F 1s (CF_2) signal at 689.2 eV. Atomic percentages were calculated from the high-resolution data. Peak assignments were based on the binding energies of reference compounds. Peak assignments: C₁ is C-R (R=C, H); C₂ is C-OR or C-N; C₃ is R-C=O; C₄ is R-C=O or O=C-OR; C₅ is C-F or CF₂; C₆ is CF₂; C₇ is CF₃.

This study investigated whether plasma polymerization would provide a modified adherable layer to PTFE which eliminates problems reported by previous researchers. The rapid plateauing in the ammonia activation study supports the hypothesis that an equilibrium is rapidly achieved in which backbone chain scission eliminates 'activated or modified' chain segments almost as soon as they are formed. Similar results have been found when polymethylmethacrylate (PMMA) is treated in an oxygen plasma.⁶ Plasma polymerization was investigated as a means of placing a covalently bonded coating onto the PTFE surface. It was hypothesized that even if PTFE chain fragmentation occurred, the fragments created in the plasma polymerization would stabilize the PTFE bulk. It is particularly surprising that ammonia plasma pretreatment improved the adhesive performance of the plasma-polymerized coated PTFE (Table 6). The mechanism which permits the observed performance improvement is not understood. The plasma-polymerized surface was functionalized via conventional plasma activation treatment prior to adhesive bonding.

Any model that is to be proposed must accommodate the following results obtained from this study:

- (1) The sodium-etched PTFE shows a much higher adhesion strength than either of the two plasma-modified samples: 1871 psi *vs.* ~400 psi (12.9 *vs.* 2.8 MPa).
- (2) The adhesion strength of the plasma deposition sample is roughly comparable to that of the ammonia plasma-activated sample: 402 *vs.* 360 psi (2.8 *vs.* 2.5 MPa).

Table 6. Effect of plasma pretreatment on plasma deposition^a

Pre-treatment plasma ^b	Pull strength ^c (psi)
None	101
Argon	182
Ammonia	396
Ammonia	402 ± 70 ^d
Sodium-etched	1871 ± 50

^a Proprietary hydrocarbon deposition process.

^b Plasma Science 0500 plasma system at 1200 W and 0.100 Torr.

^c PATTI[®] tester; procedures conform to ASTM D4541; Miller Stephenson 907 adhesive (two-part epoxy).

^d Repeat set of five samples.

- 3) All three samples show comparable carbon chemistry on the PTFE side of the debonded surface.
- 4) The sodium-etched sample contains 7.4 at.% C—R groups (where R = C or H), which is a much higher percentage than either of the plasma-treated samples or virgin PTFE.

The ESCA data of Table 1 show that the failure mechanism in the plasma-activated case is cohesive within the bulk PTFE. Analysis of the failed surfaces after debonding was found by ESCA to be essentially pure PTFE. Both the plasma-deposited and the Tetra-Etch® samples fail mostly by cohesive failure, with some evidence of islands of adhesive failure. This conclusion is supported by the fact that more C—R groups are found on the bolt side of the debonded surface for the latter two specimens (Table 5). The C—R groups are believed to be epoxy resin.

CONCLUSION

Prior researchers reported that sodium etch penetrates microns in depth, providing a porous or spongy structure that facilitates adhesion bonding. The high-resolution ESCA analysis reported herein suggests that sodium etching also results in cross-linking which may stabilize the modified PTFE interface. The high-resolution ESCA data also show that ammonia plasma treatment caused chain scission. Probably any plasma treatment is likely to cause chain scission because the

C—C bond is weaker than the C—F bond. Small amounts of chain scission are likely to cause a reduction of bulk tensile properties, causing a weakened interface. The tensile adhesion results, as well as the chemical structure information from ESCA scans, support the theory that a modified and weakened PTFE transition layer is established at the interface between bulk PTFE and the fully modified surface, accounting for the low adhesion strength of the plasma-treated samples compared to Tetra-Etch®-treated samples. Although the improvement in adhesion is significantly less than that achieved with the sodium etchant, the plasma process does provide some enhancement in structural bonds.

The plasma process is both safe in the workplace and environmentally clean. In addition, the economics of the plasma process as compared to conventional sodium etch processes justifies examination of joint design to take advantage of the reduced but reliable bonds achievable with the plasma process. While a plasma process to provide comparable results to a sodium etch still eludes definition, the plasma process is an effective, consistent and reliable adhesive pretreatment for structural bonding of polytetrafluoroethylene.

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