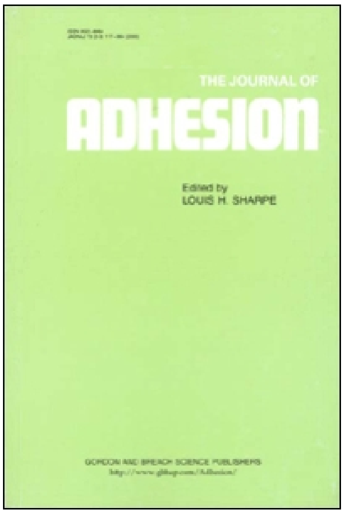

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Adhesion to Sodium Naphthalenide Treated Fluoropolymers Part I—Analytical Methodology

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Fluoropolymers may be treated with sodium naphthalenide (Na/Naphth) in tetrahydrofuran (THF) so as to increase their ability to form adhesive bonds with other polymers or metals. We describe here a quantitative analysis of the chemical modification which results from such a treatment, using a range of derivatizations coupled with infrared (IR), ultraviolet (UV), and X-ray photoelectron (XPS) spectroscopic techniques. For example, after 60 min treatment of a perfluoroalkoxy film (PFA, a copolymer of tetrafluoroethylene and perfluoroalkylvinylether), the polymer was partially defluorinated to a depth of 115 nm, with almost all the carbons in the affected region being functionalized in some fashion. Carbonyl groups were present at about 3.3×10^{-9} equivalents per cm^2 of film surface, which, averaged over the 115 nm affected depth, is equivalent to about 0.25 carbonyls per 100 carbons. The carbonyl content increased with increasing storage time in air. The other major functionalities were alkene (26 per 100 carbons), with a conjugation length of about 10, alkyne (18 per 100 C), aliphatic CH (3.5 per 100 C), hydroxyl (0.30 per 100 C), and carboxylic acid (<0.02 per 100 C). A comparison of the IR and XPS data shows that the unsaturation was distributed relatively uniformly through the 115 nm, while the carbonyl and hydroxyl species were concentrated in the top few nm.

INTRODUCTION

Fully fluorinated polymers are characterized by their low dielectric loss, high dielectric strength and good thermal stability, and so find widespread use in electronics applications. However, it is often necessary to coat the fluoropolymer with metals or to bond electrical components adhesively. In such a situation, a chemical pretreatment of the fluoropolymer is necessary to increase "bondability," and one of the most common is immersion in Na/naphth solution, which defluorinates the surface and introduces a range of chemical functionalities.[1–5]

While qualitative analysis (and partial quantification) of the treated polymer has demonstrated that the incorporation of unsaturation and oxygenated functionality accompany defluorination, a comprehensive and quantitative analysis of

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chemical functionality in the surface is not available in the open literature. Such an analysis is necessary if one wishes to establish a complete structure/adhesive property correlation for the treated surface, or if one wishes to use the Na/naphth treated surface as the base for further chemical reaction. The purpose of this publication is to describe a protocol for the quantification of surface functionality in the treated fluoropolymer. The effects of varying treatment conditions and of different fluoropolymer types and morphologies will be described in the second part of this series.

EXPERIMENTAL

The data reported here refer to a commercial, 25 micron thick, unoriented film of perfluoroalkoxy (PFA, Dupont, a copolymer of tetrafluoroethylene and perfluoroalkylvinyl ether). As will be shown later, this polymer responds to Na/naphth treatment in a manner similar to other fluoropolymers but, unlike polytetrafluoroethylene (PTFE), it is relatively easy to extrude in the form of a smooth-surfaced film. The film was Soxhlet extracted with THF and dried in vacuum at 60°C before treatment. The surface of the film appeared completely flat by scanning electron microscopy (at 10,000×), with the only features being occasional surface scratches.

The Na/naphth solution was prepared in a three-necked 500 mL flask, with a nitrogen inlet, a serum stopper, a 500 mL dropping funnel with a pressure equalization arm, and a glass-coated magnetic stirrer bar. The naphthalene (freshly sublimed, 38.45 g, 0.33 mol) was discovered in THF (300 mL, reagent grade, freshly distilled from lithium aluminum hydride) under 99.999% nitrogen. Metallic sodium (9.9 g, 0.43 mol, cut in small pieces and washed with hexane) was added and reaction began almost immediately to produce the dark green color characteristic of Na/naphth. The solution was stirred under nitrogen for three hours at room temperature, and then transferred under nitrogen to a sealed darkened bottle, using serum caps and a double-ended needle. The solution was sorted at 4°C. The concentration of sodium naphthalenide was determined by removal of aliquots which were then reacted with methanol and titrated with 0.10 N hydrochloric acid, using phenolphthalein indicator, giving a concentration of Na/naphth of 0.90 M.

Surface treatment of the PFA film (3 × 5 cm) took place at room temperature in a 25 mL Schlenk tube. The specimen was purged for 10 minutes with 99.999% nitrogen, and then 20 mL of Na/naphth added *via* a syringe. After the desired treatment time, the films were washed with THF (6 times) and water (7 times, both solvents deoxygenated), still under nitrogen in the Schlenk tube, before being dried in vacuum at 60°C. The depth to which defluorination had taken place was determined by immersing the Na/naphth treated films in fuming nitric acid at 60°C, and allowing the system to cool to room temperature. The film was then immersed in acid dichromate ($K_2Cr_2O_7 : H_2O : H_2SO_4 = 5:8:100$) at 60°C and allowed to cool. Finally, the film was washed with 6 N hydrochloric acid to remove residual chromium salts, washed with water and dried in vacuum. PFA specimens without Na/naphth treatment experienced no mass loss by this treatment, but the oxidizing acid environment could degrade and dissolve the defluorinated layer which resulted from the Na/naphth treatment, leaving virgin PFA (as evidenced by a contact angle increase to >100°). The thickness of the defluorinated layer was calculated from the total mass loss (original film minus (Na/naphth + acid) treated film) assuming a density of 2.15 g/cm^3 for the fluoropolymer.

The concentration of the various functionalities was determined after a series of derivatization reactions.

(a) *2,4-dinitrophenylhydrazine (DNPH) treatment* This allowed quantification of carbonyl groups through the formation of a hydrazone, which has characteristic UV and IR absorptions. The Na/naphth treated film was immersed for 30 minutes in an ethanolic DNPH solution (0.2 g recrystallized DNPH, 1 mL hydrochloric acid, 1 mL water, 20 mL carbonyl free ethanol), then Soxhlet extracted with ethanol for 4 hours to remove residual DNPH, followed by drying in vacuum. An increased immersion time of 22 h in DNPH did not change the yield of hydrazone, although 48 h immersion did increase the yield slightly. A model hydrazone was prepared for calibration purposes by reaction of DNPH with acetone.

(b) *Bromination* This was used to identify the characteristic absorptions of alkyne functionality. We note that this technique is also often used for the determination of alkene functionality but, in the case of fluorosubstituted alkenes, bromination is difficult and incomplete. The treated film was placed in the upper part of a Schlenk tube, which was purged with 99.999% nitrogen for 10 minutes. One mL of bromine was then injected into the bottom of the Schlenk tube through a serum cap. The film was then left in contact with the bromine vapor for 24 hours in the dark, then washed twice with carbon tetrachloride and dried in vacuum. After 24 h, the alkyne absorptions (see later) were completely removed and so the derivitization was stopped at that point.

(c) *Diborane treatment* This reduced alkyne and alkene groups to hydrocarbons, and (more slowly) ketones to alcohols. It does not reduce aromatic unsaturation. The Na/naphth treated film was placed in a Schlenk tube and purged with nitrogen for 10 minutes. Twenty mL of 1 M BH_3 in THF (Aldrich) was then added. After the desired reaction time (24 hours), the specimen was rinsed three times with THF, three times with water, soaked five minutes in 1.0 N hydrochloric acid (twice), rinsed four times with distilled water, and dried in vacuum.

(d) *Trifluoroacetic anhydride treatment* This converted hydroxy groups to perfluoroacetates, which have a characteristic sharp IR absorption at 1791 cm^{-1}. The Na/naphth treated film was placed in the upper part of a Schlenk tube and purged with 99.999% nitrogen for 10 minutes. One mL of trifluoroacetic anhydride

(TFAA, Aldrich) was injected into the bottom of the tube through a serum cap. After the desired exposure to the TFAA vapor (8 hours), the film was dried in vacuum. Increased exposure time did not increase the yield of fluoroester.

(e) *Sulfur tetrafluoride treatment* This derivitization converts carboxylic acids to acid fluorides, which have a characteristic IR absorption at 1838 cm^{-1}. The Na/naphth treated specimen was placed in a polyethylene bottle, with polyethylene fittings, so that first nitrogen then SF_4 gas could be flushed through the system and discharged into 10% sodium hydroxide solution. After 30 minutes purging with SF_4, the system was sealed and reaction allowed to proceed for 24 hours. Increased reaction time did not further increase the yield of acid fluoride. The SF_4 was then flushed from the system with nitrogen. The SF_4-treated specimen was stored in a desiccator before analysis, to eliminate hydrolysis of the acid fluoride. In a second experiment to test for the presence of carboxylic acid salts, the Na/naphth treated film was immersed in 1.0 N hydrochloric acid for five minutes, rinsed with distilled water, then vacuum dried, so as to convert carboxylates to carboxylic acids for SF_4 derivatization.

XPS analysis was performed using a Leybold–Heraeus LHS-10 spectrometer equipped with a dual anode Mg/Al source. Specimens were approximately 1 cm × 2 cm, and were held in place using gold-coated screws. This sample size was large enough to prevent the detection of any sample rod background. The instrument was operated using Mg K_α X-radiation at an applied voltage of 13 kV and an operating current of 10 mA. Under these conditions, the sampling depth is 3–5 nm. Analysis chamber pressures were typically 5×10^{-9} mbar, and never exceeded 9×10^{-9} mbar. Survey spectra were collected using a constant ΔE, with a retarding ratio of three. Detailed spectra were collected keeping $\Delta E/E$ constant and using a pass energy of 150 eV. Sensitivity factors of C 1*s* = 0.25, O 1*s* = 0.66, F 1*s* = 1.00, *N* 1*s* = 0.42. and Br 3*d* = 0.77 were used in calculating atomic percentages. UV-visible spectra were obtained with a Perkin Elmer Lambda 3840 array spectrometer, operated in the transmission mode, and controlled by a 7300 Professional Computer.

The major analytical tool for this study was infrared (IR) spectroscopy, using a Mattson Cygnus 100 FT-IR and a Nicolet SX-60 FTIR, both operated at 4 cm^{-1} resolution. When spectra with very low noise levels were required, up to 5000 scans were averaged. IR spectra were obtained by the internal reflection spectroscopy (IRS) method, using a germanium IRS element and 60 degrees incidence. Under these conditions, and at 1700 cm^{-1}, the penetration depth (i.e. the distance from the element surface at which the intensity of the evanescent field has dropped to 36% of its intensity at the surface) is 290 nm.[6] Note that this penetration depth exceeds the depth affected by the etchant (see later). Because very small absorbances were being measured, extreme care was taken to avoid contamination of specimens and holders. For example, the IRS element was cleaned in an air plasma before every spectrum. Unless stated otherwise, spectra were recorded at a fixed time after preparation (i.e. after vacuum drying overnight) so as to reduce the possibility of surface restructuring.

RESULTS

This section will describe the results of analysis of one type of film sample (25 micron PFA) subject to a single treatment procedure (1 hour Na/naphth). The effects of etching time, wash procedure, and fluoropolymer type will be described in the second part of this series. Analysis of mass loss data after acid dichromate treatment indicates that the Na/naphth treatment produced partial defluorination to a depth of 115 nm. As will be shown later, continued treatment can increase the affected depth to over 300 nm. The film surface remained smooth and featureless at 5000× magnification both after Na/naphth treatment and after the subsequent acid dichromate etch. Some fine structure was observable at 10,000× magnification. The water droplet contact angle was reduced from 104 to 41 degrees by the Na/naphth treatment.

1 Examination of underivitized surface

Figures 1 and 2 show the results of XPS and IR-IRS analysis after Na/naphth treatment. The surface *ca.* 5 nm deep is changed from an initial atomic composition of 34% C, 66% F, < 1% O, to a defluorinated and oxygenated state of

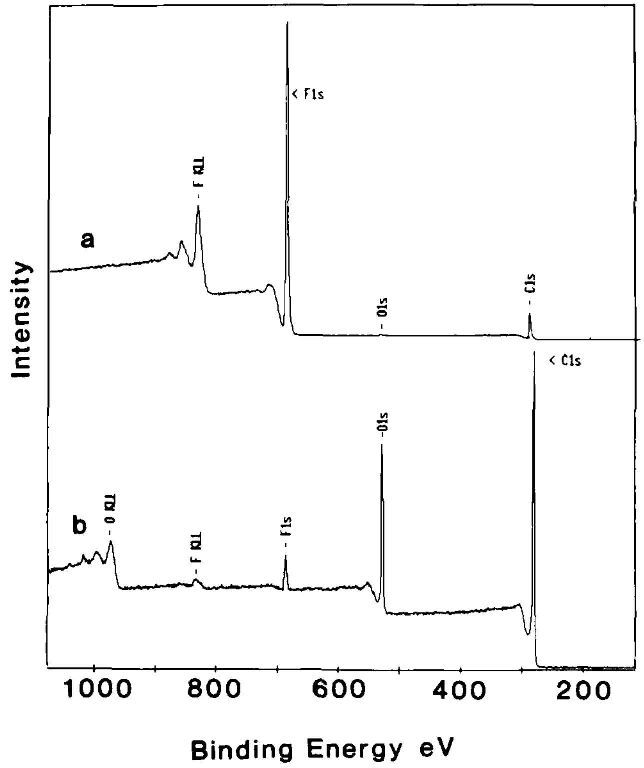


FIGURE 1 XPS survey scan of PFA surface (a) before and (b) after 1 h Na/naphth treatment.

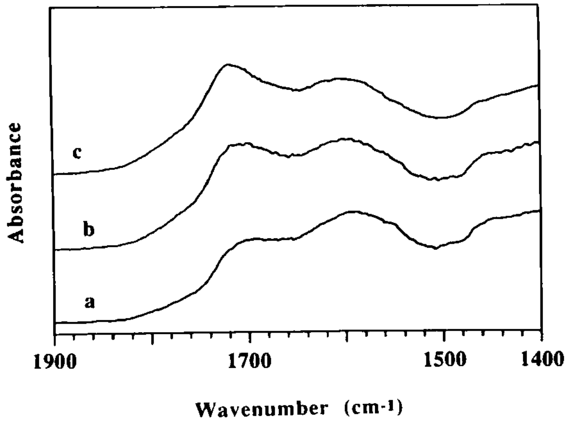


FIGURE 2 IR-IRS spectra of PFA surface (a) immediately after Na/naphth treatment (b) treated surface after 24 h at 60°C (c) treated surface after 2 weeks at 25°C.

87% C, 2% F, and 11% O (the percentages refer to atomic percentages of all atoms except hydrogen, as is conventional in XPS analysis). The non-symmetrical nature of the C 1*s* peak implies that a range of species are present but, without a more detailed understanding of what the products might be, we considered it unwise to curve fit the spectra quantitatively.

The mid-IR region of the IRS spectrum shows broad absorptions at about 1690 cm^{-1} and 1590 cm^{-1}, associated with carbonyl and unsaturated products respectively, but again the breadth of the absorptions makes quantification difficult. Also shown in Figure 2 is the effect of aging in air on the surface chemistry. The carbonyl concentration (*ca.* 1700 cm^{-1}) in the near-surface region increases significantly (about a factor of 2) with short term aging at 60°C, or with longer term aging under ambient conditions, implying that oxidation by air is responsible for a large fraction of the carbonyl products. A spectrum obtained after 4 weeks aging at room temperature was similar to the 2 weeks spectrum. XPS analysis of the surface <5 nm shows a smaller increase in oxygen content (11% O to 15% O after two weeks storage at room temperature in the dark), which implies storage in air increases the depth of the oxidation rather than the local oxygen content. Interestingly, in spite of an increase in oxygen content, the water contact angle increased from about 40 to about 60 degrees during storage, implying that there was some reorganization of the first few Angstroms of the surface or adsorption of contaminants. We will report on this aging effect separately.

The UV-Vis spectrum of the Na/naphth treated PFA showed a broad, steadily-increasing absorption typical of conjugated unsaturation, with an absorbance at 450 nm of 0.70 (1 hour treatment). No distinct peak maximum was observable with which to determine the conjugation length, although the spectral changes after derivatization were more informative (see later).

2 Quantification of surface functional groups

2.1 *Carbonyl-containing species* The classical chemical technique of derivatization with DNPH was shown to be applicable to carbonyl functionalities in the surface of PFA. An examination of the time dependence of the IR and UV-Vis data indicate that hydrazone formation was complete after 30 min immersion in the DNPH solution. Extraction of the derivatized film in ethanol for 4 hours was adequate to remove residual DNPH. Figure 3 shows the UV spectrum (difference DNPH derivatized minus underivatized) of the resultant hydrazone. The absorption maximum at 368 nm indicates that the carbonyls were in the form of unsaturated ketones. We synthesized a model hydrazone in a separate experiment and found that the extinction coefficient at 351 nm (in CCl_4 solution) was 21,600 $M^{-1}\,cm^{-1}$. The UV-Vis spectrum in Figure 3, therefore, indicates that ketonic carbonyls were present at a level of 3.3×10^{-9} equivalents per cm^2 of film surface. The data are presented in this way because the distribution of products clearly is not uniform with thickness, and reaction can occur at both surfaces of the film. The surface area is nominal (i.e. assuming a flat surface, which is reasonably true for this film but, as will be seen later, surface roughness can play a major role in etching rate). If reaction is assumed to be restricted to the depth indicated by the mass loss experiments, the average concentration in the affected region is 3.0×10^{-4} equivalents/cm^3. If the affected surface layer is assumed to consist almost entirely of carbon (a reasonable assumption based on the data for unsaturated species, see later) and to have a density of 1.5 g/cm^3, such a concentration corresponds to 0.25 carbonyl groups per 100 carbons. The major source of error in quantification of the UV-Vis data is the necessity to assume a smoothly curving baseline surrounding the hydrazone absorption.

The IR-IRS data (Figure 4) of the DNPH-derivatized film show the characteristic phenyl and nitro absorptions of the hydrazone and a greatly diminished carbonyl absorption at 1700 cm^{-1}. The aromatic absorption at 1617 cm^{-1} is

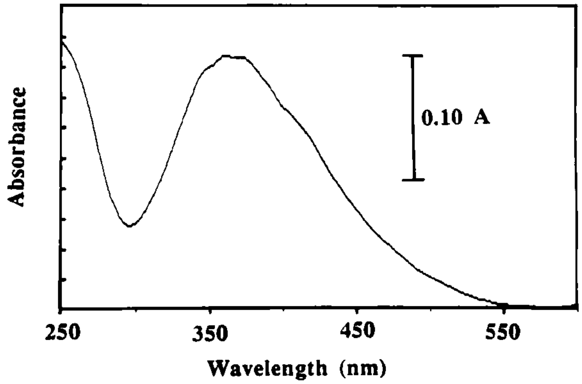


FIGURE 3 Difference UV-Vis spectrum (DNPH derivatized–underivatized) of Na/naphth treated PFA film.

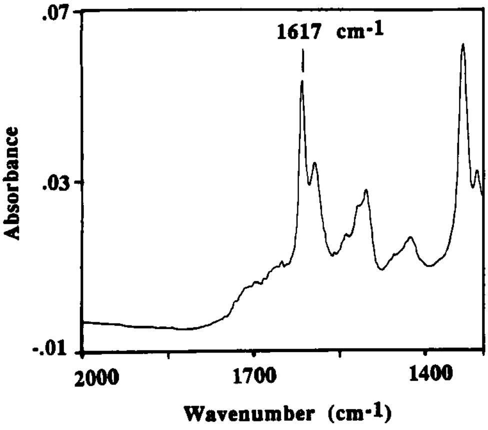


FIGURE 4 IR-IRS spectrum of Na/naphth treated PFA film after derivatization with DNPH.

particularly useful since, when combined with the UV-Vis data above, it allows "calibration" of the IR-IRS technique. It is notoriously difficulty to quantify IR-IRS data for solid samples because of the difficulty in obtaining perfect optical contact between the sample and the IRS element. Since the thickness of the chemically modified region is appreciably less than the IR sampling depth, our sampling procedure approximates to the "thin film case" described by Harrick,[6] where the relative concentrations of absorbing species can be determined simply from their relative IR absorptions and extinction coefficients. Therefore, the UV-Vis data provide the absolute concentration of carbonyl species, while the IR-IRS data can then provide relative concentration data for the other chemical functionalities. It is necessary only to normalize the IR-IRS spectra to a constant (but unknown) optical contact using an invariant CF absorption, rather than to determine quantitatively the exact degree of optical contact in each case. The extinction coefficient of the 1617 cm^{-1} band in a model hydrazone was found to be 1350 M^{-1} cm^{-1} in carbon tetrachloride solution.

The XPS data from the derivatized surface (Fig. 5) support the assignment of hydrazone formation. The N 1*s* peaks at 405.9 eV and 400.1 eV are from the nitro and hydrazone nitrogens respectively. The atomic percentage of nitrogen (5%) is consistent with about 1 in 60 of the carbons to a depth of 5 nm in the underivatized surface originally having carbonyl functionality. Note that these data refer to a sampling depth of <5 nm, and that the act of derivatization may change the absolute quantity of carbonyl groups in this near surface region because of molecular restructuring (driven by the desire of the polymer to minimize its surface energy), and so the number 1 in 60 should be considered as a lower limit of the original carbonyl surface concentration. The assignment of hydrazone formation was also supported by diffuse reflectance IR (DRIFT) analysis of powdered PFA after Na/naphth treatment. This technique gives better spectral quality than the IR-IRS technique at >3000 cm^{-1}, and so allows

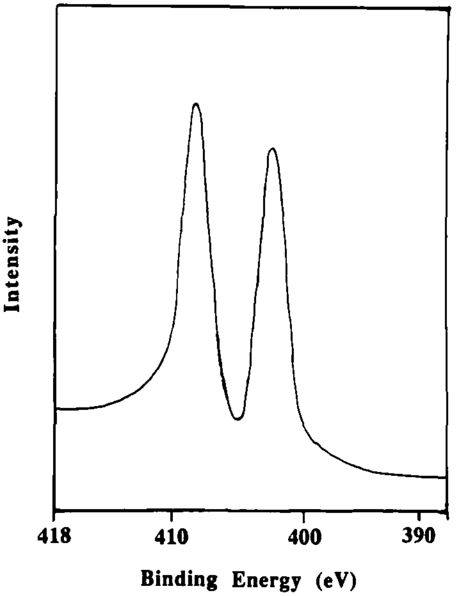


FIGURE 5 XPS spectrum (N 1*s*) region of DNPH derivatized PFA film.

examination of the NH stretching region of the spectrum. The observed NH stretching mode at 3303 cm^{-1} is consistent with a ketone-derived hydrazone, rather than an aldehyde-derived species (<3280 cm^{-1}), or residual hydrazine (3327 cm^{-1}).

2.2 *Hydroxyl species* Figure 6 shows the carbonyl region after derivatization with TFAA. The relatively sharp fluoroacetate absorption at 1791 cm^{-1} is well

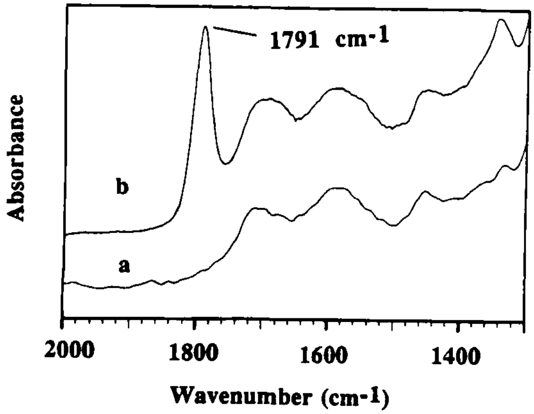
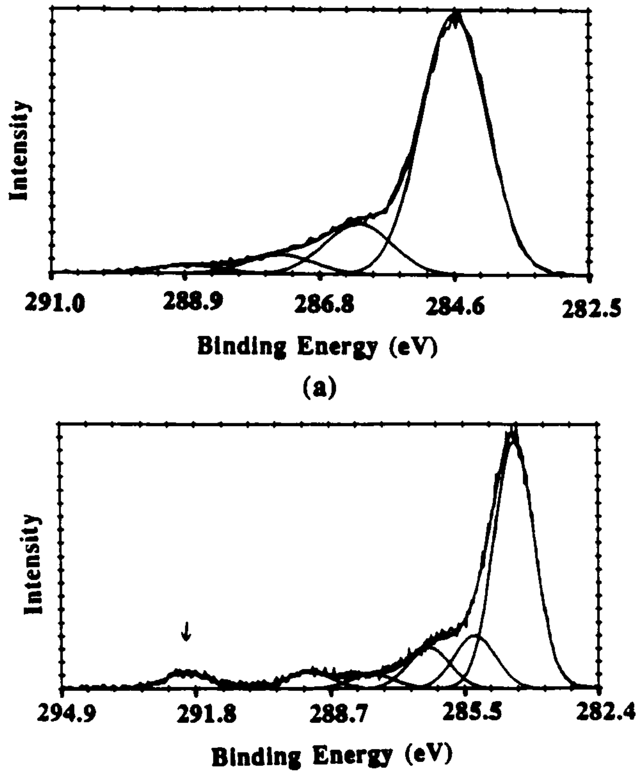


FIGURE 6 IR-IRS spectrum of Na/naphth treated PFA (a) before and (b) after TFAA derivatization.

separated from the broader carbonyl and unsaturation bands. The extinction coefficient of a model trifluoroacetate (in carbon tetrachloride) was found to be 675 M^{-1} cm^{-1}. Before derivatization the only option open for determination of hydroxy functionality was the broad OH stretch at about 3400 cm^{-1}, which was difficult to quantify and prone to interference from adsorbed water.

We therefore determined the hydroxy functionality in the Na/naphth treated film to be 1.2 times the carbonyl concentration or 4.2×10^{-9} equiv/cm^2. XPS analysis of the TFAA derivatized surface (Fig. 7) supports the assignment of a trifluoroacetate, since a noticeable CF_3 peak is introduced into the C 1*s* spectrum. Quantification of this peak indicates that 4.9% of the carbons in the derivatized surface are associated with the trifluoroacetate, which implies that one carbon in 20 to a depth <5 nm in the surface was originally hydroxy substituted. The absolute value of this number is subject to the same caveat regarding restructuring described for the carbonyl species.



(a)

(b)

FIGURE 7 XPS spectrum (C 1*s* region) (a) Na/naphth treated PFA (b) after derivatization with TFAA.

2.3 *Alkyne functionality* A comparison with the spectra of model compounds indicates that the absorption at 2155 cm^{-1} (Fig. 8) is likely associated with the alkyne functionality. This was confirmed by bromination, which rapidly eliminated the absorption, as did diborane treatment. Because this region of the spectrum is relatively uncomplicated by overlap with other bands, we could quantify alkyne directly from the Na/naphth treated spectrum without derivatization. The breadth of the absorption necessitated the use of band area as opposed to band height in the quantification. The intensity of the alkyne carbon-carbon stretch also varies appreciably with the molecular structure of the alkyne, and we chose a "typical" value of 213 M^{-1} cm^{-2} (based on area), as we determined for 1-heptyne. In such a way we determined the alkyne concentration to be 73 times the carbonyl concentration or 2.4×10^{-7} equiv/cm^2.

2.4 *Alkene functionality* A comparison with the spectra of model compounds indicates that the broad 1600 cm^{-1} absorption is associated with conjugated alkene functionality, although the presence of fluorine may produce some broadening and displacement of the band. This assignment was confirmed by diborane treatment, which produced a marked decrease in absorption at 1600 cm^{-1} and an increase in CH absorptions. Our primary method of analysis of alkene was direct quantification of the 1600 cm^{-1} band after Fourier Self Deconvolution[7] to reduce spectral overlap. The original and deconvoluted spectra are shown in Figure 9. We then quantified the area of the band relative to a reasonable pseudobaseline and combined this with a typical extinction coefficient for such a band of 414 M^{-1} cm^{-2} (1-heptene in CCl_4). In such a way we calculated the concentration of alkene functionality to be 103 times the carbonyl concentration or 3.4×10^{-7} equiv/cm^2.

An estimate can be made of the conjugation length of the unsaturation by

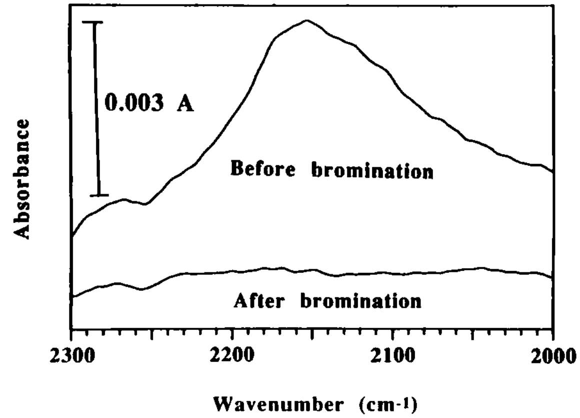


FIGURE 8 IR-IRS spectrum (triple bond region) of Na/naphth treated PFA before and after bromination.

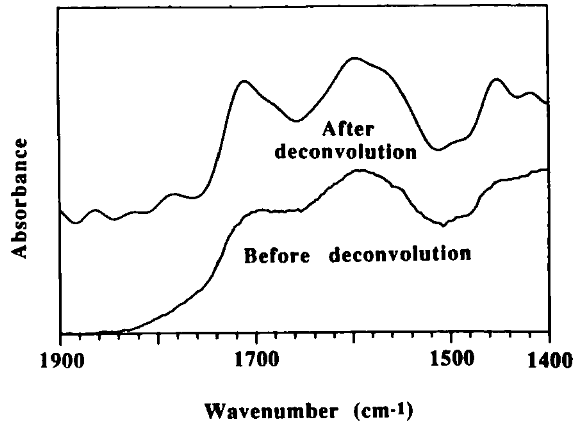


FIGURE 9 IR-IRS spectrum (double bond region) of Na/naphth treated PFA (a) before and (b) after Fourier Self Deconvolution.

examination of the changes in the UV-Vis spectrum after diborane treatment. Figure 10 shows the difference spectrum for the Na/naphth treated PFA before and after diborane treatment. The "negative" absorption at about 450 nm and the "positive" absorptions at 213 nm and 244 nm indicate[8] that the original conjugation length was about 10, which was then reduced by diborane to dienes and trienes. The term "conjugation" here also includes conjugation of the alkene to an alkyne or a carbonyl group since, to a first approximation, they produce a similar bathochromic shift. The assignment of conjugation length was also supported semi-quantitatively by the electron spin resonance (esr) spectrum of the Na/naphth treated specimen (data not shown here). The esr singlet had a peak-to-peak line width of 7.5 Gauss, consistent with a polyenyl radical species with an average conjugation length of about 20. Note that the nature of the esr

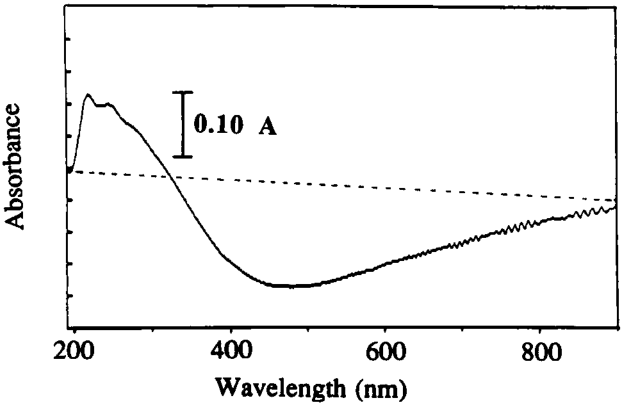


FIGURE 10 Difference UV-Vis spectrum (after diborane derivatization minus before) for Na/naphth treated PFA.

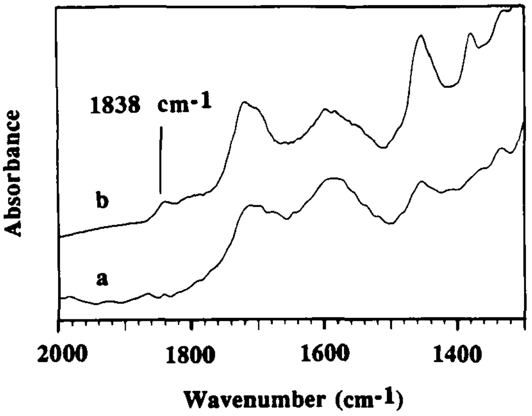


FIGURE 11 IR-IRS spectrum of Na/naphth treated PFA (a) before and (b) after SF_4 derivatization.

averaging process preferentially weights the longer conjugation lengths in the distribution, so producing a higher average value.[9]

2.5 *Carboxylic acid species* The IR-IRS spectrum after SF_4 treatment (Fig. 11) shows that the carboxylic acid content of the surface was low. Using an extinction coefficient of 690 M^{-1} cm^{-1} for the 1838 cm^{-1} absorption,[10] we calculate the carboxylic acid content to be less than 0.05 times the ketonic carbonyl content or $<1.5 \times 10^{-10}$ equiv/cm^2.

2.6 *Aliphatic CH species* The CH stretch region (about 3000 cm^{-1}) is amenable to direct quantification because of the absence of interference from the fluoropolymer. Figure 12 shows that although the absorptions are weak, it is possible to resolve methylene functionality (2926 cm^{-1}) from a wide range

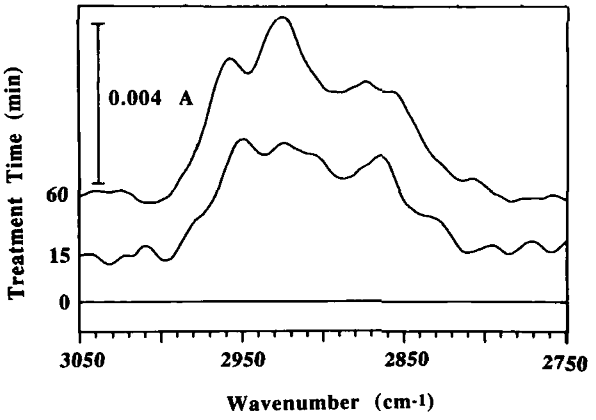


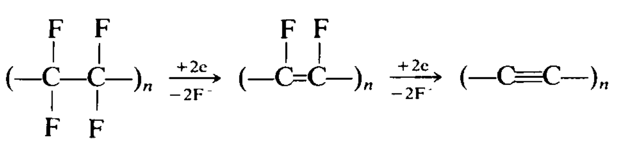
FIGURE 12 IR-IRS spectrum (CH stretch region) of Na/naphth treated PFA film after various treatment times.

of other hydro-carbon structures, including beta-fluorinated hydrocarbons (>2955 cm^{-1}). Again, using a reasonable extinction coefficient of 1520 $M^{-1}\,cm^{-2}$ (based on peak area), we calculate the CH content of the surface 115 nm to be 14 times the carbonyl content, or 4.5×10^{-8} equivalents/cm^2.

DISCUSSION

The well-established qualitative picture of Na/naphth treatment of fluoropolymers is that it leads to partial defluorination and the introduction of unsaturation, hydroxyl, and carbonyl groups. The quantitative data reported here supplement this picture in the following areas. Within the affected depth (115 nm in our case), almost all the carbon atoms have reacted in some form, but the form of the reacted species varies with the distance from the surface. The most easily visualized manner of quantifying the data is as atomic ratios. If, as a first approximation, the density of the defluorinated layer is assumed to be 1.5 g/cm^3 (polyacetylene = 1.2, graphite = 2.09), and is assumed to consist almost entirely of carbon, the number of carbon atoms in the affected layer can be calculated. The data of functional group concentration are calculated by comparison with the carbonyl concentration (0.25 per 100 carbons, averaged over the first 115 nm). This leads to concentrations of alkene functionality of 26 per 100 carbons, alkyne of 18 per hundred carbons, C—H of 3.5 per hundred carbons, hydroxyl of 0.30 per 100 carbons, and carboxylic acid of <0.02 per 100 carbons.

The unsaturation is highly conjugated, and distributed relatively uniformly throughout the reaction depth, with the amount of alkyne functionality almost as high as alkene functionality. This high extent of reaction presumably provides the route for the continued increase in the reaction depth, in that such a structure will have significant electrical conductivity. It is, therefore, not necessary for the Na/naphth to penetrate over a hundred nm into the polymer; electron transfer can occur and the rate limiting step then becomes the diffusion of the fluoride ion out of the polymer.



$$(\text{—}\underset{F}{\overset{F}{C}}\text{—}\underset{F}{\overset{F}{C}}\text{—})_n \xrightarrow[-2F^-]{+2e} (\text{—}\overset{F}{C}{=}\overset{F}{C}\text{—})_n \xrightarrow[-2F^-]{+2e} (\text{—}C{\equiv}C\text{—})_n$$

Although the presence of oxygenated species is particularly noticeable in the XPS and IR spectra, these data show that carbonyls are one of the minor products, and that hydroxyl groups (possibly from reaction during the water wash) outnumber carbonyl groups. The highly surface-specific nature of the oxygenated species (mostly <5 nm from the surface) supports a mechanism for their formation involving the transport of molecular species such as THF solvent, oxygen, or water, rather than the electron transfer involved in the formation of unsaturation.

The XPS spectra may be misleading in their picture of the composition of the first 5 nm in from surface, in that XPS does not detect hydrogen atoms, and the IRS spectra indicate that the CH content of the affected layer is about 14 times the carbonyl content. It is reasonable to assume that the aliphatic CH is produced largely by reaction with the solvent (particularly the CH_2 component), and so is likely to be highly surface specific in a fashion similar to the carbonyl and hydroxyl functionality. The detailed nature of the CH component, such as whether it is in the form of non-polar methylene functionality or the more polar CHF group, will determine what effect it has on the wettability of the surface.

The accuracy of the quantitative data depend strongly on two factors—the completeness of the derivatization, and the transferability of extinction coefficients from model compounds to the polymers. The completeness of the derivatization was confirmed by prolongation of the reaction time until no further change was observed or, in the case of the alkyne, until the alkyne absorption disappeared. The most crucial extinction coefficient is of the hydrazone, since all other species are ratioed to carbonyl. Treatment with DNPH is the accepted analytical technique for analysis of ketones and aldehydes, and the extinction coefficients have been shown to vary little within any structural class.[11] The question of the extinction coefficient of the acid fluoride in solids and solution has been addressed by Carlsson *et al.*[10] The extinction coefficients of alkene and alkyne functionalities are the least reliable, since they are known to vary with structure. However, Truemann and Wall[12] have demonstrated that the extinction coefficients of low molecular weight alkenes are directly transferable to unsaturated polymers.

Clearly, this highly functionalized surface provides many opportunities for further reaction, such as grafting. The physical and mechanical properties of the affected layer will also be markedly different from the bulk polymer, and this will have important consequences for the adhesion process, such as in the formation of a weak boundary layer. This and other aspects of fluoropolymer adhesion will be described elsewhere.

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