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### **Adhesion to Sodium Naphthalenide Treated Fluoropolymers. Part III. Mechanism of Adhesion**

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# Adhesion to Sodium Naphthalenide Treated Fluoropolymers. Part III. Mechanism of Adhesion

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Adhesion of fluoropolymers to copper and to other polymers is examined using a range of fluoropolymer types (PTFE, PFA, extruded, skived and cast films), surface modification techniques such as sodium naphthalenide (Na/naphth), acid stripping and lamination to produce surfaces of controlled roughness, and three tests of adhesion (90 degree peel tests, torsional shear tests and stripping of transmission electron microscopy (TEM) replicas). A combination of chemical and physical modification is required to produce good adhesion, with the relative importance of each dependent upon the specific adhesion test used. For relatively smooth-surfaced films, Na/naphth appears to function by increasing both the chemical functionality and the mechanical integrity of a surface layer. Untreated PTFE and PFA show interfacial failure and negligible adhesion. Smooth-surfaced PTFE with superficial surface modification, e.g. after lamination to shiny copper foil or after acid stripping of defluorinated material, often fails by fibrillation of the fluoropolymer surface. For short sodium etch times, adhesion is improved and the failure mode is interfacial. For long etch times, there is a mixed mode of failure. Fibrillation in smooth-surfaced PFA systems was not observed. Adequate adhesive strength in these systems could only be achieved by an increase in the surface roughness. The best adhesion could be achieved by surface roughening, followed by Na/naphth treatment. For such PTFE surfaces plated with copper, peel and shear tests showed a mixed mode of failure, with copper and fluoropolymer found on both failure surfaces by x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDS). Extensive fibrillation occurred at the locus of failure. Provided chemical modification is adequate to allow wetting, the roughness of the surface dominates the properties of the adhesive bond. Prolonged Na/naphth treatment (e.g. one hour) causes a reduction in peel strengths.

**KEY WORDS** Fluoropolymers; sodium etch; chemical adhesion; mechanical adhesion; PTFE; PFA; surface roughness; surface chemistry.

## INTRODUCTION

Fluoropolymers have historically enjoyed widespread use to provide anti-friction and non-stick surfaces. More recently, interest in adhesion to fluoropolymers has increased, especially in electronics applications, due to the excellent thermal stability and low dielectric loss which these materials provide. Mechanisms of adhe-

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sion are generally categorized by chemical contributions, *e.g.* covalent bonding, dispersive, electrostatic or acid-base interactions, and by mechanical contributions, *e.g.* interdiffusion or interfacial topography.<sup>1,2</sup> The experimental separation of these variables has proven to be a difficult task. For the study of mechanical contributions, surface topography is varied and analyzed using scanning electron microscopy (SEM). The adhesive joint is then formed and measurements of adhesive strength are related to the macroscopic roughness observed.<sup>3</sup> It has been noted that mechanical interlocking in polymer systems can provide a much higher level of apparent adhesion than would be expected solely from an increase in surface area, and that a considerable amount of energy is dissipated by deformation of material during testing.<sup>4</sup> For the study of chemical contributions, the surface topography is held constant while the surface chemistry is varied and analyzed using a variety of techniques such as XPS, EDS, Auger and Infrared spectroscopies. Once the interface is characterized, it is possible to relate the interfacial chemistry to adhesive strength and locus of failure.<sup>5,6</sup> Some recent studies have focused on the copper-polymer interface,<sup>7-9</sup> since copper is used so frequently in electronics applications. In these investigations, it is not always clear that the surface has been altered only physically or only chemically. Changing both the physical and the chemical character of the surface simultaneously complicates the interpretation of adhesive results.

For fluoropolymer surfaces, numerous methods of chemical and physical modification are used.<sup>10</sup> Frequently, adhesion is effected by pretreating the fluoropolymer substrate with a strong reducing agent, such as sodium naphthalenide (Na/naphth), which defluorinates the surface thereby increasing the surface energy and hence, wettability. These surfaces are now chemically reactive, and McCarthy *et al.*<sup>11-14</sup> have shown that specific functionalities can be introduced, although their influence on adhesive strength has not been studied. Ion sputtering<sup>15,16</sup> and lamination<sup>17</sup> are known to change both the physical and chemical character of fluoropolymer surfaces. The effect of interfacial chemistry on adhesion has been examined using chemical evaporation of various metals onto fluoropolymers.<sup>18</sup> Again, it is assumed that the physical structure of the interface is kept constant so that the relation of interactions to adhesion is straightforward. However, similar studies with polyimides have shown migration of some evaporated metals away from the interface, creating a diffuse interphase.<sup>5</sup> Investigations of fracture surfaces in metal-fluoropolymer and metal-adhesive-fluoropolymer systems have claimed cohesive failure in the fluoropolymer exclusively.<sup>19</sup>

We have previously quantified the chemical functionalities and the extent of modification which result from the Na/naphth treatment and reported the influence of treatment conditions and fluoropolymer structure on these results using a combination of gravimetric analysis, x-ray photoelectron spectroscopy (XPS), infrared internal reflectance spectroscopy (IR-IRS), and derivatization techniques.<sup>20,21</sup> The Na/naphth synthesis, standard etching procedure, and the process of removing the defluorinated layer using hot chromic acid (acid strip) were described in these papers. Table I summarizes the chemistry of several fluoropolymer surfaces. Here, ranges indicate results for multiple samples. Use of various take-off angles in XPS indicated the presence of large concentration gradients from the surface through ~10nm depth. Generally, fluorine signals increased and oxygen decreased with

TABLE I  
Chemistry of various fluoropolymer surfaces

Fluoropolymer sample	[F/C] <sup>a</sup>	[O]at% <sup>a</sup>	Affected depth
PTFE, PFA theoretical	2.0	—, ~1 <sup>b</sup>	—
PTFE, skived	1.5	<1	
PTFE, PFA after lamination	0.9–1.6	3–9	<2nm (superficial)
PTFE, PFA after 1 min–1 hr sodium etch	<0.1	10–15	25–150nm
PTFE, PFA after acid strip	1.2–1.5	3–4	superficial

<sup>a</sup>By XPS, using F 1s/C 1s and O 1s signals at 62° TOA.

<sup>b</sup>Oxygen concentration varies with copolymer content for PFA.

sampling depth. For example, even for skived but otherwise untreated PTFE, the theoretical fluorine-to-carbon ratio was obtained only when the sampling depth was increased by the use of the F 2s signal. The sampling depth for F 1s and F 2s electrons is estimated to be 2nm and 6nm respectively.<sup>22</sup>

We have also shown that Na/naphth does not change the topography of fluoropolymers but that topological differences can be obtained by lamination to foils of various roughnesses.<sup>21</sup> With lamination, we can alter and control the physical character of the fluoropolymer surface, from relatively smooth (shiny foil) to very rough (electrodeposited foils) while keeping the surface chemistry constant. The purpose of this paper is to relate the chemical and physical surface variables to the adhesion process in fluoropolymer systems, particularly to copper and solution-deposited polymers.

## EXPERIMENTAL

Polytetrafluoroethylene (PTFE) and tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA) were manufactured by DuPont. The PTFE specimens were commercially available films prepared by either skiving or casting. PFA specimens were either laboratory or commercially extruded films (textured and smooth, respectively) 25–200 $\mu$ m thick. In some instances, the fluoropolymer films were modified by lamination to copper foils of various roughnesses (shiny foil, 0.5-, 1-, and 2-oz. ED foils, Gould Corp.).<sup>21</sup> Removal of copper from the laminates was accomplished using a heated aqueous solution of ammonium persulfate. For samples which were subsequently subjected to electroless copper plating, a Shipley CP-78 pretreatment and plating system was used (Shipley Co.). For peel and torsional shear testing, copper thickness was then built up to a total thickness of 25 $\mu$ m by electrolytic deposition.

Samples examined by transmission electron microscopy (TEM, Philips EM300) were replicated using solutions of polyacrylic acid (PAA) in distilled water, of cellulose acetate (CA) in acetone or of atactic polystyrene (a-PS) in distilled toluene, all at 5% by weight. After drying, detached replicas were shadowed with Pt/C at  $\tan^{-1}(1/2)$ , coated with carbon at normal incidence, mounted on 200-mesh copper screen, and the replicating polymer dissolved away.

Loci of failure from 90° peel and torsional shear tests were examined by SEM

(Amray 1200B, tungsten source) after coating with Pd/Au or after coating with carbon when energy dispersive x-ray spectroscopy was performed (Amray 1000A, LaB<sub>6</sub> source and KEVEX Quantum IV EDS with thin window). XPS spectra were recorded using a PHI 5300 spectrometer (Perkin Elmer, Physical Electronics Division). The instrument was operated using monochromatic AlK $\alpha$  x-radiation at 600W and an applied voltage of 15.0kV. Pressures in the analysis chamber were typically  $6.7 \times 10^{-7}$  Pa and never exceeded  $2.7 \times 10^{-6}$  Pa. Spectra were collected in the survey mode for qualitative analysis and in the utility mode for quantitative atomic composition. Unless otherwise noted, the take-off angle was 62° from the plane of the sample. Sample charging was minimized by using a charge neutralizer and a high-purity, high-transmission, nickel screen (Buckbee-Mears) suspended above the samples.

The 90° peel testing was performed at a rate of 2"/min, parallel to the original copper foil machining direction. Shear strength testing for bulk PTFE was performed using a punch-type die according to ASTM D732-46 (Instron, Model F/CLM). Torsional shear tests were performed on Cu/PTFE/Cu sandwich specimens with a range of surface treatments to provide data for an adhesive joint geometry very different from peel testing. A modified tubular butt joint (napkin ring) geometry was used, as described by Lin and Bell.<sup>23</sup> Samples were cut into rings using a manually operated arbor press, with a two piece tool-steel die which was machined to match the napkin ring inner and outer diameters. After degreasing all surfaces with acetone, the rings were affixed to the torsional joints using an epoxy resin (EPON 828®:MDA, 1:0.264 by weight). The joints were assembled and cured at 120°C for one hour, then 150°C for two hours and cooled to room temperature at 1°C/min. The joints were tested on Instron (Model TTCML, Instralab torsional attachment) with a crosshead speed of 0.5 cm/min. Several samples from the above experiments were examined by optical microscopy (Nikon Metaphot, bright field reflected light). FT-IR microscopy was also used to examine fracture surfaces (Nicolet 60SX FT-IR spectrometer, Spectra Tech IR-Plan infrared microscope).

## RESULTS

### 1 Adhesion to Smooth Surfaces

In the conventional approach to replication for TEM analysis, it is desirable for the replicating medium to conform physically to the sample surface with minimal adhesion, so that detachment is facile and involves interfacial separation only. We are using this technique in an unconventional way to study the effect of interfacial chemistry on adhesion and locus of failure. By varying the chemical attraction between the fluoropolymer surface and the replicating medium, changes in the ease of detachment and in the condition of the parted surfaces can be observed. In this study, three replicating media were chosen based on differences between expected polar and dispersive contributions to adhesion: polyacrylic acid (strongly polar and acidic), cellulose acetate (intermediate), and atactic polystyrene (slightly basic, adhesion mainly dispersive in character). The chemistry of the fluoropolymer sur-

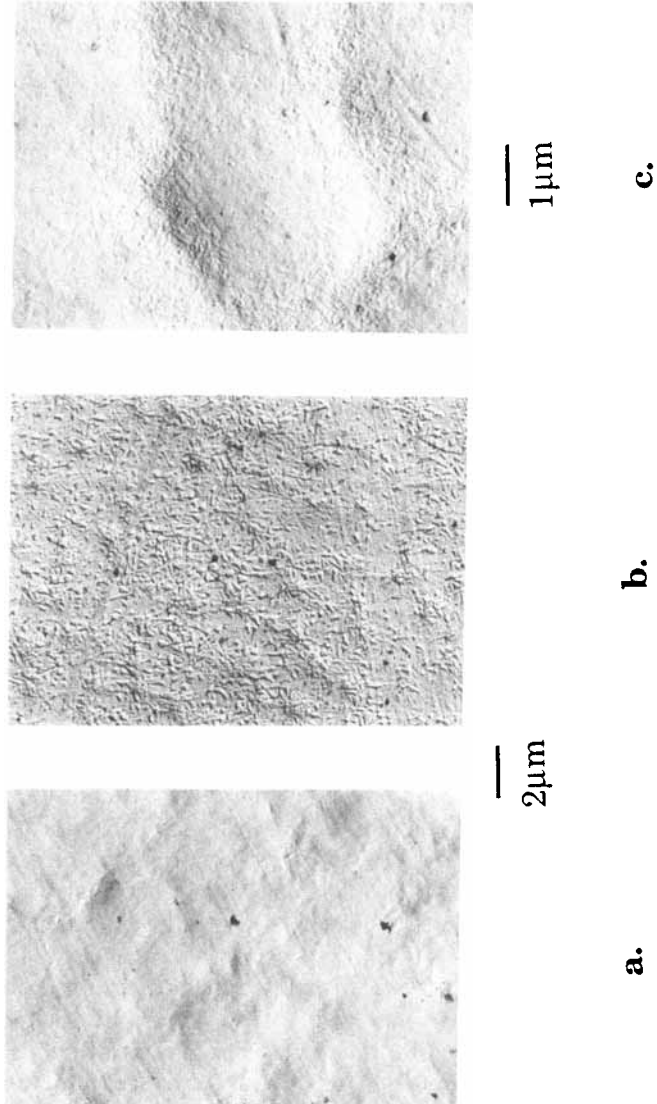


FIGURE 1 TEM results for replication of a. skived PTFE with PAA, b. cast PTFE with a-PS, c. extruded PFA and PAA.

face was also varied, depending upon manufacturing history and treatment (Table I). Not unexpectedly, this technique could not be used for rough-surfaced laminates or for skived PTFE after sodium etch and acid strip, which is known to have a very irregularly pitted sub-surface.<sup>21</sup> Figure 1 shows typical TEM results for three unmodified fluoropolymer surfaces. Here there is clean separation between the replicas and the fluoropolymer substrate, revealing only surface marks associated with the skiving, casting or extrusion process.

Figure 2 shows replicas of a PTFE surface which had previously been laminated to shiny copper foil, *i.e.* a PTFE surface with superficial chemical modification, but a relatively smooth topography. The least polar replicating medium, a-PS (Fig. 2a), shows a topography which closely resembles the unreplicated fluoropolymer surface (see Fig. 6 in Ref. 21). When the replicating media are materials which are capable of significant chemical interactions with the surface, *e.g.* PAA and CA, fibers are observed to be attached to the replica (Figs. 2b and 2c). The fibers were confirmed to be PTFE by electron diffraction, and indicate a failure mode which is no longer interfacial. At points of stress concentration, the failure strength of PTFE appears to have been exceeded and failure to have moved into the substrate. Some features of the original PTFE surface (machine lines in the original foil) are visible beneath the fibers. Similar results were found by SEM for copper peeled from the fluoropolymer surface.

It is clear from Figures 1 and 2 that the TEM result depends on both the fluoropolymer surface treatment and the nature of the replicating medium. Figure 3 shows a comparison of three different surface treatments with a single replicating medium (a-PS). The starting point (Fig. 3a) is PTFE after lamination to shiny foil. Failure between the replica and the PTFE substrate appears to have been interfacial, with no signs of fibrillation at either medium or high magnifications. Figure 3b shows the replica from a 15-second sodium-etched surface. Failure again appears to be interfacial, with no signs of fibrillation, although the replica was appreciably more difficult to remove from the surface than previously (see below). When the defluorinated surface which results from Na/naphth treatment was removed by acid stripping, a superficially modified surface was again produced. This surface was previously shown to have no gross difference in topography from the untreated or etched samples.<sup>21</sup> This time, the replica had a highly fibrillar surface (Fig. 3c), and at high magnifications the fibers are seen to be nodular, interconnected, and to have a characteristic width of 10–90nm.

The failure mode on stripping the replica was entirely different when longer (1 hour) Na/naphth treatment times were used. The replica in Figure 4a was very difficult to remove, and a pattern characteristic of a mixed mode of failure can be observed (note featureless areas surrounded by “ridges”). This type of fracture surface could be duplicated in peel testing of copper/PTFE specimens where the PTFE had experienced 1 hour Na/naphth treatment. Figure 4b shows an SEM image of the copper side of a peel strip, and has the same featureless areas surrounded by ridges. It is also apparent from Fig. 4b and at higher magnifications on the specimen in Fig. 4a, that the ridges contain fibers, while few fibers are attached to the smoother areas. To determine the nature of the surface shown in Fig. 4b, we dissolved the copper away from the peel strip with ammonium persulfate

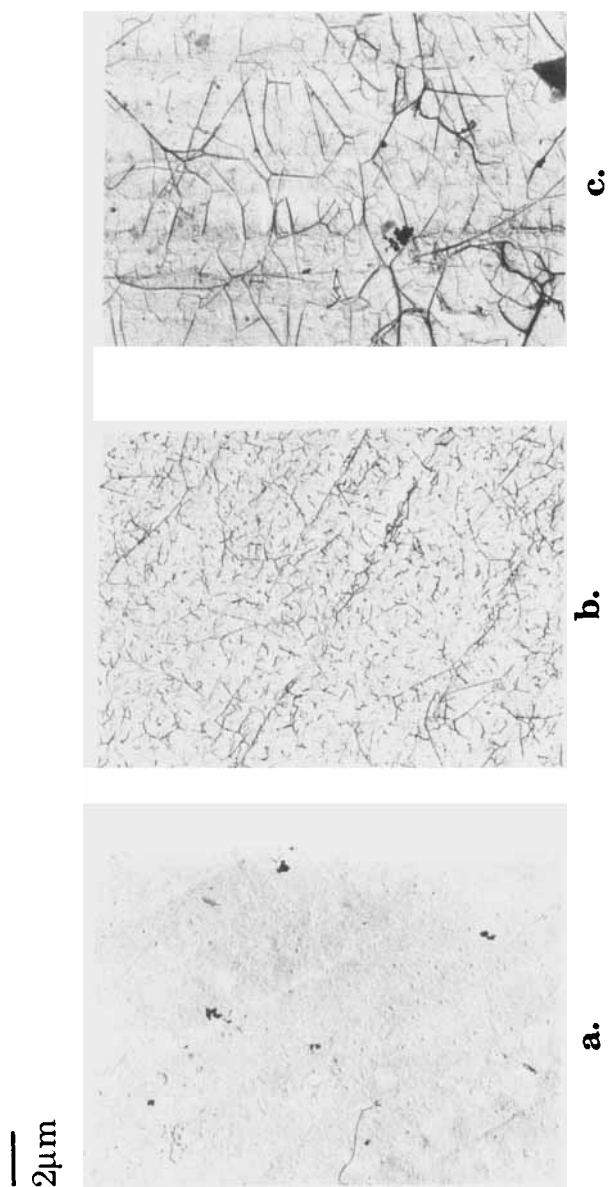


FIGURE 2 TEM of the failure locus for laminated PTFE and a. a-PS replica, b. PAA replica, and c. CA replica.



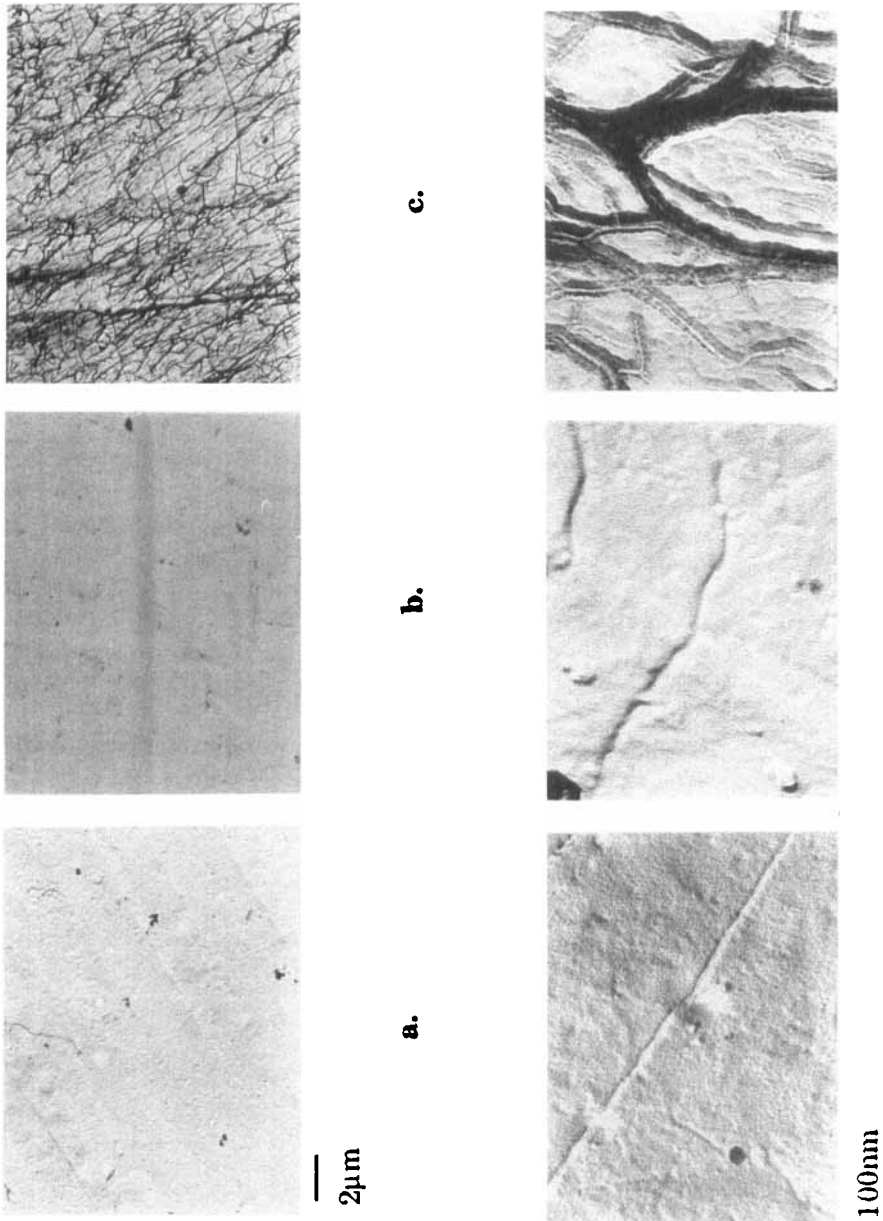


FIGURE 3 TEM of a-PS replicas from PTFE after a. lamination, b. short-time sodium-etch, c. etch and acid strip at medium (top row) and high (bottom row) magnifications.

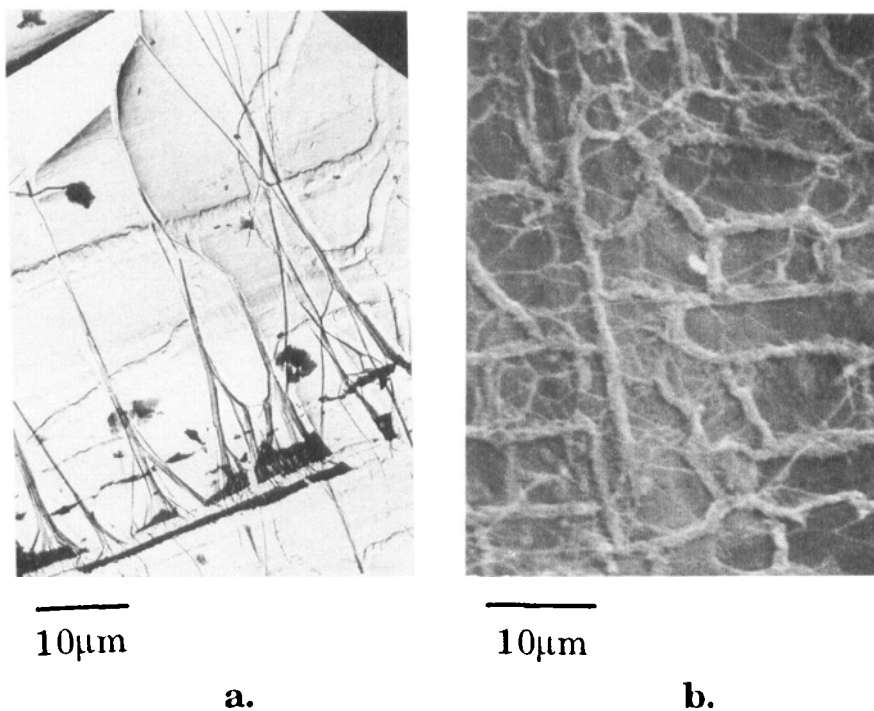


FIGURE 4 Locus of failure for smooth-surfaced 1-hour sodium-etched PTFE and a. PAA replica, by TEM and b. Cu peel strip, by SEM.

solution. The material which remained had a net-like, discontinuous structure, which was analyzed by IR microscopy to be fluoropolymer based, with appreciable amounts of carbonyl and unsaturated functionality at  $1600\text{--}1850\text{cm}^{-1}$ . Qualitatively, the IR spectrum of the transferred material resembled a mixture of PTFE and the defluorinated fluoropolymer which results from Na/naphth treatment.

No quantitative data on adhesion strength are accessible to this experiment, but we could make qualitative comparison of adhesion using the following system of classification:

- a = no adhesion (spontaneous detachment of the dried replica)
- b = poor adhesion (removed easily with gentle manipulation)
- c = good adhesion (very difficult to remove without tearing, fragmenting or otherwise damaging the replicating film)
- \* = fibers present on the replica

Table II summarizes the data from 46 specimens. The results for cellulose acetate replication closely resembled those for polyacrylic acid, so CA was not used to replicate the entire sample set. For the relatively smooth specimens examined here, "good adhesion" occurred only with the Na/naphth treated PTFE and the polar replicating media. When only superficial chemical modification of the surface was achieved (*e.g.* by acid stripping or by lamination), adhesion was classified as "poor,"

TABLE II  
Adhesion and locus of failure for smooth fluoropolymer surfaces by TEM replication

Replicating medium	PAA	CA	a-PS
<i>Sample Description</i>			
PTFE	1. skived or cast (untreated)	a/b	b
	2. after lamination to shiny foil	b*	b*
	3. #2 after 15 sec/1 min sodium etch	c	b
	4. #2 after 1 hr sodium etch	c*	b
	5. #2-4 after acid strip	b*	b*
	6. #1 (cast) after acid strip only		b*
PFA	7. laboratory extruded	a/b	a
	8. after sodium etch		b
	9. after sodium etch and acid strip	b	a
	10. after lamination to shiny Cu foil	b	
	11. #10 after sodium etch and acid strip	b	

a = no adhesion    b = poor adhesion    c = good adhesion    \* = fibers present

\*This replica could not be removed. Fiber content unknown.

often associated with fibrillation of the PTFE surface. Fibrillation was not observed with PFA specimens, even under conditions which most favored fibrillation of the PTFE surface (acid stripped, PAA replicated). The effects of surface treatment on PTFE and PFA are only comparable when the surface topographies are the same (compare #10 and 11 with #2 and 5 in Table II, laminated specimens). In all cases, adhesion was classified as "poor," with the most marked difference being that failure of the PTFE/replica interface was accompanied by fibrillation of the PTFE.

Several other qualitative, but important, observations are not recorded in Table II. PTFE sample #4 (*i.e.* laminated to shiny foil, then sodium etched for 1 hour) was acid stripped and then was repeatedly re-etched by Na/naphth, and then restripped by the oxidizing acid. A similar thickness of fluoropolymer (*ca.* 125nm) was removed in each etch-and-strip step. The replicas made after the first etch-and-strip (Fig. 3c) are similar to those observed after later etch-and-strip steps, showing significant fibrillation. This observation confirms that the mode of failure which we see is not associated with an anomalously weak surface layer on the PTFE.

If a second PAA replica was made of an area which had previously been replicated (a commonly used TEM method to "clean" surfaces), then the number of fibers observed decreased appreciably. This was particularly noticeable for the acid-stripped samples. We attribute this to the removal of the superficially modified material during the first replication, returning the surface to its original state (Fig. 1) for the second replication. Without chemical interactions between the surface and the replicating medium, enough force cannot be applied during detachment to either remove fibers from the PTFE surface or pull them from the bulk.

## 2 Adhesion to Rough Surfaces

The effect of surface roughness was studied using both 90 degree peel and torsional shear testing. These two tests were chosen to see how the influence of surface roughness and surface chemistry differs with test geometry. Samples of 800 $\mu$ m

skived PTFE films were first laminated to give surfaces of different roughnesses. The laminating foil was then removed chemically and the PTFE was exposed to different surface treatments and then plated with copper. Peel tests were not performed on the laminates directly due to the thickness variability and inflexibility of the foils. The copper-plated PTFE specimens were peeled and the peel strength was recorded as pounds per linear inch (pli). Peel tests are known to show considerable scatter. For this reason, strengths for 3–4 strips per sample were averaged for each reading. Table III shows the influence of interface roughness and sodium etch time on peel strengths. Where ranges are shown, multiple samples were tested. Previous gravimetric results indicate relative surface areas of 1:3:4:4 for shiny:½ oz.:1 oz.:2 oz. foils.<sup>21</sup>

The unetched PTFE samples showed some increase in peel strength with increasing interface roughness, although none of these values indicate strong adhesive bonding. The 1-minute sodium-etched sample from the 1 oz. foil laminate gave the most significant increase in peel strength. The peel strengths of the 1 hour-etched smooth (shiny foil) and rougher surface (½ oz. foil) samples were quantitatively similar, although there was a qualitative difference in their peel traces. The peel trace for the smoother sample showed much less force oscillation than that for the rougher surface. There was some loss in strength associated with a thicker defluorinated layer, in that the one-hour sodium-etched sample from the 1 oz. foil laminate showed a decrease in peel strength from the one-minute etched sample. The 1 oz. foil-PTFE surface gave the highest peel strength in each set, and so was chosen for subsequent locus of failure studies. Using this system and 90° peel testing, both sides of the fracture surfaces were examined by SEM, EDS and XPS.

The signals used for EDS analysis are generated from a depth of approximately 1µm, while the depth for XPS analysis is approximately 1–10nm, and so is more surface sensitive. However, EDS gives lateral resolution to 0.5µm, whereas the XPS signal is averaged over several square millimeters. The combination of these techniques gives a very useful picture of the physical and chemical state of fracture surfaces. Figure 5 shows a typical SEM and EDS result for this study. For this 1-minute sodium-etched sample, copper and fluorine were consistently found on both

TABLE III  
Effect of surface roughness and etch time on the 90° peel strength  
of Cu from PTFE

Foil type for original laminate	PTFE surface treatment	Average peel strength (pli)
—(skived)	no etch	0
Shiny	no etch	<0.5
1 oz. ED		0.5–3
2 oz. ED		~0.5
1 oz. ED	1 min sodium etch	9–13
Shiny	1 hr sodium etch	1
½ oz. ED		1–3
1 oz. ED		4–9
2 oz. ED		5–6

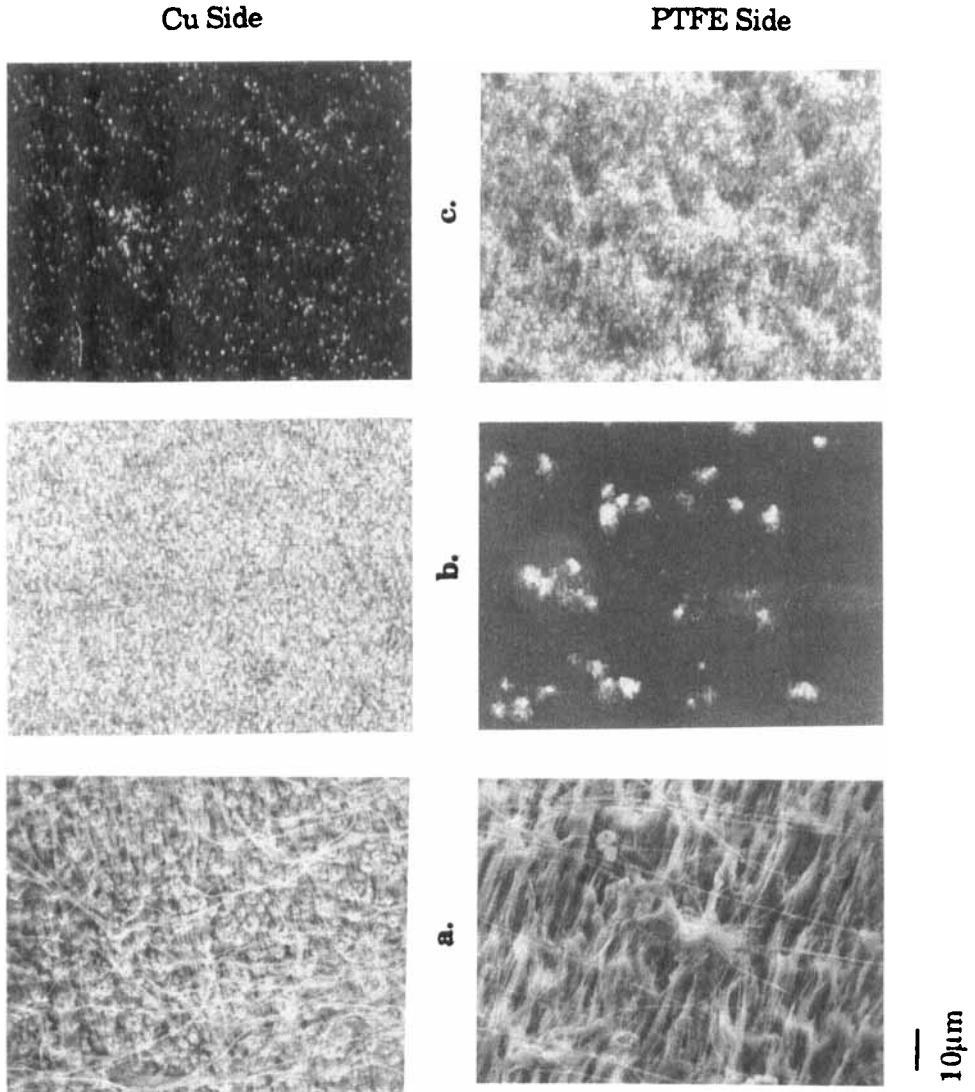


FIGURE 5 SEM/EDS of failure locus for 90° peel of Cu from rough-surface PTFE after 1 min sodium etch a. SEM image, b. copper map, c. fluorine map of the Cu side (top row) and PTFE side (bottom row).

surfaces, indicating a mixed mode of failure. The SEM images in Figure 5 show PTFE fibers on both sides of failure. The original interface contours are visible beneath the fibers on both surfaces. The EDS maps show copper islands on the PTFE side of failure and a less localized fluorine distribution on the copper side of failure.

Figure 6 shows XPS survey spectra of both fracture surfaces from a 1-hour sodium-etched sample. Angle-resolved XPS analysis ( $45\text{--}75^\circ$ ) did not give useful results for depth profiling due to the roughness of the surfaces. As with EDS analysis, the presence of copper is evident on both sides of fracture. Responses for the Cu 2p electrons are in the binding energy ranges of 925–965 eV, and one small peak for the Cu 3p response occurs just below 75 eV. Table IV gives the XPS ratios for fluorine and carbon 1s signals from the fracture surfaces of the peel samples. The 1-minute sodium-etched samples showed a similar fluorine-to-carbon ratio for both sides of the fracture surface, and these values were less than the theoretical ratio for PTFE. From Figure 5, the quantity of fibers is similar on both sides of the fracture surface. One-hour etched samples consistently gave a higher F/C ratio on the copper side of failure than on the PTFE side. For these surfaces, the copper side of the fracture surface showed more fibers than the PTFE side. These fibers, being thicker than the XPS sampling depth, should generate a significant fluorine signal by XPS. The etched layer appears to dominate the signal from the PTFE side of the 1-hour sodium-etched sample (low fluorine content).

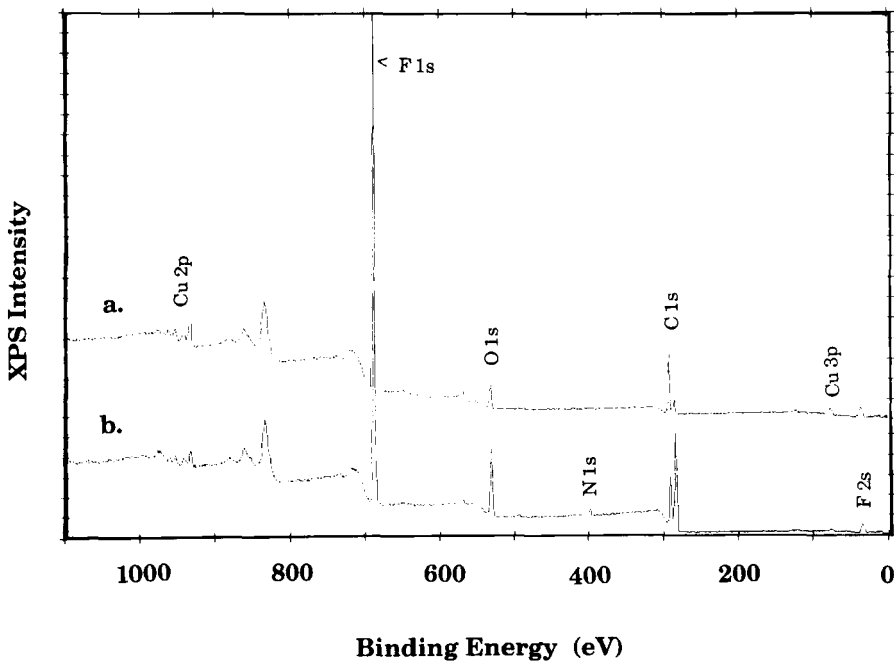


FIGURE 6 Survey XPS spectra of the failure locus for copper peeled from rough-surfaced PTFE after 1-hour sodium-etch a. Cu side, b. PTFE side.

TABLE IV  
Locus of failure of XPS results for 90° peel of Cu  
from rough-surfaced PTFE

Sample description	[F]/[C]	
	Cu side	PTFE side
1. no etch	0.6–1.4*	1.2–1.5*
2. 1 min sodium etch	1.4*	1.2
3. 1 hr sodium etch	0.8–1.1*	0.4–0.5*

\*Copper present.

Torsional shear testing was also performed on these materials. The napkin ring torsional shear geometry is generally used to test a homogeneous ring of polymer resin, and is known to give reproducible results (<5% relative standard deviation). The conventional shear trace shows a steady increase in force as torque is applied followed by a sudden decrease to zero force when the resin fractures. The maximum load reached before failure, which should vary with sample thickness, is used to calculate the resin shear strength.<sup>23</sup> For a load recorded in pounds, the shear strength is calculated in pounds per square inch (psi). In this study, the compressive shear strength of PTFE was determined for comparison with torsional shear values, and was found to be 4460psi with a standard deviation of 520psi for nine trials. This shear trace showed the typical yielding and drawing behavior of PTFE, and should correspond to the maximum possible shear strength of the Cu/PTFE/Cu sandwiches tested in torsional shear (*i.e.* for cohesive failure in the PTFE).

In our system, there is a primary leak (local maximum) at low load prior to complete failure, which seems to mark the onset of yielding and drawing. As different types of samples were tested, this primary peak was found to occur at the same load regardless of sample thickness, interface roughness or sodium etch time. Torsional shear test results for this primary peak load are presented in Table V.

Cross-sectional viewing of a torsional shear sample before testing and then after the primary peak showed that angular displacement of the PTFE bulk had occurred during the test, indicating shear movement. Complete failure was typically characterized by full delamination of the sample, *e.g.* the copper rings were still affixed to each side of the test joint while the bulk of the PTFE remained on one side only. After joint failure, both sides of the fracture surface were examined using SEM and EDS. Figure 7 shows these results for one test piece. The original interfacial structure is still apparent on the copper side of the test piece (Fig. 7a), with the nodular copper surface visible below the PTFE fibers. Failure appears to have closely followed the Cu/PTFE interface. As with the peel test samples, the locus of failure consistently contained fluorine and copper on both sides of the fracture surface. There was no obvious difference between the peak loads and fracture surfaces for any of the samples listed in Table V. The SEM images in Figure 7 show substantial smearing of the fluoropolymer on the PTFE side of fracture. This contrasts with fibers alone, as seen in the TEM and peel studies.

TABLE V  
Effect of sample thickness, interface roughness and sodium etch on torsional shear test results for Cu/PTFE/Cu sandwich systems

Sample description (original foil type:treatment)	Peak load (pounds)	Std. dev. (pounds)
50 $\mu$ m PTFE		
shiny:laminated	45.2	0.8
1 oz. ED:laminated	48.2	1.0
	48.0	2.7
1 oz. ED:1 min sodium etch	46.6	1.6
800 $\mu$ m PTFE		
1 oz. ED:laminated	45.2	2.6
1 oz. ED:no etch (replated)	54.2	1.7
1 oz. ED:1 min sodium etch	54.6	0.9

## DISCUSSION

In the TEM study, the observed variability in ease of detachment of replicas for the smooth samples correlates well with expectations, based on the chemical affinity between the polymer surfaces involved. From previous contact angle work on these surfaces and generally accepted models of chemical adhesion and interfacial energetics, it is expected that the PAA solution would not adhere to a pure fluoropolymer surface but would adhere quite strongly to a sodium-etched fluoropolymer surface. Similarly, the PAA should not adhere strongly to an acid stripped surface, since the advancing contact angle with water changes from 41° after sodium etching to over 100° after removal of the etched layer by acid stripping (nominal contact angles are >100° for unetched PFA and PTFE).

It is interesting that the acid-stripped and laminated surfaces give qualitatively similar adhesive strengths (Table II). Lamination defluorinates and oxygenates fluoropolymer surfaces superficially. The more polar media should then give better chemical adhesion to the laminated surface than to the acid-stripped surface, so that enough force can be applied/transferred/locally concentrated upon peeling to cause drawing in the fluoropolymer at the interface. From Table I, XPS analysis shows that the acid-stripped surfaces have a similar chemistry to the laminated surfaces, with slightly less oxygen. If concentrated on the acid-stripped sample surface, the oxygen present may provide enough chemical adhesion to match that observed for the laminated surface. Advancing contact angles might not reflect this oxygen content if the surface is very mobile (reorganization) or if the surface chemistry is not homogeneous (low energy fluorinated areas dominate, and contact angle hysteresis increases).

It is also interesting that the laminated and acid stripped PTFE surfaces gave quite different failure loci. In the former case, fibers are not always formed (Figs. 2a and 2b) and in the latter, they are always present, even for a-PS replication (Figure 3c and Table II). While a concentration of oxygen at the acid-stripped surface may provide the additional chemical adhesion necessary to fibrillate the fluoropolymer upon detachment of the replicas, an alternative explanation may be that defluorination of the fluoropolymer by lamination strengthens the surface through conjugation



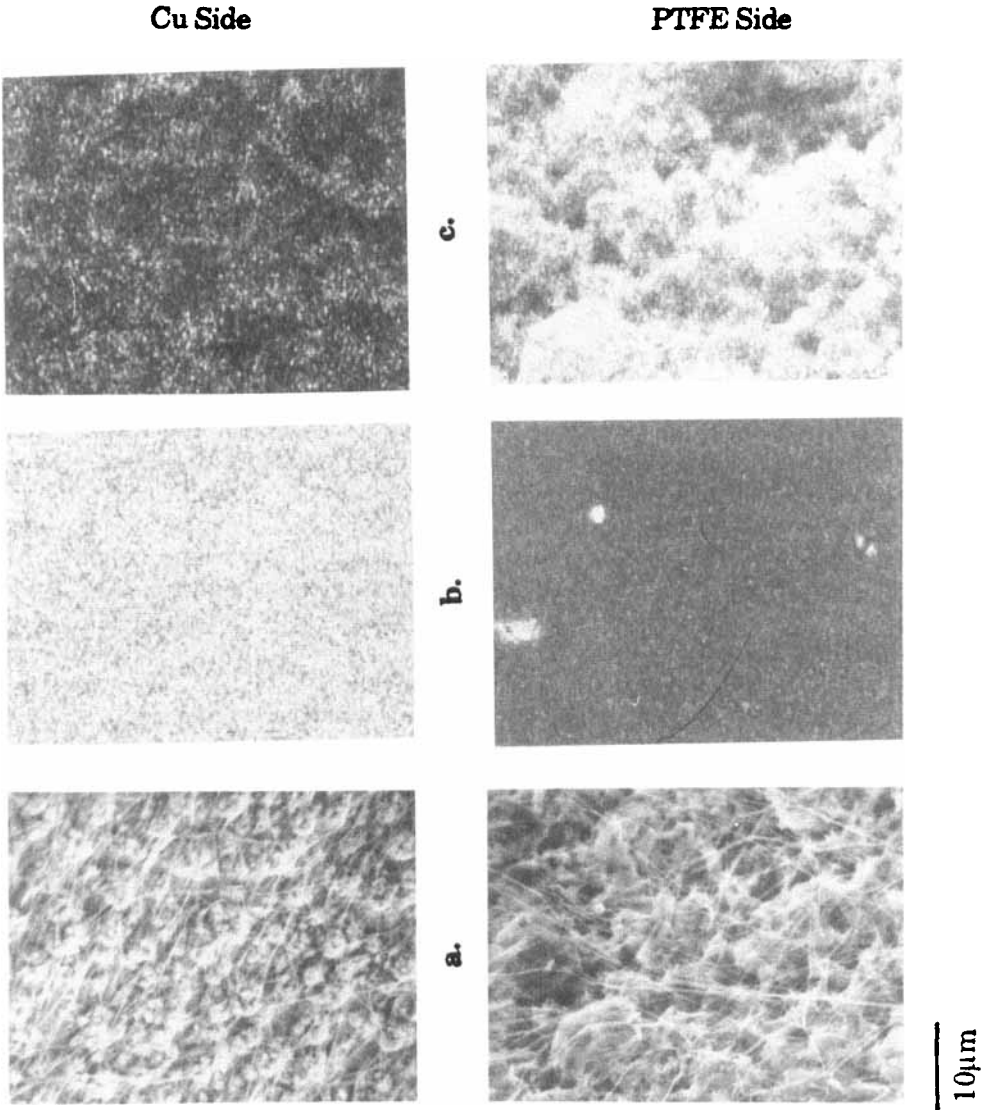


FIGURE 7 SEM/EDS of the failure locus for torsional shear of a Cu/PTFE/Cu specimen without sodium etch a. SEM image, b. copper map, c. fluorine map of the Cu side (top row) and PTFE side (bottom row).

of the polymer backbone, providing some resistance to fibrillation. Because the depth of modification produced by lamination is superficial ( $\sim 2\text{nm}$ ), this resistance may be adequate to prevent fibrillation upon detachment of a non-polar replica (Fig. 3a) but inadequate to prevent fibrillation upon detachment of more polar replicating films (Figs. 3b and 3c).

Fibrillation appears to be a bulk property of PTFE rather than associated with a weak boundary layer, since fibers are formed not only from the original surface but also from exposed material within the PTFE sample. One difference between the laminated and the acid-stripped surfaces is the location of testing relative to the original surface. For the acid stripped samples, the surface which we are replicating was originally more than 100nm into the bulk PTFE. As we have already noted, the acid stripping does not cause a gross change in surface topography, the surface chemistry is similar to the laminated fluoropolymer, yet fibers are always formed during removal of the replicas from these surfaces.

One interpretation of the variation we have seen in failure modes involves the mechanical integrity of the surface. The skived, cast, and extruded surfaces have little potential for chemical adhesion (highly fluorinated) and clean interfacial separation between the replica and the fluoropolymer surface would be expected, *i.e.* no fibers should be formed. After lamination, the surface is superficially modified so that the potential for chemical adhesion is increased. Where there is little chemical affinity between this surface and the replicating medium, *e.g.* with *a*-PS replication, separation is interfacial. As the replicating media become more polar, enough interaction occurs to lead to fibrillation. For the sodium etched surfaces, we know that defluorination has taken place to a significant depth and an unsaturated carbonaceous layer results. This layer is brittle and continuous. It is also an integral part of the PTFE bulk, since the material was part of the original PTFE sample. For short etch times (15 sec, 1 min) the modified surface has affinity for the polar replicating media and chemical adhesion is maximized, but interfacial separation still occurs. Now the modified layer has enough mechanical integrity to withstand the peel force, and separation occurs without fibrillation. For a thick modified layer at this higher level of chemical adhesion, *e.g.* between the PAA replica and the 1-hour sodium-etched PTFE surface, the etched layer is broken and fibers are pulled from the bulk PTFE. The thicker defluorinated layer cannot transfer energy away from the interface as efficiently as the thinner layer and is also less flexible, fracturing under the load. Once the chemical adhesion at the interface exceeds the force required to break the modified layer, a mixed mode of failure ensues, PTFE strands are drawn, and the apparent adhesion is determined by the fracture path and material deformation. This same trend is seen in the data for skived samples (no chemical functionality, no fibers) acid stripped samples (no physical skin, superficially functionalized, fibers always present) and laminated samples (weak physical skin, superficially functionalized, fibers present if polar replicating media used). The absence of fibers from all PFA surfaces may be due to differences in morphology (crystallinity) between PFA and PTFE. Although the morphology of PFA has not been studied extensively, the side chain in TFE copolymers is known both to increase the flexibility of the fluorocarbon backbone and to disrupt the helical structure, decreasing chain alignment and, hence, crystallinity.<sup>24</sup> As a result, the mechanical properties

of the fluoropolymer are influenced, *e.g.* the yield stress for PFA is 30–50% higher than for PTFE.<sup>25</sup>

Based on the results in Table III for smooth fluoropolymer surfaces, only minimal adhesion of copper and solution-deposited polymers can be achieved through chemical modification by Na/naphth treatment. Once surface roughness is introduced, apparent adhesive strength improves, although roughness alone does not give optimal results. In every case for rough surfaces, a mixed mode of failure occurs. While failure closely follows the contours of the interface, the actual path moves between the bulk PTFE and the bulk adherend (copper), as determined by XPS and SEM/EDS analyses (Table IV and Figure 5). This more tortuous path in the rough-surfaced specimens may result in higher apparent adhesion.<sup>3</sup> The sodium-etched interface provides more resistance to fibrillation and better (more even) force distribution to the bulk PTFE than the superficially modified surface. Apparent strength is increased by forcing the fracture path to move repeatedly through the etched layer.

While the results of this study may be open to various interpretations, in our view they suggest the following progressive model for adhesion of polar materials to fluoropolymers, beginning with adhesion to a smooth, inert fluoropolymer surface. The effects of chemical functionality and roughness can be added separately. This is presented in Figure 8, along with a summary of the TEM failure-mode and peel-strength data. For smooth surfaces, chemical modification improves adhesion only marginally in this test geometry. Surface roughness contributes to apparent adhesive strength to a much greater extent. The optimal 90-degree peel strength observed for this system requires a combination of both surface chemical modification and roughness. For PTFE systems with the highest observed adhesive strengths, the failure mode is mixed rather than cohesive in the PTFE.

Torsional shear testing was chosen as a test configuration which differs substantially from the peel test. Results showed no observed dependence of the peak load on PTFE thickness, surface treatment or surface roughness. This contrasts with the peel test results, where surface treatment and roughness affected the apparent adhesive strength to a great extent. Assuming an even distribution of shear force through the thickness of the sample, the peak load should be proportional to the sample thickness.<sup>23</sup> The values for peak load presented in Table V show no such correlation, and translate to apparent shear strengths of 7300 psi for 50 $\mu$ m films and 500 psi for the 800 $\mu$ m films. This should be compared with a bulk shear strength for PTFE of approximately 4500 psi. It seems likely that the shear force is being concentrated near the interface rather than being evenly distributed through the thickness of the sample. Otherwise, the shear strengths among samples would be much more similar, and the peak load values would show fluctuation. Also, the SEM/EDS results (Fig. 7) show a mixed mode of failure rather than interfacial separation or cohesive failure in the PTFE. The interface roughness in these experiments appears to exceed some critical roughness which would allow differentiation between sodium etched and unetched interfaces. We predict that, once the interface roughness approaches the thickness of the etched layer in magnitude, differences will be found. That the influence of surface chemistry and roughness varied for the two different tests (90 degree peel and torsional shear) underlines the importance

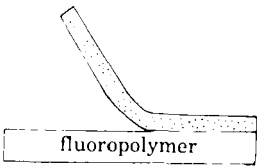
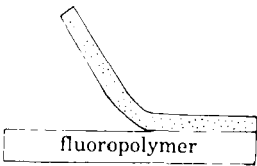
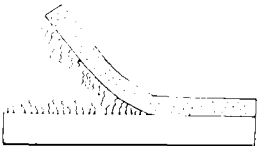
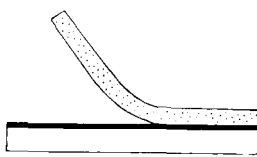
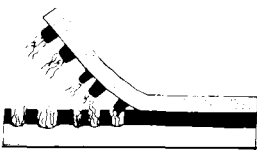


<u>Surface Type</u>		<u>Failure Mode</u>	<u>Strength</u>	
			<u>TEM</u>	<u>Peel (pli)</u>
smooth, no functionality		interfacial	a	0
smooth, superficially modified		fibrillation	b*	<0.5
smooth, thin polar skin		interfacial	c	
smooth, thick polar skin		mixed	c*	1
rough, superficially modified		mixed		0.5 - 3
rough, polar skin		mixed		4 - 13

FIGURE 8 Model for adhesion of polar materials to fluoropolymers.

in adhesion studies of the test geometry. Prior knowledge of the most likely in-use stress modes assists in the appropriate choice of test configuration.

In this series of papers, we have attempted to shed some light on the complicated phenomenon of adhesion to fluoropolymers by choosing, defining and controlling various system parameters in a systematic fashion. Together, these results support several conclusions about adhesion to fluoropolymers that have previously been based on (enlightened) speculation. They also contradict the notion that PTFE systems of any significant strength always fail cohesively in the fluoropolymer. While not all possible fluoropolymer systems have been covered, this work establishes a foundation on which further investigators can build.

## CONCLUSIONS

Several conclusions can be reached based on the results of this study:

1. For smooth fluoropolymer surfaces, only minimal adhesion of copper and solution-deposited polymers can be achieved through sodium naphthalenide chemical modification.
2. Surface roughness is required for good adhesion to fluoropolymers. However, roughness alone does not give optimal results.
3. Fibrillation is a bulk property of PTFE, and not associated with a weak boundary layer.
4. For a smooth surface, where a surface layer with mechanical integrity exists, the bulk PTFE resists fibrillation, and the apparent adhesive strength is improved.
5. Adhesion to fluoropolymers is optimized where the surface is:
  - a. wettable
  - b. rough
  - c. mechanically strong and continuous
6. For PTFE systems with the highest observed adhesive strengths, the failure mode is mixed rather than cohesive in the PTFE.

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