

The Effect of Ultraviolet Radiation on Sodium-Etched Poly(tetrafluoroethylene) Bonded to Polyurethane Elastomer

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Synopsis

Peel strength values of sodium-etched poly(tetrafluoroethylene) film bonded to polyurethane substrates have been monitored and found to decrease as a function of exposure to ultraviolet radiation. Attenuated total reflectance (ATR) spectra were monitored on unbonded sodium-etched poly(tetrafluoroethylene) surfaces for the same environmental aging conditions and were found to vary significantly in the region of 1650 cm^{-1} . Techniques are proposed to retard UV-initiated etch degradation and thereby prolong bond integrity.

INTRODUCTION

Although several methods¹⁻⁷ have been described to improve the bondability of poly(tetrafluoroethylene) (PTFE), the most widely accepted surface treatment on a commercial scale is to etch the PTFE in a solution of sodium metal and liquid ammonia² or in a bath consisting of the 1:1 complex of sodium and naphthalene in tetrahydrofuran.⁸ During etching, the white PTFE surface in contact with the alkali metal etchant turns a dull brown to almost black color (depending on the severity of etch), indicating a significant change in surface properties. A useful quality control check for procurement of uniformly and reproducibly etched PTFE is to employ Federal Color Specification 595 (color chip 37056 deep etch, color chip 30099 target color and color chip 30140 light color or low degree of etch)⁹ to compare the etched PTFE surface with predetermined color parameters. Color is related to etch depth, and bond strength has been related to etch depth as well.¹⁰

It has been postulated that the effect of the etching operation is to extract fluorine from the PTFE surface and leave a carbonaceous surface to which adhesives can readily bond. Recently, carbon-to-carbon double bonds have been reported by Miller et al.¹¹ to result from etching PTFE with potassium in liquid ammonia. These authors also report a 10,000-fold increase in surface area as measured by nitrogen absorption using

the B.E.T. method. Although spectral proof of the double bond character is not presented, monomer grafting or chemical reaction at the residual double bonds is cited as evidence for the unsaturation.

Attenuated total reflectance spectra (ATR) of virgin (unetched) PTFE have shown an increase in carbonyl absorption after etching. Additionally, a large amount of adsorbed water on the etched surface, which also suggests the presence of polar functional groups on an activated surface, is evident from the ATR spectra.

Equally as important as the etching process itself is the etch stability at the adhesive-etched PTFE interface. Several references to the instability of the adhesive bond of sodium-etched PTFE to other substances in the presence of UV light appear in the literature,^{8,12} but no quantitative peel data indicating the extent of the UV attack on the bonded surface could be found. However, the gross effect of UV radiation on virgin unetched PTFE is to cause ~10% reduction in tensile strength and ultimate elongation after 100 hr of irradiation with a G30T8 ultraviolet light source.¹³

It is the purpose of this paper to show adhesive strength decay of sodium-etched PTFE bonded to polyurethane as a function of UV exposure, to present ATR data on the etched PTFE surface as a function of exposure to the same environmental conditions, and to suggest techniques to obviate the effect of UV attack and thereby prolong bond integrity from a practical user standpoint.

EXPERIMENTAL

Environmental Conditioning of Peel Samples

Two devices were chosen to simulate UV exposure in wet and dry environments. These are the Atlas Weather-Ometer and an instrument containing a series of fluorescent sunlamps/blacklamps which is commercially available (American Ultraviolet Co., Summit, New Jersey). The latter unit has been used to evaluate the stability of other polymers such as polyesters, polyolefins, PVC, and ABS and results were found to correlate well with sunlight exposure data.¹⁴ The ultraviolet spectral energy distribution curves for these two sources compared with sunlight are shown in Figure 1.

Samples were exposed in the Weather-Ometer using a sunshine carbon arc with Corex D filters. Sample distance from the light source was approximately 9 in., and an exposure cycle (Cam no. 7) was used giving a cycle consisting of 102 min of light, 18 min of light and water. The temperature inside the unit was 113°F. This test was performed in accordance with ASTM 1499 and E42.

In the fluorescent sunlamp/blacklamp unit, an equal number of fluorescent sunlamps (Westinghouse 40WFS40) and blacklamps (Westinghouse 49BL) are alternately mounted inside the circular rotating drum

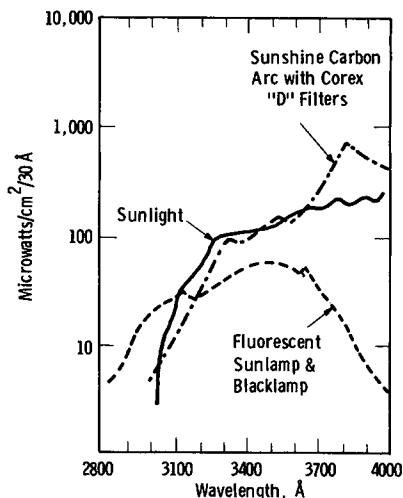


Fig. 1. Radiation of fluorescent sunlamp/blacklamp, carbon arc, and sunlight.

upon which samples are placed. The energy output is maintained relatively constant by a staggered replacement of the lamps. In this case, two lamps were changed every 100 hr. The sample distance from the light source was 4 in. and the temperature inside the unit was approximately 97°F. The major advantage of this unit is that it provides uniform illumination over the entire height of the sample rack compared to other devices in which the radiation emanates from a small central area of the light source.

Peel Testing

Sample panels of sodium-etched PTFE film (0.010 in.) bonded to urethane sheets (0.125 in.) with suitable adhesives were periodically removed from the weathering devices, and a peel specimen, 1 in. × 4 in., was cut from the panel. The PTFE film was hand peeled from the elastomer for approximately 1 in., and the specimen was then tested for peel strength on a Dillon Universal Tester, Model M-1. Peel rate was maintained at 0.5 in./min, and the angle of peel was approximately 180°.

Attenuated Total Reflectance (ATR) Spectra

In order to investigate the mechanism of etch degradation, ATR spectra were determined on etched and virgin PTFE surface as a function of aging in the fluorescent sunlamp/blacklamp unit. Samples of 10-mil etched film were exposed to UV radiation with the etch directly facing the light source, and the identical samples were exposed with the etched surface turned away from the light source. Control specimens were aged for similar periods of time in a black envelope at laboratory ambient conditions.

All ATR spectra were obtained using a Wilk's reflectance attachment, Model ATR-131. With this equipment, the sample beam is reflected between two faces of a KRS-5 crystal against which the sample has been pressed to provide intimate contact. Penetration of the sample surface by the light beam is estimated to be 3-5 μ . Therefore, spectra obtained in this fashion represent primarily surface effects.

The reflectance attachment was used in conjunction with a Digilab Fourier transform spectrometer, Model FTS-14. The sample spectrum was scanned 100 times with a resolution of 4 cm^{-1} , and the computer collects and averages the scans obtained and presents them in almost any fashion required. After the spectra had been obtained and plotted, they were then stored in the computer memory. It was then possible to bring any spectrum out of the memory files and use it as either the "sample" or "reference" spectrum. In this fashion, differential spectra between the control samples and the samples which had been exposed to a particular environment were obtained.

The amount of energy transmitted through the crystal and samples comprised roughly 10% of the total energy available and was automatically expanded to full scale by the computer in individual plots. In the differential spectra, the automatic scale expansion was not used. Here, the samples were compared by plotting the energy throughput of a specific sample against the energy throughput of the control sample.

RESULTS AND DISCUSSION

Field Analysis

Although the peel strength of PTFE-urethane composites¹⁵⁻¹⁷ bonded with a polyurethane adhesive is initially 8-12 lb/in. of width,¹⁸ some cases have been reported from the field where PTFE film is either peeling or has separated completely from polyurethane launch tube liner pads in the Fleet Ballistic Missile Poseidon launch system.¹⁹ All of the reported failures have occurred on the top three rows of polyurethane pads where exposure to direct sunlight is most prevalent. To determine the extent of UV degradation on the adhesive bond, samples of sectioned pads were aged in the Weather-Ometer and examined periodically. After only 400 hr of aging, the PTFE film was completely detached from the polyurethane substrate. Based on these results, an investigation was initiated to evaluate possible solutions.

The various composites evaluated in this investigation are listed and described in Table I. To evaluate the effect of adding a UV absorber to the film, PTFE billets containing 0.5-0.7% by weight of carbon black were manufactured into etched tape and evaluated along with unfilled etched PTFE film. The carbon-filled tape is referred to as "black PTFE" in Table I, and the unfilled tape, as "white PTFE." Also evaluated in this investigation were polyurethane adhesive systems incorporating hydro-

TABLE I
Composite Sample Codes

Sample code	Etched liner film (0.010 in.)	Adhesive
A	White PTFE	polyurethane-1; a proprietary two-part room-temperature curing system
B	Black PTFE	polyurethane-1
C	White PTFE	polyurethane-1 with hydroquinone added at 5% by weight
D	Black PTFE	polyurethane-1 with hydroquinone added at 5% by weight
E	White PTFE	polyurethane-1 with carbon black added at 2% by weight
F	White PTFE	polyurethane-2, a commercially available two-part room-temperature curing system
G	White PTFE	epoxy-1, polyamide hardener, room-temperature cure
H	FEP	polyurethane-1
I	FEP	polyurethane-1 with hydroquinone added at 5% by weight
J	FEP	epoxy-1

quinone, an antioxidant, and carbon black, a UV absorber, directly into the adhesive. An epoxy adhesive system cured with a polyamide was also investigated. A new fluoroethylenepropylene (FEP) film, Teflon XC (du Pont), was also evaluated because of its surface treatment that is claimed to provide outstanding adhesion and weatherable properties. The FEP film was also 0.010 in. thick.

Peel Test Results

Table II presents peel strength data for the sample composites after aging in the Weather-Ometer, and Table III presents similar data after aging in the fluorescent sunlamp/blacklamp unit. After peel testing,

TABLE II
Peel Strength of Composites Aged in the Weather-Ometer

Sample code	Peel strength after aging, lb/in. of width					
	0 hr	100 hr	200 hr	300 hr	400 hr	500 hr
A	11.5	4.5	2.0	0.0	0.0	0.0
B	12.0	6.0	3.0	1.0	2.3	3.5
C	10.5	3.5	0.4	0.0	0.0	0.0
D	10.0	8.5	5.8	5.5	4.5	6.0
E	10.3	7.8	3.4	2.8	2.3	1.7
F	7.0	1.0	0.0	0.0	0.0	0.0
G	6.4	1.2	0.0	0.0	0.0	0.0
H	2.5	2.5	1.5	0.0	0.0	0.0
I	3.0	1.5	0.0	0.0	0.0	0.0
J	11.5	2.5	0.2	0.0	0.0	0.0

TABLE III
Peel Strength of Composites Aged in Dry Fluorescent Sunlamp/Blacklamp Unit

Sample code	Peel Strength after aging, lb/in. of width					
	0 hr	100 hr	200 hr	300 hr	400 hr	500 hr
A	11.5	3.2	1.8	1.2	1.4	1.0
B	12.0	4.5	7.8	7.5	8.0	8.0
C	10.5	4.4	2.6	2.0	2.0	1.5
D	10.0	11.5	10.8	10.3	10.5	10.3
E	10.3	9.0	6.0	5.2	3.5	3.0
F	7.0	3.8	2.5	2.1	1.9	1.5
G	6.4	2.3	2.0	1.5	1.5	1.2
H	2.5	0.4	0.2	0.2	0.0	0.0
I	3.0	1.0	0.3	0.2	0.0	0.0
J	11.5	0.3	0.0	0.0	0.0	0.0

the failure was noticed to occur at the etched PTFE-unetched PTFE interface. The dark etched surface appeared to adhere to the adhesive during peel, leaving the PTFE whiter and free of etch.

Samples aged in the Weather-Ometer degraded faster than those in the fluorescent sunlamp/blacklamp cabinet. This is probably due to the harsher environments experienced in the Weather-Ometer. Moisture and temperature cycling may have reduced the bond life, and the extra heat generated by the Weather-Ometer would cause faster degradation. Additional observations have been made that samples of etched PTFE appear to "lose" their etch after aging in a dark oven at 250°F.

Composites prepared with PTFE tape containing carbon black possess substantially better UV stability than composites prepared with unfilled PTFE. Composites with hydroquinone formulated into the adhesive at 5% by weight possess slightly greater peel strength retention after exposure than composites lacking hydroquinone in the adhesive. Carbon black, Vulcan 9A32 (Cabot Corp.), in the adhesive formulation at 2% by weight also increased bond life to a lesser extent. The addition of hydroquinone and/or carbon black at the concentrations used in this investigation has little effect on the unaged peel strength of the urethane adhesive. The peel strength data obtained with composites bonded with other adhesives show universal bond decay during exposure to UV radiation. The FEP-lined composites deteriorated more rapidly than PTFE-lined specimens. The epoxy adhesive exhibited better initial strength to FEP than the polyurethanes.

To further determine the spectral region in the ultraviolet area that causes etch degradation, T-peel specimens of carbon-filled and unfilled PTFE films and FEP film were bonded with an epoxy-polyamide adhesive per ASTM D-1876 and aged in light of various ultraviolet wavelengths. The UV lamps used in this analysis were low-intensity laboratory models having a sharply defined wavelength. A 3660-Å lamp produced an intensity of 131 microwatts/cm² on the sample surface; a shorter-wavelength

(2537 Å) lamp produced 120 microwatts/cm². Table IV shows the results of periodic peel tests after aging under these lamps. The shorter-wavelength UV light was most destructive, but the carbon-black filled PTFE once again offered the greatest protection to the etched interface.

TABLE IV
Peel Strength of T-Peel Specimens After Aging in Light of Various Wavelength
(Epoxy Adhesive, 0.010-in. Substrates)

Substrate	Wave-length, Å	Peel strength, lb/in. of width					
		0 hr	100 hr	200 hr	300 hr	400 hr	500 hr
White PTFE	2537	8.0	5.0	3.5	4.3	4.0	4.0
White PTFE	3660	8.0	6.0	5.4	5.5	6.5	6.5
Black PTFE	2537	9.5	8.3	6.5	6.8	7.4	7.5
Black PTFE	3660	9.5	9.0	8.5	8.0	8.3	8.5
FEP	2537	11.5	12.5	6.5	7.0	5.7	5.5
FEP	3660	11.5	10.5	10.0	11.0	10.0	9.5

ATR Results

Infrared spectra were scanned over the region 3800 cm⁻¹ to 600 cm⁻¹ and plotted differentially with respect to the crystal with no samples and then with respect to the crystal in contact with a control sample. All significant changes in these spectra occur in the region 1900 cm⁻¹ to 1300 cm⁻¹.

Spectra of unfilled PTFE film aged in the fluorescent sunlamp/black-lamp unit with etch down and etch exposed to the light source are shown in Figures 2 and 3, respectively. Assuming that the main effect of sodium etching of PTFE surfaces is the oxidation of surface sites to acids followed by sodium salt formation, the primary bond in sodium-etched PTFE which is not found in virgin PTFE would be the carbonyl frequency associated with —COO⁻Na⁺. In the spectra of Figures 2 and 3, this band appears to be centered near 1600 cm⁻¹, with secondary bands appearing at 1650 cm⁻¹, 1705 cm⁻¹, and 1730 cm⁻¹.

Samples exposed to ultraviolet light for as little as 100 hr exhibit a universal weakening in the absorption at 1650 cm⁻¹ and a strengthening of the absorption at 1750 cm⁻¹. Continued exposure to the environmental conditioning reinforces the pattern.²⁰⁻²⁴

Literature data of fluoroacid carbonyls indicate that they generally occur in the region of 1770–1790 cm⁻¹; and for PTFE endgroups²⁵ the carbonyl frequency is observed at 1811 cm⁻¹ and 1779 cm⁻¹. A conjugated acid-salt carbonyl frequency has been observed²⁰ to be positioned near 1625 cm⁻¹ for CF₃CCONa·2CF₃COOH, but none of these observed assignments fit the required literature data.

The band near 1600 cm⁻¹ is not greatly changed by UV exposure while the band occurring near 1650 cm⁻¹ could be a —C=C— conjugated to a carbonyl bond. Its disappearance would then be related to the for-

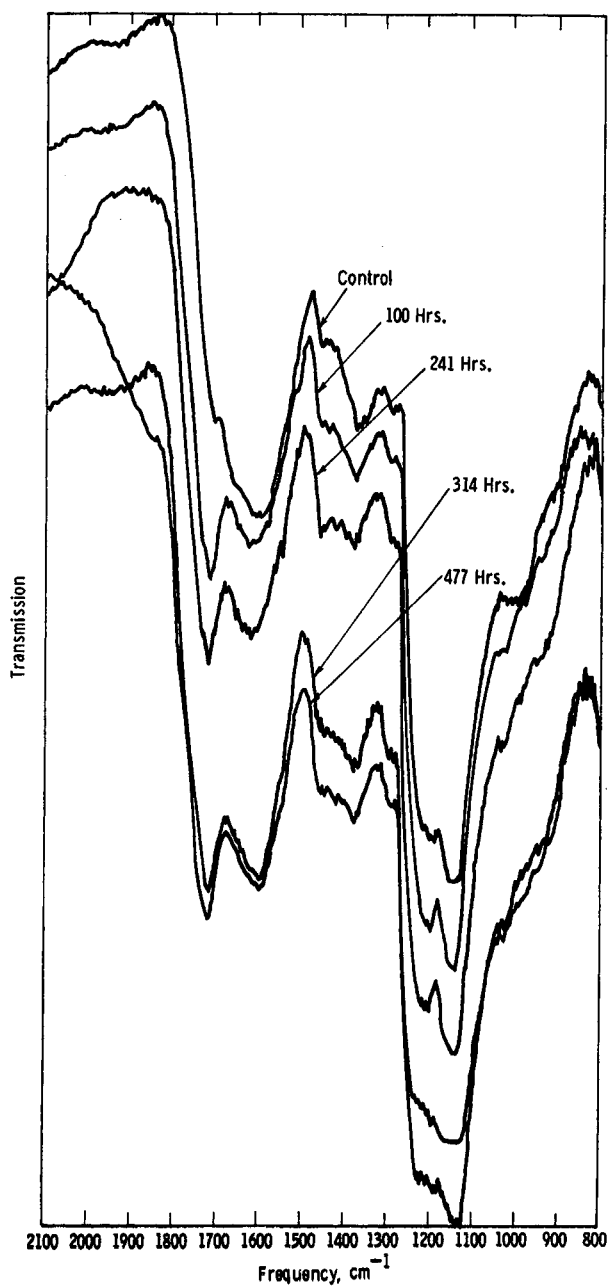


Fig. 2. ATR spectra of sodium-etched Teflon exposed to UV radiation with etch down.

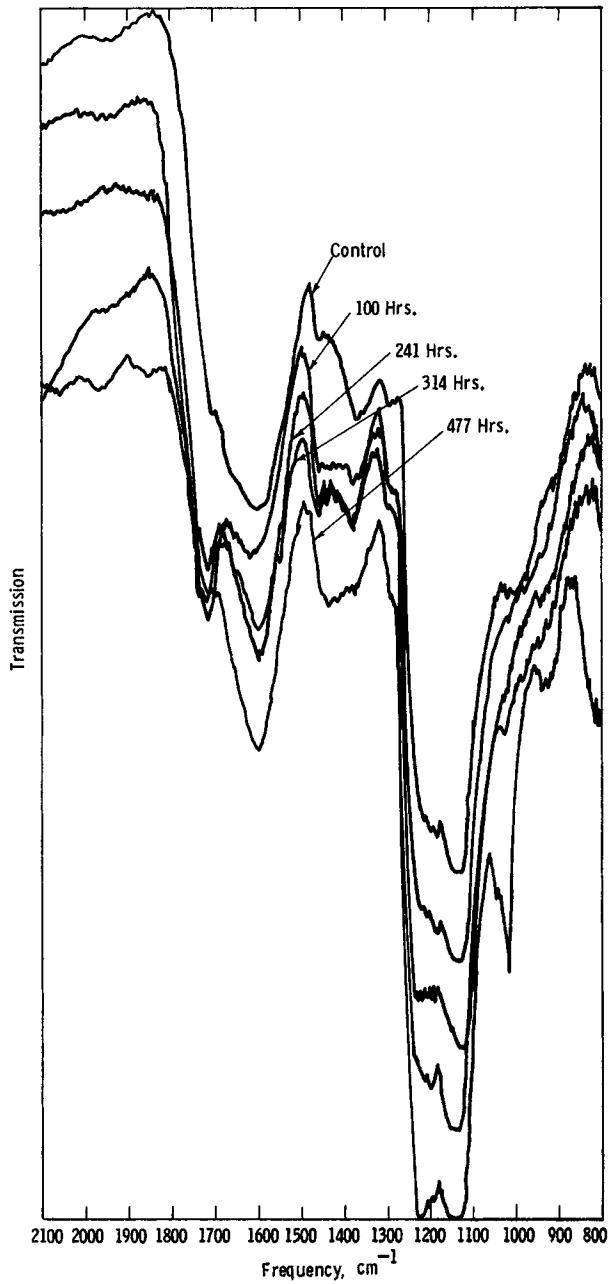


Fig. 3. ATR spectra of sodium-etched Teflon with etch exposed to UV radiation.

mation of the acid reflected in the growth of the 1705 cm^{-1} band. The bond failure could then be explained as a breakdown in the PTFE surface which no longer adheres to the PTFE film.

CONCLUSIONS

Quantitative peel strength data clearly demonstrate that the adhesion of sodium-etched PTFE film bonded to polyurethane substrate is markedly degraded by spectral radiation. After 300 hr of aging in a Weather-Ometer, peel strength of adhesive-bonded composites is decreased from 12 lb/in. width to ~ 0 .

Adhesion retention is improved by the incorporation of a UV absorber such as carbon black into the PTFE film and/or hydroquinone into the adhesive. The most significant improvement occurs with a combination of both carbon black and hydroquinone, resulting in a 60% retention of bond strength after 500 hr in the Weather-Ometer. Based on these data, it is now possible to approximate expected service life for adhesive-bonded composites.

ATR spectra show a marked increase in absorption in the region of $1700\text{--}1600\text{ cm}^{-1}$ as a function of time of exposure to ultraviolet radiation while peel strength decreases uniformly with the spectral change. No evidence for —C=C— unsaturation on the etched PTFE surface could be found.

The authors wish to acknowledge Mr. John Ray for determination of ATR spectra and for useful interpretative comments and Mr. G. B. Rosenblatt for guidance throughout this investigation.

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Received July 26, 1972

Revised September 1, 1972