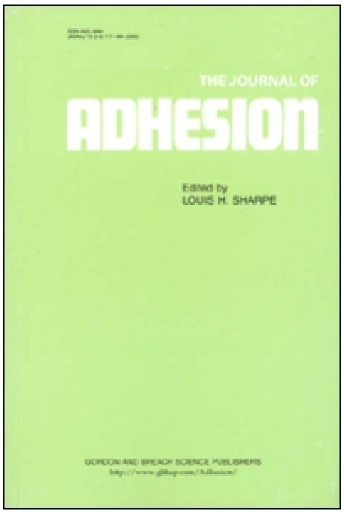

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# Pretreatments of Fluoropolymers

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# Pretreatments of Fluoropolymers*

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In the present study the mechanisms and effectiveness of various pretreatments for fluoropolymers were studied. The pretreatments were "Tetra-Etch," various plasmas, flame and potassium hydroxide. "Tetra-Etch" was found to be much more reactive than potassium hydroxide (KOH) towards fluoropolymers. The plasma treatment of PTFE showed that it was possible to get substantial increases in adhesion with little or no chemical change to the polymer. However, to obtain large increases in adhesion it may be necessary to modify PTFE chemically as with "Tetra-Etch." Consideration of the bonding of these fluoropolymers shows that sharp interfaces between these substrates and adhesives do not exist.

KEY WORDS adhesion; pretreatment; X-ray photoelectron spectroscopy XPS; fluoropolymers; polytetrafluoroethylene PTFE; poly (vinyl fluoride) PVF; poly (vinylidene fluoride) PVdF; plasma; flame; "Tetra-Etch"; weak boundary layer.

## INTRODUCTION

Fluoropolymers have been utilised for many years on the basis of their "non-stick" properties and their high chemical resistance. It is often necessary to bond fluoropolymers to other materials and a pretreatment is usually required to achieve satisfactory adhesion.

Two pretreatments to enhance the adhesion to fluoropolymers have been used commercially for over 25 years. These treatments involve immersion in a solution of sodium in liquid ammonia[1] or in a solution of sodium naphthalenide in tetrahydrofuran (THF).[2] A number of other pretreatments have been shown to give large increases in adhesion. These methods include plasma treatment,[3] direct electrochemical reduction,[4] treatment with an alkali metal amalgam,[5] reduction with benzoin dianion[6] and deposition of aluminium by evaporation.[7] It is likely that plasma treatment of fluoropolymers will become more important commercially.

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The two theories given to explain the poor adhesion to untreated fluoropolymers are the existence of weak boundary layers (WBL), or low surface energies. This paper seeks to provide information on the relative merits of these explanations for particular fluoropolymers.

In the present study, polytetrafluoroethylene (PTFE), was treated with various plasmas, flame, potassium hydroxide (KOH) and with "Tetra-Etch"; poly (vinylidene fluoride) (PVdF) was treated with KOH and "Tetra-Etch"; poly (vinyl fluoride) (PVF) was treated with various plasmas, flame, KOH and "Tetra-Etch"; ethylene-chlorotrifluoroethylene (ECTFE) was treated with flame and "Tetra-Etch." The chemical changes caused by the various treatments were examined, mainly by X-ray photoelectron spectroscopy (XPS) and, in most cases, the corresponding adhesion levels were determined.

## EXPERIMENTAL

### Materials

PTFE, "Fluon," was supplied by ICI in the form of skived film 100 μm thick. The PVF film was Du Pont's "Tedlar," grade T TR 20 SG 4, and was 50 μm thick. PVdF was obtained from Atochem Sensors Ltd; it was in the form of film 100 μm thick. ECTFE, "Halar" 300 grade, was supplied by Ausimont, in the form of sheet 1.6 mm thick.

The adhesive used throughout the study was a two-part epoxide, namely Ciba Geigy's Araldite AV100 and HV100 hardener, mixed in the ratio 1:1 by weight. These were supplied by B and K Resins Ltd., Bromley, Kent. To ensure constant glue line thickness, 1% (by weight) of ballotini spheres (0.21 mm maximum diameter) were incorporated into the adhesive.

"Tetra-Etch," an organic ether solution of a sodium aryl complex, is a product of W. L. Gore and Associates Ltd; it was supplied by R. D. Taylor & Co., Glasgow. The exact nature of the product is not known, but the authors have obtained very similar results with a 1M solution of sodium naphthalenide in THF. Fluoropolymers were treated without prior cleaning at room temperature in air. After treatment the following washing procedure was carried out twice: methanol (AR), high purity water (>80°C) and methanol. The samples were dried in an oven at 60°C and stored in the dark.

Aqueous potassium hydroxide (KOH) solutions were made up from AR grade pellets, supplied by Fisons, Loughborough, and high purity water supplied by Romil Chemicals Ltd, Loughborough. Alcoholic KOH solutions (5 M) were made up by dissolving the appropriate amount of KOH pellets in 5% high purity water and 95% HPLC grade absolute ethanol by volume (supplied by Romil Chemicals Ltd). After treatment the samples were washed 6 times with high purity water, then 6 times in high purity water within an ultrasonic bath and, finally, twice with methanol (AR) in an ultrasonic bath; the samples were dried in an oven at 60°C.

### Treatment Equipment and Bond Testing

Plasma treatment was carried out using a Chemex Plasma Equipment, "Chemprep" plasma barrel reactor 230-D instrument at 13.56 MHz, 70 Watts and a gas pressure of 0.40 Torr. After the sample had been exposed to the plasma for the specified time, the gas was left to flow in the chamber for one minute before purging with nitrogen to atmospheric pressure. The gas supplies were nitrogen (ring main supply), oxygen (BOC "High Purity") and argon (Air Products 99.999% pure).

The flame treatment rig consisted of a burner containing a large number of closely spaced jets and a conveyer system with controllable speeds that transported a detachable metal plate; the fluoropolymer to be treated was attached to the metal plate and passed in front of the burner. The distance from the burner to the sample was 15 mm and the air:gas ratio was 11:1. The contact time of the flame on the polymer surface was 0.04 or 0.06 seconds.

A composite lap shear test was employed for bond strength measurements. The joint consisted of a steel strip/adhesive/fluoropolymer/adhesive/steel strip with an overlap area 20 mm wide × 10 mm long. The adhesive was cured for two hours at 70°C and the joints were tested on a Hounsfield Tensometer Type W at a rate of 12.5 mm $\text{min}^{-1}$. Values were taken from an average of seven tests; the error was ±200 N.

### X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were recorded using a VG ESCALAB MK1 instrument. The X-ray source was $\text{Alk}_\alpha$ with an analyser at a constant pass energy and a take-off angle of 90° with respect to the sample surface. The following instrument parameters were used: aperture = 4 mm slit, pass energy = 85 eV, 5 scans (1 minute per scan), X-ray anode power = 50 watts. These conditions were chosen to minimise X-ray exposure and power, based on evidence of beam damage on materials such as PVF and also to exclude pulse overlap encountered for the intense 1s photoelectron peaks for F. Relative sensitivity factors of core-level photoelectrons were calculated for this instrument according to Ref. 8.

## RESULTS

The results of various pretreatments are given in Tables I–IV.

### Tetra-Etch

"Tetra-Etch" is a very effective pretreatment for PTFE, PVF and ECTFE (see Table I). However, the changes in surface chemistry introduced by the treatment on these polymers differed markedly: chemical changes on PVF occurred more slowly than the other polymers and a high failure load was achieved with markedly less defluorination and oxidation of the surface. It was also not discoloured by the process. Even at longer treatment times, in which more than half of the fluorine was removed, the oxygen incorporation was small. For all the other polymers defluorination was accompanied by extensive oxidation. It is clear that the beneficial effects of "Tetra-Etch" on adhesion cannot be associated in all these cases simply with an increase in surface functionality.

The "Tetra-Etch" treatment causes substantial roughening of PTFE but causes

TABLE I
Effect of "Tetra-Etch" treatment on PTFE, PVF, PVdF and ECTFE

| Polymer | Colour | XPS (Atom %) C | Cl | F | O | Failure load/N |
|---|---|---|---|---|---|---|
| PTFE none | White | 38.4 | — | 61.6 | — | 420 |
| PTFE 10 secs | brown | 87.6 | — | 0.8 | 11.6 | 4280 |
| PTFE 1 min | black | 82.2 | — | 0.9 | 16.9 | 4260 |
| PVF none | colourless | 70.4 | — | 28.8 | 0.8 | 360 |
| PVF 10 secs | colourless | 72.4 | — | 26.7 | 0.9 | 800 |
| PVF 1 min | colourless | 75.4 | — | 23.0 | 1.6 | 2080 |
| PVF 60 mins | colourless | 87.3 | — | 11.4 | 1.3 | 3020 |
| PVdF none | colourless | 51.4 | — | 47.9 | 0.7 | — |
| PVdF 1 min | faint br | 77.4 | — | 12.9 | 9.7 | — |
| PVdF 60 mins | faint br | 79.5 | — | 9.2 | 11.3 | — |
| ECTFE none | cream | 53.2 | 14.3 | 32.5 | — | 240 |
| ECTFE 1 min | cream | 72.5 | 3.7 | 17.7 | 6.0 | 3300 |

br—brown

no significant change in topography with PVF and PVdF; the ECTFE shows an intermediate behaviour. The high failure loads for PTFE noted in Table I may well be due to a combination of a relatively large number of oxygen-containing groups together with a favourable topography.

XPS examination of the failed joints involving PTFE that had been treated with "Tetra-Etch" for 2 seconds was carried out. The two sides of the failed joint gave the following analysis; Side 1 was the epoxide side.

|  | C/% | F/% | O/% |
|---|---|---|---|
| Side 1 | 54.7 | 39.1 | 6.2 |
| Side 2 | 48.5 | 46.0 | 5.5 |

The fluorine and oxygen concentrations are intermediate to those of untreated PTFE and PTFE treated with "Tetra-Etch" (Table I). The results cannot be explained by partial interfacial and partial cohesive failure because no nitrogen (from the adhesive) was observed. This demonstrates that the black layer produced by the treatment is not uniform down to the untreated PTFE and that failure occurred in an interphasial region.

### Potassium Hydroxide

Treatment of PVF and PVdF with potassium hydroxide (Table II) usually resulted in major changes in surface composition; PTFE was unchanged under the conditions studied. However, the conditions required to bring about such large changes in chemistry were relatively severe and in some cases did not result in correspondingly large changes in failure loads (compare with results in Tables I, III and IV). At

TABLE II
Potassium hydroxide treatment of PVF, PVdF and PTFE

| Polymer and treatment | Colour change | XPS (Atom %) | | | Total impurities* | Failure load/N |
|---|---|---|---|---|---|---|
| | | C | F | O | | |
| PVF untreated | — | 70.4 | 28.8 | — | 0.8# | 360 |
| PVdF untreated | — | 51.4 | 47.9 | — | 0.7# | — |
| PTFE untreated | — | 38.4 | 61.6 | — | — | 420 |
| PVF (5 M 2 h) 56°C | none | 69.6 | 25.8 | 4.5 | 0.1 | 460 |
| PVF (5 M 2 h) 80°C | none | 74.1 | 17.6 | 7.7 | 0.6 | 720 |
| PVF (10 M 2 h) 90°C | none | 75.1 | 10.9 | 12.7 | 1.3 | 960 |
| PVF (15 M 1 m) 80°C | none | 68.4 | 29.9 | 1.7 | — | 2900 |
| PVdF (15 M 1 m) 80°C | faint br | 55.2 | 38.9 | 4.8 | 1.1 | — |
| PVF (15 M 30 m) 140°C | br | 80.6 | 1.0 | 17.6 | 0.8 | 4330 |
| PVdF (15 M 30 m) 140°C | dark br | 74.7 | 1.9 | 20.9 | 2.5 | — |
| PTFE (15 M 30 m) 140°C | none | 35.1 | 64.9 | — | — | — |
| PVF alc (5 M 30 m) 90°C | br | 71.5 | 24.1 | 4.0 | 0.4 | 3350 |
| PVdF alc (5 M 30 m) 90°C | bl | 71.6 | 16.8 | 11.1 | 0.5 | — |

*—Impurities on treated samples were predominately zinc but, for more severe treatments, traces of tin and sodium were evident.

#—Oxygen was present as an impurity.

br—brown

bl—black

alc—alcoholic KOH

m—minute

h—hours

concentrations of 5 and 10 molar and a treatment time of 2 hours, significant defluorination and oxidation of the PVF surface had occurred but with only a modest increase in failure load. However, at a higher concentration (15 M) and only a short treatment time (1 min) failure load was high with relatively small changes in surface chemistry. Increasing the temperature to 140°C gave a further improvement in bond strength, a substantial amount of oxygen and almost complete defluorination.

No significant topographical changes have been observed with this treatment.

### Plasma

Plasma treatment, Table III, in contrast to "Tetra-Etch," produced greater changes in the surface composition of PVF than in PTFE. The plasma treatment produced the highest level of bond strength observed for PVF in this study; higher bond strength levels were associated with higher surface oxygen and lower fluorine levels. The topography of the PVF was usually unchanged with plasma treatment, except for the 30-minute argon plasma when shallow pitting of the relatively smooth surface was evident using scanning electron microscopy.

In the case of PTFE, bond strengths were increased but the values obtained were much lower than those reached with "Tetra-Etch." Changes in surface composition were very small. The topography was only slightly changed.

TABLE III
Plasma treatment of PVF and PTFE

| Polymer | Plasma | XPS (Atom %) C | O | F | Failure load/N |
|---|---|---|---|---|---|
| PVF | None | 70.4 | 0.8 | 28.8 | 360 |
| | Ar 1 m | 71.3 | 11.0 | 17.7 | 4060 |
| | Ar 30 m | 78.0 | 11.9 | 10.1 | 4540 |
| | $O_2$ 1 m | 66.3 | 12.4 | 21.3 | 3420 |
| | Air 1 m | 66.8 | 8.0 | 25.2 | 3080 |
| | $N_2$ 1 m | 66.5 | 5.8 | 27.7 | 2720 |
| PTFE | None | 34.6 | — | 65.4 | 420 |
| | Ar 1 m | 42.1 | 4.5 | 53.4 | 1340 |
| | Ar 5 m | 33.1 | 1.6 | 65.3 | 1400 |
| | Ar 30 m | 33.5 | 0.9 | 65.6 | 1860 |
| | Ar 60 m | 32.8 | 0.2 | 67.0 | 1660 |
| | $O_2$ 1 m | 34.4 | — | 65.6 | 1080 |
| | $O_2$ 10 m | 33.6 | 0.2 | 66.2 | 1440 |
| | $O_2$ 30 m | 34.0 | 0.5 | 65.5 | 640 |

m—minute

## Flame

There were some interesting contrasts in the flame treatment of PVF, ECTFE and PTFE (Table IV). With PTFE there was no significant change in the surface chemistry and the bond strength level actually fell; with PVF and ECTFE large increases in bond strength were obtained and substantial changes in surface chemistry occurred. Treatment of PVF resulted in the introduction of oxygen, presumably due to the attack of the $CH_2$ groups, and no detectable defluorination. However, with ECTFE, introduction of oxygen was accompanied by a large degree of dehalogenation.

No topographical changes were observed with this treatment.

## DISCUSSION

This preliminary study on several fluoropolymers subjected to a number of different surface treatments has demonstrated that there is no simple chemical explanation for the mechanism of adhesion enhancement. Significant differences have been seen in the surface chemistry of different polymers subjected to the same treatment.

PVF treatment with "Tetra-Etch," and with KOH under certain conditions, produced high levels of bond strength without large changes in surface composition. However, with plasma and flame treatment the reverse was the case; higher levels of bond strength were associated with major changes in surface composition. For PTFE, the results in Table III show that it is possible to obtain substantial increases in bond strength without significantly altering the elemental composition of the surface. However, to obtain large increases in bond strength it may be necessary to introduce new functional groups into the PTFE, as with "Tetra-Etch."

TABLE IV
Flame treatment of PVF, PTFE and ECTFE

| Treatment/seconds | XPS (Atom %) C | Cl | F | O | Failure load/N |
|---|---|---|---|---|---|
| PVF none | 70.4 | — | 28.8 | 0.8 | 360 |
| PVF 0.06 | 67.6 | — | 28.0 | 4.4 | 3240 |
| PTFE none | 38.4 | — | 61.6 | — | 420 |
| PTFE 0.04 | 34.0 | — | 66.0 | — | 80 |
| ECTFE none | 53.2 | 14.3 | 32.5 | — | 240 |
| ECTFE 0.06 | 68.8 | 8.0 | 17.2 | 6.0 | 2980 |

There is significant evidence for the removal of weakly-bound material in the case of PVF. Previous work on PVF,[8] using multiple bonding experiments in which untreated PVF/epoxide joints were repeatedly fractured and the PVF rebonded, resulted in large increases in joint strength. Substantial quantities of fluorinated material was transferred, at low stress, to the epoxide adhesive. This supports the view that the poor joint strength obtained with untreated PVF in the present study was due to a weakly-held material. It also helps to explain the changes in surface chemistry following "Tetra-Etch" treatment. Here an increase in joint strength was accompanied by some defluorination but a small increase in oxygen concentration. A possible explanation for the change in stoichiometry is that the surface molecules become crosslinked, hence strengthening the surface layer.

When PVF was treated with KOH and little joint strength improvement was attained, it is probable that the treatment chemically modified a region of low cohesive strength; only under more severe treatment conditions was this layer removed. In the reactions of PVdF with aqueous KOH at 140°C or with alcoholic KOH at 90°C, brown and black surfaces were observed, respectively. It is likely that a combination of reactions is occurring. Carbon could be formed by the elimination of two molecules of HF from each repeat unit. The carbon formed will be highly reactive towards oxygen, leading to the incorporation of oxygen-containing functional groups. Dehydrofluorination of PVF would result in a conjugated double bond structure and this is consistent with the coloration produced after the more severe treatments. Oxygen may also be introduced into PVF and PVdF by nucleophilic substitution. Surface infra-red experiments show double bonds with treated PVF. With PVdF, triple and double bonds are observed;[9] this is in agreement with the findings of other authors studying the dehydrofluorination of PVdF powders and film with Group I hydroxides.[10,11,12]

## CONCLUSIONS

The study shows that factors other than surface chemistry are also important in determining joint strength levels.

There is significant evidence for the presence of weakly-bound material on PVF which is strengthened or removed by at least some of the surface treatments. For example, the "Tetra-Etch" treatment of PVF gave large increases in joint strength without introducing substantial quantities of oxygen-containing functional groups.

The plasma treatment of PTFE showed that it was possible to get substantial increases in joint strength with little or no chemical change to the polymer. However, to obtain large increases in joint strength it may be necessary to modify PTFE chemically as with a sodium naphthalenide treatment (*e.g.* "Tetra-Etch").

A comparison of Tables I and II indicates that "Tetra-Etch" is much more reactive towards PVF and PVdF than is KOH.

Consideration of the bonding of these fluoropolymers shows that sharp interfaces between these substrates and adhesives do not exist. There is clear evidence that mechanically-weak layers exist on untreated PVF and PTFE. Likewise, the black layer on "Tetra-Etch"-treated PTFE is not uniform into the polymer.

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