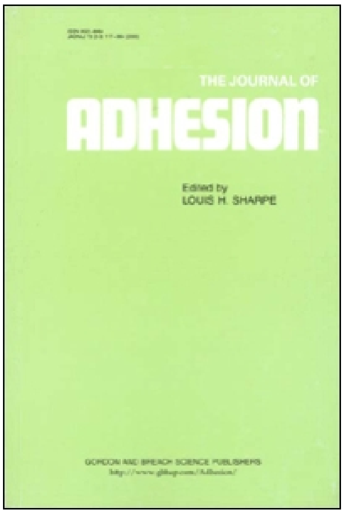

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Pretreatments of Hydrocarbon and Fluorocarbon Polymers

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Pretreatments of polyolefins and fluoropolymers are usually necessary to achieve satisfactory adhesion for bonding and related technologies. In this paper results for various pretreatments of these polymers are presented. These are the treatment of polyolefins with aqueous reagents, dilute fluorine and a natural gas flame, the treatment of PTFE with sodium naphthalenide and the treatment of ECTFE with sodium naphthalenide and a flame. X-ray photoelectron spectroscopy was used to investigate the chemical changes caused by the treatment and the adhesion levels were discussed in relation to wetting, interactions across interfaces and weak boundary layers.

KEY WORDS Pretreatments, polyolefins, fluoropolymers, X-ray photoelectron spectroscopy, wetting, interactions, weak boundary layers.

1 INTRODUCTION

A number of polymers, especially hydrocarbons and fluorocarbons, require a pretreatment to achieve a satisfactory level of adhesion for printing, bonding, painting, coating and metallising. Very effective methods of pretreatment for most of these types of polymers exist,[1-3] although there is room for improvement in at least one case, namely butyl rubber.[4] There has been considerable discussion regarding the reasons for the need to pretreat hydrocarbon polymers and fluoropolymers. These reasons centre around poor wettability, low interactions across interfaces and weak boundary layers.

In this paper a summary of several current projects on pretreatments for low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), ethylene-chlorotrifluoroethylene copolymer (ECTFE) and polytetrafluoroethylene (PTFE) is presented.

These polymers represent two important groups of plastics. The polyolefins are widely used especially in packaging applications, whereas the fluoropolymers, because of their high cost are only used in specialised applications particularly where chemical resistance is critical. Both groups usually require pretreatment to achieve a satisfactory level of adhesion.

The object of this work is to identify the reasons for the effectiveness of the above pretreatments and hence to increase the understanding of the relative importance of weak boundary layers, wetting, specific interactions and topography.

2 EXPERIMENTAL

2.1 Materials

A range of plastics has been used in the various projects described in this paper. These are given at the end of each table of results. The plastics were used in film form, except in the case of ECTFE, which was in the form of thin sheet.

'Tetra-Etch' is a proprietary etching solution for fluorinated polymers and is a product of W. L. Gore Associates.

The paint used in the flame treatment study of polypropylene (Table IV) was a 2-pack polyurethane system (M615-122, M210-763) supplied by ICI.

The adhesive used in all cases was Araldite AV100 plus HV100 used in the ratio of 1:1 by weight. This adhesive is a product of Ciba-Geigy Plastics.

2.2 Pretreatments

Pretreatment of LDPE with aqueous reagents[5] Aqueous solutions of the following reagents were prepared in the ratios (parts by weights):

Ammonium peroxydisulphate	H_2O	100
	$(NH_4)_2S_2O_8$	5.9
Potassium permanganate	H_2O	97.5
	Conc. H_2SO_4	2.5
	$KMnO_4$	6.0
Chromic acid	H_2O	12
	Conc. H_2SO_4	150
	$K_2Cr_2O_7$	7

The LDPE film was immersed in the various solutions either for five minutes at 30°C or 30 minutes at 70°C and then washed several times in triply-distilled water and dried.

Fluorination of LDPE and HDPE Mixtures of fluorine/nitrogen and fluorine/oxygen/nitrogen were used to maintain bubbles of LDPE and HDPE in a modified blown film unit. The rate at which the blown film was reeled was chosen to give treatment times of about 20 seconds.[6]

Flame treatment of PP[7] *and ECTFE*[8] PP film or ECTFE sheet was attached to an aluminium sheet and passed through a natural gas flame by means of a chain conveyor system which permitted variations in the speed of travel. The flame was produced using a 150 mm double row burner supplied by WSA Components. The conditions used are described in the results section.

'Tetra-Etch' treatment of ECTFE[8] *and PTFE*[9] 'Tetra-Etch' which had been stored at -5°C was allowed to warm to room temperature and solids were dissolved with the aid of gentle stirring. ECTFE sheet and PTFE film were immersed in 'Tetra-Etch' for one minute at room temperature. The plastics were then washed in meth-

anol, followed by water at 80°C for 10 minutes, followed by an ultrasonic wash in methanol for 10 minutes. This washing procedure was carried out twice.

Sodium naphthalenide treatment of PTFE[9] A solution of sodium naphthalenide in tetrahydrofuran (THF) was prepared as follows: 16g Naphthalene were dissolved in 125 ml dry THF and 2.9 g sodium in the form of small cubes were added. Dissolution in the dark was achieved in 2–3 hours with the aid of a magnetic stirrer in conjunction with a PTFE-coated follower.

PTFE film was immersed in this solution for one minute at room temperature and then washed according to the 'Tetra-Etch' treatment.

2.3 Surface Analysis

X-ray Photoelectron Spectroscopy (XPS) XPS spectra were recorded on a VG ESCALAB Mk 1 spectrometer using Al K_α radiation. Quantification was obtained from measurement of peak area, with corrections being made for photoelectron cross-section, energy dependence of the energy analyser and the energy dependence of the inelastic mean free path. The spectra were deconvoluted to remove the broadening effect of the unmonochromatised Al K_α line.

Attenuated total reflectance, Fourier transform infra-red analysis (ATR-FTIR) Infra-red spectra were recorded on a Nicolet 20DXC FTIR spectrometer using a variable angle ATR attachment manufactured by Spectratech. A multiple reflecting 50 mm KRS-5 prism was used.

2.4 Measurement of Contact Angles

Contact angles between treated PP and triple-distilled water were measured using a Krüss G40 goniometer. The values given in Figure 2 are the mean of eight determinations.

2.5 Joint Strength Determination

Composite butt test The faces of the steel cylinders (area 650 mm^2) to be bonded were abraded and debris removed by immersing the ends of the cylinders in a beaker of trichloroethylene contained in an ultrasonic bath. After drying, a thin layer of the adhesive was spread onto each cylinder. Squares of the films with a length slightly greater than the diameter of the cylinders were placed between two cylinders, giving a composite structure as follows: cylinder-adhesive-film-adhesive-cylinder. Six joints were constructed for each film and then placed in a special bonding jig to avoid any movement during the curing of the adhesive. The jig was placed in an oven at 55°C for 20 hours to ensure complete curing of the epoxide adhesive. After this time, the joints were removed from the oven and allowed to cool to room temperature. The strengths of the joints were then determined at a strain rate of 4.9 mm per minute using a Monsanto 2000 tensile testing unit.

For the results described in Table IV, the polyurethane paint was sprayed onto the film using a Badger 250 spray gun and dried at 90°C for 30 minutes. The bonding procedure described above was then used.

Composite lap shear test The results in Tables V and VI involved strips rather than cylinders of steel. Otherwise, the procedures were similar to those used in the composite butt test.

3 RESULTS

The changes in adhesion levels and in surface chemistry due to the pretreatments are summarised in Tables I–VI. The elemental analyses, which exclude hydrogen, were determined using X-ray photoelectron spectroscopy.

In Figure 1, the FTIR-ATR spectra from untreated and LDPE-treated with a fluorine/nitrogen mixture are given. In Figure 2, the effect of the air:gas ratio on the flame treatment of PP is shown; the ratio is related to the oxygen introduced into the polymer surface and the contact angle between PP and water.

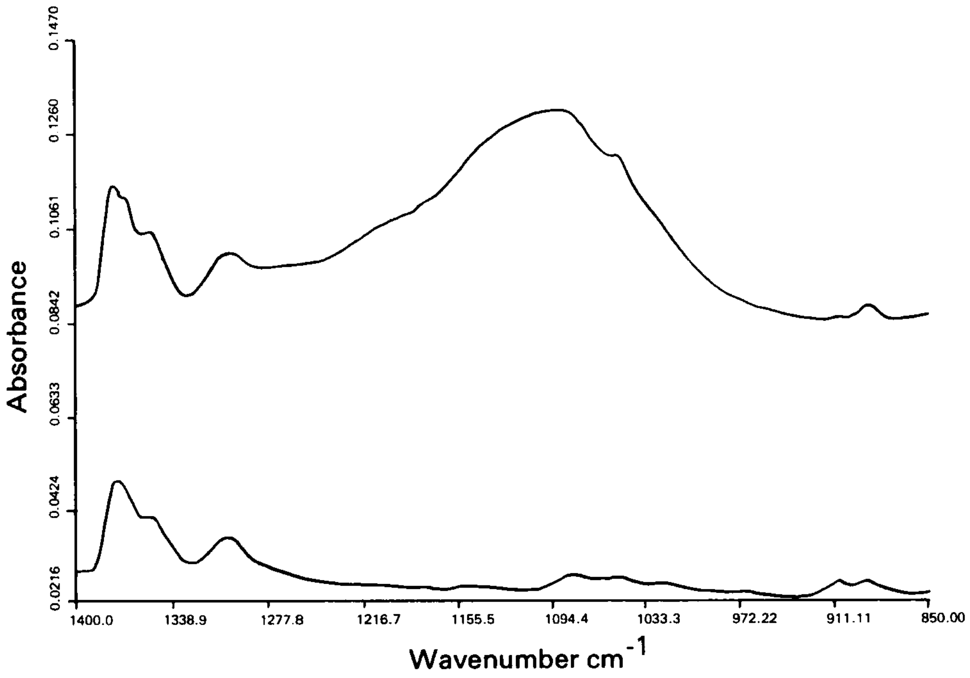

FIGURE 1 FTIR-ATR spectra from untreated LDPE (lower) and LDPE treated with a fluorine/nitrogen mixture (upper). C-F stretching vibrations are clearly visible at about 1090 cm^{-1}. From FTIR and XPS data, it is estimated that the thickness of the fluorinated layer in this sample is 10–100 nm.

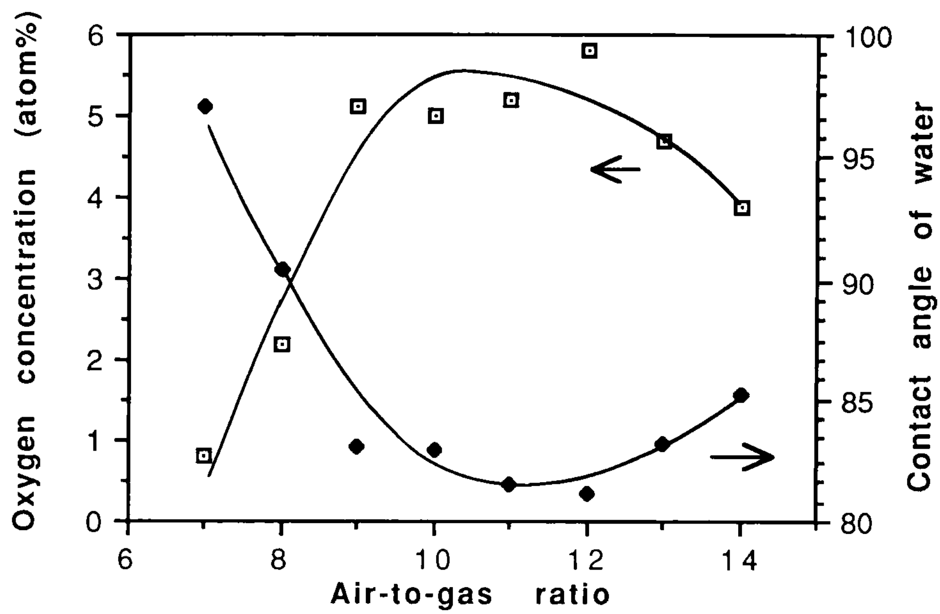

FIGURE 2 The effect of composition of the flame on contact angle and oxygen concentration in the treated surface as measured by XPS. The distance from the inner cone tip was 10 mm and the total flow rate was 24 l min.$^{-1}$

4 DISCUSSION

4.1 Pretreatment of Polyethylene with Aqueous Reagents

Treatment of polymers with aqueous reagents is generally undesirable for environmental reasons and the need to wash and dry the specimens. However, the shape of an item or some other reason may mean that flame, plasma and corona treatments are unsuitable.

Treatment of polyolefins with chromic acid is a well-established method and has been the subject of a number of studies.[10-12] Studies of other aqueous reagents including potassium permanganate[13] and ammonium peroxydisulphate[14] have been carried out, but these have not involved the use of modern surface analytical techniques to elucidate changes in surface chemistry.

The results in Tables I and II reveal some interesting differences between chromic acid, potassium permanganate and ammonium peroxydisulphate. Under the mild conditions described in Table II, chromic acid treatment causes major changes in adhesion levels and surface chemistry, whereas changes due to ammonium peroxydisulphate are small. Potassium permanganate causes intermediate changes.

The results in Table II also show some large differences in the treatments. Potassium permanganate now appears as effective as chromic acid in enhancing adhesion, but discrimination is limited at these failure loads because of failure within the polyethylene. The difference in surface chemistry caused by these two pretreatments is very interesting. With chromic acid, very little 'metal' is introduced into

TABLE I
Pretreatment of LD polyethylene[a] with various aqueous reagents for five minutes at 30°C

Treatment	Analysis (atom %) C	O	Mn	Joint strength[b] MPa
None	99.8	0.2	—	1.0
$(NH_4)_2S_2O_8$	99.6	0.4	—	1.4
$KMnO_4$	97.0	2.8	0.2	7.7
$K_2Cr_2O_7$	95.3	4.7	—	20.0

[a] 'Alkathene' WJG33, a product of BP Chemicals.
[b] Composite butt test.

TABLE II
Pretreatment of LD polyethylene[a] with various reagents for 30 minutes at 70°C

Treatment	Elemental analysis (atom %) C	O	S	Cr	Mn	K	Joint strength[b] MPa
None	99.8	0.2	—	—	—	—	1.0
$(NH_4)_2S_2O_8$	96.2	3.8	—	—	—	—	12.0
$KMnO_4$	52.8	33.6	—	—	12.6	1.0	21.6
$K_2Cr_2O_7$	82.3	14.9	2.2	0.5	—	—	20.9

[a] 'Alkathene' WJG33, a product of BP Chemicals.
[b] Composite butt test.

the polymer surface, whereas with potassium permanganate large quantities of manganese are apparent. The LDPE treated with the permanganate had a brown discoloration and much of the oxygen observed is probably in the form of manganese dioxide. In contrast, the oxygen in the chromic acid treated surface is mainly due to modification of the polymer chains, i.e. the introduction of carbonyl and other groups.[11] This is consistent with the greater symmetry of the high resolution C 1s peak in the case of potassium permanganate, indicating less chemical modification of the LDPE.

Treatment with ammonium peroxydisulphate for 30 minutes at 70°C, although less effective than the other two treatments, still results in a large increase in adhesion. The enhanced adhesion is accompanied by pronounced changes in oxygen level showing major chemical modification to the LDPE. This is in contrast to the work of Morris,[14] who, using ATR-IR found no chemical change to the PE. Morris concluded that the enhanced adhesion was due to the elimination of a weak boundary layer. The results in Table II provide an alternative explanation, i.e. the introduction of chemical groups causes improved wetting and increased interaction across the interface.

4.2 Pretreatment of Polyethylene with Diluted Fluorine

There are at least two explanations for the poor adhesion normally achieved with untreated PTFE. Firstly, PTFE has a very low surface energy and the poor adhesion

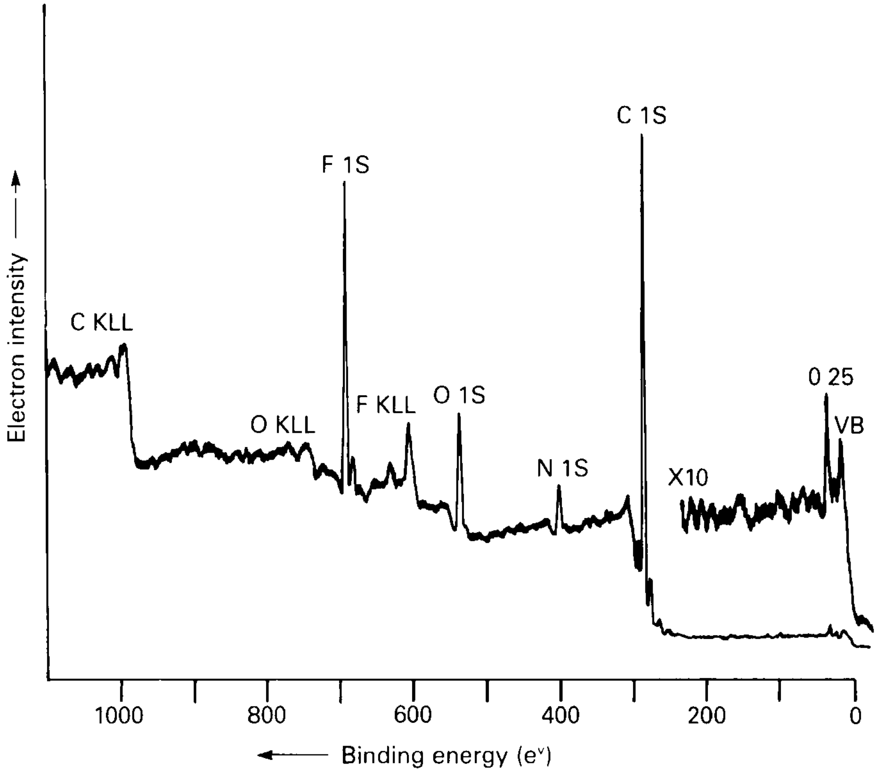

FIGURE 3 XPS survey scan of the surface of an epoxide adhesive cured in contact with PTFE. The PTFE was detached at a very low failure load, but transfer of fluorinated material occurred.

has been attributed to inadequate wetting by adhesives and other coatings. Others have attributed the poor adhesion to a weak boundary layer on the surface of the polymer and there is evidence that such a layer exists, as can be seen in Figure 3; fluorine-containing material is transferred to the adhesive at low failure loads, but quantification of the data was not provided.

With partially fluorinated polymers, the situation appears to be complicated by variations in different grades or batches of these polymers. For example, moderately high levels of adhesion have been obtained[15] with untreated poly(vinyl fluoride), PVF, whereas in other studies poor adhesion was observed.[9] In the latter case transfer of fluorine to the adhesive was observed, although this was in a relatively small quantity. Good adhesion with untreated poly(vinylidene fluoride), PVdF has also been observed.[16,17] PVF and PVdF differ from PTFE and polyolefins in that they have relatively high polar components to their surface energies.[18] This may be the reason why good adhesion can be achieved provided weak boundary layers are absent.

The results in Table III show that treatment of LDPE and HDPE with mixture of fluorine/nitrogen and fluorine/oxygen/nitrogen at room temperature results in large increases in adhesion. In all cases there were large changes in the chemical

TABLE III
Pretreatment of LD[a] and HD[b] polyethylenes with diluted fluorine

Polymer[c]	Elemental analysis (atom %) C	O	F	Joint strength[d] MPa
L1	100	—	—	0.6
L2	52.0	7.1	40.9	17.3
L3	67.0	18.2	14.8	18.3
H1	100	—	—	0.6
H4	58.9	20.2	20.2	18.3
H6	48.2	1.9	49.9	23.5

[a] Riblene (470421/71 ZF 2000) from Enichem.

[b] HD 6007 EA from BP Chemicals.

[c] L and H represent LD and HD polyethylenes respectively. L1 and H1, which were untreated, showed apparent interfacial failure. The other joints showed mixed cohesive failure within the film and adhesive.

[d] Composite butt test. As only one side of the film had been treated, the other side was treated with chromic acid.[6]

compositions of the polyolefins. Even with the fluorine/nitrogen mixture a substantial quantity of oxygen is introduced into the polymer surfaces, either due to small quantities of oxygen in the mixture and/or attack by oxygen or subsequent exposure of the polymers to air.

The outer surfaces of the PE bubbles showed no evidence of any chemical change. As the concentration of oxygen in air is greater than in the fluorine/oxygen/nitrogen mixture, it is apparent that activation of the polyethylenes by the fluorine was necessary for the introduction of oxygen-containing groups.

The surface free energies ranged from 56 mJ m^{-2} for H4 to 28 mJ m^{-2} for H6.[6] The pretreatment of HDPE with a mixture of fluorine and nitrogen (H6) therefore represents another example where good adhesion can be achieved despite a surface energy lower than that of untreated PE; again, this is consistent with a relatively high polar component to surface energy, in this case 4.4 mJ m^{-2}.

The FTIR-ATR spectrum of a sample of LDPE treated with a fluorine/nitrogen mixture (L2 in Table III) is shown in Figure 1. Based on the intensities of the carbon-fluorine stretching vibration and the inelastic electron background of the XPS spectrum, it is estimated that the thickness of the fluorinated layer is in the region of 10–100 nm.

4.3 Flame Treatment of Polypropylene

The flame treatment of LDPE and HDPE bottles especially to enhance print adhesion has been used successfully for many years. In recent years, flame treatment has been used to enhance the adhesion of paint to polypropylene components for cars, e.g. bumpers.

In Table IV, results on the effect of varying the conditions of the flame treatment are presented. The results show that large increases in paint adhesion can be achieved using a wide variety of conditions in terms of air:gas ratio, total flow rate

TABLE IV
Effect of flame treatment on the surface chemistry of polypropylene[a] and the adhesion of a polyurethane paint to the polypropylene

Treatment conditions[b]		Elemental analysis (atom % O)	Joint strength[c] MPa
Air:gas	8:1	2.8	24.7
	9.1	3.1	25.4
	11:1	6.1	26.4
	13:1	4.4	26.7
	14:1	2.8	25.8
Total flow rate (1 min^{-1})	12	1.9	26.0
	18	2.6	25.6
	24	6.1	26.4
	36	6.9	27.2
	48	8.2	24.0
Distance from inner core tip (mm)	2.5	10.5	22.8
	10	6.1	26.4
	20	4.1	22.1
	40	2.8	6.5
	60	1.2	4.2

[a] Homopolymer grade VB 8050B supplied by Nesté.

[b] The standard treatment conditions were:

Treatment time	0.04s
Air: gas ratio	11:1
Total flow rate	24 litre min^{-1}
Distance from inner core tip	10mm

[c] Composite butt test.

and distance from the inner cone tip of the flame. At joint strengths above 22 MPa material failure, either in the PP or the paint, occurred and it is not possible to distinguish between specimens with joint strengths above this level.

The amount of oxygen introduced into the PP surfaces ranges from 1.2 to 10.5 atomic percent. Large increases in adhesion can be obtained with relatively small changes in surface chemistry. Thus with an air:gas ratio of 11:1 and a total flow rate of 12 litres per minute, only 1.9% of oxygen is introduced into the PP surface, but the adhesion level increases more than tenfold. On the other hand, when the plastic is moved to a distance of 40 mm from the inner cone tip, 2.8% oxygen is introduced into the PP surface, but the adhesion level increases by less than threefold. This indicates that in the former case more of the oxygen is in the form of functional groups which are very effective in promoting adhesion.

4.4 Flame Treatment of Ethylene-Chlorotrifluoroethylene Copolymer

The results in Table V show that the flame treatment can provide large improvements in adhesion levels in ECTFE. The pretreatment leads to partial dehalogenation of the polymer and the introduction of a substantial quantity of oxygen. The treatment leads to a large increase in the polar component of surface energy.[8] Improved wetting and increased interaction across the interface between the adhe-

TABLE V
Flame treatment of ethylene-chlorotrifluoroethylene copoylymer (ECTFE)[a]

Treatment time(s)[b]	Elemental analysis (atom %) C	F	Cl	O	Joint strength[c] MPa
0	52.5	33.4	14.1	—	1.2
0.04	72.5	14.0	7.3	6.1	8.2
0.06	68.8	12.2	8.1	6.0	14.9

[a] 'Halar' 300 is supplied by Ausimont.
[b] The standard conditions described in Table IV were used.
[c] Composite lap shear test.

sive and the oxygen-containing groups of the treated ECTFE will lead to enhanced adhesion.

4.5 'Etching' Treatments of Polytetrafluoroethylene and Ethylene-Chlorotrifluoroethylene Copolymer

The results in Table VI confirm that sodium naphthalenide in THF and its commercial equivalent cause almost complete defluorination of PTFE and the introduction of a substantial quantity of oxygen into the polymer surface. The dehalogenation of ECTFE is less complete, but again substantial quantities of oxygen are introduced. It is known[19] that material of low cohesive strength exists on the surface of PTFE (see Figure 3 and Section 4.2). It is not possible, therefore, to state whether in the absence of a layer of low cohesive strength, good adhesion would be obtained with PTFE, or whether the oxygen-containing groups introduced by the pretreatment are necessary for good adhesion.

TABLE VI
Effect of pretreatment of PTFE and ECTFE with 'Tetra-Etch' or sodium naphthalenide for one minute at room temperature

Polymer	Treatment	Elemental analysis (atom %) C	F	Cl	O	Joint strength MPa
PTFE	No	37.4	62.6	—	—	2.1
PTFE	TE	82.0	1.0	—	17.0	21.3
PTFE	SN	87.1	0.4	—	12.4	21.4
ECTFE	No	52.5	33.4	14.1	—	1.2
ECTFE	TE	74.9	12.2	3.8	9.1	10.0

TE "Tetra-Etch."
SN Sodium naphthalenide.

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