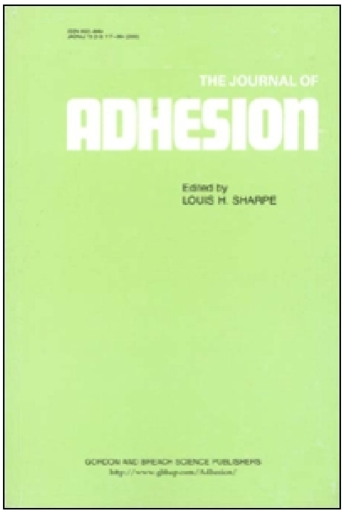

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion Studies of Fluoropolymers

D. M. Brewis[a]; I. Mathieson[a]; I. Sutherland[a]; R. A. Cayless[b]
[a] Loughborough University of Technology, Loughborough, UK [b] BP Research, Sunbury-on-Thames, Middlesex, UK

To cite this Article Brewis, D. M. , Mathieson, I. , Sutherland, I. and Cayless, R. A.(1993) 'Adhesion Studies of Fluoropolymers', The Journal of Adhesion, 41: 1, 113 — 128

To link to this Article: DOI: 10.1080/00218469308026557

URL: http://dx.doi.org/10.1080/00218469308026557

J. Adhesion, 1993, Vol. 41, pp. 113–128
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America.

Adhesion Studies of Fluoropolymers*

D. M. BREWIS, I. MATHIESON and I. SUTHERLAND

Loughborough University of Technology, Loughborough, LE11 3TU, UK.

R. A. CAYLESS

BP Research, Sunbury-on-Thames, Middlesex, TW16 7LN, UK.

(Received June 11, 1992; in final form September 8, 1992)

A comparative study of the treatment of polytetrafluoroethylene (PTFE) and poly(vinyl fluoride) (PVF) with "Tetra-Etch" has been carried out. The treatment of PTFE resulted in extensive changes in surface chemistry and topography, whereas with PVF there was no significant change in topography and the chemical changes were much less marked. However, treatment of both polymers resulted in large increases in bond strength.

Multiple bonding experiments in which samples are repeatedly fractured and re-bonded were carried out with untreated PTFE and PVF. These resulted in moderate increases in bond strength with PTFE and large increases with PVF. The results indicate that weak boundary layer (WBL) removal is a key element in adhesion improvement by "Tetra-Etch" on PVF. With PTFE, WBL removal also improves adhesion, but the chemical and/or topographical changes introduced by the "Tetra-Etch" are required for optimum performance.

KEY WORDS Adhesion; pretreatment; X-ray photoelectron spectroscopy XPS; scanning electron microscopy SEM; fluoropolymers; polytetrafluoroethylene PTFE; poly(vinyl fluoride) PVF; weak boundary layer.

1. INTRODUCTION

Good adhesion to fluoropolymers for printing, bonding or metallising is generally not possible without pretreatment of the fluoropolymer surface. Pretreatments to promote adhesion of fluoropolymers include: a) immersion in a solution of sodium in liquid ammonia,[1] b) immersion in a solution of sodium naphthalenide in tetrahydrofuran (THF),[2] c) reduction with electrochemically-generated tetraalkylammonium radical anion salts,[3] d) direct electrochemical reduction in THF,[4] e) treatment with alkali metal amalgam,[5] f) reduction with benzoin dianion,[6] g) plasma treatment,[7] h) deposition of aluminium by evaporation.[8] Pretreatment with sodium naphthalenide is the most widely used method commercially. It was first reported to increase the adhesion of polytetrafluoroethylene (PTFE) by Benderly.[2,9] Bond strengths, with epoxy, in the range of 6.9–13.8 MPa were reported.

---

*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

Early surface analysis of fluoropolymers treated with sodium complexes was carried out by Dwight and Riggs,[10] and Brecht *et al.*[11] From X-ray photoelectron spectroscopy (XPS) results they reported almost complete defluorination of the surface of fluorinated ethylene propylene (FEP) and PTFE, respectively. Oxygen incorporation with carbonyl and carboxyl type carbon were observed. From post treatment reactions with bromine they concluded the presence of unsaturation.

Sodium complex treated fluoropolymer surfaces are susceptible to degradation by ultra violet radiation (UV).[12] In an adhesion test the dark brown treated surface of PTFE returned to white after 400 hours in a "Weather-Ometer" and became detached from the polyurethane adhesive. Addition of a UV absorber gave typically a 60% retention in bond strength even after 500 hours in the "Weather-Ometer." Exposure to light, abrasion, heat and certain oxidising agents also causes depletion of the treated layer, as shown by XPS.[10]

Dwight and Riggs[10] used soft X-ray spectroscopy to estimate the depth of the treated layer, and quote about 0.3 μm for PTFE and 0.07 μm for FEP. Post treatment oxidation with fuming nitric acid followed by chromic acid was used by Ha *et al.*[13] to estimate the thickness of the treated layer by measurement of the total mass loss. They estimated a depth of 0.115 μm for a 60-minute sodium naphthalenide treatment of a copolymer of tetrafluoroethylene and perfluoroalkylvinylether, (PFA).

Using a combination of infra-red, UV and XPS, Ha *et al.* have presented a detailed surface study of PFA. Quantifications *via* derivatisation techniques of various functionalities were averaged over the 0.115 μm depth *via* infra-red data and over 0.005 μm with XPS data. The infra-red data indicated a high level of unsaturation (alkene and alkyne groups) and few oxygen-containing groups; however, XPS suggested a higher concentration of oxygen. As XPS has a shallower sampling depth (0.005 μm), they therefore concluded that the carbonyl and hydroxyl groups were concentrated in the top few nanometres, whereas the unsaturation was distributed more uniformly through the 0.115 μm.

Topographical changes due to sodium complex treatments depend on the polymer; whereas PTFE and FEP suffer severe roughening from both sodium naphthalenide solution and sodium in liquid ammonia, PFA shows no such change in topography with the sodium naphthalenide treatment.[13]

In general terms, adhesion to a surface may be increased by one, or a combination, of the following: 1) A change in surface chemistry can bring about improved wetting and increased interaction across the interface. 2) An increase in roughness increases the potential degree of contact between substrate and adhesive and the possibility of mechanical keying. 3) The removal of a weak boundary layer (WBL) will increase the cohesive strength near the interface.

The purpose of the present study was to increase understanding of bond failure mechanisms and examine the means by which pretreatments improve bonding. In particular the effect of "Tetra-Etch" (sodium/naphthalene/ether complex solution) on a fully-fluorinated system (PTFE) and a partially-fluorinated polymer, poly(vinyl fluoride) (PVF) was examined to assess the relative importance of the changes brought about by the pretreatment. To investigate the importance of WBLs, multiple bonding experiments were carried out with untreated PTFE and PVF (see section 3.2). The properties studied were bond strength to a conventional epoxy adhesive, water contact angles, surface chemistry (using XPS and attenuated total reflectance—Fourier transform infra-red, ATR-FTIR), and topography (by scanning electron microscopy, SEM).

2. EXPERIMENTAL

2.1 Materials

The PTFE used for this study was "Fluon," supplied by ICI in the form of skived film, 100 μm thick.

PVF "Tedlar" film, grade: T TR 20 SG 4 was supplied by DuPont; the film thickness was 50 μm.

"Tetra-Etch," an organic ether solution containing sodium aryl radicals is a product of W. L. Gore and Associates Ltd; this was supplied by R. D. Taylor and Co, Glasgow. The concentration of the active species is not stated, but the authors have obtained very similar results using a 1 M solution of sodium naphthalenide in THF.

The adhesive used throughout the study was a two-part epoxy namely Araldite AV100 and HV100 hardener, used in the ratio 1:1 by weight. These are products of Ciba Geigy and were supplied by B and K Resins Ltd, Bromley, Kent.

2.2 Treatment of Fluoropolymers

The fluoropolymer films were used as received. The "Tetra-Etch" treatment was carried out in air at room temperature. After treatment the films were washed as follows: methanol AR grade, hot high purity water (>80°C), and methanol; the washing procedure was repeated and then the films were dried in an oven at 60°C. Prior to bonding and analysis the treated films were stored in the dark. The films were normally used the following day. Aging tests showed no change in water contact angle or XPS results after 10 days in the dark.

2.3 Analysis

Bonding A composite lap shear test consisting of steel strip/epoxy/polymer/epoxy/steel strip with an area of 20 mm × 10 mm overlap was employed for bond strength measurements. 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 min^{-1}. Values were taken from an average of seven tests.

For multiple bonding tests, fluoropolymer film (about 100 mm × 120 mm) was bonded with epoxy adhesive between poly(ethylene terephthalate) (PET) film on both sides. A small pressure was applied to the "sandwich" during the curing time by placing it between two aluminium plates that were held together with bull dog clips. Once the adhesive had cured, the PET film (and attached epoxy) was peeled by hand from the fluoropolymer.

X-ray photoelectron spectroscopy (XPS) XPS spectra were recorded using a VG ESCALAB Mk 1 instrument. The X-ray source was AlK_α with the analyser at a constant pass energy and a take-off angle of 90° with respect to the sample surface. Relative sensitivity factors of core level photoelectrons were calculated for this instrument taking into account: the photoionisation cross-section,[14] the angular asymmetry parameter,[15] the transmission of the energy analyser[16] and the energy dependence of the inelastic mean free path of the photoelectron.[17] The values were F1s = 1.00, C1s = 0.23, O1s = 0.67, N1s = 0.42. 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.

Attenuated total reflectance—Fourier transform infra-red (ATR-FTIR) Surface infra-red analysis was carried out on a Nicolet 20DXC instrument with a variable angle ATR attachment. A KRS-5 (TlBr/TlI) crystal was used. The energy resolution was 4 cm^{-1} and 500 scans were taken for each sample.

Contact angles Water contact angles (triply distilled) were measured on a Krüss G40 goniometer. Advancing angles were recorded by expanding the volume of a 2 μl drop till the periphery moved along the surface; the value was taken as soon as the drop came to rest.[18] The values quoted are the average of four measurements.

The measurement of solid surface energies is possible by the use of several liquids of known surface tension;[19] the thermodynamic theory assumes the surface is both smooth and chemically homogeneous. It was noted that even in the case of untreated PTFE that the surface was very rough and porous (Figure 3); hence, surface energy measurements based on contact angles would not have been reliable. Water contact angles were used to give a guide to the wettability/polarity of a surface.

Scanning electron microscopy (SEM) Electron micrographs were produced on a Cambridge Stereoscan 360 SEM; the original magnification was ×3000. Samples were vacuum coated with gold (<5 nm) to give a conducting surface.

3. RESULTS AND DISCUSSION

3.1 Pretreatments

The bond strengths of PTFE and PVF were compared over a range of pretreatment times. PTFE is known to react rapidly with sodium naphthalenide solutions, giving large improvement in bond strength. In this study a bond strength increase from 2.1 MPa to 18.3 MPa was observed for the shortest treatment time of two seconds; a bond strength plateau of around 21 MPa was reached only seconds later. PVF, however, exhibited a slower response to the treatment; the maximum bond strength of around 14 MPa had not developed after 60 seconds (Table I).

The improved adhesion of PTFE is probably due to a combination of factors. Wettability of the surface was increased as shown by a very rapid initial decrease in contact angle (the slight subsequent increase in advancing contact angle over longer

TABLE I
Bond strengths and water contact angles for "Tetra-Etch" treated PTFE and PVF

	Treatment time (seconds)	Advancing water contact angle (deg)	Bond strength (MPa)*
PTFE	0	118	2.1
	2	79	18.3
	10	64	21.4
	30	68	20.5
	60	69	21.3
	600	71	22.2
	1800	72	20.8
	3600	73	22.3
PVF	0	78	1.8
	2	77	3.6
	10	78	4.0
	30	81	5.0
	60	84	10.4
	600	87	15.9
	1800	89	13.4
	3600	91	14.1

*Error is ± 1 MPa

periods of treatment is likely to be a roughness effect). This rapid decrease over the first few seconds is accompanied by an increase in bond strength. The increased wettability with respect to water should result in an increase in the degree of contact between the PTFE and the adhesive. Oxygen functionality was incorporated as a result of the treatment and this is likely to increase the interactions across the interface and also provides the possibility for chemical bonding. XPS data (Figure 1) shows almost complete defluorination of the PTFE surface within a few seconds, with a maximum of around 20% oxygen incorporation. An ATR-FTIR spectrum of a one-hour treated sample (Figure 2) shows at least some of the oxygen is present as carbonyl and hydroxyl.

SEM (Figures 3 and 4) shows that the treatment caused severe roughening of the surface, increasing the potential area of contact between the PTFE and the adhesive and the possibility for mechanical keying.

The fact that fluorinated material was transferred to the epoxy adhesive at low failure loads is a strong indication that a WBL existed on the untreated PTFE (see Table II in section 3.2). This WBL must have been removed by the "Tetra-Etch."

PVF behaves very differently from PTFE, particularly with respect to wettability and roughness. Table I shows that with increased treatment time there was a slight *increase* in the advancing water contact angle, hence improved contact between the epoxy and the treated PVF is unlikely to occur. Figure 5 shows untreated PVF and even the longest treatment time (one hour) did not cause any detectable change in topography. Hence a change in wettability and roughness were not responsible for the observed increase in adhesion; this is consistent with removal of a WBL.

XPS data for PVF reveals that there is a reduction in surface fluorine, about 29% to 12% after a one-hour "Tetra-Etch" treatment, and little or no oxygen incorporation; this may indicate the production of unsaturation through dehy-

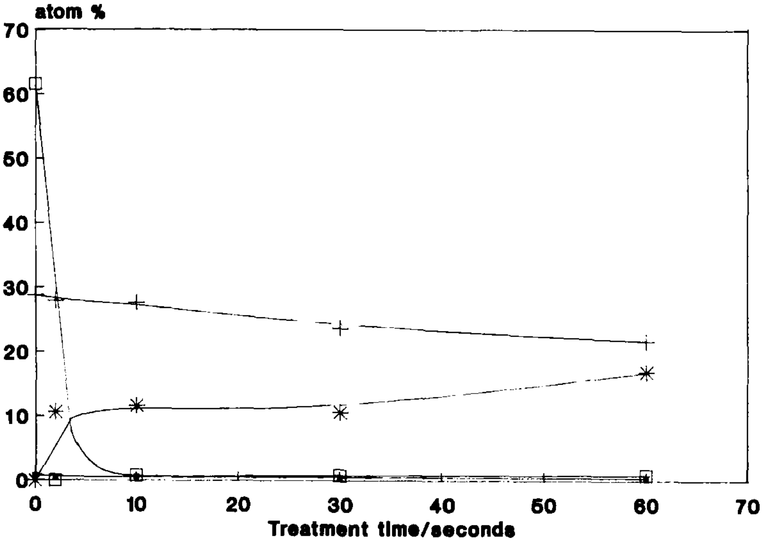

FIGURE 1 Short term XPS data for "Tetra-Etch" treated PTFE and PVF. □ PTFE fluorine concentration, * PTFE oxygen concentration, + PVF fluorine concentration, ■ PVF oxygen concentration.

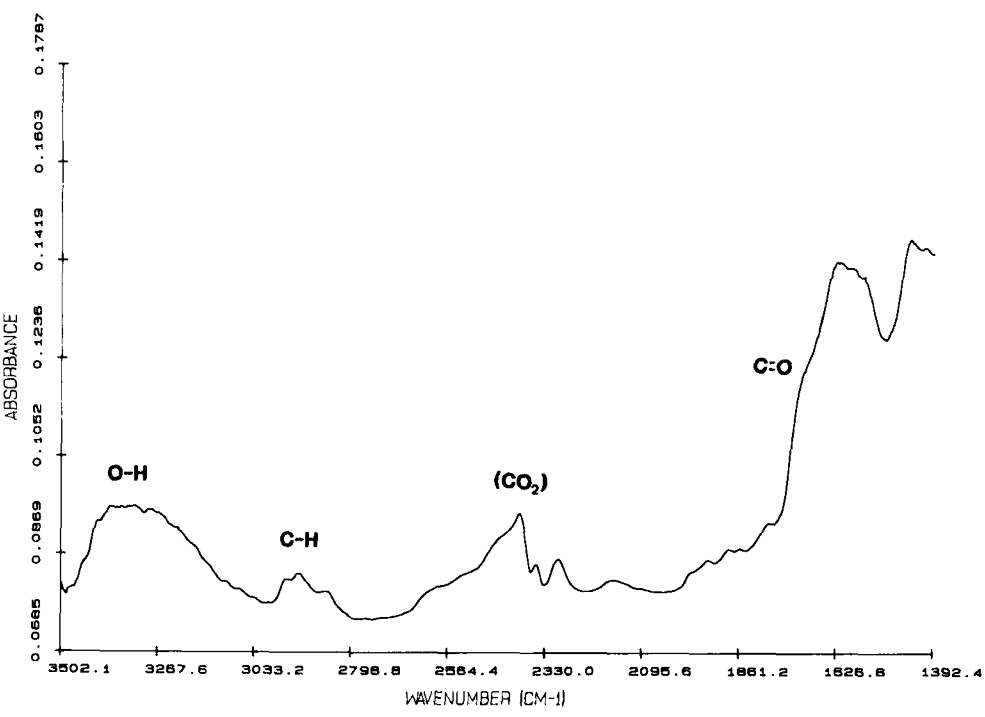

FIGURE 2 An ATR-FTIR spectrum of PTFE treated with "Tetra-Etch" for one hour.

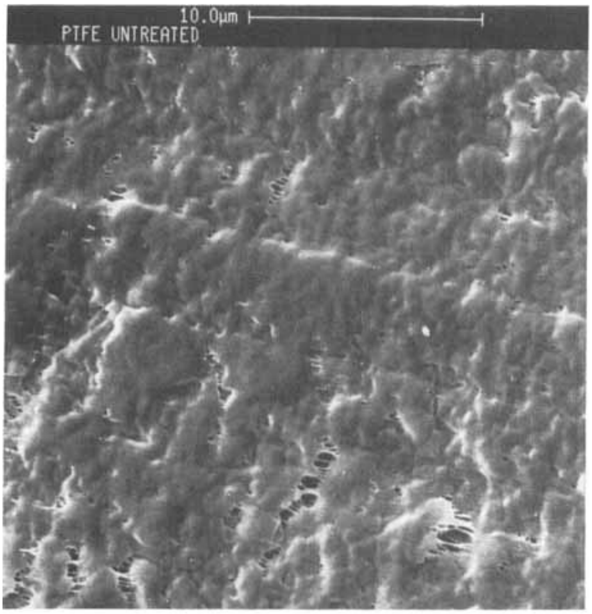

FIGURE 3 A scanning electron micrograph of untreated PTFE.

FIGURE 4 A scanning electron micrograph of PTFE treated with "Tetra-Etch" for 1 min.

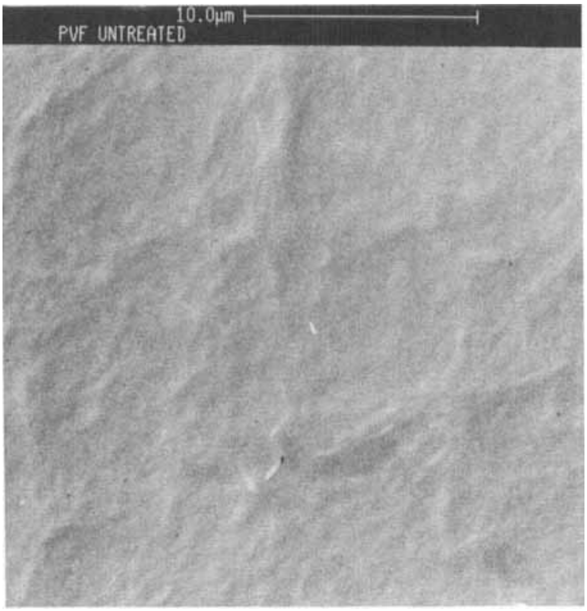

FIGURE 5 A scanning electron micrograph of untreated PVF.

drofluorination and/or cross linking of the surface. This, in turn, could account for the slight increase in water contact angle through loss of polarity. Figure 1 shows the XPS data for treatments up to one minute.

"Tetra-Etch" is much less reactive toward PVF than toward PTFE. This is probably because the first stage of the reaction involves attack of the fluoropolymer at positive carbon atom sites by solvated electrons. The electron-withdrawing effect of the fluorine atoms in PTFE is much greater than that of the single fluorine atom in PVF. This means that the positive charges on the carbon atoms in PTFE will be significantly greater than those in PVF.

The results in Table II indicate there is at least a partial WBL on the untreated PVF. This was probably removed by the "Tetra-Etch" treatment.

3.2 Multiple Bonding

The idea of a weak boundary layer existing on the surface of polymers, consisting of low molecular weight material and being responsible for poor adhesion, was first introduced by Bikerman.[20] This idea was supported by Schonhorn and Hansen[7] who reported an improvement of adhesion without change in wettability when polyethylene (PE), PTFE, PVF and poly(chlorotrifluoroethylene) (PCTFE) were exposed to an activated inert gas (the technique was named CASING). The so-called WBL was said to be cross linked as a result of the treatment producing a surface of high cohesive strength. Schonhorn and Hansen reported using ATR-IR that no surface oxidation was evident as a result of the treatment. Contrary to the results of Schonhorn and Hansen, Sowell *et al.*[21] and Malpass and Bright[22] found large increases in the wettability of activated gas plasma treated PE, indicating introduction of

TABLE II
Bond strengths and XPS data for multiple bonding of PTFE and PVF

Material	No of bondings	Bond strength (MPa)*	% of F on epoxy side
PTFE	1	2.0	16.9
	10	4.7	19.2
	20	4.5	20.1
PVF	1	2.9	1.3
	10	9.0	10.1
	20	12.1	6.5

*Error is ± 1 MPa

substantial quantities of oxygen into the surface. In the case of PTFE Schonhorn and Hansen obtained much smaller increases in adhesion than with PE; in a composite lap shear test the maximum strength obtained was about 7 MPa. In some recent work[23] it was found that plasma treatment increased the composite lap shear strength of PTFE from 2.1 MPa to 9.3 MPa while only introducing very small quantities of oxygen into the surface. These facts are consistent with the view that to obtain high bond strengths (say > 20 MPa) it may be necessary to bring about major changes in surface chemistry and/or topography as is caused by "Tetra-Etch" as well as removing any WBL.

The problem with treatments such as CASING (plasma) and sodium complexes is that there is more than one mechanism to account for adhesion improvement, *i.e.* changes in topography, surface chemistry and the cohesive strength of the interfacial region. PTFE bonded with an epoxy adhesive is known to have low strength and to fail cohesively; XPS provides evidence of fluorine on the adhesive side of a debonded joint.[24] It was for this reason that the multiple bonding experiment was carried out (Table II). This showed that substantial improvements in bond strength for PTFE can be achieved without altering the surface chemistry; with PVF large increases were obtained.

Unbonded PTFE (Figure 3) has a characteristic grooved surface that is the product of the skiving process; it also contains deeper holes containing fibrous material. After the PTFE had been bonded once, the surface appeared more uniform (Figure 6). The epoxy side of this bond (Figure 7) showed a replica of the initial PTFE surface (compare with unbonded epoxy (Figure 8)).

Both surfaces were very different after the PTFE had been bonded twenty times (Figures 9 and 10). The PTFE surface contained a mass of fibres: with higher magnification it was possible to see that they were attached to, and emerged from, a very porous bulk. The epoxy surface appeared very rough and contained fibrous material. Clearly the fibres alone did not account for the twenty percent of fluorine observed in the XPS data. The inelastic electron background to the low kinetic energy side of the F1s photoelectron peak is not flat as would be expected if the fluorine atoms were distributed uniformly throughout the sampling depth of the instrument. The background is seen to decrease with increasing separation from the F1s peak. This indicates the presence of a high concentration of fluorine atoms in the near surface region and would be consistent with a very thin layer of PTFE present on the epoxy surface.

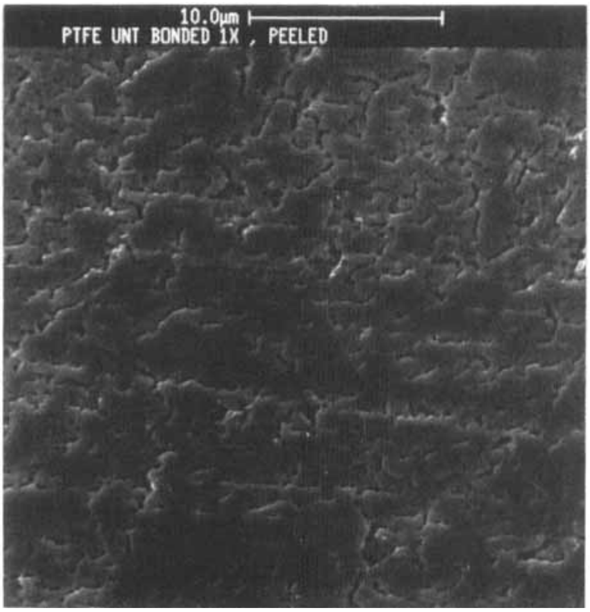

FIGURE 6 A scanning electron micrograph of PTFE after it had been bonded once.

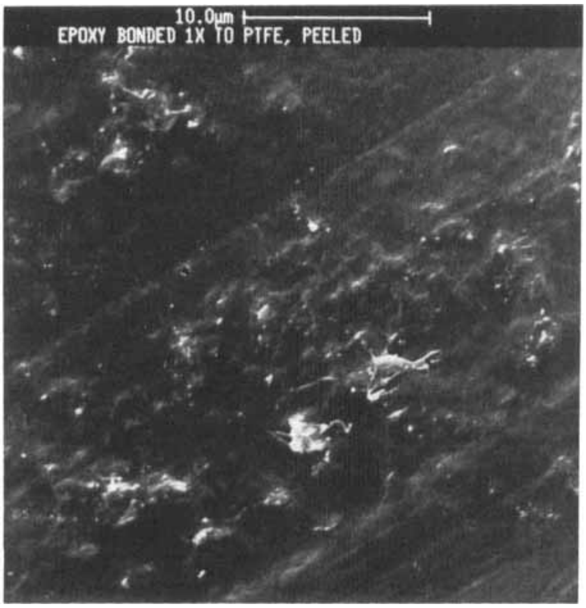

FIGURE 7 A scanning electron micrograph of the epoxy side of an adhesive joint to PTFE that had been bonded once.

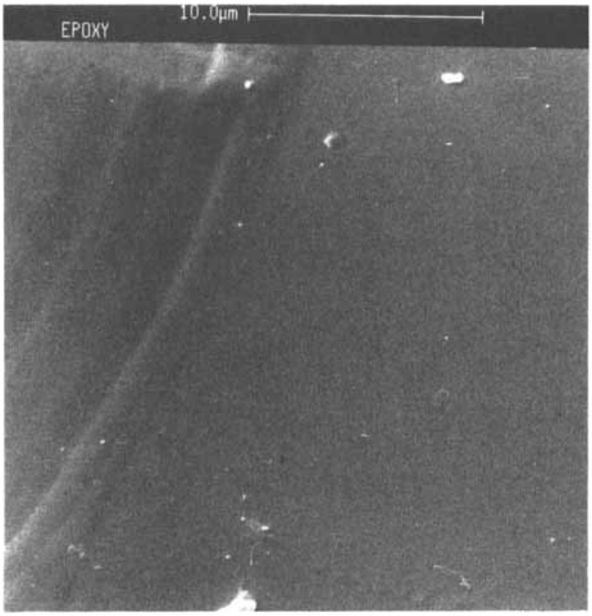

FIGURE 8 A scanning electron micrograph of cured epoxy adhesive.

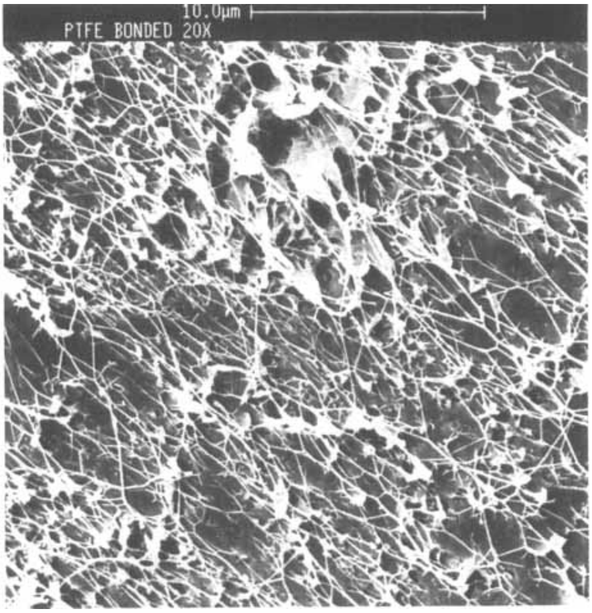

FIGURE 9 A scanning electron micrograph of PTFE that had been bonded twenty times.

FIGURE 10 A scanning electron micrograph of the epoxy side of an adhesive joint to PTFE that had been bonded twenty times.

The above observations would suggest that initially material of low cohesive strength is removed from the surface of the PTFE as a result of the first few bondings. At some point bond strength must increase to cause cohesive failure *via* plastic deformation with production of the fibres. There seems to be an upper limit of about 4.5 MPa for the bond strength even when the amount of fibres increases. Although the topography of this fibrous surface may enhance adhesion after many bondings, it can be said that there has been a transition, during multiple bonding, from bondings that produced no plastic deformation to a time when the bond strength was great enough to cause plastic deformation.

Moderately high bond strengths have been obtained with untreated PVF.[25] This might be expected due to the polar nature of the polymer (the polar contribution to surface energy, $\gamma_s^P = 5.4$ mJ m^{-2} compared with PTFE which is 0.5 mJ m^{-1});[26] likewise, good adhesion can be obtained with poly(vinylidene fluoride) PVdF without pretreatment ($\gamma_s^P = 7.1$ mJ m^{-2}).[26,27] Surface energy measurements on PVF in this present work were consistent with the literature values, yet poor adhesion was obtained; this suggests that the low strengths obtained were due to a WBL, probably originating in the manufacturing process. Large improvements were obtained in the multiple bonding experiment (Table II) and were probably mainly due to the removal of the aforementioned WBL. However, as in the case of PTFE, topographical changes occurred: Figures 11 and 12 show both sides of the joint where the PVF had been bonded just once; there was no change in the PVF surface and the epoxy gave the replica. XPS data show fluorine on the epoxy side, suggesting

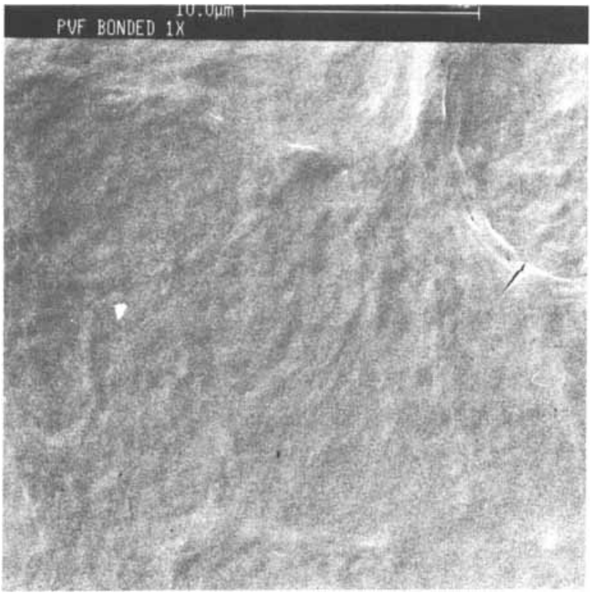

FIGURE 11 A scanning electron micrograph of PVF that had been bonded once.

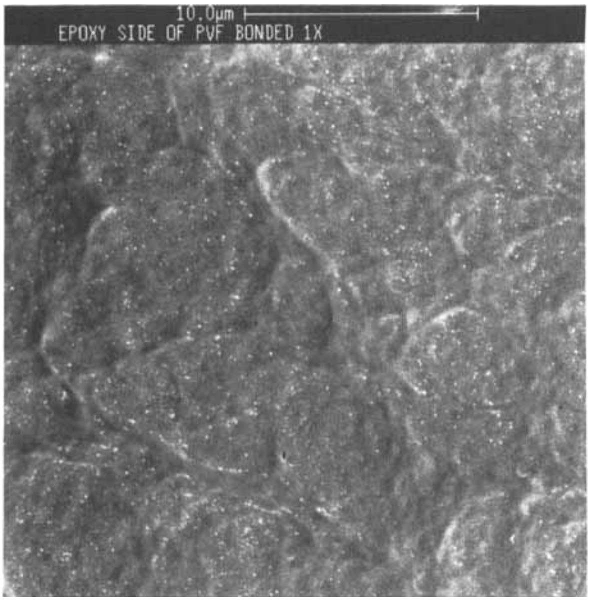

FIGURE 12 A scanning electron micrograph of the epoxy side of an adhesive joint to PVF that had been bonded once.

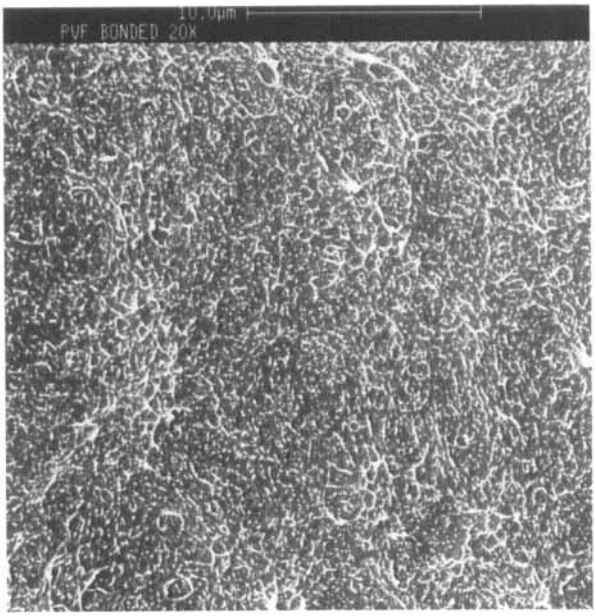

FIGURE 13 A scanning electron micrograph of PVF that had been bonded twenty times.

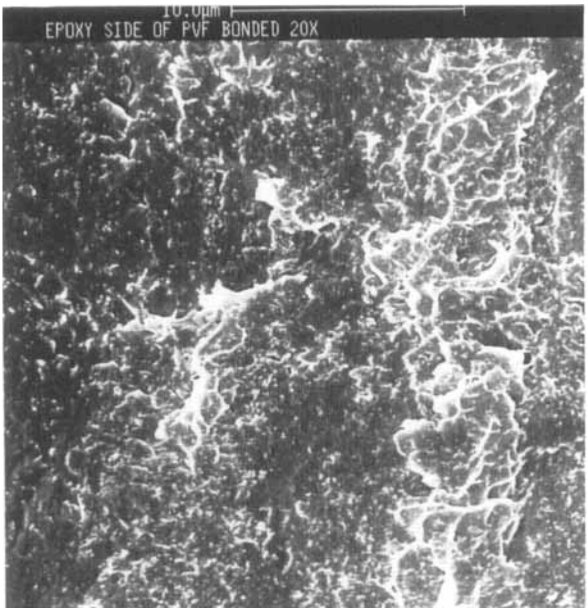

FIGURE 14 A scanning electron micrograph of the epoxy side of an adhesive joint to PVF that had been bonded twenty times.

transfer of low molecular weight material. After the PVF had been bonded twenty times (Figures 13 and 14) plastic deformation of the PVF is evident; the lack of nitrogen in the XPS spectrum of the PVF side eliminates the possibility that the observed topography was due to epoxy. XPS reveals transfer of the fluorinated material to the epoxy.

4. CONCLUSIONS

1. For both PVF and PTFE, treatment with "Tetra-Etch" produced large improvements in the strength of bonds made with epoxy resin.
2. With PTFE, "Tetra-Etch" treatment resulted in almost complete defluorination and substantial oxidation within a few seconds. Extensive roughening of the surface also occurred. Chemical modification of PVF is less rapid and much less marked, with incomplete defluorination and little oxidation. Unlike PTFE there were no significant changes in topography.
3. Multiple bonding experiments aimed at removing weak boundary layers (WBL) resulted in moderate increases in bond strength with PTFE; with PVF the effect was greater, approaching the strength obtained with "Tetra-Etch." For both polymers, evidence for WBL removal was found by XPS detection of fluorinated material on the epoxy surface. Multiple bonding also caused topographical changes on both polymers which may contribute to the improvement in measured adhesion.
4. "Tetra-Etch" did not affect wettability or topography of PVF. The improved adhesion is, therefore, likely to be due to a combination of WBL removal and some chemical modification. The multiple bonding experiments support the view that WBL removal is paramount to obtaining good adhesion. Further improvements might be obtainable if greater chemical and topographical effects could be introduced.
5. On PTFE, WBL removal by multiple bonding improved adhesion significantly but not to the levels (>20 MPa) attainable with "Tetra-Etch." This indicates that with PTFE, in addition to WBL removal, the extensive chemical and/or topographical modifications introduced by "Tetra-Etch" are essential for optimum performance.

References

1. R. J. Purvis and W. R. Beck, US Patent 2,789,063 (16 April 1957) to Minnesota Mining and Manufacturing Co.
2. A. A. Benderly, *J. Appl. Polym. Sci.* **6**(20), 221 (1962).
3. D. M. Brewis, R. H. Dahm and M. B. Konieczko, *Makromol. Chem.* **43,** 191 (1975).
4. R. H. Dahm, D. J. Barker, D. M. Brewis and L. R. J. Hoy, *Adhesion 4* (Applied Science Publishers, London, 1979), p. 213.
5. J. Jansta, F. P. Dousek and J. Riha. *J. Appl. Polym. Sci.* **34,** 3201 (1975).
6. C. A. Costello and T. J. McCarthy, *Macromolecules* **17,** 2941 (1984).
7. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.* **11,** 1461 (1967).

8. R. F. Roberts, F. W. Ryan, H. Schonhorn, G. M. Sessler and J. E. West, *J. Appl. Polym. Sci.* **20,** 255 (1976).
9. E. R. Nelson, T. J. Kilduff and A. A. Benderly, *Ind. Eng. Chem.* **50,** 329 (1958).
10. D. W. Dwight and W. M. Riggs, *J. Coll. Int. Sci.* **47**(3), 650 (1974).
11. V. H. Brecht, F. Mayer and H. Binder, *Makromol. Chem.* **33,** 89 (1973).
12. J. F. Meier and E. M. Petrie, *J. Appl. Polym. Sci.* **17,** 1007 (1973).
13. K. Ha, S. McClain, S. L. Suib and A. Garton, *J. Adhesion,* **33,** 169 (1991).
14. J. H. Scofield, *J. Electron Spec.* **8,** 129 (1976).
15. R. F. Reilman, A. Msezane and S. T. Manson, *J. Electron Spec.* **8,** 389 (1976).
16. M. P. Seah, *Surf. Int. Anal.* **2,** 232 (1980).
17. M. P. Seah and W. A. Dench, *Surf. Int. Anal.* **1,** 1 (1979).
18. A. W. Neumman and R. J. Good, *Surf. Coll. Sci.* **11,** 31 (1979).
19. R. Krüger and H. Potente, *J. Adhesion* **11,** 113 (1980).
20. J. J. Bikerman, *Adhesives Age* **2**(2), 23 (1959).
21. R. R. Sowell, N. J. DeLollis, H. J. Gregory and O. Montoya, *J. Adhesion* **4,** 15 (1972).
22. B. W. Malpass and K. Bright, in *Aspects of Adhesion-5* (University of London Press, London, 1969), p. 214.
23. D. M. Brewis, R. A. Cayless, I. Mathieson and I. Sutherland, unpublished work.
24. D. Briggs, in *Industrial Adhesion Problems* (Orbital Press, Oxford, 1985), p. 17.
25. M. Levine, G. Ilkka and P. Weiss, *J. Polym. Sci.* **B 2,** 915 (1964).
26. D. K. Owens and R. C. Wendt, *J. App. Polym. Sci.* **13,** 1741 (1969).
27. D. M. Brewis, *Progress in Rubber & Plastic Technology* **1** (No. 4), 1 (1985).