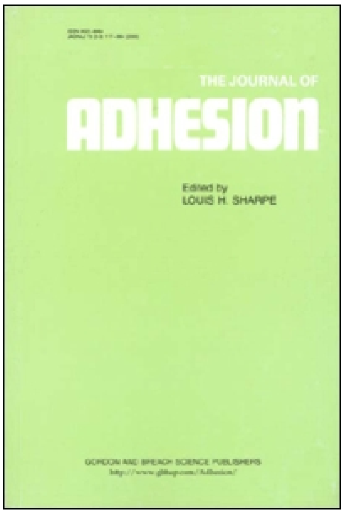

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Adhesion to Sodium Naphthalenide Treated Fluoropolymers. Part II. Effects of Treatment Conditions and Fluoropolymer Structure*

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Films of polytetrafluoroethylene (PTFE) and perfluorinated copolymers (PFA and FEP), with a range of fabrication histories, were exposed to sodium naphthalenide (Na/naphth) etchant so as to defluorinate the surface for improved wettability, and hence adhesion. The depth of defluorination was measured gravimetrically and the nature of the chemical functionalities determined spectroscopically. For smooth films, the fluoropolymer type and crystallinity had little effect on the defluorination process. Surface area was the major variable affecting defluorination rate, although the presence of surface defects and deformation in skived films also increased the rate of defluorination. For all but the skived PTFE, there was little change in surface texture either after defluorination or subsequent stripping of the defluorinated layer by an acid etch. Acid stripping of the defluorinated layer on skived PTFE left a porous surface texture. The chemical nature of the surface could be changed by modifying the post-etch treatment of the specimen, for example by modifying the rinse procedure and the storage history of the specimen before the adhesive bond is made.

KEY WORDS fluoropolymers; PTFE; sodium etch; surface chemistry; adhesion; morphology.

INTRODUCTION

The "non-stick" nature of fluoropolymers has been widely exploited to technological advantage, but can hinder exploitation of other outstanding fluoropolymer properties, such as low dielectric loss and good thermal stability. One such application is in electronic circuit boards, and a commonly-used method for adhering copper and electronic components is pretreatment of the fluoropolymer in a strong electron donor such as Na/naphth.[1–6] We have shown previously that a combination

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of gravimetric analysis, x-ray photoelectron spectroscopy (XPS) and infrared internal reflection spectroscopy (IR-IRS), coupled to derivatization reactions, can provide a detailed molecular picture of the *ca.* 100 nm defluorinated surface layer.[1] The purpose of this paper is to describe the response of a range of fluoropolymer structures to Na/naphth etching, so as to understand better the role of the many specimen variables in this complex process. The next, and final, paper in this series will then attempt to relate these chemical and structural variables to the process of adhesion of fluoropolymers to copper.

EXPERIMENTAL SECTION

The fluoropolymers were polytetrafluoroethylene (PTFE), a fluorinated ethylene-propylene copolymer (FEP), and a copolymer of TFE and perfluoroalkylvinylether (PFA), all manufactured by DuPont. These polymers were in the form of 25–150 micron films, with a range of different morphologies induced by their different fabrication histories (skiving, extrusion, lamination, quenching, annealing) as described in Table I. The laboratory-extruded PFA specimens were prepared from commerically available polymer (DuPont Teflon PFA 340) as blown films on a 1.5″ Killion extruder (l/d ratio of 36:1, 20 RPM screw speed) using a melt temperature of 670°F and a blow up ratio of 4.67:1. The melt-draw ratio was adjusted to give the desired thickness (50–150 microns).

The PTFE specimens were commercially available films prepared by "skiving", *i.e.* cutting a continuous film from a rotating cylinder. In some cases, the PTFE films were further modified by lamination against copper foils, with the copper then being etched away. The surface area of the laminated specimens was varied by using copper foils of varying roughnesses ("smooth", and 0.5–2 oz. electrodeposited foils, Gould Corp.). Lamination took place in a nitrogen atmosphere at 100 psi pressure.

TABLE I
Fabrication history of fluoropolymer specimens

Specimen	Description
1. Smooth PFA	PFA film, commercially extruded, 25 micron
2. Smooth FEP	FEP film, commercially extruded, 25 micron
3. Textured PFA	Laboratory-extruded, 50–150 microns thick
4. Controlled cool PFA	#1, laminated against smooth copper, and cooled at 1°F/min, 25 microns thick
5. Quenched PFA	#1, laminated against smooth copper, and quenched in liquid nitrogen, 25 microns thick
6. Skived PTFE(1)	Commercially skived PTFE film, 25 microns
7. Skived PTFE(2)	Commercially skived PTFE film, 50 microns
8. Lamin. PTFE(1A)	#6, laminated against smooth copper and cooled at 1°F/min, 25 microns thick
9. Lamin. PTFE(2A)	#7, laminated against smooth copper and cooled at 1°F/min, 50 microns thick
10. Lamin. PTFE(2B)	#7, laminated against 0.5 oz. electrodeposited (ED) copper and cooled at 1°F/min, 50 microns thick
11. Lamin. PTFE(2C)	#7, laminated against 1.0 oz. ED copper and cooled at 1°F/min, 50 microns thick
12. Lamin. PTFE(2D)	#7, laminated against 2.0 oz. ED copper and cooled at 1°F/min, 50 microns thick

The temperature profile involved heating at 3°F/min to 650°F, then 1°F/min to 700°F, followed by a "soak" time of 30 min at 700°F, and finally cooling at 1°F/min to <500°F for those laminates classified as "controlled cool". Specimens described as "quenched" were removed from the press at 700°F and immersed in liquid nitrogen. The copper foils were then removed with ammonium persulfate solution, leaving a fluoropolymer surface which mimicked the original copper surface texture.

The synthesis of the etchant and the derivatization procedures are described elsewhere.[1] Etching and rinsing were carried out at ambient temperature, under nitrogen, in a Schlenk tube. The depth affected by the etchant was determined by removing the defluorinated layer with an acid etch, and measuring the total mass loss. The term "apparent depth" was then calculated from the mass loss, on the basis of nominal surface area (*i.e.* assuming a perfectly flat surface). Water contact angles were determined at 23°C by the sessile drop method using an Imass contact angle analyzer (model GAA2). The surface texture was examined by scanning electron microscopy (SEM, Amray 1200B), using gold/palladium coated specimens, and by transmission electron microscopy, (TEM, Philips EM300), using a polyacrylic acid replica shadowed with Pt/C at $\tan^{-1}(\frac{1}{2})$ and coated with carbon at normal incidence.

RESULTS AND DISCUSSION SECTION

1. Effect of Etching Variables

The effect of etching time on the apparent depth of etching for the smooth 25 micron PFA (#1, Table I) is shown in Figure 1. Even a few minutes etching produced an

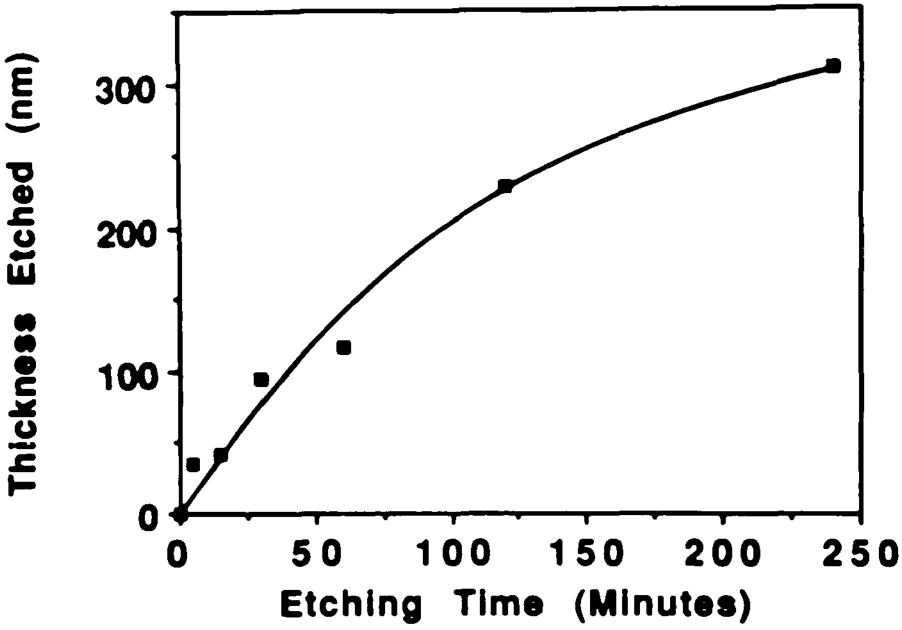

FIGURE 1 Apparent defluorination depth as a function of Na/naphth treatment time.

affected depth of several tens of nanometers, while prolonged etching increased the affected depth to several hundred nanometers. Note, again, that these depths are calculated assuming a flat film surface, which is valid for this specimen, but is not the case for rougher specimens described later. A standard etching time of 1h was selected (112 nm depth) for comparative work. We realize that this exceeds normal industrial practice, but it provided sufficient chemical change to allow precise quantification. The water contact angle decreased from about 110 degrees to about 40 degrees after 5 min. etching, and then varied little with etching time up to 4h.

Table II summarizes data from the first paper in this series[1] concerning the chemical functionality of the surface. These data were obtained by a combination of Infrared Internal Reflection Spectroscopy (IR-IRS) and X-ray Photoelectron Spectroscopy (XPS). Almost all carbons in the affected region were functionalized in some fashion. The unsaturation was distributed relatively evenly through the 112 nm affected depth, while the oxygenated species were concentrated in the top few nanometers.

The subsequent washing conditions had a marked effect on the surface chemistry. When the smooth PFA film was washed with only tetrahydrofuran (THF) after etching, there was little evidence of hydroxyl functionality, and the IR-IRS spectrum showed the presence of a large amount of sodium carbonate remaining on the surface (1427 cm^{-1} and 883 cm^{-1}). This presumably resulted from the low solubility of NaF in THF, followed by its reaction with water and carbon dioxide in air. The usual washing procedure was to wash with THF several times, then water.[1] We believe that the wash step is the major source of hydroxyl functionality, which is the primary oxygenated product, not carbonyls as is usually supposed. If the washing step involves D_2O, not H_2O, then there is a strong OD stretch absorption at 2582 cm^{-1}, implying that the water wash is associated with hydroxyl group production (we realize the OD-OH exchange is also a mechanism for incorporation of deuterium). Washing with water alone (*i.e.* no THF rinse) increased the hydroxyl functionality of the surface, but is a highly exothermic process and is not recommended as a routine specimen fabrication technique. The possibility of deuteration of carbon during this step could not be confirmed or refuted because of overlap of the CD stretch mode at 2150 cm^{-1} with the broad alkyne absorption.

The effect on the surface chemistry of aging of the treated surface in air was described in general terms in the first paper of this series.[1] The carbonyl absorption

TABLE II
Functional groups in PFA after 1h Na/naphth treatment data summarized from Ref. 1

Group	Averaged over 112 nm IR-IRS	Averaged over <5nm XPS
C=C	1 per 4 carbons	1 per 2.9 carbons
C≡C	1 per 5 carbons	
C—H	1 per 30 carbons	
—OH	1 per 300 carbons	1 per 20 carbons
—C=O	1 per 400 carbons	1 per 60 carbons
—COOH	<1 per 2000 carbons	
—CF		1 per 80 carbons

in the IR-IRS spectrum increased at least 50% after two weeks of storage in air, while the XPS spectrum showed a small, but significant, increase in oxygen content. Surprisingly, this was accompanied by an increase in water contact angle (oxygenation usually increases surface energy, but other effects may be compensating here). More detailed XPS data are shown in Figure 2, for PTFE film specimens after Na/naphth treatment. These specimens were subsequently derivatized with bromine to provide further information on changes in the level of unsaturation. Aging of the

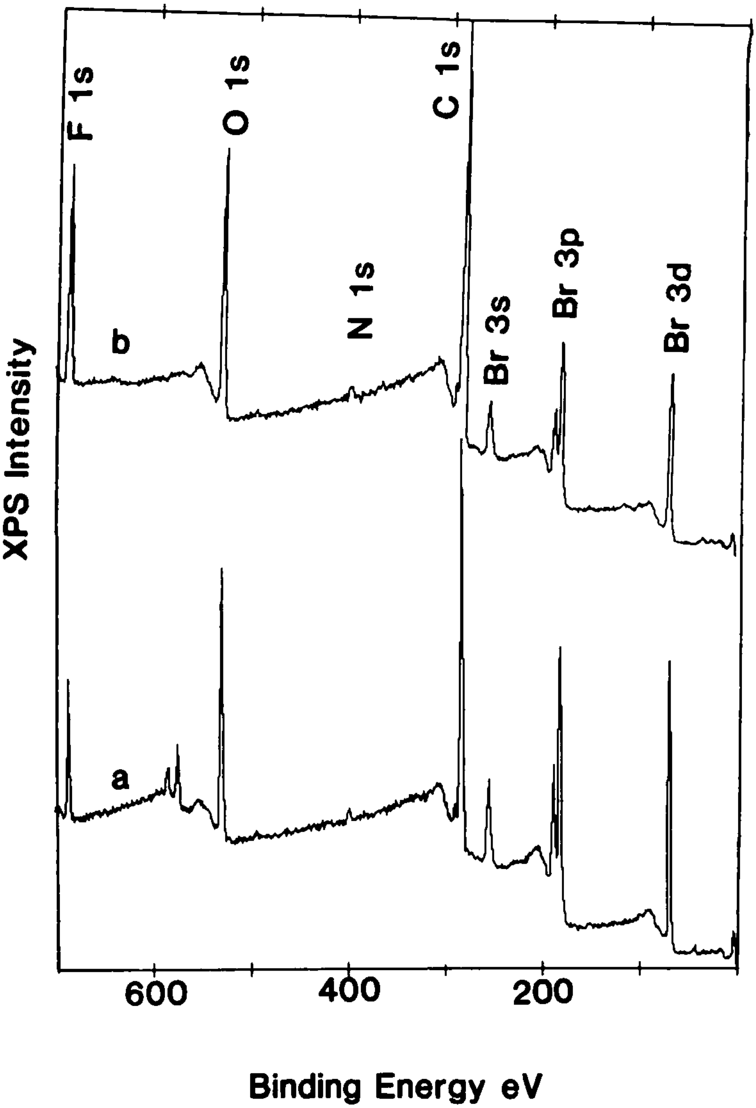

FIGURE 2 XPS spectra of PTFE surfaces after Na/naphth treatment and derivatization with bromine; (a) freshly Na/naphth treated surface, (b) Na/naphth treated surface aged in air for 3 months.

specimen in air for 12 weeks after bromination led to a doubling of the fluorine content of the surface (from 1 per 40 carbons to 1 per 20 carbons), a slight increase in oxygen content, and a decrease in the amount of unsaturation detected by bromination (16% bromine for freshly Na/naphth treated to 11% for the aged specimen). Such changes in surface functionality have a marked effect on adhesive bonding to the surface, as will be described in the third part of this series.

2. Effect of Fluoropolymer Specimen Variables

2.1 Effect of the Fluoropolymer Type

Relatively smooth-surfaced fluoropolymer films (extruded PFA and FEP, PTFE laminated against smooth copper) were compared in terms of apparent depth of etching, the average composition of the top 5 nm (XPS), and the average composition over the affected depth (IR-IRS). Table III shows a similar apparent depth for four smooth-surfaced films (#1,2,8,9) spanning the range of perfluorinated polymer types.

The chemical functionality of the treated surfaces also did not appear to vary greatly with the fluoropolymer type. The IR-IRS spectra in Figure 3 show the qualitative similarity of the reaction products in extruded PFA and skived PTFE. Similar spectra were obtained for treated FEP films. The IR-IRS data are quantified in Table IV and show a similar level of unsaturation and oxygenation in PTFE and PFA after Na/naphth treatment. The XPS data also support the hypothesis that the surface functionality is independent of fluoropolymer type. Figure 4 shows the XPS spectrum of Na/naphth treated PFA, after derivatization with bromine so as to quantify unsaturation. This spectrum can be then compared directly to the PTFE spectra shown in Figure 2a. The surface atomic compositions (Table IV) are in reasonable agreement, particularly when one considers the difficulty in obtaining reproducible XPS data at about the 1 atomic percent level. Similar data were obtained for treated FEP.

TABLE III
Apparent defluorination depth for different fluoropolymers

Specimen	Number	Heat of fusion	Apparent depth
smooth PFA	1	15.9 J/g	112 nm
smooth FEP	2	14.7 J/g	121 nm
lam. PTFE(1A) (smooth)	8	31.8 J/g	125 nm
lam. PTFE(2A) (smooth)	9	—	150 nm
lam. (PTFE)(2B) (0.5 oz. E.D.)	10	—	384 nm
lam. PTFE(2C) (1 oz. E.D.)	11	—	589 nm
lam. PTFE(2D) (2 oz. E.D.)	12	—	609 nm
skived PTFE(1)	6	29.4	223 nm
skived PTFE(2)	7	—	370 nm
Textured PFA	3	20.2 J/g	151 nm
Controlled cool PFA lam.	4	22.6 J/g	160 nm

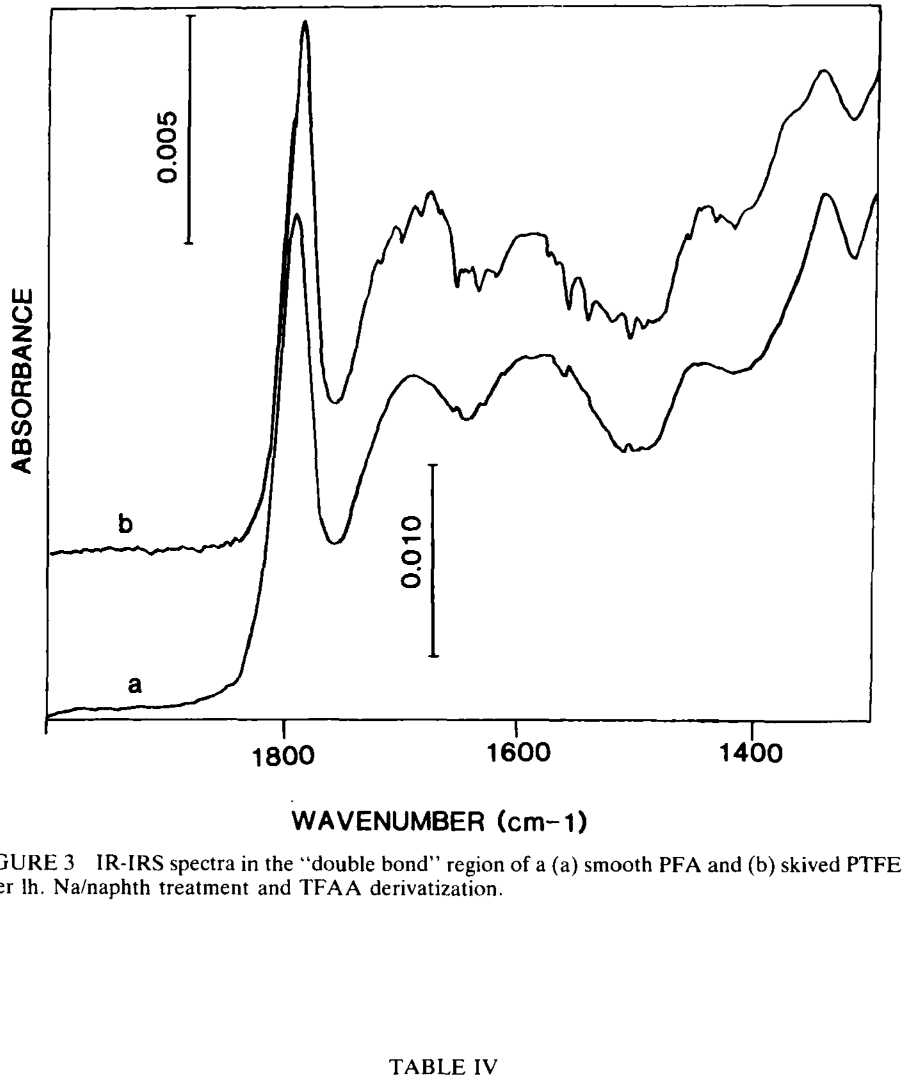

FIGURE 3 IR-IRS spectra in the "double bond" region of a (a) smooth PFA and (b) skived PTFE(2) after lh. Na/naphth treatment and TFAA derivatization.

TABLE IV
A comparison of surface functionality for 1 h. Na/naphth treated PFA and PTFE films

Group	PFA	PTFE
	Average over affected depth by IR-IRS	
C=C	1/4 carbons	1/3 carbons
C≡C	1/5 carbons	1/7 carbons
—OH	1/300 carbons	1/200 carbons
—C=O	1/400 carbons	1/300 carbons
	Average over top 5 nm by XPS	
C=C, C≡C	1/2.9 carbons	1/3.7 carbons
—OH	1/20 carbons	1/18 carbons
—C=O	1/60 carbons	1/ca. 100 carbons
—C—F	1/80 carbons	1/40 carbons

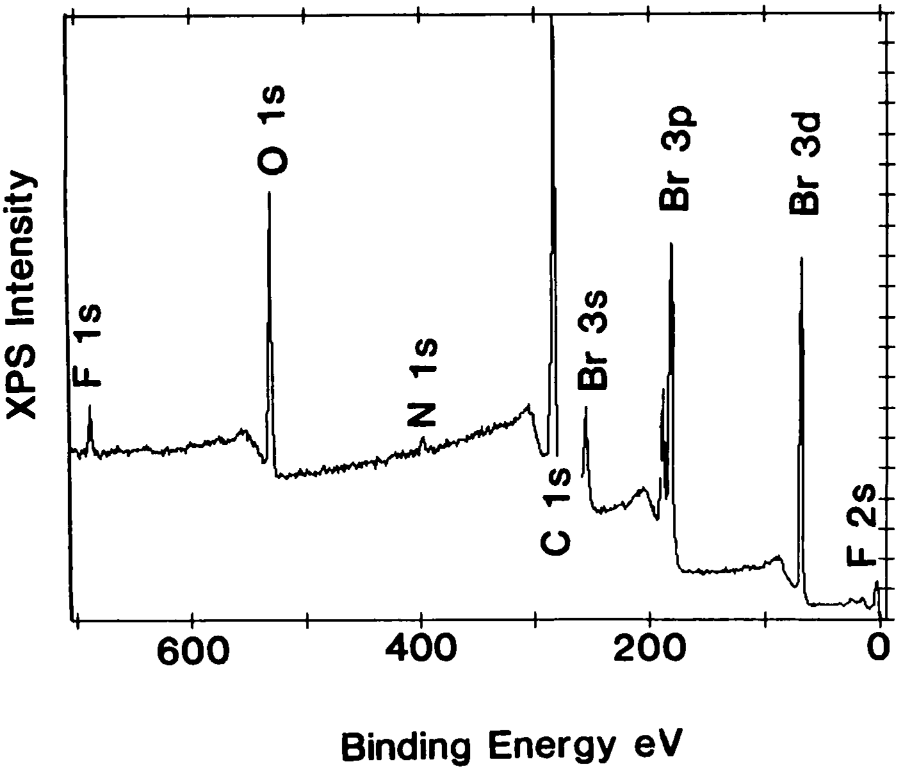

FIGURE 4 XPS spectra of PFA fluoropolymer film after Na/naphth treatment and derivatization with bromine.

2.2 *Effect of Fluoropolymer Crystallinity*

Again comparing the smooth-surfaced films (Table III), it is clear that there is no correlation between specimen crystallinity (taken here as proportional to the heat of fusion) and the extent of defluorination. The smooth-surfaced films show little difference in apparent depth despite a 100% difference in heat of fusion. It is also noteworthy that the skived and laminated PTFE had similar crystallinities but very different etch rates. We attribute this and other variations from the "smooth-surfaced" values to the effect of surface area and surface defects on the etch process. The changes in UV absorbance after Na/naphth treatment are also indicative of the depth of defluorination,[1] and using this criterion we also demonstrated that quenching the laminate in liquid nitrogen was effective in reducing PFA fluoropolymer crystallinity, but had little effect on the rate of defluorination (*i.e.* comparing specimen #4 with specimen #5). Similar laminated FEP films also showed an insensitivity of defluorination depth to changes in crystallinity induced by differences in thermal history.

We realise that heats of fusion are indicative only of bulk crystallinity, and that the surface crystallinity may be appreciably different from the bulk value, particularly for laminated specimens where transcrystallinity (*i.e.* columnar crystallites initiated at the surface) may occur.[3] We see no evidence that transcrystallinity, if it occurs, has any ability to reduce the defluorination rate. For example, the "controlled cool" PFA laminate (#4) is likely to have the highest degree of transcrystallinity, yet is defluorinated to a greater depth than the extruded PFA film (#1), which should have a relatively low tendency for transcrystallization as a result of its cooling rapidly in air during manufacture.

We attribute the apparent insensitivity of the etch process to either fluoropolymer type (section 2.1) or crystallinity (section 2.2) to the electron transfer mechanism of defluorination described in the first paper of this series.[1] Migration of the Na/naphthalenide etchant into the fluoropolymer is not necessary for defluorination to occur. Electron transfer takes place through the conjugated, unsaturated (*i.e.* semiconducting) structure of the defluorinated layer, and the rate limiting step is then migration of the fluoride ion out of the polymer. Such a process will be much less sensitive to polymer morphology and comonomer content than migration of a large etchant molecule, as is required in, for example, permanganic acid etching of polymers, where morphology controls the etching process.[7] The parameter controlling the rate of defluorination will then be the extent of contact between the etchant and the polymer, *i.e.* the surface area of the fluoropolymer film.

2.3 *Effect of Specimen Surface Area*

The hypothesis that surface area was the dominant variable was tested further with "textured" PFA extruded films and laminated PTFE specimens. The commercially extruded PFA had a flat, featureless surface with occasional scratches. The TEM micrograph in Figure 5a shows that the laboratory extruded PFA had a nodular surface texture, and observation of the replica at various viewing angles indicated that the surface area resulting from the textured surface was about 40% greater than that of a perfectly flat specimen. Table III shows that the apparent depth of defluorination increased in proportion to the increase in surface area, compared with the smooth-surfaced control.

The largest effect on apparent defluorination depth came with lamination against high surface area copper foils. Scanning electron microscopy (SEM) of the copper foils showed that the electrodeposited copper surfaces have a highly contoured, nodular texture with apparent surface roughness in the order 2 oz. ED >1 oz. ED >0.5 oz. ED >> "smooth" copper. Surface area measurements by the BET method supported this trend, but the small areas involved (<10 m^2/g) limit the quantitative precision of the method. SEM of the laminated fluoropolymer surfaces, after dissolution of the copper, showed a highly contoured polymer surface which had largely conformed to the original copper surface profile (see Figure 7 in section 3). Table III shows that the mass loss follows the trend in surface area, although we have yet to quantify this relationship, because of a lack of accurate surface area data.

The skived PTFE films form somewhat of a special case which we attribute to the extent of surface damage (chain scission, void formation) induced by the skiving process, as well as to the increase in surface area compared with the smooth extruded films. After lamination to smooth copper, the defluorination rate falls to a value similar to that of the other laminated fluoropolymers (Table III), even though the surface roughness does not appear to have changed greatly (see micro-

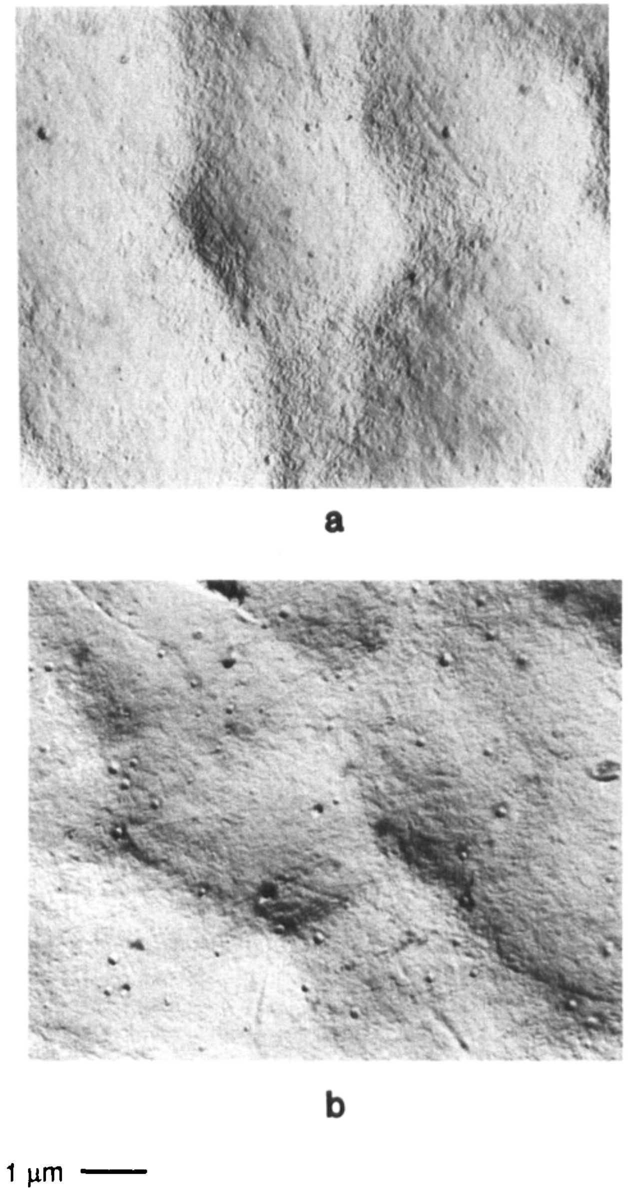

FIGURE 5 Transmission electron micrographs of textured PFA (#3) (a) before and (b) after 1h Na/naphth treatment.

graphs in section 3). The two skived films also show appreciable differences in defluorination rate, which may reflect their different fabrication histories, but these differences diminish after lamination. The structural difference between the skived PTFE and the other fluoropolymers (or laminated PTFE) become most noticeable when the defluorinated layer is removed with chromic acid (see section 3). For skived PTFE, this leaves a porous surface texture, which may be a consequence of the original damaged polymer surface, while the other specimens show relatively small changes in surface texture after stripping of the defluorinated layer.

3. Changes in Surface Texture on Na/Naphth Treatment

The property of adhesion is strongly influenced by the texture of the adherend surface, due to effects such as mechanical interlocking.[2] It is, therefore, important to understand the effect of Na/naphth treatment on fluoropolymer surface texture. The smooth-surfaced PFA film showed no change in surface texture (at >10,000× by SEM) either after Na/naphth treatment or even after stripping of the 112 nm defluorinated surface layer by chromic acid. However, featureless micrographs make uninteresting illustrations, and so instead we compare in Figure 5 TEM micrographs of the textured PFA (#3) before and after Na/naphth treatment. The untreated surface shows a nodular texture of about 2–3 microns dimensions, on which is superimposed fine surface texture (crystallites?) of <0.1 microns dimensions. Other than occasional surface pitting, the Na/naphth treated specimen appears little different.

Figure 6 compares the laminated PTFE(2A) in its original state, after Na/naphth treatment, and after removal of the defluorinated layer by chromic acid. The embrittled nature of the defluorinated layer is evidenced by occasional surface cracking, but the defluorination process produces little change in surface texture. It also appears that defluorination occurs to a relatively uniform depth since, when the defluorinated layer is stripped away (Fig. 6c), the freshly exposed surface duplicates the original surface texture.

PTFE laminated against rough copper has a much more highly contoured surface (Figure 7), but this again is little changed by the Na/naphth treatment, or even by the subsequent chromic acid etch. In some cases, a coarsening of the surface texture can be observed, possibly as a result of undercutting some of the finer surface texture of the untreated specimen.

The exception to this general rule of unchanging surface texture is skived PTFE. Figure 8 shows that the Na/naphth treatment produces some surface cracking but no major change in surface texture. However, subsequent chromic acid stripping of the defluorinated layer leaves an irregular and porous structure, implying that the defluorination was highly non-uniform. The literature concerning the surface texture of Na/naphth-treated fluoropolymers is unclear. It has been reported that extended treatment of fluoropolymers produces a porous surface texture,[2,3,4,8] but it is not always clear what the nature and processing history was of the fluoropolymer. The temperature and concentration of the etchant may also play a role in the final surface texture. The information here indicates that skived PTFE is not comparable with extruded PFA or FEP in terms of surface structure, and also differs from PTFE which has been laminated (*i.e.* melted against a metal surface) before exposure to the etchant. Our initial evidence indicates that these differences play an important role in the subsequent adhesive bonding performance of the fluoropolymer surface. This is a point which will be expanded upon in the third, and final, paper of this series.

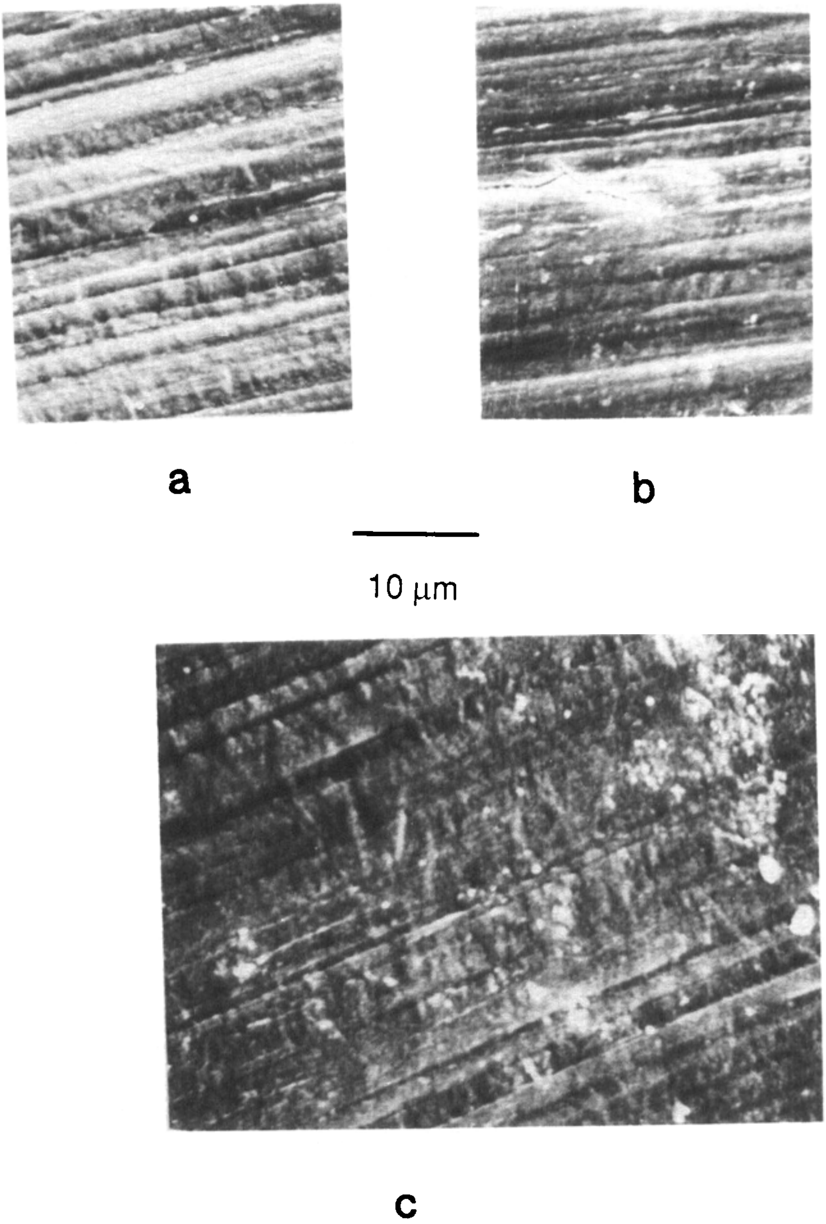

FIGURE 6 Scanning electron micrographs of PTFE laminated against "smooth" copper; (a) original, (b) after lh Na/naphth treatment, (c) after Na/naphth treatment and chromic acid stripping of defluorinated layer.

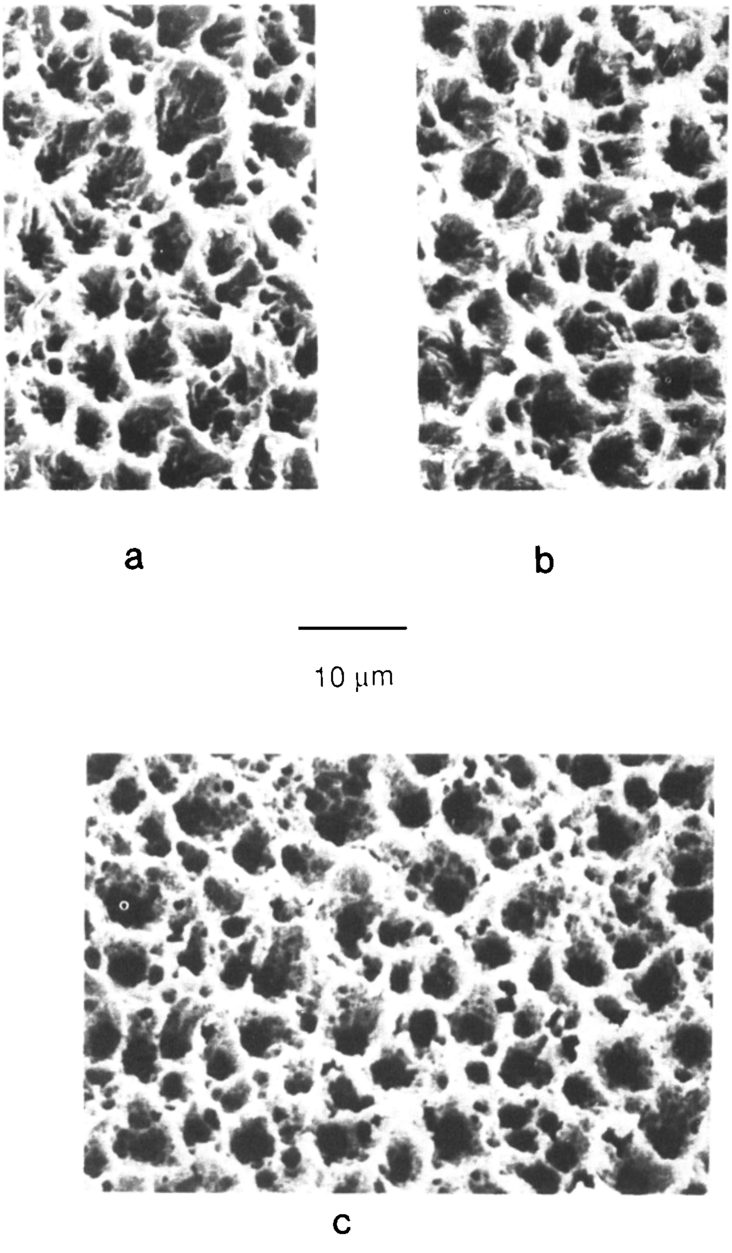

FIGURE 7 SEM of PTFE laminated against 1.0 oz. E.D. copper; (a) original, (b) after Na/naphth treatment, (c) after Na/naphth then chromic acid stripping.

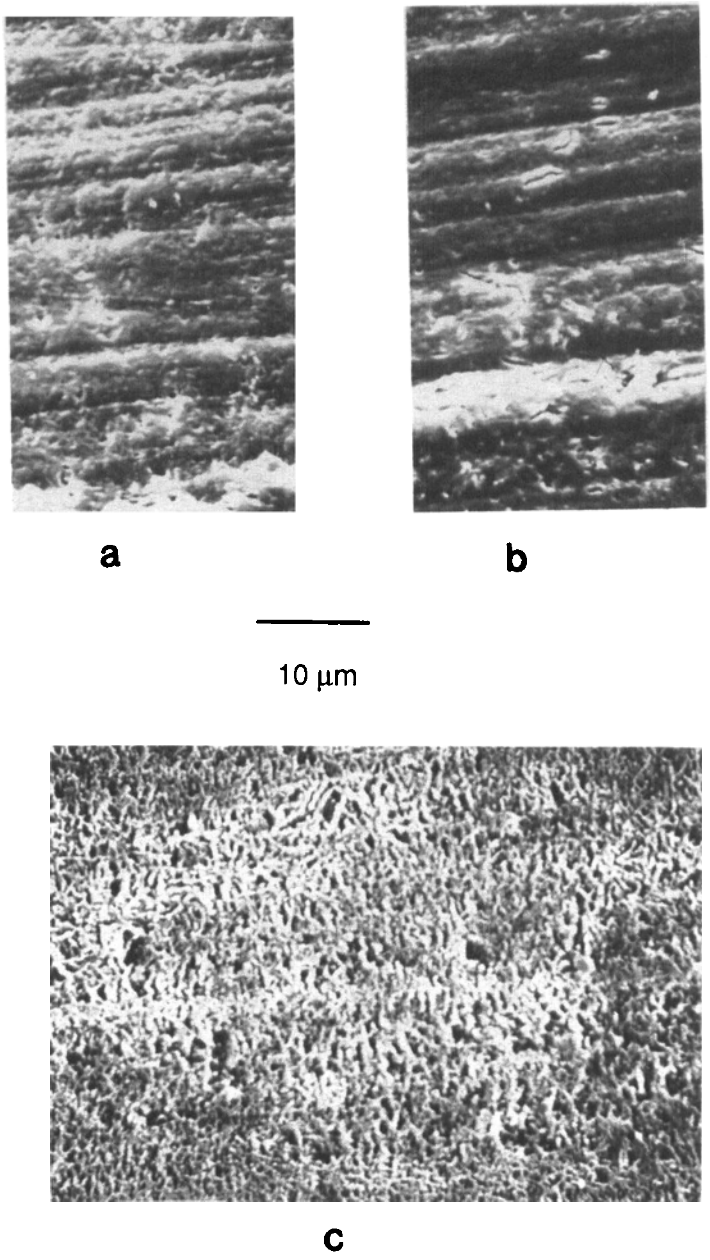

FIGURE 8 SEM of skived PTFE film; (a) original, (b) after Na/naphth treatment, (c) after Na/naphth then chromic acid stripping.

CONCLUSIONS

1. The depth of defluorination and the chemical functionality of the defluorinated surface may be modified by variation of the Na/naphth etching conditions and the post-etch treatment (rinsing and storage).
2. The defluorination process is little affected by the nature of the fluoropolymer (at about 5% perfluoro-comonomer content) and the crystallinity, which is consistent with an electron transfer mechanism of defluorination.
3. The surface area of the fluoropolymer is the dominant variable affecting the amount of defluorination.
4. For all but the skived PTFE films, defluorination occurred in a uniform fashion, to a constant depth, with little change in the surface texture of the polymer.
5. Skived PTFE films have a porous surface texture after Na/naphth treatment and subsequent stripping of the defluorinated layer by chromic acid, which may be a consequence of the surface deformation involved in the skiving process.

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