Pretreatments of fluoropolymers to enhance adhesion

By

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Abstract

The aim of the project was to gain a better understanding of the factors that affect adhesion of fluoropolymers. This was achieved by employing various analytical techniques to the treated and untreated polymers. The effects of novel pretreatments, and established treatments, on Polytetrafluoroethylene, PTFE, Poly (vinyl fluoride), PVF, and poly (vinylidene fluoride) PVdF, were characterised using: adhesion tests, X-ray photoelectron spectroscopy (XPS), including derivatisation reactions, Fourier Transform Infrared (FTIR), contact angles and scanning electron microscopy (SEM)

For untreated PVF and PTFE it was found that a certain degree of adhesion improvement was achievable without any chemical modification of the surfaces. This was observed when the substrates were repeatedly bonded. It is proposed that weakly cohesive material was present in the polymers and these acted as weak boundary layers when bonded.

Removal of weak boundary layers alone was found to be insufficient to obtain high adhesion with PTFE. Surface functionality, increased wettability and favourable topography all contributed to the high bond strengths observed with 'Tetra-Etch' treated PTFE. 'Tetra-Etch' treatment is used commercially on PTFE but prior to this programme was unreported on PVF and PVdF. The treatment was effective at promoting adhesion for PVF though at a much slower rate than for PTFE. Additional mechanisms to that for PTFE (i.e. electron transfer) are proposed for the action of 'Tetra-Etch' on PVF. These are dehydrohalogenation through electron transfer and an elimination reaction. The same mechanisms are proposed for PVdF.

Flame and low pressure plasma treatments were carried out on PVF and PTFE. Flame was found to be ineffective for PTFE but with PVF chemical modification (oxidation) occurred at the carbon/hydrogen sites. No defluorination was observed; this was in contrast to the mechanism of oxidation via plasmas on PVF, where defluorination, oxidation, ablation, and crosslinking may have all contributed to the high bond strength obtained. Certain plasma treatments were effective at improving the adhesion of PTFE but were slower and caused less modification. Removal of weak boundary layers was proposed as the major factor since oxidation was often slight.

Reaction with solutions of potassium hydroxide (KOH), sodium hydroxide (NaOH) and lithium hydroxide (LiOH) were effective as adhesion pretreatments for PVF and PVdF but not for PTFE. For PVF and PVdF rates of reaction and chemical modification varied with time, temperature, molarity of solution and the nature of the solution i.e. aqueous or alcoholic. The greatest improvement in rate and effectiveness of the treatment for adhesion improvement was on the addition of a phase transfer catalyst to the aqueous solution. It was found for PVF that substantial surface oxidation could be achieved without improving the adhesion. It was suggested that oxidation occurred at sites present in a weakly cohesive layer. Mechanisms of the reactions were considered in terms of neucloephilic substitution and elimination; for PVF and PVdF both are likely. The mechanism of the phase transfer catalyst was investigated and found to be complex. It was found not to be simply a wetting agent but had inherent reactivity on its own. A combination of mechanisms was proposed.

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Chapter 1.

Introduction

1.1 Aims and outline of work

Pretreatments are usually required when fluoropolymers are adhesively bonded or before printing, painting or metalising. The aim of the project was to gain a better understanding of the factors that affect the adhesion of some fluoropolymers. This was achieved by employing various analytical techniques to treated and untreated fluoropolymers. The effects of novel pretreatments, and established treatments, on Polytetrafluoroethylene, PTFE, Poly (vinyl fluoride), PVF, and poly (vinylidene fluoride) PVdF, were characterised using: adhesion tests, X-ray photoelectron spectroscopy (XPS), including derivatisation reactions, Fourier Transform Infrared (FTIR), contact angles and scanning electron microscopy (SEM). The results are discussed in terms of the relative importance of the surface changes brought about by a pretreatment to improve adhesion.

In this chapter the fluoropolymer materials used in the project are introduced and general theories of adhesion are presented. A review of polymer pretreatments is included and the various analytical techniques are discussed.

1.2 Properties and applications of fluoropolymers and adhesives

Fluoropolymers are utilised for their chemical resistance, their "non-stick", low friction and electrical properties. They represent only a small proportion of the world polymer production. Polytetrafluoroethylene (PTFE), for example, is produced in quantities of a few thousand tonnes per year compared with polyethylene which is manufactured in millions of tonnes world wide. In comparison polyolefins are much cheaper and they are used extensively in the packaging market whereas fluoropolymers are reserved for specialist applications.

PTFE was the first fluoropolymer to be exploited for its exceptional properties. More recently, other fluoropolymers have been developed to overcome the processing difficulties that are inherent with PTFE, whilst maintaining the desirable properties such as chemical resistance, electrical properties etc. For example, PTFE has been copolymerized with ethylene and partially fluorinated monomers enabling them to be melt processable.

To reduce costs or enhance properties, fluoropolymers are often used in conjunction with other materials, hence joining of these plastics is an important technology. When the "non-stick" property of PTFE is required the problem of adhering it to the supporting material becomes important. Much research and development has been undertaken to establish methods that enhance the adhesion of fluoropolymers and these are outlined in Section 1.4 of this chapter. For the remainder of this section the properties and applications of the fluoropolymers used in this project are outlined.

1.2.1 Polytetrafluoroethylene (PTFE)

Tetrafluoroethylene gas was first seen to polymerise in 1938 by R.J.Plunket who found it as a white solid within a gas cylinder.

Polymerisation is now carried out with free radical initiators at high temperatures in the presence of water. The resulting polymer has a highly crystalline structure; 93-98 % is typical and it is insoluble in all reagents except under extreme conditions.

The crystalline melting point of PTFE is 327°C and at 300°C it is possible to dissolve it in perfluorokerosine fractions, from which a solution viscosity can be measured and hence an estimation of molecular weight. Molecular weights of millions are typical.

PTFE has a very high melt viscosity (about a million times that of most thermoplastics) arising from the restriction of rotation about chain bonds and the very high molecular weight. The stress required to cause flow in the melt is so high as to cause fracture of the polymer itself, hence conventional melt extrusion processes are not used in the fabrication of PTFE. Typically, PTFE powder is compressed at room temperature into the desired shape then sintered at a temperature greater than the crystalline melting point e.g. 380°C. The rate of cooling after sintering will determine the final crystallinity. If the material is cooled slowly (at around 15° per hour) then 70 % crystallinity is likely; or around 50% if the material is quenched rapidly. The crystalline structure of PTFE is made up of lamellae with the polymer chain direction at 90°. Chain folding occurs outside of the crystal structure. In the case of the material used in this project a cylindrical block had been compressed and sintered. The exact rate of cooling was not known however, there will be a difference in degree of crystallinity between the periphery and the centre of the block. In the centre, where cooling would have been slower the polymer chains will have had more time to be oriented and form crystal structures. At the surface where cooling was more rapid there would be a larger proportion of amorphous regions. A long narrow rectangular film is produced from the cylindrical block by continuous skiving by means of a blade. In terms of the bulk properties of this film there will be a crystallinity gradient along the film as described above. However, the skiving process will result in a different morphology on the new surface. Skiving will cause drawing of the PTFE and subsequent orientation of molecules but also give rise to chain rupture and disorganisation. For adhesion studies the morphology of the skived surface predominates, as PTFE consistently gives low adhesion values.

PTFE has a high impact strength but is strained easily to plastic deformation and creeps under moderate stress. Its desirable properties include high heat resistance and a broad working temperature range (-260 to +260°C), low coefficient of friction, good electrical insulating properties (low dielectric constant and high volume resistivity) and excellent chemical resistance. The material is expensive so applications are limited.

Some examples of applications where PTFE is used are:

Electrical properties - wire and cable insulation although other polymers such as polyimides are growing in preference.
Chemical resistance - chemical plant lining, biological implants
Low friction and 'non stick' properties - non lubricated bearings, cookware, bakeware, mould release agent as a film or as a low molecular weight material in aerosol form.

Fillers are sometimes used to improve certain properties e.g. short glass fibres improve the creep resistance.

1.2.2 Poly (vinyl fluoride) (PVF)

Poly (vinyl fluoride) PVF has the following repeat unit, $-CH_2-CHF-$. It has similarities to the chlorine containing counterpart PVC, except PVF is transparent to (ultra-violet) UV radiation and therefore has excellent resistance to weathering and is used often in laminates.

PVF is a highly crystalline, tough and flexible material. It has excellent chemical resistance and is stable for continuous working up to temperatures of 204°C. Usage at temperatures greater than this can lead to the evolution of hydrogen fluoride (HF) gas, which is highly toxic and corrosive. The PVF used in this project was Du Pont's 'Tedlar' film. Unlike PTFE, this polymer film will have been melt processed. However, such processing will still give rise to some differences between the surface and the bulk morphology due to different stresses in the polymer melt when being extruded. Rate of cooling and time for relaxation of internal stresses are important parameters which may affect the final morphology. The film used in this work is marketed as a release film for purposes including the manufacture of printed circuit boards. The commercial bulletin quotes: " 'Tedlar' films provide outstanding release from phenolic, acrylic and epoxy resin as well as from Cu, oxide and standard press plate surfaces either hot or cold". No release agents had been used in the processing of the PVF and there were no silicones, plasticizers or reinforcing agents present.

1.2.3 Poly (vinylidene fluoride) PVdF

Poly (vinylidene fluoride), $-CH_2-CF_2-$ is crystalline with a melting point of around 160°C. It degrades at temperatures > 380 °C producing HF but can be melt processed safely at 220 - 240 °C. PVdF has good mechanical strength and good chemical resistance

A unique quality of this material is its ability to be made piezoelectric. If a substrate is piezoelectric, mechanical deformation of the substance will produce an electric current, and visa versa, an electric field will result in mechanical deformation of the material. When PVdF is stretched and poled in an extremely high electric field at high temperature the level of piezoelectric property is much more than obtained with other polymers.

The material used in this project had no orientation or poling carried out on it. As in the case of PVF the morphology of the surface regions might be expected to be different to the bulk as a result of melt processing.

1.2.4 Epoxy adhesive

There is a wide variety of epoxy adhesives available with different structural properties. The adhesive has a 'resin' component containing an epoxide ring and a 'hardener' which is usually an amine. Reaction of the two is often accelerated by increased temperature. The product is a cross-linked thermoset plastic. Once cured the adhesive is hard and rigid but can be brittle unless modified. They have advantage over other reaction-setting adhesives in that there is less shrinkage and no volatile products are released on cure. They are classified as structural adhesives and are used in aerospace, automotive and general engineering applications. In addition, they are often used as the matrix resin in composite structures. The product used in this work was a two component, general purpose, untoughened adhesive. The resin was a bisphenol A derivative and the hardener was a polyaminoamide.

1.2.5 Cyanoacrylate adhesive

Cyanoacrylate adhesives are not in general, regarded as structural adhesives due to poor thermal and moisture durability on glass and metal substrates. They cure by an anionic polymerisation mechanism which is catalysed by traces of bases on the adhered; even water is sufficient. The curing is very rapid but can be incomplete on thick sections of adhesive. Additives to the adhesive formulation can alter the cure rate and alter the mechanical properties i.e. reduce the inherent brittleness. The product used in this work had an additive to increase the viscosity.

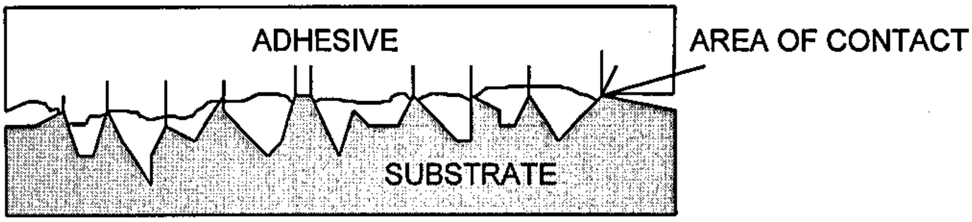
1.3 Theories of adhesion

Adhesion may be considered as the intermolecular force that acts across an interface or the mechanical force required to separate two materials. Studies to improve adhesion between materials might therefore, seek to increase the intermolecular forces, one way or another. However, the requirements for good adhesion are more complex. This section outlines the main theories of adhesion and summarises the requirements for good adhesion.

1.3.1 Mechanical theory

According to this theory the adhesive fills the irregularities of the substrate, so providing a mechanical key resisting separation. Modification of a substrate to increase surface roughness would therefore be considered as advantageous; the resulting increase in surface area of contact would also potentially contribute to improved adhesion. In practice however, because of a high viscosity or surface energy an adhesive may not be able to penetrate the holes in a very rough surface, resulting in voids which may weaken the joint through stress concentrations. In extreme cases the bonding area may even be reduced (Fig 1.1)

Figure 1.1 Extreme case of rough surface and adhesive being unable to penetrate causing poor contact



Alternatively an adhesive may have a very low viscosity but lack gap filling properties resulting in a similar problem.

There is evidence to suggest that for certain systems an increase in roughness is important for improvement in bond strength. For example Packham *et al.*[1] showed its advantage in the bonding of metals to polyethylene.

1.3.2 Adsorption theory

This is probably the most popular theory of adhesion and its focus is the nature of forces acting across the interface of an adhesive and substrate.

There are various forces of attraction that could occur across such an interface ranging from strong bonds, i.e. ionic and covalent (this would then be termed as chemisorption), to weaker intermolecular forces such as van der Waals forces and hydrogen bonding. Van der Waals forces can be dispersion forces, dipole-induced dipole and dipole-dipole attractions. Fowkes[2] proposed that specific interactions can be grouped into two categories: London dispersion forces and acid-base interaction, within which hydrogen bonding is included.

Tabor[3] and others have shown theoretically that dispersion forces alone could account for the highest joint strengths if coverage of the adhesive was complete. In practice however, this would be unlikely and other factors such as stress concentrations may reduce the measured joint strength.

On the basis of this theory it is necessary to wet the substrate so intermolecular forces may operate. By changing the chemistry of the substrate, wetting may be improved. The nature of the interaction (van der Waals, hydrogen bonding etc.) may also be affected by changing the surface chemistry.

There is evidence for the importance of hydrogen bonding in the self adhesion of corona treated polyethylene by Briggs and Kendall[4].

There is limited evidence for chemical bonding at interfaces. Gettings and Kinloch[5] however, detected $FeOSi^+$ ions using Secondary Ion Mass Spectrometry (SIMS) to study a silane primed steel. This indicates the presence of Fe-O-Si bonds.

1.3.3 Diffusion theory

This theory envisages mutual diffusion of substrate and adhesive molecules thereby eliminating the interface and creating an interphasial region. Voyuskii[6] proposed evidence for such a theory in the autoadhesion of rubber under different conditions such as temperature. This theory probably operates in special cases such as bonding an elastomer with an adhesive of similar composition. Solvent or thermal welding of similar plastics is another example and priming of polypropylene with a chlorinated polypropylene primer. A recent symposium has been conducted on the evidence of interphases in adhesion[7].

1.3.4 Electrostatic theory

Derjaguin and Smilga[8] proposed that adhesion was due to the transfer of electrons from one material to another at an interface thereby producing electrostatic attraction. It was observed that some failed joints were charged, but this could have been as a result of the testing. He claimed certain high peel strengths could not be explained by van der Waals or chemical bonds alone. Doubt was thrown on some of Derjaguin's claims by Schonhorn[9] and others who showed that deformation of substrates in peel tests needed to be considered.

1.3.5 Weak boundary layer theory

Before any of the above mechanisms can operate, good wetting of one substrate onto another must be achieved. However, sometimes even when good wetting occurs, the adhesion is poor due to a weak boundary layer in the adhesive joint

The weak boundary layer theory may more appropriately be described as a theory of abhesion, of why substrates are difficult to adhere to. Bikerman[10] first proposed that if a region of low cohesive strength existed between the substrate and the adhesive when bonded, then low bond strengths would result. This region of low cohesive strength he named a 'weak boundary layer' and it could arise from the adhesive or the adherend or external contamination. It is important to note that the terminology refers to a bonded system. Regions of low cohesive strengths on substrates before bonding may not necessarily result in a weak boundary layer when joined. Brewis[11] deliberately contaminated chromic acid treated polyethylene with hydrocarbon grease (about 1 μm thick) to simulate a potential weak boundary layer; the bond strength with epoxy decreased slightly but still remained 7x greater than untreated. In this case the region of low cohesive strength was absorbed by the adhesive and a weak boundary layer did not result. A more recent example is given by Strobel *et al.*[12] who studied the corona treatment of polypropylene (PP). They proposed that treatment produced low molecular weight oxidised material (LMWOM). The adhesion of ink to a surface containing LMWOM was not impaired, in fact in some cases the adhesion was apparently greater.

Possible sources of weak boundary layers (WBLs) in polymers are: external contamination e.g. dust, grease and moisture, or internal components e.g. low molecular weight bulk species, processing aids or any additive that could potentially migrate to the substrate surface.

In a recent review on the importance of WBLs in adhesion, Brewis[13] outlines early examples that report adhesion improvement without chemical modification and which conclude strengthening of weakly cohesive material as the mechanism by which adhesion improvement is achieved. The review also outlines research carried out on similar systems at a later date within which X-ray photoelectron spectroscopy (XPS) was used to analyse the surfaces of the treated substrates. The development of this very surface sensitive technique caused much of the earlier findings to be invalidated as oxygenated species on, for example, treated polyolefins was clearly detected.

In conclusion then, although in regard to polyolefins, there is little direct evidence to suggest removal of weakly cohesive material at a surface to be the major mechanism by which a pretreatment improves the adhesion, there is no evidence to disprove its existence on a substrate before treatment or bonding. It must therefore remain a possibility that a pretreatment may improve adhesion through removing or strengthening surface material as well as introducing functionality. Also adhesion of an oxidised surface containing weakly held material will only result in a weak boundary layer if the LMWOM cannot be incorporated into the adhesive

However, there is clear evidence of WBLs with bonded fluoropolymers which will be discussed in detail in Chapter 4.

Pretreatments can in principle enhance adhesion to polymers by three mechanisms, namely: removal of potential weak boundary layers, increased surface roughness and introduction of new chemical groups

1.3.6 Summary

As far as this thesis is concerned, the most generally accepted theory of adhesion, i.e. adsorption will be assumed. However, continual attention will be given to potential weak boundary layers.

1.4 Pretreatments for polymers

In general polyolefins and fluoropolymers are some of the most difficult polymers to adhere to and they usually require some form of pretreatment before adhesive bonding, painting, printing or metalising can take place.

Theories of adhesion and criteria for good adhesion have been outlined in the previous section. This section describes the various pretreatments that seek to bring about the requirements for good adhesion i.e. good contact between substrate and adhesive, favourable interactions across the interface and the absence of a weak boundary layer at the interface. Roughening of a surface by a pretreatment may be beneficial due to increased surface area and the possibility of mechanical keying

Several reviews of polyolefin and fluoropolymer adhesion have been published[14-20] Some of the major pretreatments are now discussed with emphasis on those used with fluoropolymers.

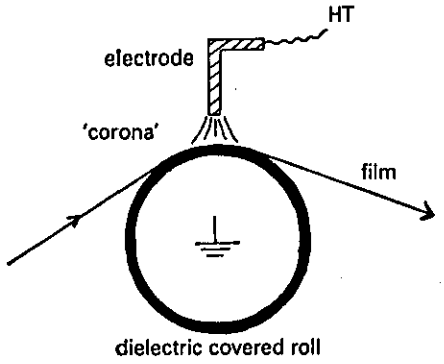
1.4.1 Corona discharge

In around 1950, corona treatment was introduced to enhance print adhesion to low density polyethylene (LDPE). Corona discharge treatment is still the major pretreatment for polyolefin film and some simple shaped products such as cylinders. It is also used for other films including poly (ethylene terephthalate) (PET).

A schematic diagram of the film treating process is shown in Figure 1.2.

A high voltage made across the electrode and the roll generates a plasma between them (atoms, ions and electrons from the air). A plasma at atmospheric pressure is commonly called a corona discharge. Low pressure plasmas will be discussed as a separate pretreatment in section 1.4.3.

Figure 1.2 Schematic diagram of the corona discharge treatment of film



Briggs and co-workers[21,22] first applied the use of XPS and surface derivatisation to polyolefins to identify the oxidised species introduced by a corona treatment[21-24]. Information from XPS and other methods identified the following species: carbonyl, enol, carboxylic acid, esters, ethers, nitrite and hydroxyl groups. It was shown that an oxygen to carbon ratio of ~4% on LDPE gave good adhesion with ink and that adhesion to ink was facilitated through enolic -OH groups in the discharge treated surface. In the autohesion of corona treated PE it was shown that OH groups were the most crucial to autoadhesion. Just 0.4% of C-H converted to C-OH was capable of giving good adhesion.

The mechanism of corona treatment[15] is based on free radical formation resulting in oxidation and possibly crosslinking of the surface.

Brewis and Briggs[14] first reported that overtreatment of polyolefin film caused low molecular weight oxidised material that may or may not affect subsequent adhesion. More recently Strobel *et al*[25-27] investigated the generation, properties and practical effect of low molecular weight oxidised material (LMWOM) on corona treated polyolefins. They showed that washing polypropylene with polar solvents like water after corona treatment gave less oxygen and a less wettable surface than unwashed corona treated polypropylene. This underlined the importance of checking the reliability of contact angle measurements. They gave further evidence of removal of LMWOM by measuring weight change after washing; 0.3-0.4% weight loss was recorded (equivalent to a 150 nm layer). Aging effects on the polypropylene were minimal. Only a small decrease in wettability was observed on aging at ambient temperatures and was attributed to the reorientation of oxidised functionalities within the treated-surface region. In contrast corona treated poly (ethylene terephthalate) showed extensive migration and reorientation of oxidised groups resulting in decreased wettability and loss of oxygen at the surface. Ink adhesion was seen to be better on unwashed samples.

1.4.2 Flame treatment

Flame treatment was developed around 1950 to enhance print adhesion to LDPE bottles. The majority of thick section articles are still treated in this way.

Burners, such as shown in Chapter 2.3.2 (Figure 2.1) are used to treat the product by passing it in front of the flame; treatment times are usually a fraction of a second. The burners are fed with an air:alkane gas mixture. An optimum treatment is achieved with an oxidising flame; an excess of 10 % oxygen over the stoichiometric value is recommended[28].

Flame treatment of LDPE was carried out by Briggs *et al.*[29] and using XPS they showed that the level of oxidation was similar to that achieved with a chromic acid treatment e.g. oxygen concentration of typically 20 atom %. The introduction of 0.02 % of an antioxidant into the polymer did not reduce the level of incorporated oxygen nor did it have a detrimental affect on adhesion. The depth of oxidation was estimated at 4-9 nm and no aging effects were observed.

Garbassi *et al.*[30] carried out multiple flame treatments on polypropylene and used secondary ion mass spectrometry (SIMS) to establish that oxidation had taken place in the pendant methyl groups. They also supported the idea that OH groups were most influential on the adhesion between a polyolefin (polypropylene) and paint.

Some recent work by Sutherland *et al.*[31] showed how the oxygen incorporation in a polypropylene (PP) surface increased as the air to gas ratio was increased from oxygen deficient to that of complete combustion. Further increase of air gave rise to less PP surface oxidation The maximum oxygen incorporation was ~ 5.5 atom

% (air:gas = ~10) . In the same study they showed how other variables such as intensity of the flame, separation between the sample and the flame's cone tip and contact time affected oxygen incorporation and wettability. Surface oxygen concentration increased as the flame intensity increased (from a flow rate of 10 to 50 l min^{-1}) but at high flow rates there was not a close correspondence between water contact angle and oxygen concentration. Increased sample-flame separation reduced oxygen incorporation but contact time showed little effect on oxygen concentration under the conditions studied. The adhesion to paint was assessed with butt tests and found to be good for all, even mild treatments.

Although the majority of literature on flame treatment is applied to polyolefins, partially fluorinated polymers have been found to be effectively pretreated with a flame[32,33]. Ethylene-chlorotrifluorethylene copolymer was treated for 0.04 and 0.06 seconds using the apparatus described in this work[33]. Adhesion was improved 7 and 12 fold respectively and both treatment times produced similar levels of oxygen and dehalogenation. Hong *et al.*[32] flame treated poly (vinyl fluoride) (PVF) and observed oxidation using XPS. In the same study, surface infrared (ATR-IR) results showed there was a decrease in the concentration of hydrogen and fluorine species in the amorphous polymer. Both XPS and ATR-IR results suggested that for an optimum treated sample, ether linkages were the major environment for the oxygen, with little evidence of any other oxygenated species. This lead them to conclude that the flame treatment eliminated a region of weakly cohesive material at the surface through crosslinking.

1.4.3 Plasma treatment

A plasma has been described as the fourth state of matter; i.e. a gas that has been elevated to a higher energy state; it will include atoms, ions, electrons, free radicals and activated molecules. In the context of this work 'plasma' is used to describe a low pressure plasma i.e. a gas containing activated species that is neutral overall. The two previous treatments outlined, i.e. corona and flame are examples of plasmas at atmospheric pressure.

Chemical modification of materials by plasma treatment is based on a free radical mechanism. Free radicals may be generated at sites within the material by impingement of free radicals contained in the plasma, or alternatively UV radiation, also present in the plasma, can create free radicals in the substrate[34].

The plasma may have a number of effects on the material being treated: ablation, roughening, crosslinking and introduction of new chemical groups. A review of plasma treatment for bonding improvement is given by Liston[35]

A plasma treating system consists of a vacuum system, a power supply which could be radio, microwave frequency etc. connected to an impedance matched network and a reaction chamber into which the gas flows. Unless otherwise stated the following examples employ a radio frequency generator (13.56 MHz).

In 1966 Hansen and Schonhorn were among the first to report the use of activated inert gases (helium) at reduced pressure to pretreat polyethylene and PTFE[36,37]. They reported the loss of hydrogen and fluorine, respectively, from the polymers after treatment and an increased adhesion to epoxy adhesive to around 20 MPa in the case of polyethylene; this is comparable to strengths obtained using chromic acid treatment. They proposed that the improved adhesion was due to the formation of a crosslinked surface layer, which in the case of polyethylene, they managed to isolate as an insoluble gel. For PTFE this was not possible due to the insolubility of PTFE. However, they showed that exposure of perfluorokerosine to a prolonged plasma (16 hours) resulted in the formation of a hard, brittle, solid and attributed the improved adhesion of PTFE to the formation of a crosslinked surface too. They reported no change in the wettability for either polymer after treatment. The treated surfaces were analysed using ATR-IR and the presence of trans-ethylenic unsaturation in the treated polymers was confirmed by the removal of peaks at 964 cm^{-1} for polyethylene and 982 cm^{-1} for PTFE after exposure to bromine in carbon tetrachloride in the dark. The adhesion after bromination was equally good as samples before characterisation with bromine, hence the presence of unsaturation was not thought to contribute the improved adhesion. They named the treatment CASING (Crosslinking by Activated Species of INert Gases).

In the same study PVF and poly (vinylidene fluoride) (PVdF) were treated with the CASING process. The adhesion of PVF was improved but untreated PVdF had a relatively high joint strength and no further improvement was achieved with treatment.

A dispute of Schonhorn's claim came in 1968 when Malpass and Bright[38] reported glow discharge (plasma) treatment of polyethylene in argon and helium and they did observe a reduction in contact angle on the treated samples and suggested that oxidation would explain their observations. Sowell *et al.*[39] also used an argon plasma to improve the adhesion of polyethylene and found an increase in wettability of the treated surface.

In 1969 Hall *et al.*[40] treated a number of polymers including polyethylene, polypropylene and PVF with activated helium and oxygen plasmas. They carried out composite lap shear adhesion tests using an epoxy adhesive. The oxygen plasma treated polyethylene gave bond strengths of the same order of magnitude as the inert gas plasma treated samples and in the case of low density polyethylene (LDPE) the failure was cohesive within the polymer. The bond strength of polypropylene however, was increased by an oxygen plasma but not a helium plasma. They explained the difference in response of polypropylene and polyethylene to a helium plasma was due to the fact that polypropylene had a greater tendency to chain degradation. This was suggested from ATR-IR results of the polypropylene showing unsaturation produced by chain scission. The adhesion of PVF was increased nearly 5 fold after both oxygen and helium plasmas.

In further studies by Hall *et al.*[41] they treated PVdF with helium and oxygen plasmas and found an increase in adhesion of ~ 10 times that of untreated. This was in contrast to the work of Schonhorn and Hansen[37] mentioned earlier. However, the Schonhorn work reported high bond strengths with untreated PVdF. It is important to note the variation in untreated values of some polymers that may be indicative of batch to batch variation in these substrates or different adhesives.

The growing importance of XPS in the 1970s gave greater understanding to the effects of plasma treatment of polymers. Collins *et al.*[42] used XPS together with ATR-IR, SEM, contact angles and adhesion tests to look at the effect of ammonia and air plasmas on PTFE. They showed that the depth of chemical modification of the PTFE with the NH_3 increased as the reaction time increased; only at greater than 30 mins treatment time were nitrogen functionalities observed with ATR-IR whereas nitrogen was seen in XPS spectra even at the shortest time of 2 minutes. The adhesion tests gave values greater than 3.2 MPa for a one minute treatment time (they did not give an untreated value). They report that the modified region was brown in colour which could be removed by immersion in nitric/perchloric acid. This also reduced the wettability of the surface in most cases. Re-examination with XPS indicated surface compositions close to that of untreated. For air plasma treated samples they found that 0.08 mm thick tape had disintegrated after extended treatment which they explained as the result of surface ablation.

Inagaki *et al.*[43] also employed an ammonia plasma on PTFE with similar analysis and results. In this case the modified PTFE was bonded to a nitrile rubber using a phenol type adhesive and peel tests were carried out. They found that the maximum peel strengths of 8.1×10^3 N/m were achieved at a modification temperature of 200°C; the failure was cohesive within the PTFE. XPS results showed no nitrogen when the treatment was carried out at room temperature. The F/C was 1.66 and O/C was 0.06. Treatment at 230°C yielded F/C ratios of 0.61 and O/C 0.52.

Yasuda *et al.*[44] used XPS to characterise the surfaces of nitrogen and argon plasma treated polymers. Quantification was not reported but a substantial amount of oxygen was incorporated in argon and nitrogen plasma treated polyethylene; a large amount of nitrogen was also found in the nitrogen plasma treated sample. Argon and nitrogen plasma treated PTFE gave rise to a 10 fold increase in the O1s intensity (a small amount was evident in the untreated material) and a 75 % decrease in F1s intensity.

An XPS study on the effect of a series of inert gases on one particular fluoropolymer (ethylene-tetrafluoroethylene copolymer) was carried out by Clark and Dilks[45]. Helium, neon, argon and krypton were compared. Helium was found to be the most effective gas plasma for crosslinking the outer few monolayers of the polymer, but crosslinking of subsurface and bulk was best effected by neon.

In a later study, Clark and Hutton[46] treated PTFE and PVdF with a hydrogen plasma for various times. They used variable angle XPS and showed there was more defluorination of the PTFE at the near surface region. This effect was seen very rapidly (treatment times of < 1 minute). Oxygen levels however, were fairly uniform within the sampling depth of XPS. PVdF also showed extensive and rapid defluorination that exceeded the levels of defluorination of PTFE at long treatment times.

Some reports of plasma treatment of PTFE show little oxidation or defluorination of the surface. For example, in a study by Golub *et al*[47] PTFE was exposed to an oxygen plasma (reaction conditions were not included in the report) and no significant amount of oxygen was seen using XPS; the same was true for a fluorinated ethylene-propylene (FEP) sample. In contrast, the same treatment on PVF showed extensive oxidation (~16%) and some defluorination.

Wettability studies of oxygen plasma treated PTFE, tetrafluoroethylene-ethylene copolymer (TFE-E) and PVdF was carried out by Hirotsu and Ohnishi[48]. Treated PTFE exhibited a fall in water contact angle from 126 to 100 degrees and was stable to aging in air. The water contact angle of treated PVdF was reduced from 102 to 77 degrees but increased slightly after 3 days aging in air.

A more recent report on surface characterisation of PTFE after oxygen and argon plasmas is given by Morra *et al.*[49]. They showed that after exposure to an oxygen plasma for 15 minutes the sample became deeply etched. Oxygen incorporation increased for treatment times of up to 2 minutes then the level fell for treatment lengths up to 15 minutes. This effect was seen in peak shifts within the C 1s XPS peak. After 2 minute plasma exposure times the C 1s peak was indicative of carbon bonded to hydrogen and oxygen functionalities, then after 15 minutes there was an almost complete restoration of the carbon peak at higher binding energy representing carbon bonded to fluorine. After an argon plasma however, although this produced the same initial high oxygen incorporation and subsequent reduction after 15 minutes (though not down to zero), the C 1s peak after 15 minutes still showed a peak due to C-H. They proposed that for both type of plasmas there were two competing reactions occurring in the chamber: firstly defluorination and oxygen incorporation, and secondly etching that revealed underlying PTFE-type porous material. They suggested that for an oxygen plasma chemical modification was dominant in the first instance but later a steady state was reached where etching predominated. In the case of an argon plasma the steady state reached was a different balance of the two processes.

Aging effects with respect to wettability were seen with an argon plasma but not with an oxygen plasma.

An example of plasma generated by microwaves rather than radio frequency was give recently by Kasemura *et al.*[50]. They in fact, used a vessel at reduced pressure within a domestic microwave oven (560 Watts, 2450 MHz). They carried out this treatment on PTFE and FEP and analysed the materials with contact angles, peel tests, XPS and SEM. XPS confirmed oxidation of the PTFE and FEP after 10 seconds of treatment which improved the wettability. Peel strengths increased as the duration of treatment increased.

It has been shown by Griesser *et al.*[51] that contact angles measured on FEP treated with an argon plasma (10 Watts, 700 KHz) varied as the samples aged in air. As a result of the treatment the sessile water contact angle was reduced from 100 to 80° The contact angles rose within a 3 week aging period then levelled off at around 90° over the next few weeks. XPS results however, did not show a corresponding reduction in oxygen to account for the apparent reduction in polarity or any indication of surface contamination. Therefore, surface reorientation within the sampling depth of XPS was concluded.

Plasmas may also be used to deposit or graft specific molecules or monomers onto the surfaces of materials but this is outside the scope of this work and will not be reviewed.

1.4.4 Chemical treatments

The three previous methods to enhance adhesion have been applied to both fluoropolymers and other polymers. In this section a review of chemical pretreatments specific to fluoropolymers is given, with greater emphasis to the sodium complex treatments due to their relevance to this work.

Sodium naphthalenide and sodium in liquid ammonia treatments

A patent for the treatment of fluoropolymers in sodium in liquid ammonia was obtained by the Minnesota Mining and Manufacturing Co. (3M) in 1957[52]. PTFE which is normally white was turned black by the mixture and this was attributed to the formation of carbon via the extraction of fluorine from the polymer chain. Evidence from this came from the detection of fluoride ions in the treatment bath[53].

Around the same time, at the Diamond Ordnance Fuze Laboratory, Washington, an organic synthesis experiment employing a sodium-naphthalene complex in tetrahydrofuran (THF) was being investigated. A PTFE coated stirrer used in the reaction vessel was found to be black after immersion in the mixture[54]. Experiments were carried out on PTFE treated with the complex to assess its bonding characteristics. A one molar solution of the complex was made up (i.e. 1 mole of sodium, 1 mole of naphthalene in 1 litre of THF) and stirred for two hours at room temperature, the PTFE was immersed for 15 minutes then washed in acetone and finally with water. In a lap shear test the bond strength was 11 MPa for a sample treated for 15 minutes but it was reported that bond strengths were similar for treatment times of 30 seconds to 2 hour treated samples.

During publication of the above a patent was granted to G.Rappaport (General Motors) covering a similar method except dimethyl glycol ether was used instead of THF[55] . A later report by Benderly[56] describes more fully the sodium naphthalene treatment and notes its effectiveness on FEP and poly (chlorotrifluoroethylene) (PCTFE - "KEL-F"). The report also gives a comparison with other treatments such as radiation induced grafting and corona; in joint strength comparisons the sodium etching treatment was more effective.

Wettability studies were carried out on untreated and 'Tetra-Etch'[a] treated PTFE by Cirlin and Kaeble[57]. Contact angles indicated that a highly polar surface was produced. The report is mainly concerned with roughness and contact angle anisotropy effects. It was found that the roughness effect on wettability of PTFE was significant for the low energy untreated material but negligible when the surface was treated and had a high surface energy.

Fluoropolymer surfaces treated with the sodium complex undergo degradation in the presence of ultraviolet light[58]. Meier and Petrie treated PTFE film with a sodium etch (details were not given) and then bonded it to a polyurethane with an unspecified adhesive. Peel strengths were found to decrease as a function of

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[a] 'Tetra-Etch' is a product of W.Gore & Associates. It is a sodium complex in organic ether; it produces almost identical surface effects as sodium naphthalenide in THF on PTFE[44].

exposure of the joints to UV (The samples were irradiated in a Weather-Ometer, temperature = 45°C, the wavelengths of the radiation were near that of sunlight). An ATR-FTIR spectrum of the treated surface showed a band at 1600 cm^{-1} which they attributed to the carbonyl of $COO^{+}Na^{-}$ based on the assumption, quote: " that the main effect of sodium etching of PTFE surfaces is the oxidation of surface sites to acids followed by sodium salt formation". In the absence of analysis such as XPS the actual presence of sodium was unconfirmed. They reported other bands around 1650 - 1730 cm^{-1}, which after exposure to UV were changed; the 1650 band was weakened and the 1705 band increased. They suggested the former was due to -C=C- conjugated to a carbonyl but apparently contradict themselves by also quoting there was no evidence for unsaturation in the etched surface. The stability of the etched PTFE bonds was improved by the incorporation of UV absorbers. Carbon black was used in the PTFE and hydroquinone in the adhesive. This gave a 60 % retention of bond strength after 500 hours in the Weather-Ometer compared with samples not containing additives.

XPS analysis of fluoropolymers treated with sodium complexes was first carried out by Brecht *et al.*[59], and Dwight and Riggs[60] independently. Brecht *et al.* treated PTFE with sodium in liquid ammonia and sodium naphthalenide in THF. XPS analysis was carried out on the treated surfaces. The results showed that PTFE treated with sodium naphthalenide for 30 seconds did not have sodium at the surface which would throw doubt on the previous reference's suggestions of the sodium salt formation[58] as part of the mechanism. The concentration of fluorine at the surface was reduced from a F/C ratio of 2 for untreated, to 0.17 after 30 seconds of treatment. Oxygen was introduced resulting in an O/C ratio of 0.2. Sodium in liquid ammonia treated PTFE was subjected to a number of post treatments. After exposure to UV the surface contained more fluorine than newly treated. A sample exposed to 400°C exhibited a surface composition equivalent to that of untreated PTFE.

Dwight and Riggs[60] carried out a similar study on FEP treated with sodium in liquid ammonia. No fluorine was evident at the surface and a large amount of oxygen was incorporated. The XPS C 1s peak from the treated FEP was peak fitted with 3 Gaussian peaks to give ratios of 4.8/1.7/1.0 for CH/C=O/COOH. ATR-IR confirmed the presence of C=O. Water contact angles were low, indicating a polar surface and hysteresis was high probably due to roughness. They reported that

PTFE gave qualitatively, very similar results to FEP and likewise with sodium naphthalenide treatment of both. They reported that ATR-IR analysis of FEP treated with sodium complex did not show unsaturation. However, after immersion in a solution of bromine in carbon tetrachloride XPS showed bromine at the surface. A shoulder to the higher binding energy side of the C1s peak was increased in this spectrum and could be said to be C-Br as the oxygen intensity remained the same. Thus the presence of unsaturation in sodium complex treated FEP was suggested.

In the same study, soft X-ray fluorescence (SXRF) spectroscopy was used to observe the increase in depth of etching with time. After just 5 seconds treatment on PTFE the SXRF fluorine intensity had fallen by 10%, this corresponded to 75% of the total decrease after 60 seconds. The rate of fluorine loss was less rapid for FEP. An estimate of the modified depth after 60 seconds of treatment based on these results was said to be 0.3 μm for PTFE and 0.07 μm for FEP.

Abrasion, heat and light all reduced the peel strength of the treated substrate and this was attributed to the removal of the oxidised material at the surface and exposure of underlying fluoropolymer. However, when a treated sample was placed in boiling water oxygen functionalities were diminished without any fluorine emerging. Immersion in sodium hypochlorite for one hour resulted in the formation of fluorocarbon and hydrocarbon peaks and some oxygen. Table 1.1 summarises the post treatments and the effect on peel strength and water contact angle.

Table 1.1 FEP treated with sodium in liquid ammonia with various post treatments

Treatment	Peel strength/Nm^{-1}	water contact angles/°	
		advancing	receding
None	0	109	93
Na/NH$_3$	1491	52	16
+ abrasion	789	66	25
+ 96 h at 200°C	439	101	74
+ 100 h in Fadeometer	0	91	36
+ 16 days in boiling water	877	54	0
+ sodium hypochlorite	*	50	0

* no value was reported but it was stated to be high

Further studies into the action of heat on PTFE which had been treated with 'Tetra-Etch' was carried out by Rye and Kelber[61]. Thermal desorption spectroscopy with mass spectrometry (TDS-MS) was used to detect products desorbing from the treated material as it was heated. It should be noted that desorption was not necessarily from just the surface. XPS was also used to analyse surfaces before and after desorption. It was found that as etch time increased the amount of desorbed products such as fluorocarbons, N_2, CO etc. decreased. Hence, it was concluded that 'Tetra-Etch' treatment removed low molecular weight species as well as oxidised the surface.

In regard to Dwight and Riggs' claim that the action of heat led to desorption of an oxidised overlayer (see above), Rye and Kelber disputed this. They observed that after heating, the increase in surface fluorine occurred at a higher temperature than the loss of surface oxidised species. They concluded that the re-emergence of fluorine at the surface after heating was a result of diffusion of low molecular weight fluorocarbons from the bulk or a rearrangement of the sponge like surface.

Ha *et al.*[62] have recently carried out a detailed study on the sodium naphthalenide treatment of PFA - a copolymer of tetrafluoroethylene and perfluoroalkyvinylether.

They used the following derivatisation reactions in conjunction with XPS, UV and quantitative IR to characterise the surface of PFA treated for one hour.

Reagent:	functional group detected:
2,4 dinitrophenyl hydrazine	$C=O$
bromine	$C\equiv C$ $C=C$
trifluoroacetic anhydride	OH
sulphur tetrafluoride	$COOH$

Mass loss results indicated partial defluorination to a depth of ~ 115 nm after treatment. Water contact angles were reduced from 104 to 41°. The results are summarised in Table 1.2.

The results suggest that the oxidised functionality is concentrated in the top few layers.

Table 1.2 Average number of functional groups per 100 carbon over a depth of 115 nm and <5 nm

Functional group	115 nm (IR)	5 nm (XPS)
carbonyl	0.25	16
hydroxyl	0.33	5
carboxylic acid	0.02	-
alkene	25	
alkyne	20	34
aliphatic carbon	3.5	

They expanded the study to different fluoropolymers i.e. PTFE and FEP, and experimented with different treatment conditions[63]. They found that the defluorination process was little effected by the nature of the fluoropolymer or the crystallinity but that the surface area was the dominant variable in affecting the amount of defluorination. Washing after treatment was found to influence the type of oxygen containing groups produced. Less OH groups were seen when the sample was washed with just THF and not water. This was confirmed by using D_2O instead of water; the OD stretch was seen in IR .

Benzoin dianion

Reduction of PTFE with benzoin dianion (K_2 { PhC(O)C(O)Ph }) in THF was reported by Costello and McCarthy[64]. The reagent forms a radical anion as in the case of sodium naphthalenide but renders the PTFE a metallic gold colour rather than black. On exposure to air for 1-2 days the colour faded. The colour was said to be due to absorbance/reflection and not interference as indicated by the morphology and by the fact that the colour was independent of thickness (after a certain treatment time). Gravimetric analysis indicated a loss of 3.8 fluorine atoms per monomer unit and XPS confirmed the presence of very little fluorine and a small amount of oxygen at the surface. The oxygen level increased on exposure to air. No adhesion tests were reported.

Iqbal *et al.*[65] proposed that benzoin dianion reduced PTFE had a surface containing mainly trans polyacetylene (trans $(CH)_x$) with polyene conjugation lengths of 12-28 olefin units based on results from Raman, FTIR and SEM studies. These results were questioned by Costello and McCarthy[66] on the grounds of the unquantitative nature of Raman spectroscopy. However, the use of deuterated DMSO in the process indicated that the protons in the polyacetylene $(CH)_x$ originated from the solvent.

A later study by Costello and McCarthy[66] involved reaction of the reduced PTFE surface with specific reagents to produce controlled functionality on the surface e.g. halogen, hydroxyl, amino, and carboxylic acid functionalities.

Electrochemical reduction

PTFE was found to be reduced with electrochemically generated tetraalkylammonium radical anion salts[67] and also with direct electrochemical reduction in THF[68]. In the latter case, PTFE was placed in contact with a cathode whose potential, compared with a saturated calomel electrode, was more negative than -1.5 V; the solvent was aprotic (e.g. THF) and contained a tetraalkylammonium support electrolyte. From the point of contact a black product grew. The appearance, and bonding and wetting characteristics were very similar to that of sodium naphthalenide treated PTFE. Anisotropic effects were obtained when skived tape, ram extruded rod and unsintered calendered films were treated compared with a pressed film[69]. This was probably due to alignment of chains and stress concentrations.

Group I hydroxides

An early report on the immersion of PVdF in 75 % aqueous potassium hydroxide at 145°C for 30 seconds was given by Brewis and Dahm[70]. They observed that the material blackened and gave an increase in bond strength from 15 MPa to 28.3 MPa in a butt test. The treatment was severe and later studies are reported on the use of phase transfer catalysts (PTC) with Group I hydroxides to enhance the reactivity of the solution towards PVdF[71-73].

Kise and Ogata[71] used 0.16g of tetrabutylammonium bromide (TBAB) in 20 ml of 0.1 M sodium hydroxide (NaOH) at 70 °C to treat PVdF powder. Using infrared they observed that carbon-carbon double and triple bonds were present in the product. These may be formed by the elimination of one or two HF molecules from the polymer chain respectively. A band was observed around 1700 cm^{-1} but for all samples it was small, hence carbonyl was not considered to be a dominant reaction product. Samples that had a high percent conversion had no CH adsorptions present and the CF bands were much diminished.

Reaction with films gave similar infrared results and showed a reduction in water contact angle from 77 to 60°. They did not carry out any adhesion tests.

In the same study they included treatment of PVdF with potassium hydroxide (KOH) in propan-2-ol; the reactivity was greater than the reagent containing NaOH and TBAB. Infrared studies gave evidence for the presence of OH groups after the alcoholic treatment

Dias and McCarthy[72,73] reported XPS, ATR-IR, UV, contact angles and SEM analysis of NaOH plus TBAB (0.1g in 150 ml of 8 M NaOH) treated PVdF film. They observed that the addition of TBAB, increased the rate of reaction by at least two orders of magnitude. They suggested that once the surface had undergone elimination, the surface then inhibited further elimination deeper into the polymer. An estimation of the depth of treatment using gravimetric analysis gave a value of 10.6 ± 0.8Å. Also, in contrast to the work by Kise and Ogata[71] they observed no difference in the ATR-IR spectra of treated and untreated PVdF.

A detailed infrared study of PVdF treated with 25% NaOH and tetrabutylammonium hydrogen sulphate TBAH[74], gave evidence for CH=CF and CF=CF bands at 1613 and 1717 cm^{-1} respectively. The later group were said to possibly originate from head to tail defects in the repeat units of the polymer.

Crowe and Badyal[75] treated PVdF with lithium hydroxide (LiOH) (no phase transfer catalyst). When the treated material was washed in water XPS showed evidence for oxidised carbon species and a decrease in fluorine concentration. The fluorine peak was a single species. All of the LiOH solution was assumed to have been removed as there was no Li 1s signal. When alcohol was used to wash the LiOH solution from the treated sample XPS analysis showed fluorine present as two different species. These they attributed to covalent and ionic fluorine. Li was also detected. They presented this as evidence of a reaction occurring between the PVdF and LiOH at the solid-solution boundary. The Li peak was too small to differentiate between Li-F and Li-OH. No colour change was seen after treatment. A simple adhesion tape test indicated an improvement in bond strength but no further quantitative tests were reported.

1.5 Theory of analytical techniques

Many techniques may be used to study the physics and chemistry of polymer surfaces. However, the techniques which have proved most useful when considering adhesion of surfaces are X-ray photoelectron spectroscopy XPS, Static Secondary Ion Mass Spectrometry SSIMS, reflection infrared, contact angle measurement and Scanning Electron Microscopy SEM. With the exception of SSIMS these techniques have been used in the present study. The principles and procedures are now outlined.

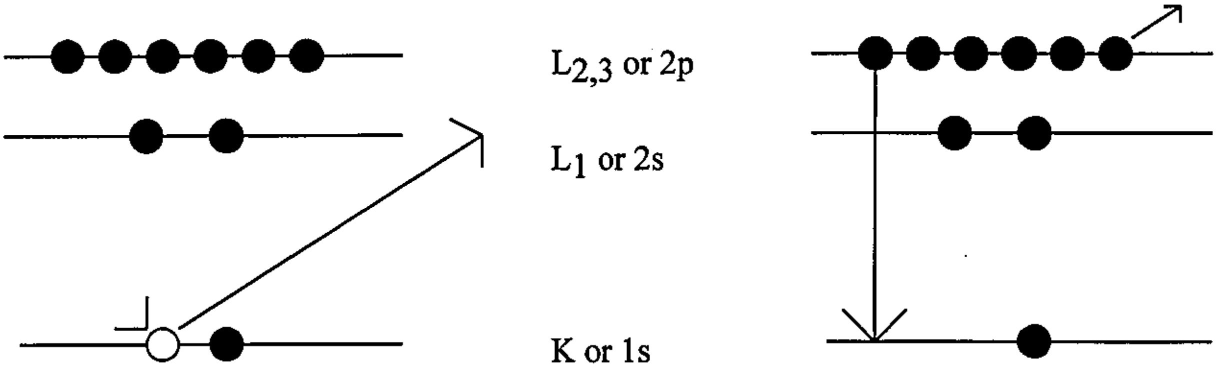
1.5.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy, XPS is a surface specific technique that can provide chemical compositional data for all atoms apart from H. For a particular atom it is also possible in some cases to determine the chemical state of the atom. More detailed chemical state information may be obtained when XPS is used in conjunction with derivatisation reactions. Different surface depths may also be probed. This section outlines the theory, the instrumentation, how quantification is achieved and the particular conditions employed in this project.

General Scheme

The sample to be analysed is placed within a vacuum chamber and irradiated with soft (i.e. low energy) X-rays; usually Al K_α or Mg K_α which have energies of 1486.6 eV and 1253.7 eV respectively. Photoemission of core level electrons within the sample may occur and the possibility of subsequent Auger electron emission; Figure 1.3 describes the two processes.

Figure 1.3 **XPS and AES emission processes**



X-ray photoelectron spectroscopy XPS

Auger electron spectroscopy AES

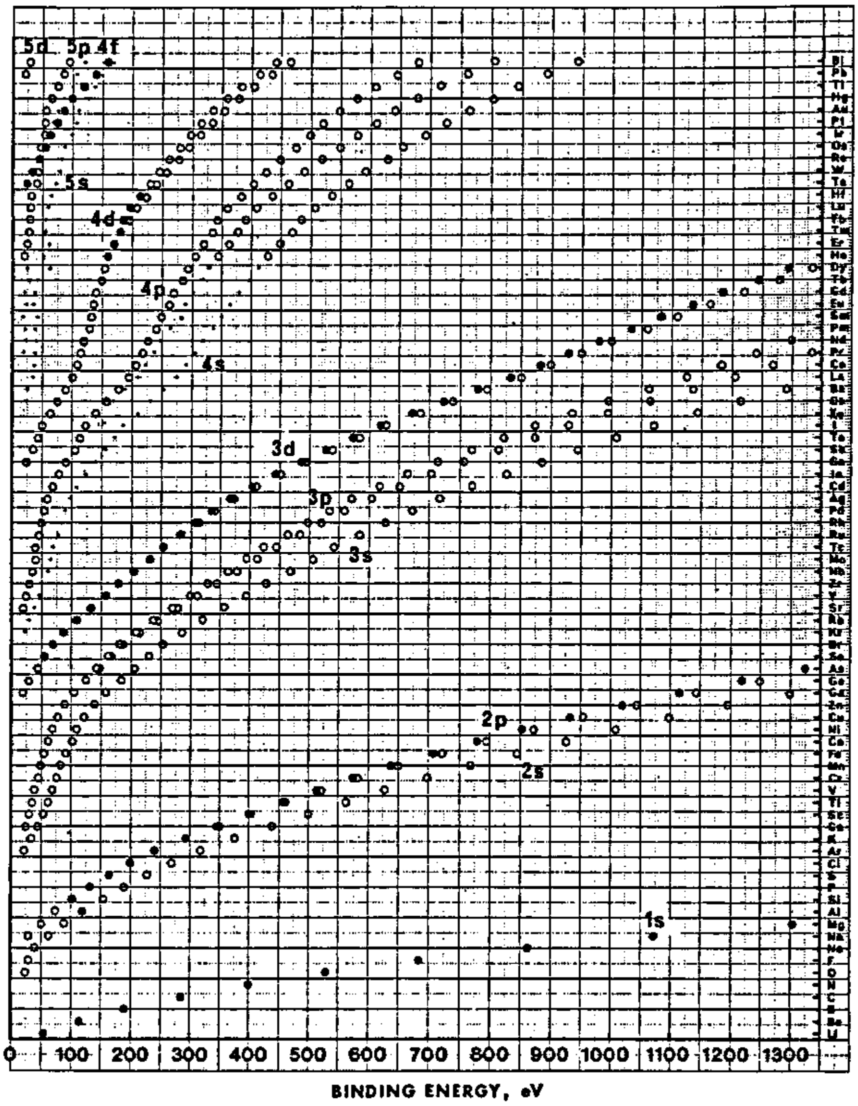
The photoelectrons are ejected with a characteristic kinetic energy E that is directly related to their binding energy to the core thus:

$$E = h\nu - E_B - \Phi \text{ ....} (1)$$

Where E_B is the binding energy , $h\nu$ is the X-ray energy and Φ is the work function of the spectrometer.

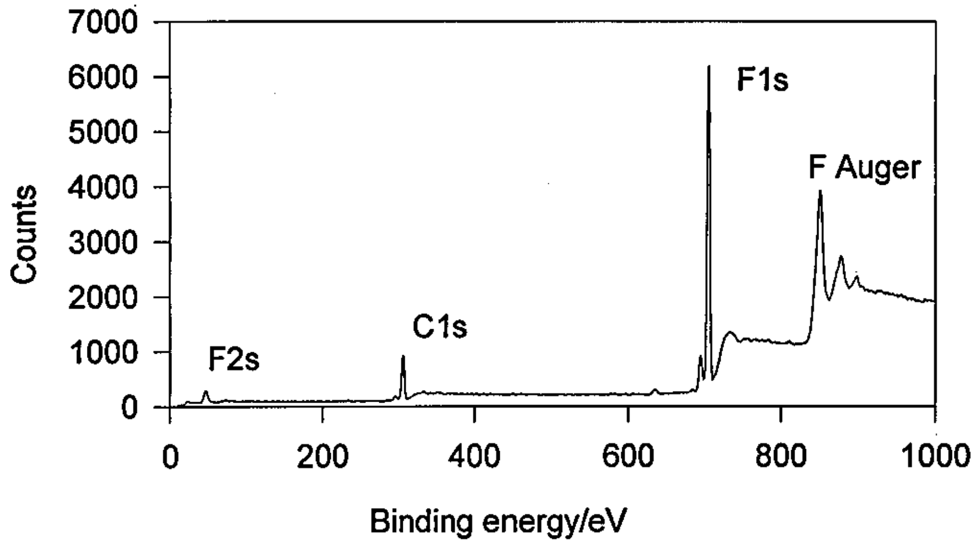
An atom's photoelectron binding energies are influenced by the charge on the nucleus That is, the binding energies within a particular shell will increase as the number of protons increase, i.e. as atomic number increases. There is a point when the core level electron e.g. 1s is so tightly held that photoemission occurs from other core levels. The relationship between binding energy and atomic number is shown in Figure 1.4.

Figure 1.4 **Elemental core level binding energies verses atomic number for all core levels in the energy range 20-1350eV[76]. ●, principle peak in broad scan; O, other main photoelectron peaks; • , peaks contributing <2% to the total photoelectron intensity.**



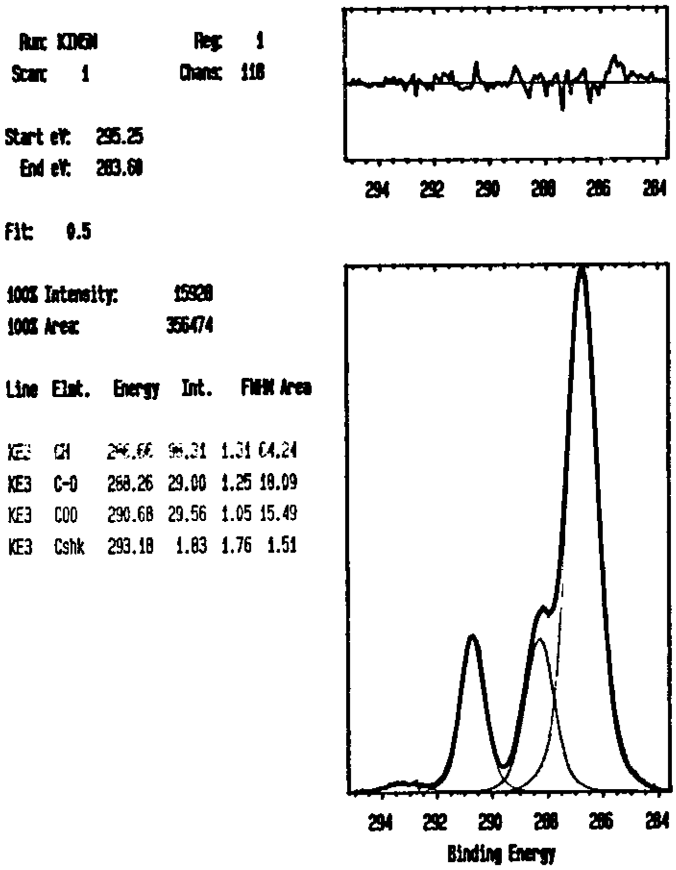
By analysing the photoelectrons according to their characteristic kinetic energy the atom from which they emerged can be identified. Fig 1.5 is an XPS spectrum of untreated PTFE film showing two core level fluorine 1s and 2s peaks, carbon 1s and peaks due to Auger electron emission from the fluorine atom.

Figure 1.5 **XPS broad scan spectrum of untreated PTFE**



Small differences in photoelectron binding energy can occur when an atom is in different chemical environments These changes can be rationalised simply, though not fundamentally, by an effective charge model. In a specimen containing, for example, hydrocarbon and carbon bonded to oxygen, the electron withdrawing nature of the oxygen atom gives the carbon atom an effective charge of δ+, so holding the core level electrons tighter. The energy required to eject the photoelectron is greater than the energy to eject a similar photoelectron from a hydrocarbon; hence the former has a lower kinetic energy. Figure 1.6 shows the different binding energies of 1s electrons from the three different types of carbon atoms in poly(ethylene terephthalate) (PET). PET contains hydrocarbons C-H in the ring structure, carbons singly bonded to oxygen >C-O-, and carboxylic carbon O-C=O; each C 1s photoelectrons have a different binding energy. The term 'chemical shift' has been used to describe this phenomenon and is the primary source of chemical state information.

Figure 1.6 **Narrow scan of the C 1s region from untreated poly(ethylene terephthalate) acquired on VG 220i XPS instrument at BP.**



```
Run: XDKGN          Reg:   1
Scan:   1           Chans: 118

Start eV:  295.25
  End eV:  283.60

Fit:   0.5

100% Intensity:      15920
100% Area:          356474

Line Elmt.  Energy  Int.   FWHM Area

KE3  CH     286.66  96.31  1.31 64.24
KE3  C-O    288.26  29.00  1.25 18.09
KE3  COO    290.68  29.56  1.05 15.49
KE3  Cshk   293.18   1.83  1.76  1.51
```

The binding energies of the different carbon atoms were as follows:

$\underline{C}H_2$ 286.7 eV $\underline{C}$-O 288.3 eV $\underline{C}$=O 290.7 eV

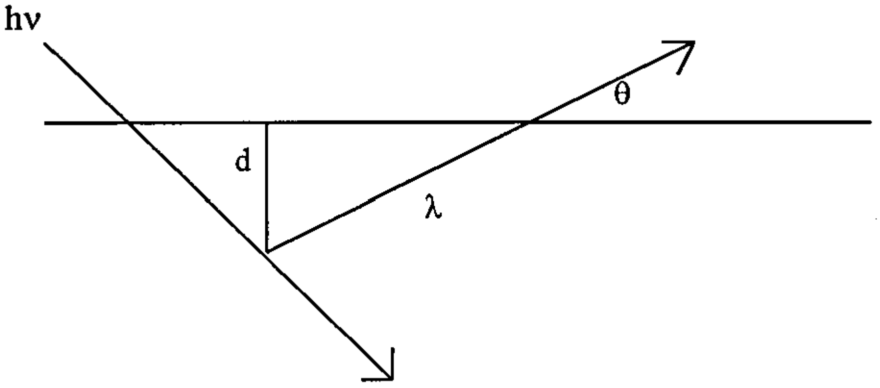
The forth peak that is resolved and fitted in the above figure is a shake up satellite arising from the ring structure.

In XPS the incident X-rays will penetrate several microns into a sample; however, the technique is surface specific because the likelihood of a photoelectron escaping from the sample without collision decreases as it emerges from an atom deeper in the sample. Near surface photoelectrons escape without loss of energy and their characteristic energies are analysed. The photoelectrons that have undergone inelastic collisions gives rise to the increased background after a photoelectron peak in a spectrum (see figure 1.5). The distance a photoelectron may be expected to travel before losing some kinetic energy is described as 'the inelastic mean free path', λ, (IMFP), or attenuation length. The probable decay in intensity of the photoelectron is described by the following equation.

$$I = I_0 \exp(-x/\lambda) \quad\text{..................(2)}$$

where: I is the intensity of the photoelectron and x is the displacement of the photoelectron from its point of origin.

The effective sampling depth 'd' of the technique may be described by the following diagram:



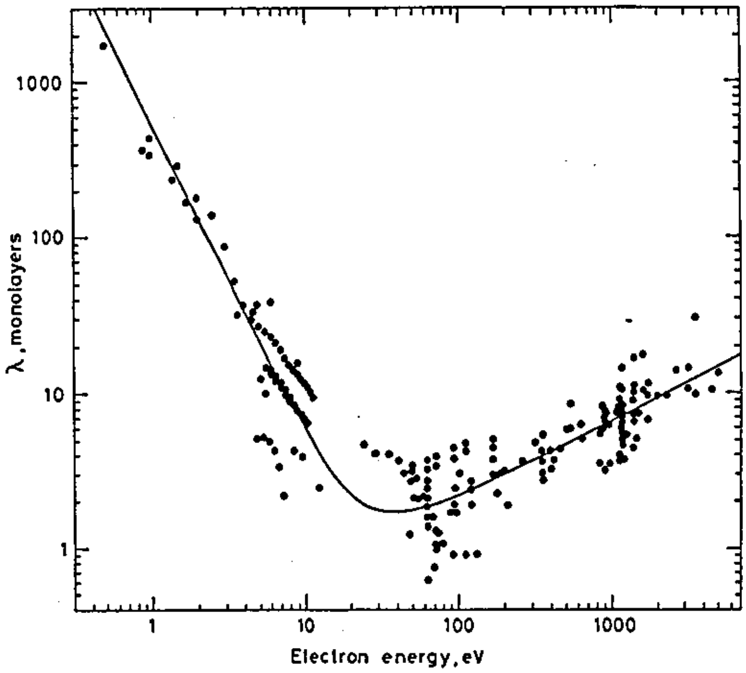
$$d = \lambda \sin\theta$$

θ is referred to as the 'take off angle', the angle at which the photoelectrons are collected. By varying the 'take off angle' the effective sampling depth can be altered; at low θ, d is small. 95% of the detected signal will have originated within a depth of 3d.

Experimental values for λ have been compiled by Seah and Dench[77]. Values of λ for organic materials vary from 1-5 nm, depending on the kinetic energy of the photoelectron. Figure 1.7 shows the relationship between IMFP and energy of photoelectrons for the elements. For example, in the sample of PTFE shown in Figure 1.5 the F2s photoelectron peak will have contributions from photoelectrons that originated from deeper in the sample, than those giving rise to the F1s peak. In the latter case the IMFP is smaller. This provides a useful tool for assessing if the

PTFE, for example, is homogeneous near the surface. Conversely if there is a sample known to be homogeneous, it can be used to check the performance of the instrument.

Figure 1.7 **IMFP in monolayers vs KE of photoelectrons**[77]



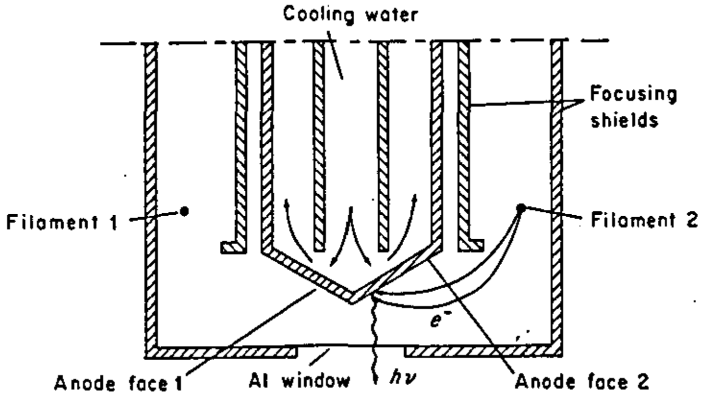
Instrumentation

There are three basic elements in the XPS instrument: the source, the analyser and the detector. These are housed in a ultra high vacuum (UHV) chamber which is constructed from stainless steel and Mu metal and is able to achieve vacua down to 10^{-10} mbar

A) The X-ray source

X-rays are produced by bombarding a water cooled anode with electrons from a thoria coated filament (Figure 1.8). The anode has two faces and may be coated either side with two different materials, usually Al and Mg. In this work both faces were Al.

Figure 1.8 The twin anode (from ref. 78)



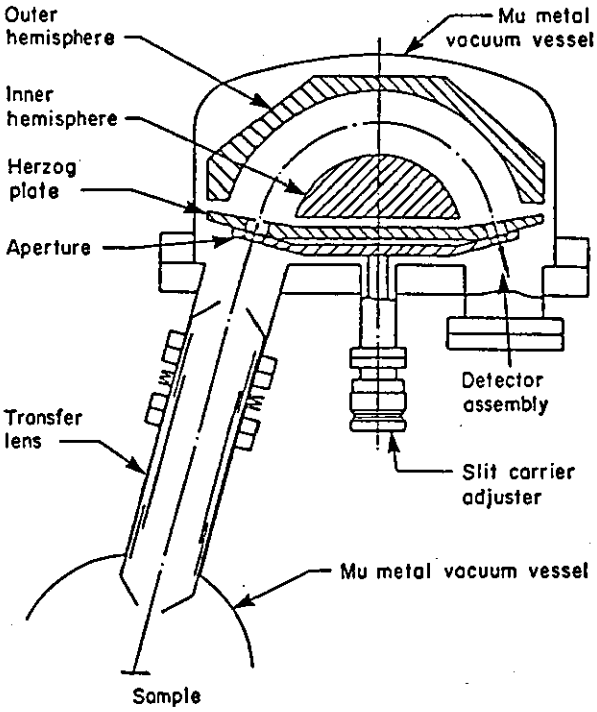
The aluminium window stops the sample being exposed to stray electrons from the filament and also protects the anode from contaminants that may outgas from the sample. The instrument used predominately in this work (ESCALAB Mk 1) did not have a monochromator for the X-rays so in a spectrum Figure 1.5 there are peaks due to the Al K_β, Al $K_{\alpha\ 1,2}$ and the Al $K_{\alpha\ 3,4}$ lines. The ratio of the intensity of the Al $K_{\alpha\ 1,2}$ and Al $K_{\alpha\ 3,4}$ lines is 10.4:1. The Al $K_{\alpha\ 3,4}$ line occurs 10.8 eV below the main Al $K_{\alpha\ 1,2}$.

The area analysed by the ESCALAB Mk1 is determined by the slit size at the entrance to the analyser. The range is 0.5 mm up to 2 cm. However, more recently instruments has been developed that have much greater spatial resolution. The ESCALAB 220i model is capable of sampling areas down to 50μm. A limited amount of work was carried out on this instrument at BP, Sunbury-on-Thames.

B) The electron energy analyser

There are two main electrostatic analysers for electron spectroscopy. There is the cylindrical mirror analyser (CMA). This gives high transmission but has a fixed resolution, and there is the hemispherical sector analyser (HSA) that gives lower transmission but variable resolution. The ESCALAB Mk 1 and 220i both employ the latter. Figure 1.9 shows a schematic of the ESCALAB 150° hemispherical analyser.

Figure 1.9 Schematic diagram of the hemispherical sector analyser



There are two modes of operation of the HSA analyser: constant retard ratio mode (CRR) and constant analyser energy mode (CAE). In this work the instrument was run in the CAE mode.

During operation of the instrument, photoelectrons emanating from the sample are transferred by the lens through an aperture and into the analyser. The electrons are retarded by means of a voltage on the Herzog plate and enter the analyser at a fixed energy (pass energy). A constant potential difference between the inner and outer hemispheres focuses the electrons on to the exit slit. The photoelectrons are then collected by an electron-multiplier. A spectrum is achieved by ramping the retard voltage at the entrance and exit of the analyser on the Herzog plate. It is important that the potential across the front and back of the electron-multiplier is constant (to keep the gain constant), so as the front end is set at the ramping retard potential the back end has to change accordingly, this is called the channeltron voltage.

The pulses emerging from the electron-multiplier are processed through the pulse counting electronics and, with the use of an interface, a computer and software a spectrum of counts verses binding energy is ultimately displayed as in Fig 1.5.

Quantification

Elemental composition is derived from a spectrum by measuring the area under a peak, dividing by the relative sensitivity factor for that photoelectron and expressing it as a percentage of the whole.

$$C_A = \frac{I_A/S_A}{\sum_n (I_n/S_n)} \times 100\% \quad ....(3)$$

C_A is the concentration of element A (atom %)
I_A is the intensity of the peak from element A
S_A is the relative sensitivity factor

Relative sensitivity factors (RSF) have been calculated for the ESCALAB at LUT (see below). To enable direct quantitative comparison with the ESCALAB at BP, RSFs for the BP instrument were determined by calibrating with standards run on both the instruments.

The intensity of a photoelectron peak is proportional to the following:

N_A the number of atoms of type A

σ_A the total photoionisation cross-section of A. The probability of photoionization occurring within a given shell increases with atomic number.[79]

$L_{A(\gamma)}$ the angular asymmetry parameter[80]. γ is the angle between the impinging X-ray beam and the ejected photoelectron. For emission from symmetrical shells e.g. K shells (1s) the probability of emission is independent of this angle and is therefore equal to one. But for L shells (2p) that are asymmetrical there is an angular dependence.

$T(E_A)$ The transmission of the energy analyser[81]. This is dependent on the pass energy of the analyser, the slit width and the kinetic energy E_A of the photoelectron.

$D(E_A)$ The efficiency of the electron detector.

$\lambda(E_A)$ The inelastic mean free path or attenuation length (as defined before).

Sample charging

During XPS analysis of an insulator the sample will become positively charged as the photoelectrons escape. The charging reaches an equilibrium level rapidly due to a counter effect of electrons from surrounding metals exposed to the x-rays and from the aluminium window of the X-ray source. Sample charging effectively changes the observed binding energy of the escaping photoelectrons due to shifts in the fermi level. This effect may be reduced by means of a charge neutralisation gun (electron gun) which is essential when an X-ray monochromator is used as there is no local source of neutralising electrons.

Spectral peak shape

The shape and width of photoelectron peak that is finally recorded is a convolution of different factors:

A) X-ray line shape - In the absence of a monochromator Al K_α and Mg K_α X-ray lines are unresolved doublets of width 0.8 and 0.7 eV respectively. The intrinsic spectra *I(E)* is 'convoluted' with the X-ray line shape (*X*) producing the observed spectrum *O(E')*.

$$O(E') = \int I(E)X(E-E')d\mathrm{E} \quad \text{.............................(4)}$$

These functions may be deconvoluted by knowing *X* and *O*.

B) The resolution of the electron analyser is also finite and a broadening effect of between 0.1-0.5 eV may occur (the resolution is also dependent on the pass energy used to acquire the spectrum).

C) The photoelectron peak itself has a finite width which is dependant on the lifetime of the excited or hole state.

D) In addition to the above factors differential charging may occur across the surface of insulating samples resulting in apparently different binding energy shifts thus broadening the peak. The extent can be anything from 0 - 2 eV. .

1.5.2 Theory of surface energies and contact angles

The use of contact angles of liquids on solid substrates, and the subsequent calculation of the solid's surface energy is a useful analysis tool. Unlike XPS and FTIR, the information gleaned is representative of the outermost surface. The measurement is achieved through the use of equations derived from thermodynamics. As such, there are certain criteria that need to be met in order to reliably implement the equations. A solid must be 'ideal' i.e. chemically homogeneous, rigid, and flat. There must be no chemical interaction with, or adsorption of the liquids used in the measurement Many substrates do not met these requirements; in certain cases these anomalies can be corrected for but it is often non-trivial.

There are different types of forces that can occur at interfaces:

Strong forces:	covalent		
	ionic		
	electrostatic		
Secondary forces:	van der Waals forces	- London dispersion forces	interaction between non polar molecules
		- Keesom forces	attraction between molecules with permanent dipoles
		- Debye forces	dipoles & induced dipoles

Hydrogen bond forces

Solids and liquids all possess an excess surface free energy quantity 'G'. When solids or liquids are brought into contact with each other there is a change in the excess surface free energy[82]. Dupré showed that the work of adhesion W_A (or the reversible work of separation) for a liquid and a solid was equal to the change in the free energy per unit area of the interface according to equation (5).

$$W_A = \gamma_{S^o} + \gamma_{LV^o} - \gamma_{SL} \quad \text{...(5)}$$

where γ_S is the surface free energy of the solid

γ_{LV^o} is the free energy at the liquid /vapour interface

γ_{SL} is the free energy at the solid/liquid interface

Young's equation states:

$$\gamma_S = \gamma_{SL} + \gamma_{LV}\cos\theta \quad \text{...(6)}$$

Where θ denotes the contact angle of drop of liquid on a solid. It may be noted here that the observed value of θ may not always be the true value. Wenzel[83] showed that when a sample is not smooth a roughness factor 'r' can be described as the following ratio.

$$r = \frac{\cos\theta}{\cos\theta^1} \quad \text{...(7)}$$

Where cos θ is the apparent contact angle of the drop to the horizontal and cos θ^1 is the intrinsic contact angle to the real surface.

Fowkes suggested that the total surface free energy γ of a solid or liquid was the sum of the individual interfacial energies (excluding the chemical bonding forces).

i.e. $$\gamma = \gamma^d + \gamma^p + \gamma^h + \text{................(8)}$$

d is the dispersion component, *p* the polar contribution and *h* is the contribution for hydrogen bonds. He also gave the following equation for the interaction of a liquid on a solid, providing the interaction was through dispersion forces only.

$$\gamma_{SL} = \gamma_{SV^o} + \gamma_{LV^o} - 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} \quad \text{........................(9)}$$

Owens and Wendt, and Kaelble and Uy combined the terms in (8) to just two terms: the sum of all dispersion and all polar contributions (including hydrogen bonds). They extended Fowkes equation (9) by assuming that the polar contributions could be expressed as a geometric mean also.

$$\gamma_{SL} = \gamma_{SV^{\circ}} + \gamma_{LV^{\circ}} - 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} - 2\left(\gamma_S^p \gamma_S^p\right)^{1/2} \text{.......}(10)$$

Combining (10) with the Young's (6) and the Dupré equations the expression below is formed:

$$\gamma_{LV^{\circ}}(1+\cos\theta) = 2\left(\gamma_s^d \gamma_l^d\right)^{1/2} + 2\left(\gamma_s^p \gamma_l^p\right)^{1/2} \text{...............}(11)$$

By rearranging (11) into the form shown in (12),

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^d} + \sqrt{\gamma_S^p}\,\frac{\sqrt{\gamma_L^p}}{\sqrt{\gamma_L^d}} \text{.........................}(12)$$

$$\equiv \quad [\text{.....Y.............}] = \text{'C'} \; + \text{'M'} \; [\text{...X..}]$$

and plotting [Y] against [X], γ_S^p and γ_S^d can be determined[84]. This may be done using a simple computer program.

More recently Fowkes equation (8) has been modified by combining the polar and hydrogen forces into one term γ^{AB}, this is named the acid-base interaction[85]. If the potential is there for proton donation or acceptance then γ^{AB} will be much greater than γ^{P}. Proton acceptors are groups such as esters, ketones, ethers, aromatics. Proton donors include partially halogenated molecules and groups that can act as acids or bases include: amides, alcohols and amines.

Contact angle hysteresis

Theoretically, because most surfaces are not 'ideal' contact angle hysteresis 'H' occurs where:

$$H = \theta_a - \theta_r \text{..}(13)$$

θ_a is the static advancing angle
θ_r is the static receding angle
(A fuller description of these terms is given in the experimental section).

One possible cause of hysteresis is roughness. Dettre and Johnson[86] describe an experimental study of the wetting of rough surfaces. They discuss the effect on advancing and receding contact angles for different levels of roughness.

In a recent review on contact angle and surface energies Good[87] outlines that if a surface is heterogeneous, containing areas of high and low surface energy then the maximum advancing angle is indicative of the lower free energy sections and the lowest receding angle representative of the high surface energy areas.

Another source of hysteresis may arise from reorientation of groups on a solid surface when in contact with the liquid.

The difficulty in obtaining a true saturated vapour of the liquid in the actual measuring instrument adds to the possibility of contact angle hysteresis. Vapour concentration gradients will occur along the path of the periphery.

Another factor should be considered when measuring contact angles. If there are components on the solid's surface that are able to dissolve in the liquid, the surface tension of the latter will change and therefore errors would occur in the estimation of surface energy of the solid. This factor may be important for polymers containing low molecular weight species on the surface; either as an untreated or as a treated substrate. The materials used in this work were therefore checked for evidence of such a phenomena. Also in this work the surface energies of rough surfaces were not measured.

Surface energies of untreated polymers

Table 1.3 displays examples the polar and dispersion values of surface energy for some untreated polymers, the materials used in this work are included.

Table 1.3 **Surface free energies for polymeric solids[88].**

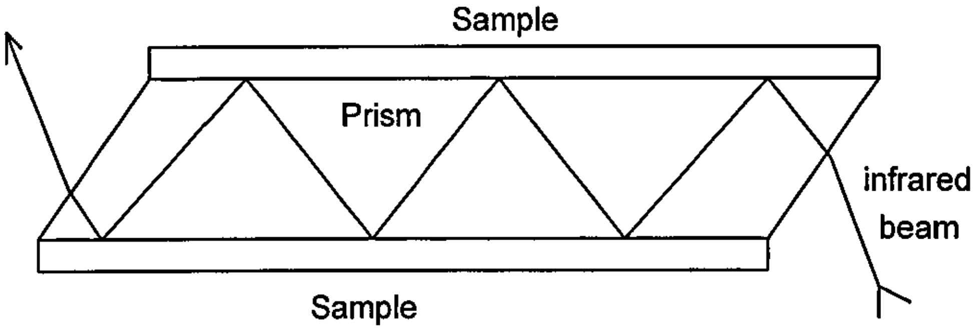
Polymer	γ_s^d / mJ m^{-2}	γ_s^p / mJ m^{-2}	γ_s / mJ m^{-2}
Polytetrafluoroethylene	18.6	0.5	19.1
Polytrifluoroethylene	19.9	4.0	23.9
Poly(vinylidene fluoride)	23.2	7.1	30.3
Poly(vinyl fluoride)	31.3	5.4	36.7
Low density polyethylene	33.2	-	33.2
Polypropylene	30.2	-	30.2
Poly(methyl methacrylate)	35.9	4.3	40.2
Poly(vinyl chloride)	40.0	1.5	41.5
Polystyrene	41.4	0.6	42.0
Poly(ethylene terephthalate)	43.2	4.1	47.3

1.5.3 Fourier Transform Infrared - Attenuated Total Reflection spectrometry (ATR-FTIR).

Infrared analysis is the measurement of absorption of radiation of a particular wavelength (or frequency), by specific chemical groups in a sample. A sample is exposed to a range of infrared wavelengths and a spectrum of absorbance (or transmission) against wavelength is obtainable.

Attenuated total reflection infrared (ATR) [or multiple internal reflection (MIR)] results in the same absorption verses wavelength output but the incident infrared beam is not transmitted through the sample. In fact, adsorptions occur from a sampling depth in the order of 1μm. Sample surfaces are held in close contact to the two surfaces of a prism, see Figure 1.10.

Figure 1.10 Arrangement of sample in ATR infrared and path of radiation



The incident infrared beam is totally internally reflected in the prism as shown in the figure above if, the angle of incidence to the inside face of the prism is greater than the critical angle θ_c

$$\text{where } \theta_c = \sin^{-1} n_s/n_p \quad \text{......................}(13)$$

n_s is the refractive index of the sample
n_p is the refractive index of the prism

The electric field however, does not fall to zero at the interface of the prism and sample. The amplitude 'E' of the evanescent wave decays exponentially as the depth 'x' into the sample increases. The relationship is described in equation 14[89]:

$$E = E_0 \exp\left(-x/d_p\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Where E_0 is the amplitude at the interface and d_p is the depth at which the amplitude has fallen to 1/e of its value at the interface; it is termed the 'penetration depth'.

The 'penetration depth' is dependent on the wavelength of the radiation in the prism, λ_1, the refractive indexes of the prism and the sample, n_p and n_s, and the angle of incidence of the radiation on the inside of the prism θ, according to the Harrick equation[89]:

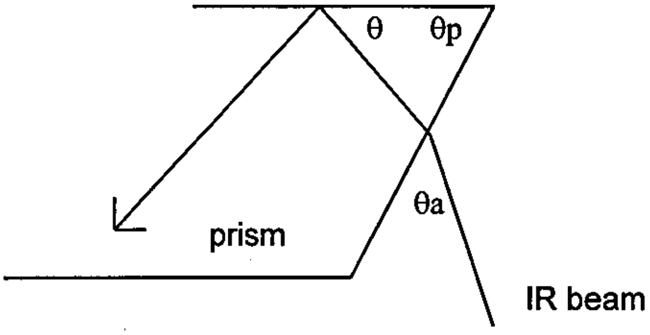
$$d_p = \frac{\lambda_1}{2\pi\left[\sin^2\theta - \left(\frac{n_s}{n_p}\right)^2\right]^{1/2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

where $\lambda_1 = \frac{\lambda}{n_p}$, and λ is the wavelength of the radiation in vacuum and,

$$\theta = \theta_a - \sin^{-1}\left[\frac{\sin\left(\theta_a - \theta_p\right)}{n_p}\right] \quad \ldots\ldots\ldots\ldots(16)$$

θ_a is the angle of incidence of the beam at the entrance to the prism
θ_p is the angle of the end face of the prism, see Figure 1.11

Figure 1.11 **Various angles in ATR prism**



Across a range of wavelengths the absorption bands seen will have arisen from groups at different depths. e.g. for a PVF sample the range of 'penetration depth' across a typical spectrum for two different prisms will be as follows (see Appendix B for calculations)

Prism	d_p at 4000 cm^{-1}(μm)	d_p 400 cm^{-1}(μm)
Germanium	0.15	1.5
KRS (TlBr-TlI)	0.32	3.2

Traditional infrared spectrometers analyse the beam emerging from the sample dispersively. Resolution is determined via the slits and one frequency is viewed at a time by the detector.

More recently Fourier Transform infrared (FTIR) instruments have gained wide acceptance as they hold various advantages over the dispersive instruments; the two main advantages are given below.

(1) Named the 'Felgett' or multiplex advantage, i.e. All frequencies are observed by the detector simultaneously. This means a spectrum may be obtained very quickly (a fraction of a second). Since acquisition time is so short it is possible to

increase sensitivity by repeating the scans and averaging the signals. The ratio of signal to noise 'S/N' is proportional to the square root of the number of scans. This enables small absorption bands to be distinguished.

(2) The 'Jaquinot' advantage. FTIR has a much greater signal throughput than a dispersive instrument. The beam diameter is about 1 cm for FTIR and has an optical aperture, whereas the dispersive instrument has slits which are much more constraining. This is a major advantage which a technique such as DRIFT (Diffuse reflectance infrared analysis) is in use where the throughput is very low, ~ 0.1 %

1.5.4 Scanning electron microscopy

A focused electron beam is scanned (or rastered) across an area on the sample surface under vacuum. There are several processes that can occur as a result of the primary incident beam. 'Secondary' electrons can be ejected or Auger electron emission (described in 1.4.1) may occur. Back scattering and reflection of electrons can also occur; these possess higher energy than the secondary electrons.

In SEM an image of the sample surface is normally produced by detecting the secondary electrons and feeding the signal to a cathode ray tube/oscilloscope that is scanning at the same rate as the primary beam. The contrast seen in the image is the variation in the yield of secondary electrons.

An insulator will become charged on exposure to a beam of electrons so such samples are generally vacuum coated with a thin layer of gold (~ 20 nm).

Chapter 2

Experimental

2.1 Materials

2.1.1 Substrates

For preliminary experiments to assess the accuracy of the bonding procedure, poly(ethylene terephthalate), 'Melinex' O grade film was used; this was supplied by ICI

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

2.1.2 Adhesives

Araldite AV100 resin and HV100 hardener, a product of Ciba-Geigy, was supplied by B & K Resins Ltd, Bromley, Kent. To ensure constant glue line thickness, 1% (by weight) of ballotini spheres of 0.21 mm diameter (max.) were incorporated into the adhesive. The normal cure schedule for adhesive was 2 hours at 70°C.

Loctite® Super Glue Gel Xtra, a cyanoacrylate adhesive, was used for certain bonding experiments.

2.2 Experiments on untreated materials

Untreated PTFE, PVF and PVdF were all bonded with epoxy adhesive and cyanoacrylate adhesive to assess the influence of different adhesives on adhesion level. Throughout the rest of the experiments epoxy was used in the bonding of PTFE and PVF, and cyanoacrylate adhesive was used for PVdF joints. The detailed reasons for this are given in the discussion (section 4.1). Briefly, a bonding system for each fluoropolymer that gave poor adhesion was chosen, in order that investigations into mechanisms of adhesion improvement could be carried out. This may be relevant when the use of a particular adhesive is unacceptable.

The effect of washing untreated PVF in methanol (AR) and trichlorotrifluoroethane (AR) was investigated and analysed using XPS and joint strength measurements.

Multiple bonding experiments were carried out on PTFE and PVF substrates. For these tests, a piece of fluoropolymer film (about 100 mm x 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 from the fluoropolymer; a sample of this was cut and the epoxy analysed by XPS for fluorinated material. The substrate was then rebonded as many times as required. Joint strengths were determined after various bonding and debonding experiments.

2.3 Treatments

2.3.1 Solutions

Sodium naphthalenide in tetrahydrofuran (THF)

This solution was prepared by dissolving naphthalene (16g) in THF (125 ml) that had been dried over calcium hydride for 72 hours and filtered before use. The solution was placed in a stoppered conical flask (250 ml), followed by sodium metal (2.9g) in the form of cubes, typically 3 mm x 3 mm x 3 mm. The flask was covered in aluminium foil to reduce degradation of the solution by light and was placed on a magnetic stirrer. The mixture was stirred for 2-3 hours using a PTFE-coated magnetic follower. Previous preparations showed that it was important to minimise the presence of air and light and that the THF should be as dry as possible. Once prepared, the solution was stored in a brown bottle within a refrigerator at O°C.

The reaction flask was cleaned by carefully adding methanol to the flask to deactivate any small amounts of unreacted sodium. Disposal was completed by flushing with water.

The procedure for treating the polymers with sodium naphthalenide was identical to the following method outlined for 'Tetra-Etch'

'Tetra-Etch'

'Tetra-Etch', a product of W L Gore and Associates (UK) Ltd., was supplied by their agent R D Taylor and Co., Glasgow. The etchant was stored in a freezer at < -5°C

On removal from the freezer the 'Tetra-Etch' solution was allowed to warm to room temperature; careful agitation ensured dissolution of any solidified components.

Samples of PTFE, PVdF or PVF were treated in 'Tetra-Etch' for a measured length of time and then washed. The trade literature from W L Gore recommended a hot water wash (>80°C) with a trace of detergent, followed by a solvent wash in acetone or similar solvent. Experimentation into washing procedures was carried out e.g.

water, with and without detergent, and monitoring any differences with water contact angles. Samples were dried in an oven at 70°C for five minutes.

The actual procedures were:

Wash A.	Water (>80°C) for 10 minutes, followed by an ultrasonic wash in acetone for 10 minutes. This procedure was carried out twice.
Wash B.	As 'A', but the water contained a small amount of detergent.
Wash C.	Initial methanol (AR) wash, followed by water (>80°C) for 10 minutes, followed by an ultrasonic wash in methanol for 10 minutes. This procedure was carried out twice.

For futher experimentation method C was adopted.

'Tetra-Etch' treatment was carried out on all the fluoropolymer substrates to compare its effectiveness. A range of treatment times was investigated ranging from a matter of seconds to one hour.

Potassium hydroxide and other Group I hydroxides

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 (5M) 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). Treatment of the polymers was carried out within a 100 ml beaker using 50 ml of reagent. Where tetrabutylammonium bromide (TBAB) was used, 0.03g or 0.15g was added to ≈ 30 ml of water before addition of the KOH pellets and made up to 50 ml.

The solutions were heated by placing the beaker in a water bath on a hot plate. For solution temperatures greater than 100°C the beaker was placed directly on the hot plate. Polymer strips 22 mm x 120 mm were coiled and attached at the overlap (about 1 cm) by threading a thin glass tube through pierced holes. This enabled the substrate to be fully immersed and for the reagent to have free access to both surfaces.

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 70°C.

Most of the work regarding the Group I hydroxides was carried out using potassium hydroxide (KOH); preliminary experiments were done using lithium hydroxide (LiOH) and sodium hydroxide (NaOH) for comparison. Experiments were conducted to explore the effects of different variables on KOH treatment. Time of treatment, molarity and temperature were investigated for PVF and PVdF, (PTFE was only subjected to the most extreme conditions).

The effect of addition of a phase transfer catalyst, namely tetrabutylammonium bromide (TBAB), to aqueous and alcoholic KOH solutions, on the adhesion of PVF and PVdF was investigated.

Investigation into the role of TBAB as an accelerator for the KOH treatment involved comparison with addition of other materials to the KOH solution, the use of different washing procedures and the effect of a TBAB solution on its own for the treatment of PVF and PVdF.

2.3.2 Flame

Flame treatment of the polymer films was carried out using a flame rig constructed in the Chemistry Department at Loughborough University of Technology. It is comprised of a burner (ex WSA Components) containing a large number of closely spaced jets, supported to produce a horizontal flame (see Figures 2.1 and 2.2). A conveyor system, with controllable speed transports a detachable metal plate. The polymer to be treated was attached to the plate. The burners were fed with an air-natural gas mixture; the flow rates of each were monitored by meters before combination.

A piece of polymer film was cut so that it was approximately 4 cm wider than the plate, this was then placed centrally on the plate and the over hanging edges of film were folded to the reverse. These were stuck down using adhesive tape ensuring that the polymer lay flat and tight.

The following conditions were employed:

- distance from burner to sample = 15 mm
- distance from flames cone tip to sample = 10 mm
- air:gas* = 11:1
- corresponding air:gas flow rates = 22:2 $\mathrm{l\ min^{-1}}$

[* - The natural gas consisted of 96% CH_4, 4% C_2H_6.]

These 'standard' conditions were chosen on the strength of previous research carried out on the apparatus.[90].

PTFE and PVF were both flame treated; the only variable used in this work was the time for a single point of the polymer to pass the flame: 0.04 secs or 0.06 secs were used. PVF samples were subjected to aging in air experiments; this was monitored using contact angles and surface energy measurements.

Figure 2.1 View of flame rig showing burner jets

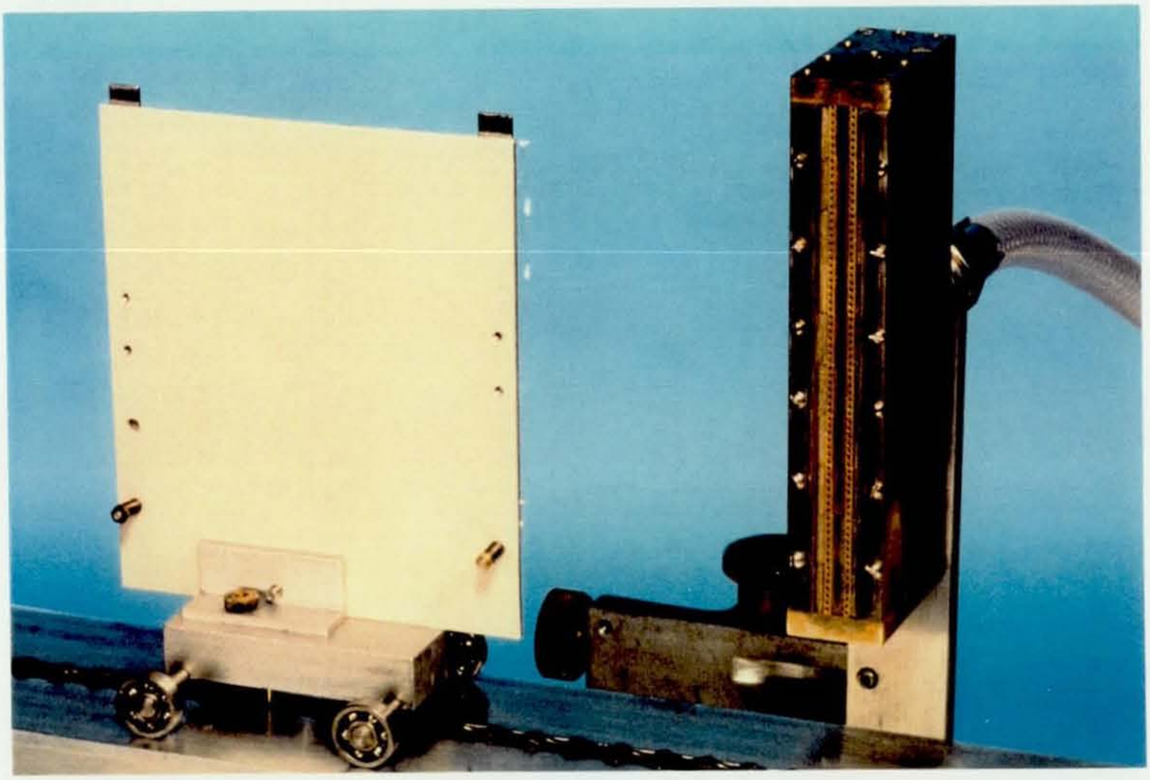
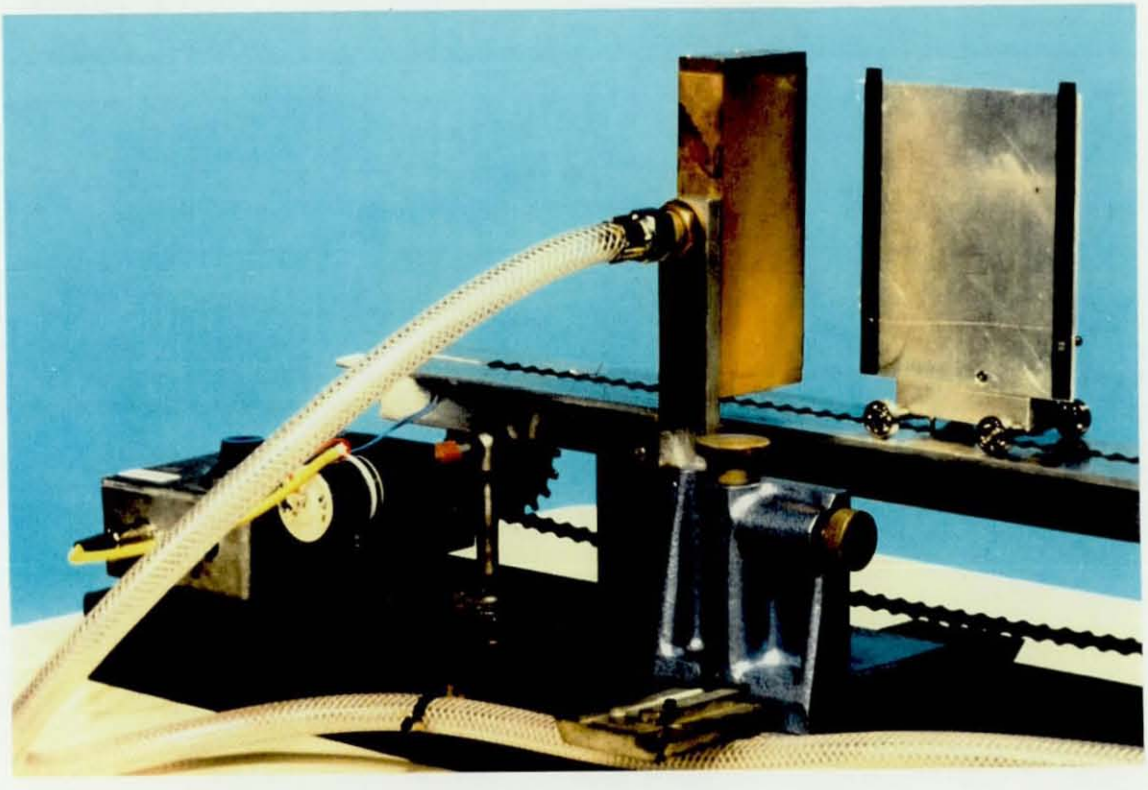


Figure 2.2 View of flame rig showing movable plate



2.3.3 Plasma

Plasma treatment was carried out at BP Research Centre, Sunbury-on-Thames using a Chemprep Plasma Barrel Reactor 230-D manufactured by 'Chemex Plasma Equipment'. The following is a summary of the equipment and operating conditions:

chamber dimensions:	23 cm in diameter, 30 cm long
chamber volume:	12.46 dm^3
maximum power supply:	500 W
radio frequency:	13.56 MHz
radio frequency power:	variable 0-200 Watts
gas pressure in chamber:	0.400 Torr
gas supplies:	nitrogen ring main oxygen and hydrogen (BOC 'High purity') argon (Air Products 99.999% pure)

The plasma chamber containing two glass plates was first cleaned by generating an oxygen plasma, this was carried out as follows. The chamber was pumped down to a minimum base pressure using the roughing pump followed by the turbo pump; the base pressure was noted. The roughing pump was re-engaged and oxygen was allowed to flow into the chamber until a pressure of 0.400 Torr was reached; the equivalent flow rate of oxygen was recorded. The radio frequency (RF) was turned on with a power reading of 200 Watts and left for about half an hour. On completion, the RF power was turned off, the roughing pump was disengaged and the chamber allowed to purge with nitrogen up to atmospheric pressure. The chamber was opened by removing the door. A 120 x 100 mm sample of polymer was placed within the chamber suspended between the two glass plates; this ensured both sides of the polymer were exposed to the plasma. The door was replaced and the chamber pumped down. The base pressure was recorded. The appropriate gas (argon, air, nitrogen, hydrogen or oxygen) was allowed to flow into the chamber until a pressure of 0.400 Torr was reached; the equivalent flow rate was noted. The RF power was turned on and a power of 100 watts was used, except in some cases with argon. At this power the reflected power was too great for the compensation system, causing it to trip out; a power of 70 watts was used instead. The samples were exposed to the plasma for the specified length of time after which the RF was turned off. The gas was allowed to continue to flow over the sample for 1 minute before purging with nitrogen to atmospheric pressure. Samples were removed from the chamber using tweezers and the edges that had been in contact with the glass were removed before the remainder was stored in clean, dry jars or envelopes. Between each experiment an oxygen plasma was carried out for 10 minutes according to the first method to reduce cross contamination.

PVF was subjected to argon, air, nitrogen, hydrogen and oxygen plasmas and PTFE was treated using argon, oxygen and hydrogen plasmas for comparison of their effects on bond strength and surface composition; in most cases the water contact angle was also monitored. Aging in air was monitored by water contact angles for an argon plasma treated PVF sample. Treatment times were varied from one second to one hour for PVF and PTFE samples and analysed using XPS and bond strength measurements.

2.3.4 Amine

PVF and PVdF were immersed in the amine hardener HV100 used for the epoxy adhesive at room temperature overnight, and at 70°C for 2 hours (these are similar to the manufacturers recommended cure profiles for the adhesive). The surface composition of both substrates were examined with XPS after washing thoroughly in acetone and drying in air. PVdF was bonded after treatment with cyanoacrylate adhesive. However, a comparison of bond strengths between untreated and amine treated PVF using cyanoacrylate adhesive was not possible as the untreated value was high.

2.3.5 Post treatments

Ultra violet irradiation of sodium naphthalenide treated PTFE

To assess the effect of UV light, samples of sodium naphthalenide-treated PTFE were placed in an Annular Photoreactor, model APQ40, from Applied Photo Physics Ltd. The lamp was 400W and provided radiation mainly between 365-366 nm; the sample was placed 30 mm from the lamp. The UV irradiation was carried out by Dr R H Dahm of De Montfort University, Leicester.

Oxidative removal of black region on 'Tetra-Etch' treated PTFE

Samples of 'Tetra-Etch' treated PTFE were immersed in undiluted domestic bleach containing hypochlorite, namely "Domestos", for 24 hours or until the black coloration was removed.

Washing and ageing after flame treatment of PVF.

PVF that had been treated with flame for 0.06 seconds was stored in clean jars. At various time intervals a sample was removed and the surface energy was measured according to the method in section 2.4.2.

PVF, 40 mm x 40 mm treated with flame for 0.06 seconds was immersed in the liquids used for surface tension measurements for two minutes then removed. The surface tension of these liquids were measured before and after immersion. The liquids are described in section 2.4.2.

2.3.6 Vapour phase derivatisation reactions

A vacuum frame had previously been designed and built for vapour-phase derivatisation in the Chemistry Department of Loughborough, University of Technology[90] (see Figure 2.3). Trifluoroethanol (TFE) and trifluoroacetic anhydride (TFAA) were used as reagents to 'tag' carboxylic acid and hydroxyl groups respectively on treated substrates. In each case a standard polymer i.e. one of known functional groups was used to measure the extent of the reaction. Figure 2.4 shows the reactions.

Figure 2.3 Gas phase derivatisation rig

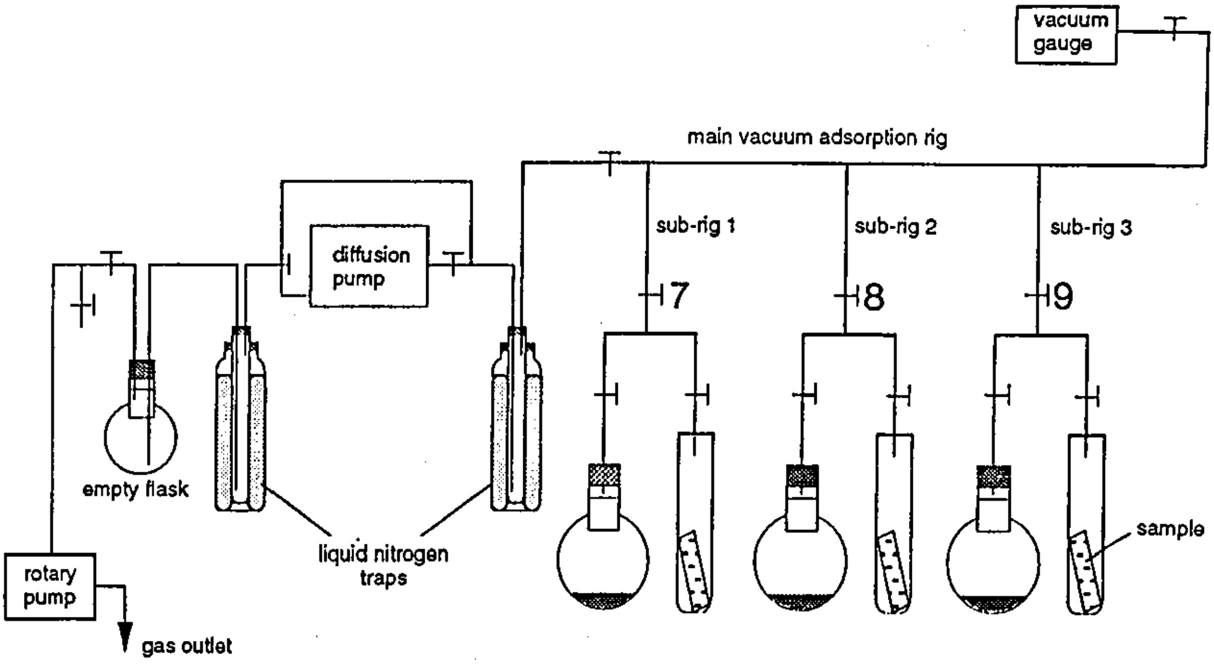
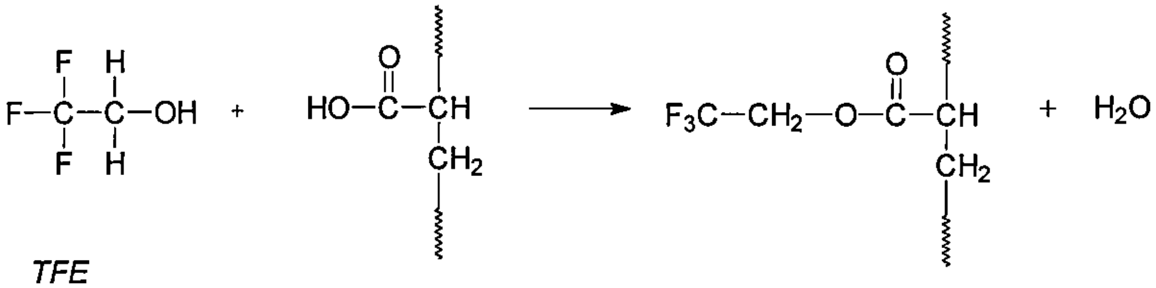
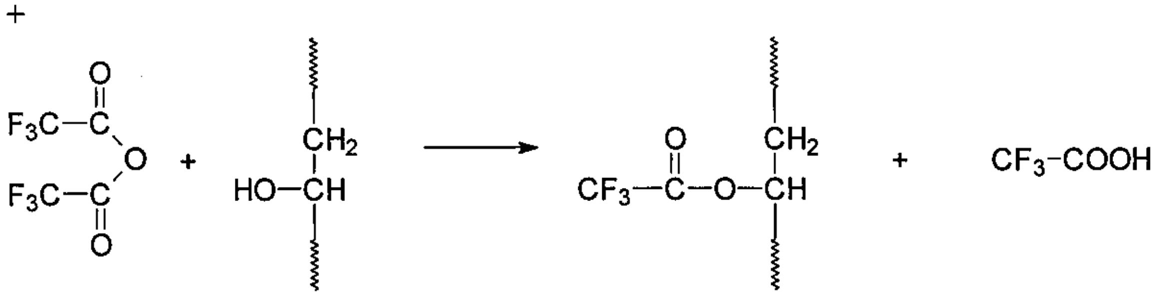


Figure 2.4 **Derivatisation reaction schemes**

Tagging carboxylic acid groups:



Tagging hydroxyl groups:



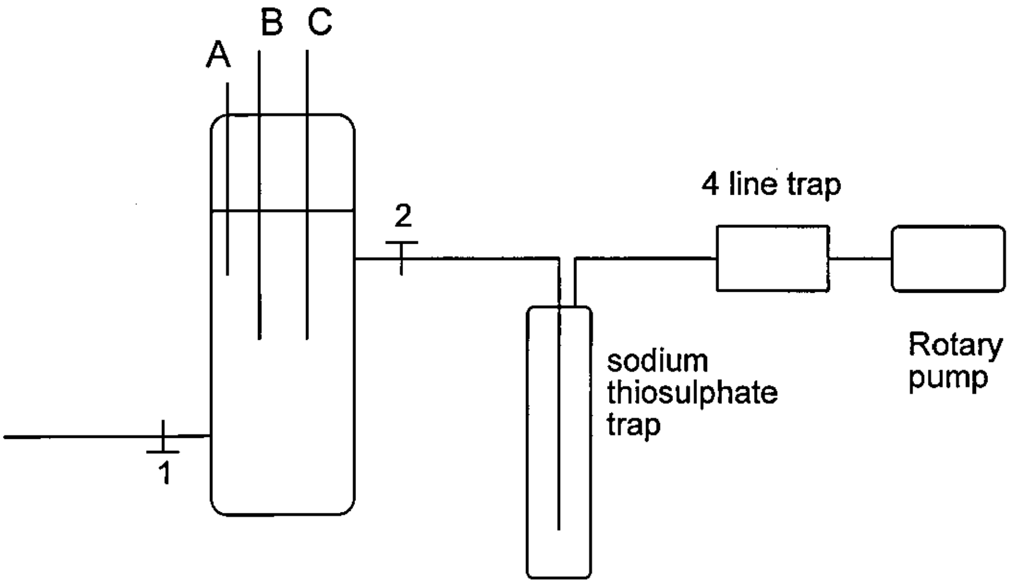
Reagents were subjected to a freeze-thaw cycle to remove dissolved gases as follows. Taps 7, 8 and 9 (Figure 2.3) were closed and Dewars containing liquid nitrogen were placed round the reagent flasks. With the diffusion pump bypassed taps 7, 8 and 9 were opened and the pressure allowed to fall to $<10^{-1}$ Torr before re-engaging the diffusion pump; the pressure was recorded when it stabilised. The taps 7, 8 and 9 were closed and the reagents allowed to defrost. The liquid nitrogen was repositioned and the reagent frozen again; the taps were then reopened. This freeze-thaw cycle was continued till a constant low pressure was obtained; then the flasks were sealed off. The manifolds containing the substrates and the standard polymers were attached and pumped down overnight.

A constant temperature for the reactions was obtained by immersing the reagent flasks in water at 20°C contained in a Dewer. With taps 7, 8 and 9 closed the flask taps were opened. Reaction time for the TFE was 16 hours and 2 hours for the TFAA. On completion the samples were pumped out for a minimum of 24 hours and kept under vacuum till XPS analysis was carried out.

Tagging of COOH and OH groups was carried out on selected treated fluoropolymers

A vessel for bromination of samples was designed and constructed for this project (see Figure 2.5).

Figure 2.5 **Vessel for bromination of treated substrates**



Sample to be brominated were placed in the apparatus, suspended on the glass hooks **B** and **C**. Addition of bromine across a carbon-carbon double bond takes place in the absence of light so the whole apparatus was enveloped in aluminium foil before introducing the bromine. A pipette was dipped in bromine so that a small amount was taken up by capillary action; this small amount was then introduced through the top of the vessel at **A** with taps 1 and 2 closed. After one hour a Dewer filled with liquid nitrogen was placed around the sodium thiosulphate trap which at this stage was empty, tap 2 was opened and the vessel was pumped out for a minimum of 72 hours. Tap 2 was closed and the bromine in the trap was disposed of using a 5M aqueous solution of sodium thiosulphate. Samples were then analysed by XPS.

Bromination of selected treated samples was carried out.

2.4 Testing procedures

2.4.1 Bonding

Metal preparation

Bright drawn steel strips of dimension 20 mm x 3 mm were obtained in three metre lengths from JPL Steel Stockists, Leicester. Bright drawn steel was chosen because of its rigidity and accurate profile. Excess grease was first wiped from the metal with a tissue and then it was cut by a guillotine into strips of 62 mm in length. The ends of the strips were then milled to achieve a length of 60.0 mm. The small burrs produced during milling were filed off the ends using a fine file.

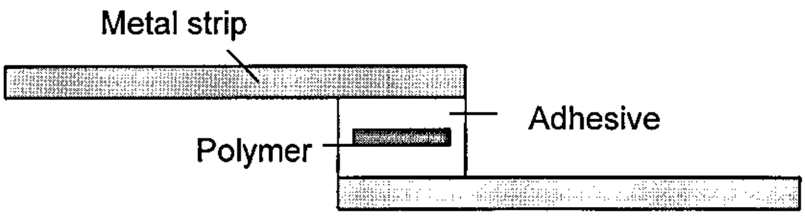
Oil was used as a coolant in the milling process; to avoid contamination of machinery the strips were degreased before grit-blasting. A wipe with trichloroethane was sufficient at this stage. The strips were then grit-blasted all over, using iron-40 grit and a pressure of 90 psi (0.62 MPa).

For cost and toxicity reasons, propan-2-ol was chosen for the final degreasing process. (Ordinarily trichloroethane is quoted as being the most effective degreasing agent for steel but propan-2-ol has proved effective for the purpose of this project). Degreasing was carried out within an ultrasonic bath for 10 minutes immediately after grit-blasting. The strips were then left to dry in air for 30 minutes and stored in clean, dry jars.

Substrate preparation

Polymer specimens, 20 mm x 10 mm, were cut accurately with a small guillotine which was kept clean and was used exclusively for this project. Tweezers and gloves were used throughout any handling of the polymer samples. The accuracy of the size of the pieces was determined by a pair of dividers to be ±0.25 mm. N.B. - the specimen size was found to be one of the most critical parameters for the reduction of experimental scatter; in particular, if the polymer film was undersized, metal-to-metal bonding could occur in the joint, see Figure 2.6.

Figure 2.6 **Schematic of error possible in lap shear joint due to metal-metal bonding**



If any joint showed evidence of metal-to-metal bonding through slippage of the polymer the bond strengths were disregarded.

Polymer samples were stored in a clean, dry jar prior to bonding.

Joint preparation

Equal proportions of epoxy resin and hardener were weighed out accurately to three decimal places together with 1% (by weight) of ballotini spheres. The components were then mixed continuously for five minutes. Mixing was aided by periodically scraping the spatula to ensure a homogeneous product. The cyanoacrylate adhesive was used as received.

Once mixed, the epoxy adhesive was used immediately. A uniform layer of adhesive was applied to a 10mm x 20mm area on the ends of two metal strips and the polymer was then placed accurately onto one. The metal strips were pressed together and, to ensure accurate and consistent overlap, the joint was located in a special jig. Figure 2.7 shows the jig and Figure 2.8 is a schematic of the lap shear joint.

Figure 2.7 Schematic of constant overlap jig, side view

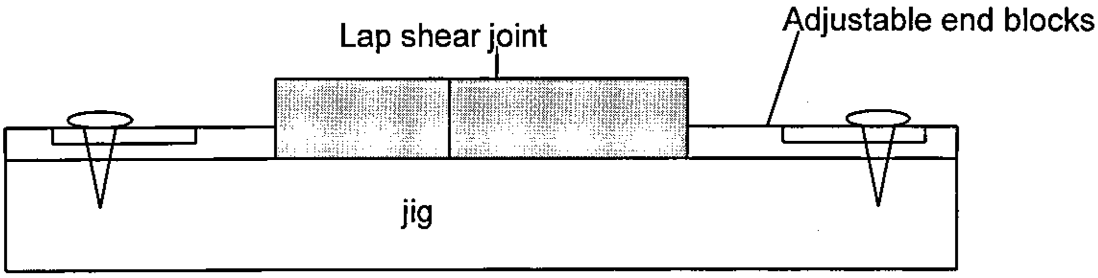
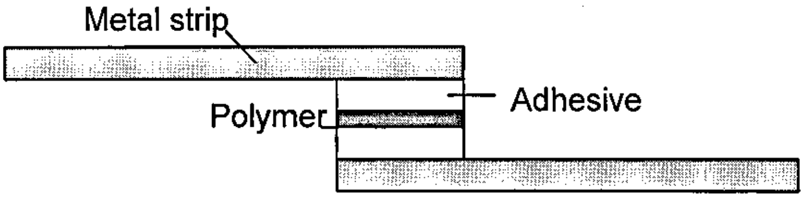
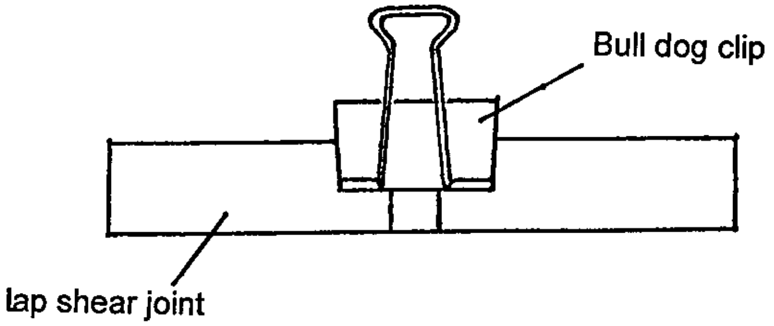


Figure 2.8 Schematic of lap shear assembly



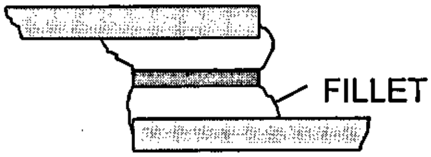
The joint was held in position at the overlap by means of a bulldog clip, positioned so that the pressure acted centrally upon it (see Figure 2.9). Any excess adhesive was removed using a microspatula before curing. The cyanoacrylate adhesive was cured in air at room temperature for at least 16 hours before testing. The epoxy adhesive was cured in a fan-assisted oven at 70°C for two hours. On removal the joints were allowed to cool at least 16 hours, before testing.

Figure 2.9 **Schematic of assembled lap shear joint**



Fillets formed during the curing of the adhesive (Figure 2.10) were removed before testing using a small file.

Figure 2.10 **Schematic of cured lap shear joint**



The joints were pulled apart on a Hounsfield tensiometer, type W, at a cross head speed of 12.5mm min^{-1}, held using 'quick grip' chucks and with an ungripped length of 40 mm. Spacers were positioned in the grips to minimise peeling forces. The failure load values quoted in the results are an average of five joints. Values are given in force (N) and force per unit area (MPa) i.e. divided by $2x10^{-4}$ m.

Bond strength measurements for some of the plasma treated substrates were carried out at BP, Sunbury-on-Thames using an Instron instrument with similar conditions.

2.4.2 Contact angles

Contact angle measurements at Loughborough University of Technology (LUT) were carried out using a 'Krüss contact angle system' G40 (version 1.0 1987). Four liquids were used: water (triply distilled), ethan-1,2-diol, dimethylsulphoxide (DMSO) and dimethylformamide (DMF). The surface tensions of these liquids were measured using a 'Krüss Digital Tensiometer K10T' instrument. Surface tensions were used to check the consistency of the liquids. Literature values for polar and dispersion components of surface tension were used for the calculation of solid surface energies and are given in Table 2.1 below.

Table 2.1 **Surface free energy of various liquids at 20°C**[91]

Liquid	γ_l	γ_l^d	γ_l^p	reference
water	72.8	21.8	51.0	92
ethandiol	48.3	29.3	19.0	93
DMSO	43.54	34.86	8.68	94
DMF	37.30	32.42	4.88	94

Separate syringes were used for each liquid and, to minimise contamination had restricted use.

Contact angle measurements were also carried out at BP Research Centre, Sunbury-on-Thames with an 'in house' constructed system. This consisted of a microscope eye piece that was mobile in three perpendicular axes, a sample plate that could be raised or lowered and a blue light source. The liquid was contained in a syringe with a micrometer screw gauge, set in a jig and positioned above the sample stage.

Method

The plastic film was cut into approximately 10 mm x 20 mm rectangles and was adhered to a small flat surface e.g. a microscope slide using double-sided tape, ensuring that the area of tape was completely covered by the film; this avoided possible contamination from components in the tape.

For the LUT instrument -
The sample was placed in the instrument and one drop of the first liquid was placed upon it. This initial drop was left for approximately five minutes to create, as near as possible, a saturated vapour of the liquid in the chamber.

A second drop was placed and allowed to rest with the syringe still within it for two minutes. The volume of the drops was kept constant throughout these experiments to 2μl, equivalent to 10 units on the Vernier scale of the microsyringe.

A. For an advancing angle measurement, liquid was added to the drop expanding it until the periphery, i.e. the point of three phase contact, moved along the surface; immediately this came to rest, the angle was noted.

B. For a receding angle measurement, liquid was extracted from the drop (aided by means of a spring on the syringe) until the periphery moved back along the surface At rest the angle was noted.

Definitions and methods of measurement vary[95,96]. For this project, 'A' is defined as the static advancing angle and 'B' as the static receding angle, as recommended by Good[96].

An average of four contact angles, 'θ' was noted for each plastic film-liquid combination and cosθ was calculated.

For the BP instrument -
The static advancing angle was measured by allowing a drop to be suspended on the syringe, the sample on the plate was then raised till the drop touched it and the

periphery advanced along the sample. The contact angle was read immediately. To measure the receding angle the plate was lowered slowly till the least contact angle was reached before the drop separated from the syringe. Note, the periphery did not actually recede along the surface and therefore cannot be directly compared to the LUT values.

Surface energy measurement[97]

Using Fowkes definitions, (outlined in Section 1.5.2) solid surface energy components can be calculated by means of a linear plot. A graph of X versus Y is plotted, where

$$X=\sqrt{\gamma_l^p/\gamma_l^d} \quad ....(17) \qquad \text{and} \qquad Y=\frac{1+\cos\theta}{2}\gamma_l\Big/\sqrt{\gamma_l^d} \quad ....(18)$$

γ_l^p = polar component of liquid surface energy
γ_l^d = dispersion component of liquid surface energy
γ_l = liquid surface energy.

The graph is a straight line with equation y = mx+c, where m = the gradient and c = the intercept on the y axis. m and c were calculated using a linear regression fit on the data, incorporated in 'Technicurve' software on a computer. The square of the gradient, $(m)^2$, is the polar contribution to solid surface energy, γ_s^p and the square of the intercept $(c)^2$, corresponds to the dispersion component, γ_s^d . The total solid surface energy, γ_s is the sum of γ_s^p and γ_s^d .

Contact angle hysteresis

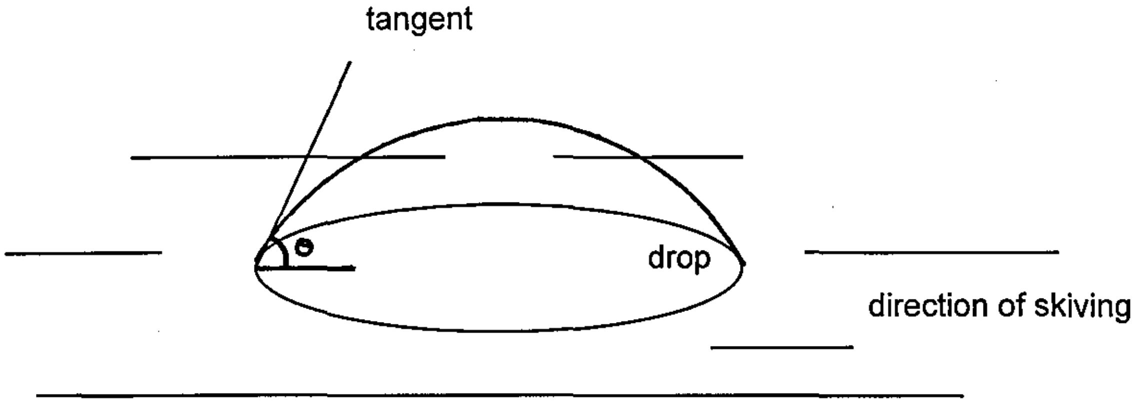
The difference between the advancing and receding contact angle is called the hysteresis; sources of hysteresis are outlined in section 1.5.2. In the cases where large hysteresis, i.e. greater than 15 degrees, was observed for the samples within this project SEM was used to observe the topography of the surface. If roughness was obviously a major cause of the hysteresis then a full surface energy calculation was not carried out, (the theory only applies to smooth, homogeneous surfaces).

Comparative studies between different samples using just water contact angles were carried out in this case.

Contact angle anisotropy

A surface containing oriented grooves, as in the case of PTFE skived film used in this project, will exhibit contact angle anisotropy[98,99], when a drop of liquid is placed on the film it is elongated along the direction of skiving. This gives rise to different contact angles parallel or perpendicular to the direction of skiving. Contact angles were measured parallel to the direction of skiving, see Figure 2.11.

Figure 2.11 **Measurement of contact angles on PTFE**



Surface energy measurements were carried out for selected polymers; more generally water contact angles were used as a guide to surface polarity.

An experiment to test the reliability of contact angles on flame treated PVF was carried out. It was possible that flame treatment could produce low molecular weight species at the surface and these could be taken up by a contact angle liquid, thereby changing the liquid's surface tension. Flame treated PVF samples were immersed in each liquid and the surface tension of the liquids were recorded with the sample remaining in the liquids. The beaker used was meticulously cleaned with chromic acid and washed with triply distilled water and dried after each liquid.

2.4.3 Fourier Transform infrared - Attenuated Total Reflection (ATR-FTIR)

Surface infrared spectra were recorded on a Nicolet 20DXC spectrometer using a variable angle ATR attachment manufactured by Spectratech. The detector was cooled using liquid nitrogen. A germanium prism (60° end surface, see Figure 1.11) or a KRS-5 (TlBr/TlI) (45° end surface) prism was used. Pressure was applied by means of a small vice on the ATR attachment and rubber pieces to bring the sample in close contact with the prism. The spectrometer's energy resolution was 4 cm^{-1} and 500 scans were taken for each sample. First a background spectrum was recorded, i.e. the absorbance from the prism alone. This was stored in the 'background' file on the computer and was automatically taken away from any other spectra.

A sample spectrum may be stored in one of two hard disk files, namely the 'sample file' or the 'reference file'; this enabled subtraction of one spectrum from another. For example, peaks due to water vapour were subtracted from sample spectra in order to identify more easily small functional groups that may have been introduced by a pretreatment. This was done by acquiring a spectrum of the sample after purging with dry nitrogen for at least 10 minutes and subtracting this, from one that had been run with the sample chamber lid open. This 'water' spectrum was then subtracted from the original sample spectrum.

Selected treated polymers were examined using ATR-FTIR. All spectra contain a strong absorbance band due to CO_2. This arises from the atmosphere within the instrument despite purging with nitrogen. CO_2 strongly absorbs infrared due to the C=O stretch. The band sometimes appears negative on the spectra given in the results, this is caused by different levels in the background or 'water' spectra that have been subtracted. The band is often very large in comparison to the bands due to surface modification of the treated polymers.

2.4.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was carried out using VG ESCALAB Mk. 1 instruments at both LUT and BP. The X-ray source was Al $K\alpha$ = 1486.6 eV in energy for both instruments. Specimens were stuck onto aluminium stubs using double-sided adhesive tape; the stub dimensions were 20 mm square at LUT and 15 mm diameter circular stubs at BP. The stubs were transported through the fast insertion lock into the UHV analysis chamber via a track system. The sample was positioned on the precision manipulator under the X-ray source so that the sample surface was normal to the analyser.

Specific instrument parameters are given with the results, but Table 2.2 has typical conditions for the acquisition of broad and high resolution scans.

Table 2.2 Instrument conditions for VG ESCALAB Mk 1 at LUT and BP

LUT Parameters	Broad scans	High resolution scans
Aperture	B1	A4
Pass energy	85 eV	18-20 eV
Scan range	1200 eV	varies
Scan width set	1250 eV	125 eV
Number of data points	2949	varies
Time for 1 scan width	60 seconds	60 seconds
No. of scans	5	30-50
X-ray anode	5-20 mA 10kV	20 mA 10 kV
Key: LUT : B1 = 4 mm x 10 mm slit. A4 = 4mm circle		
BP Parameters	Broad scans	High resolution scans
Aperture	A4	A4
Pass energy	100 eV	20 eV
Scan range	750-0 eV	Varies
Step size	1 eV	0.1
Channel time	80 ms	1000 ms
X-ray power	5-20 mA 10 kV	5-20 mA 10 kV
Time for 1 scan	60 seconds	varies
Number of scans	5	varies
Key: BP: A4 = 5 mm circle in, 10 x 4 mm out		

The spectra at LUT were recorded digitally on a microcomputer and analysed on an IBM PC using 'in house' software.

Data acquisition at BP was controlled by VG S5250 software but, data were transferred and quantified using Kratos DS800 software.

Broad scan XPS analysis was carried out on the majority of treated and untreated substrates to assess the surface compositional changes that occur as a result of the treatments. The binding energies of spectra were not corrected for charging unless peaks due the hydrocarbon were present. Broad scans of some debonded joints were also examined to gain locus of failure information.

Narrow scans of higher energy resolution were carried out on certain treated surfaces e.g. PTFE treated with 'Tetra-Etch'. Chemical shift information on treated, partially fluorinated polymers however, was complex. The C1s region consisted of peaks due to carbon bonded to one or two fluorines, plus carbon-oxygen bonds of different chemical environment; no additional quantification was obtained from these narrow scans and hence they were not generally carried out. Samples that had been subject to COOH or OH derivatisation and therefore tagged with fluorine were analysed for CF_3 groups by acquiring high resolution C1s spectra. A high resolution scan on the C1s region of untreated PVF gave an indication of the extent of X-ray damage after prolonged exposure.

When a joint strength was high, the debonded joint often failed at different surfaces. The complementary areas of both sides of the joint were too small to analyse on the VG ESCALAB Mk 1 instruments. Small spot XPS analysis was carried out on particular potassium hydroxide treated PVF samples using a VG ESCALAB 220i housed at BP, Sunbury-on-Thames. This work was carried out by Dr K. Harrison. The spectra were obtained from areas 1 mm in diameter using Mg X-rays (1235.7 eV in energy) Total acquisition times were 550 seconds for the broad scans and 500 seconds for the narrow scans (C1s, F1s, O1s and N1s). A broad scan was taken before and after the narrow scans to determine if sample degradation had taken place. Data were again analysed using the Kratos DS800 software.

Spectra of untreated PET, PTFE and PVF were acquired from the ESCALAB 220i and assumed to be 'standard' i.e. having an atomic ratio equal to the theoretical and being homogeneous in the region probed by XPS. This was to enable direct comparison of results obtained from ESCALAB 220i and ESCALAB Mk 1.

2.4.5 Scanning Electron Microscopy (SEM)

Electron micrographs were produced on a 'Cambridge Stereoscan 360 SEM' with various magnifications, typically x3000. Samples were vacuum coated with gold (< 5 nm) to give a conducting surface. Untreated and treated surfaces of PTFE, PVdF and PVF were examined. The analysis was carried out by Mr F.Page at LUT.

Chapter 3

Results

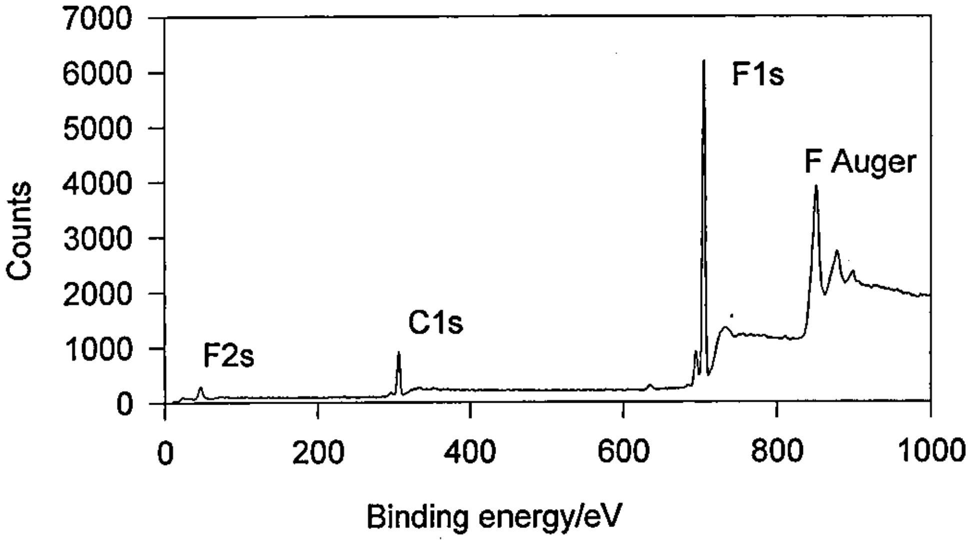
3.1 Untreated materials

3.1.1 Characterisation of untreated materials

Characterisation of the surfaces of PTFE, PVF and PVdF before pretreatment was carried out and the level of adhesion with the particular adhesives used in this work was measured via composite lap shear joint tests.

Figures 3.1, 3.2, 3.3 are broad scan XPS spectra of PTFE, PVF and PVdF in which the various peaks are identified. An example of the output from the XPS quantification software is given, displaying the surface compositions as atom % for PTFE. An X-ray anode power of 50 Watts (5 mA, 10 kV) was used for PTFE and 100 Watts (10 mA, 10 kV) for PVF and PVdF.

Figure 3.1 Broad scan of untreated PTFE and table of results from quantification software



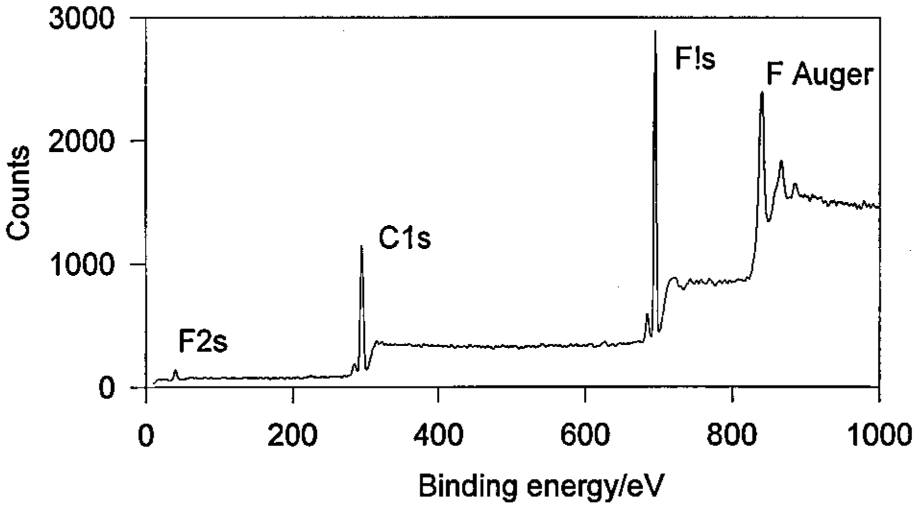
```
SPECTRUM No.    1
DIRECTORY       a:\is\data\isla7
SAMPLE          PTFE
COMMENTS        untreated
CONDITIONS      B1 Al 85

ELMT     peak     B.E.     start    stop     area     rsf      At.Wt.         % At.

C        1s                 772      801     5527.    .23      12.01          36.7
F        1s                1779     1810     41509   1.00      19.00          63.3
```

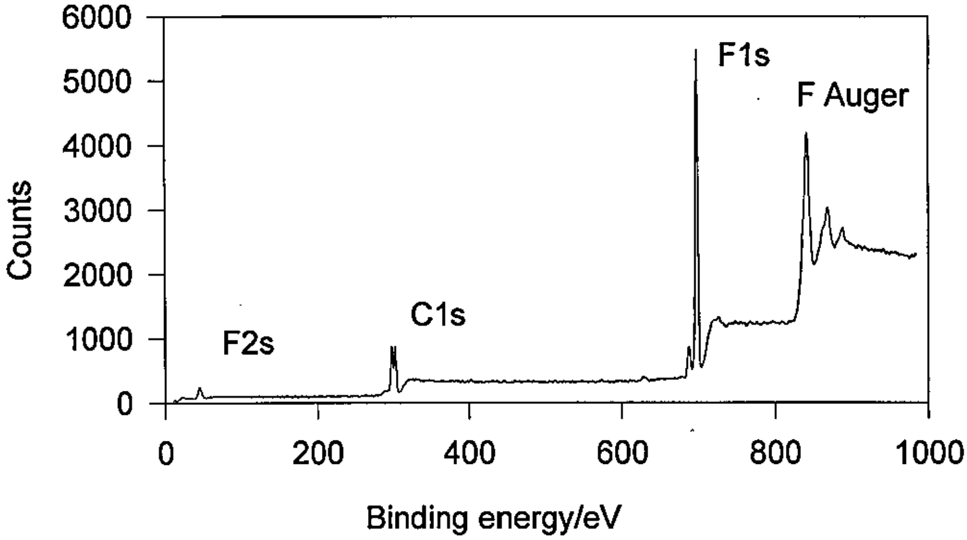
F2s/F1s = 0.05

Figure 3.2 **Broad scan of untreated PVF**



Composition: C 70.4, F 28.8, O 0.8. F2s/F1s = 0.04

Figure 3.3 **Broad scan spectra of untreated PVdF**



Composition of untreated PVdF: C 51.5, F 48.5. F2s/F1s = 0.05

High resolution C1s spectra of PVF and PVdF are included to demonstrate the binding energy shifts of carbon bonded to one or two fluorines; they are shown in Figures 3.4 and 3.5. Instrument conditions are given in Chapter 2 section 2.4.4

Figure 3.4 **High resolution C1s spectrum of untreated PVF**

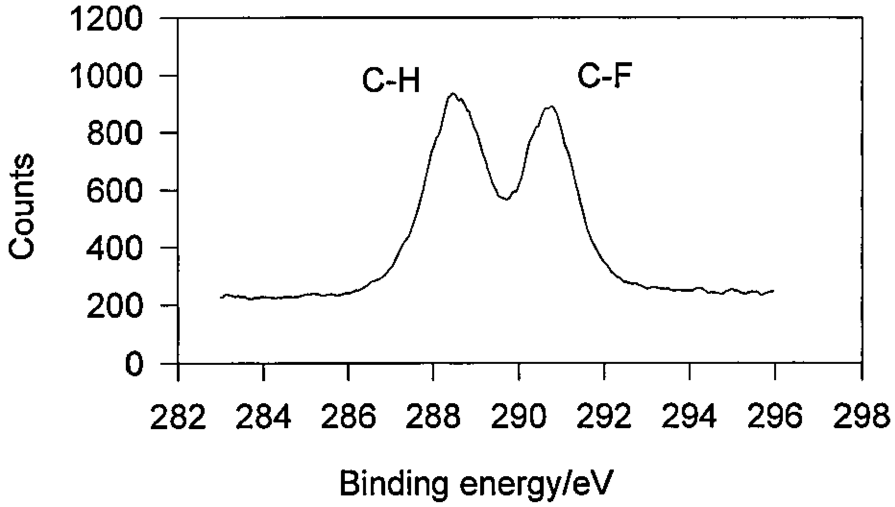
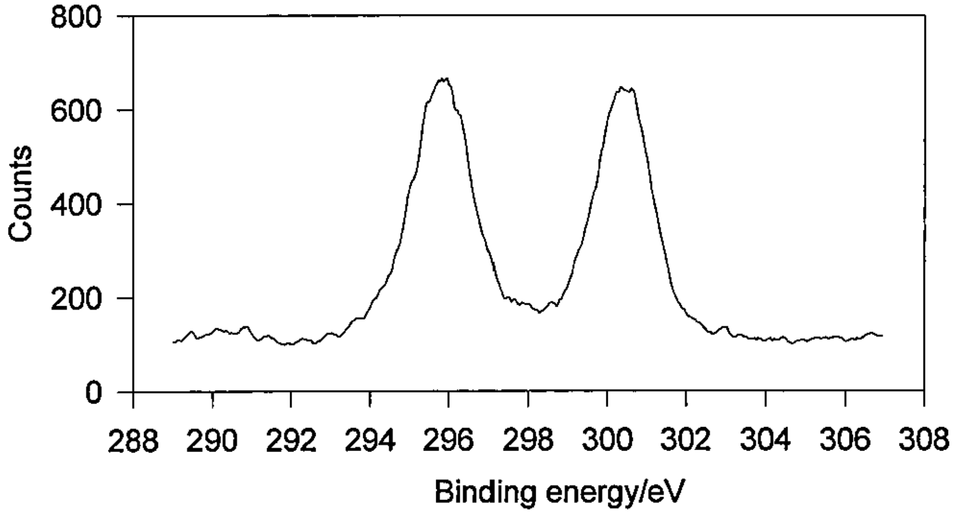
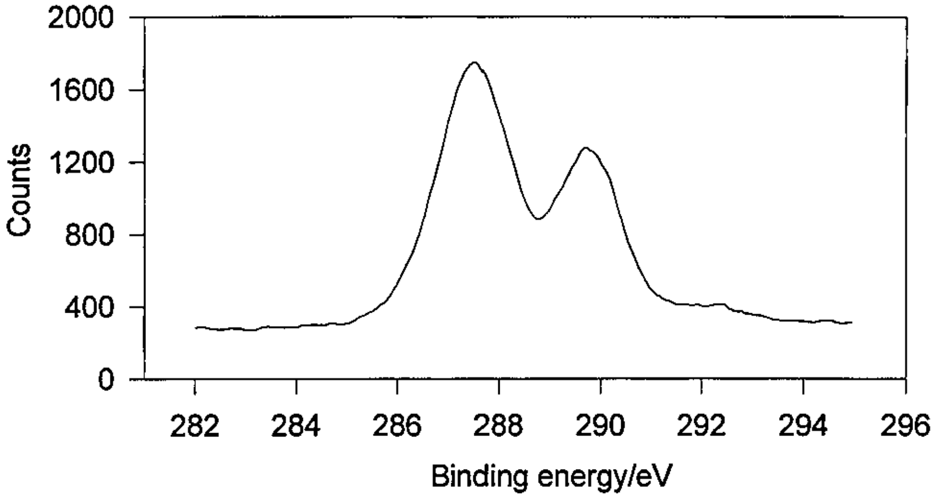


Figure 3.5 **High resolution C1s spectra of untreated PVdF**



An experiment into the effect of X-ray exposure on PVF was carried out by collecting a C1s high resolution spectra at different exposure times. Figure 3.6 shows the decrease in the carbon bonded to fluorine peak over a period of 38.4 minutes.

Figure 3.6 High resolution C1s spectrum of untreated PVF after X-ray exposure of 38.4 mins



ATR-FTIR spectra of untreated PTFE, PVF and PVdF are given for the range 4000 cm^{-1} to 400 cm^{-1} (Figures 3.7, 3.8, 3.9). A KRS crystal was used.

Figure 3.7 ATR-FTIR spectrum of untreated PTFE (KRS 55°)

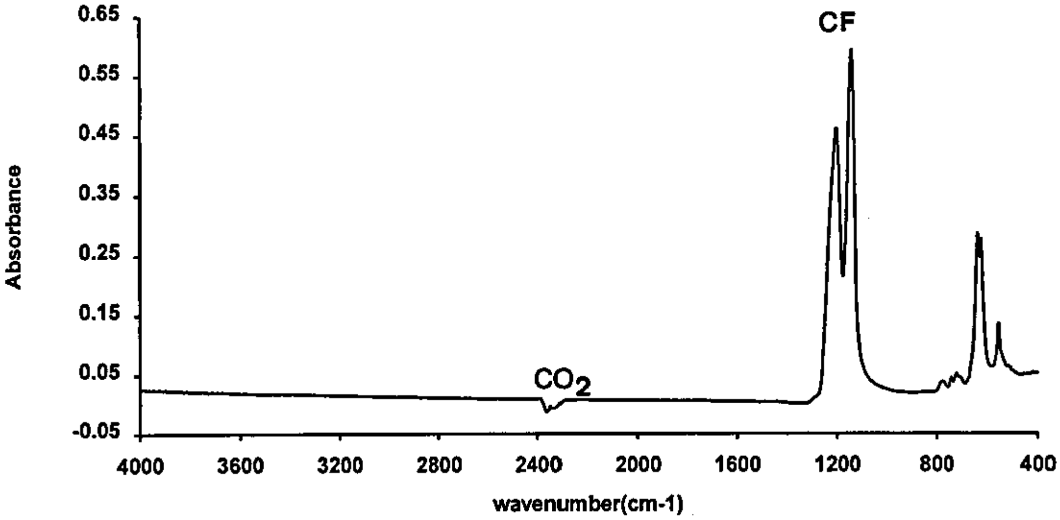


Figure 3.8 ATR-FTIR spectrum of untreated PVF (KRS 60°)

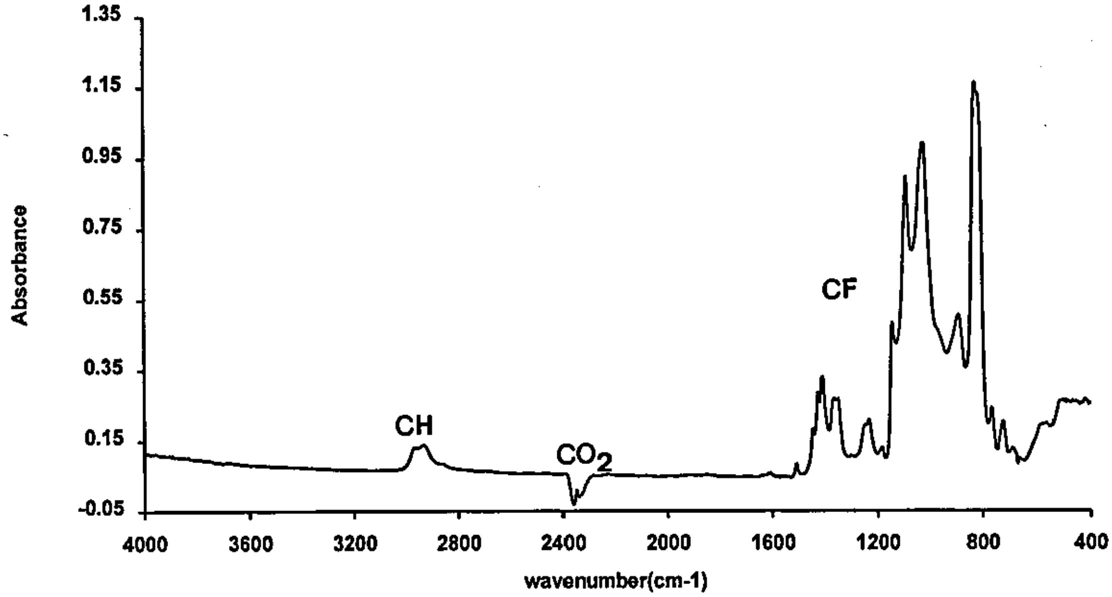
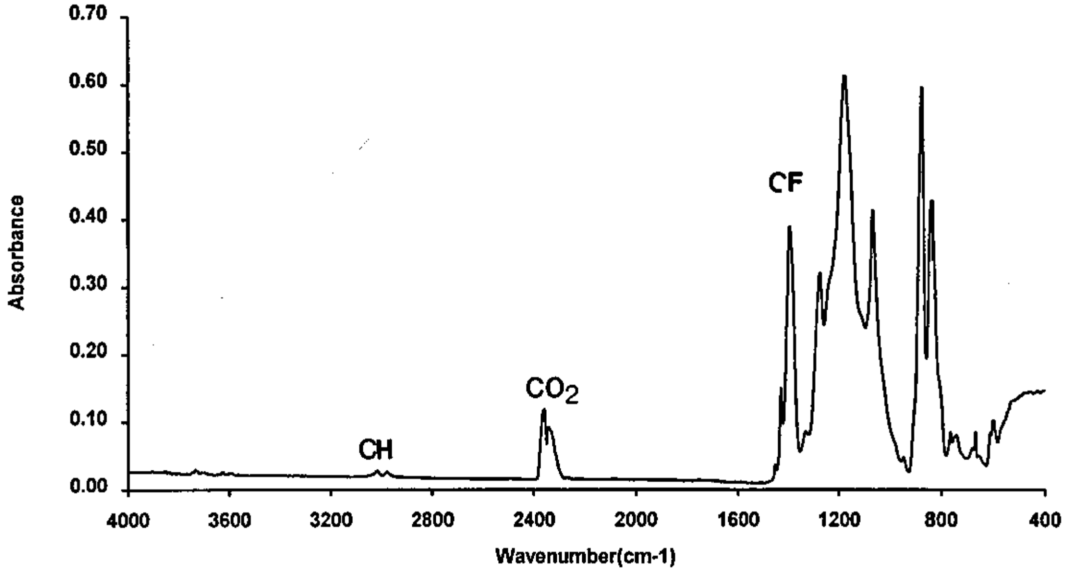


Figure 3.9 ATR-FTIR spectrum of untreated PVdF (KRS 60°)



Micrographs (Figures 3.10, 3.11, 3.12) are given below to show the topography of the untreated fluoropolymer surfaces. The scale is given on the photograph.

Figure 3.10 Micrograph of untreated PTFE

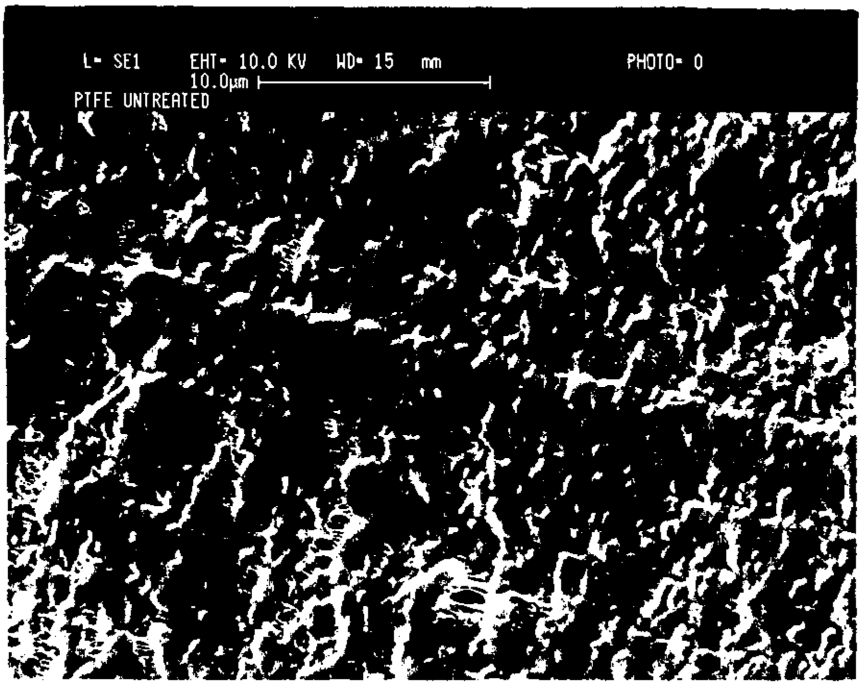


Figure 3.11 Micrograph of untreated PVF

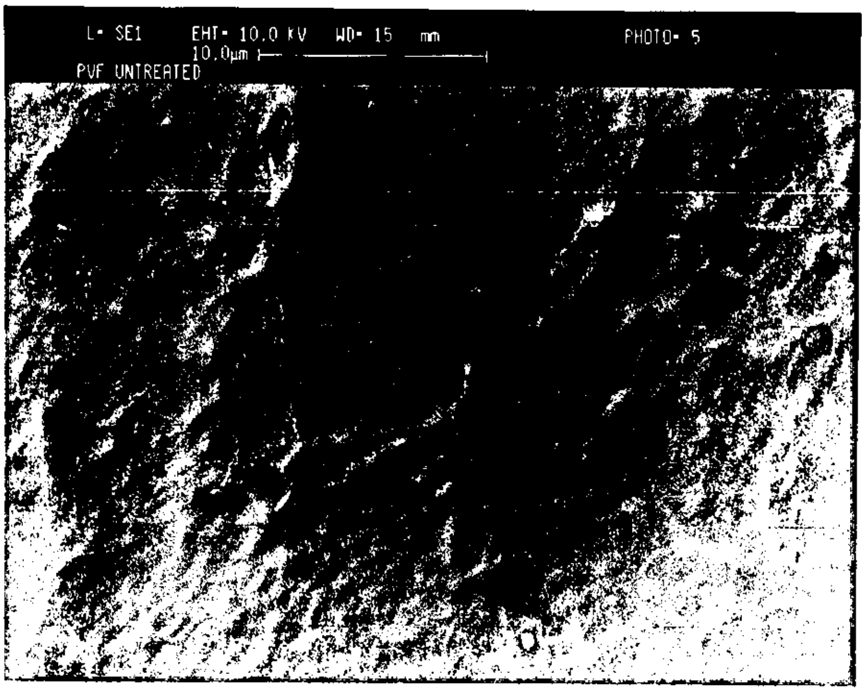
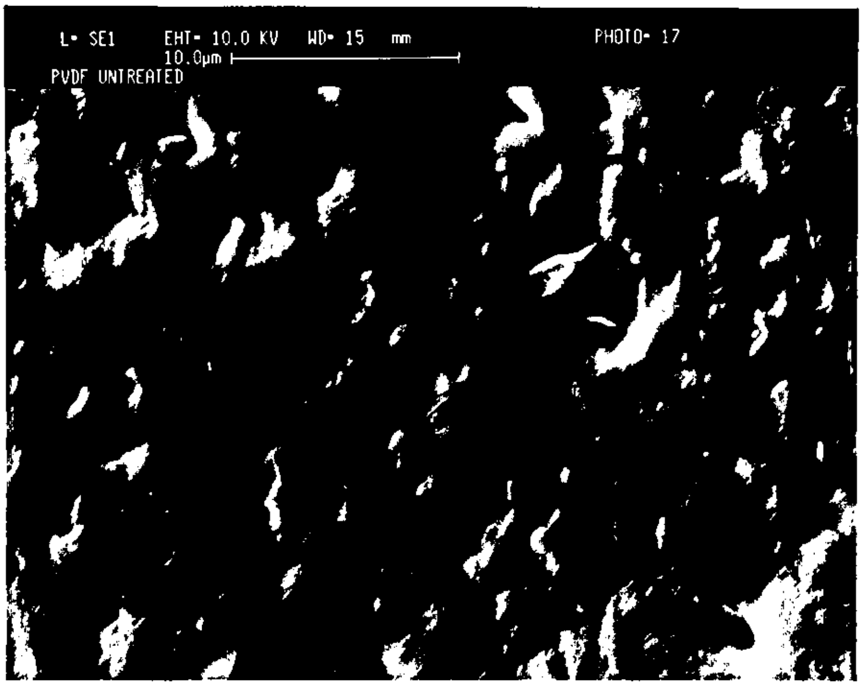


Figure 3.12 Micrograph of untreated PVdF



The surface of the PTFE was very porous and pitted whereas PVF and PVdF were relatively smooth.

Surface energy measurements were not carried out for PTFE due to the complications with surface roughness and contact angle hysteresis (hysteresis for water ~30°). PVF had a water contact angle hysteresis of ~13°, so an estimation of surface energy was determined via the Fowkes method (Table 3.1). (experimental section 2.4.2).

Table 3.1 Water contact angles of untreated PVF and PTFE and an estimation of the surface energy of untreated PVF.

	Water contact angles		Surface energy		
Polymer	advancing/°	receding/°	γ_s^p /mJ m^{-2}	γ_s^d /mJ m^{-2}	γ_s /mJ m^{-2}
PVF	78	65	6.2	31.0	37.2
PTFE	124	94			

Key: γ_s^p = Polar component to surface energy
γ_s^d = Dispersion component to surface energy
γ_s = Total surface energy

The bond strengths for untreated PVF, PVdF and PTFE are given in Table 3.2.

In order to follow one of the main aims of this project i.e. to gain understanding of the way in which pretreatments enhance the adhesion of these fluoropolymers, the adhesive joint system that gave a low failure load with untreated polymer was chosen for joint strength analysis. PVF and PTFE were consistently bonded with epoxy and PVdF was bonded with a cyanoacrylate adhesive.

Table 3.2 Adhesive joint strengths of untreated fluoropolymers bonded with two different adhesives.

Polymer	Adhesive	Conditions	Failure load/N	SD	Bond strength/MPa
PTFE	Epoxy	70°C 2 hours	420	87	2.1
	Cyanoacrylate	23°C 24 hours	213	85	1.1
PVF	Epoxy	70°C 2 hours	350	70	1.8
	Cyanoacrylate	23°C 24 hours	3500	212	17.5
PVdF	Epoxy	70°C 2 hours	6400*	379	> 32.0
	Epoxy	23°C 24 hours	1290	124	6.5
	Cyanoacrylate	23°C 24 hours	1300	294	6.5

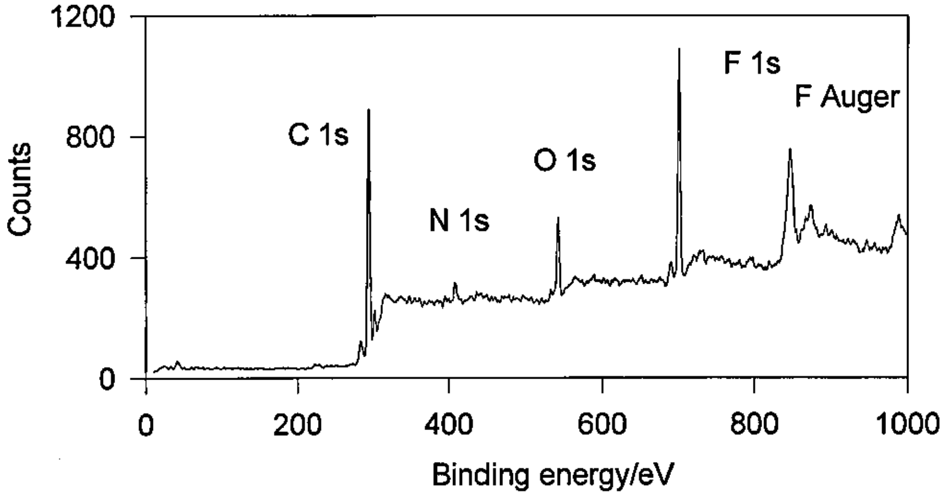
Key: SD = standard deviation

* The failure in these joints were at the metal-epoxy interface i.e. the interfacial shear strength of PVdF/epoxy was greater than 32 MPa. A lap shear test without a polymer sample i.e. metal/epoxy/metal bond gave a bond strength value of 27.5 MPa.

PVF was washed in methanol then analysed with XPS and bonded; there was no change in bond strength or surface composition. Similarly there was no change in surface composition or increase in adhesion when it was washed in trichlorotrifluoroethane.

In order to examine the locus of failure of bonded, untreated fluoropolymers, PTFE and PVF were bonded with an epoxy adhesive and then the joint was tested to failure; PVdF was bonded with epoxy at room temperature. XPS was used to examine the adhesive side of the debonded joints; Figures 3.13, 3.14 and 3.15 are the resulting spectra for the epoxy adhesive.

Figure 3.13 **Epoxy side of a debonded joint with untreated PTFE**



F2s/F1s = 0.03

Figure 3.14 **Epoxy side of a debonded joint with untreated PVF**

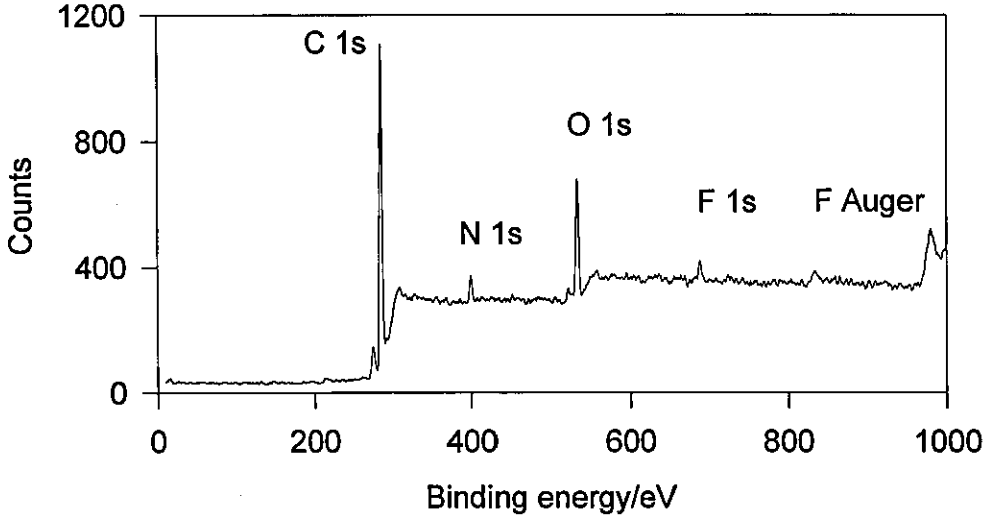
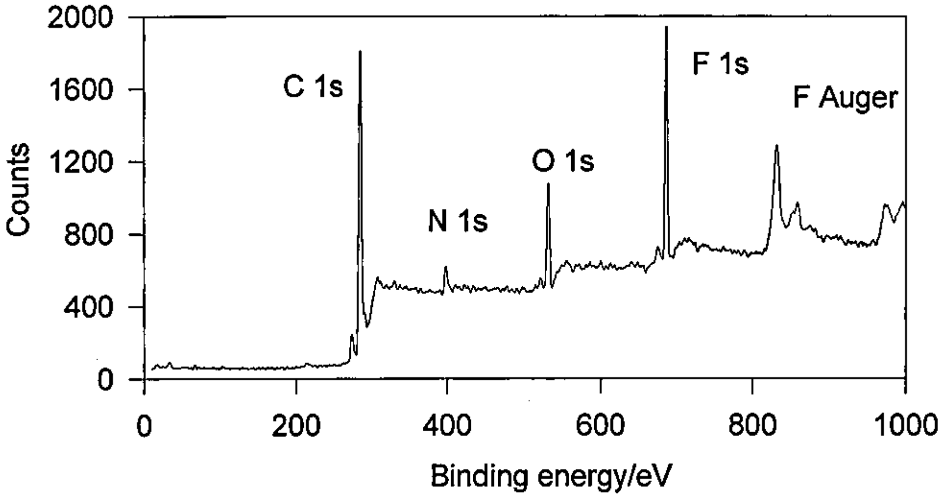


Figure 3.15 Epoxy side of a debonded joint with untreated PVdF at room temperature



F2s/F1s = 0.03

Table 3.3 summarises the quantification of the above spectra.

Table 3.3 Surface compositions of epoxy after bonding with PTFE, PVdF and PVF.

Epoxy	XPS /atom %			
	C	F	O	N
Not bonded	85.9	-	9.1	5.0
After bonding to PTFE	72.6	16.9	6.3	4.3
After bonding to PVF	84.3	1.3	10.5	3.9
After bonding to PVdF (RT)	74.8	12.2	8.8	4.3

Key: RT = room temperature

An additional experiment showing the transfer of fluorine containing material at an interface was carried out as follows. Polyethylene (PE) that had been melted and pressed between two sheets of PVF film was removed from the film and XPS carried out it. Fluorine (2.3 %) was found on the surface of the PE.

3.1.2 Multiple bonding of untreated PVF and PTFE

For multiple bonding experiments PVF and PTFE were bonded according to the method in Section 2.2 and repeatedly peeled and rebonded. At various numbers of bonds, the epoxy side of the joint was examined with XPS and the fluoropolymer was examined with SEM. Lap shear joints were also made up after particular numbers of bonds to assess the adhesion level of the material at that stage. Table 3.4 shows the results.

Table 3.4 Bond strengths of untreated PTFE and PVF, and amount of fluorine transferred to epoxy after various number of bonds

Material	No of bondings	Failure load/N	SD	BS /MPa	% of F on epoxy side
PTFE	1	396	9.6	2.0	16.9
	10	940	321	4.7	19.2
	20	897	178	4.5	20.1
PVF	1	567	29	2.9	1.3
	10	1790	188	9.0	10.1
	20	2425	330	12.1	6.5

Key: BS = Bond strength
SD = Standard deviation

The bond strength of PTFE increased by a factor of 2.2 after 20 bondings and the adhesion of PVF was improved 4.3 fold after 20 bondings.

Figure 3.11 in the previous section showed that the surface of untreated PTFE was grooved from the skiving process; it also had deeper holes containing fibrous material. After the PTFE had been bonded once (Figure 3.16) the surface appeared more uniform and the epoxy side showed a replica of the initial PTFE surface (Figure 3.17).

Figure 3.16 **Micrograph of PTFE after it had been bonded once**

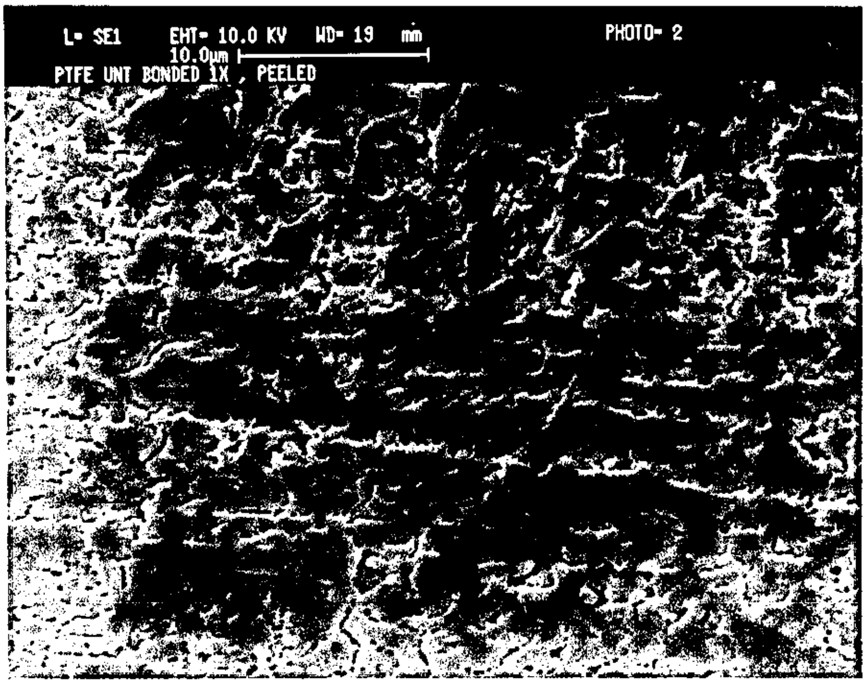
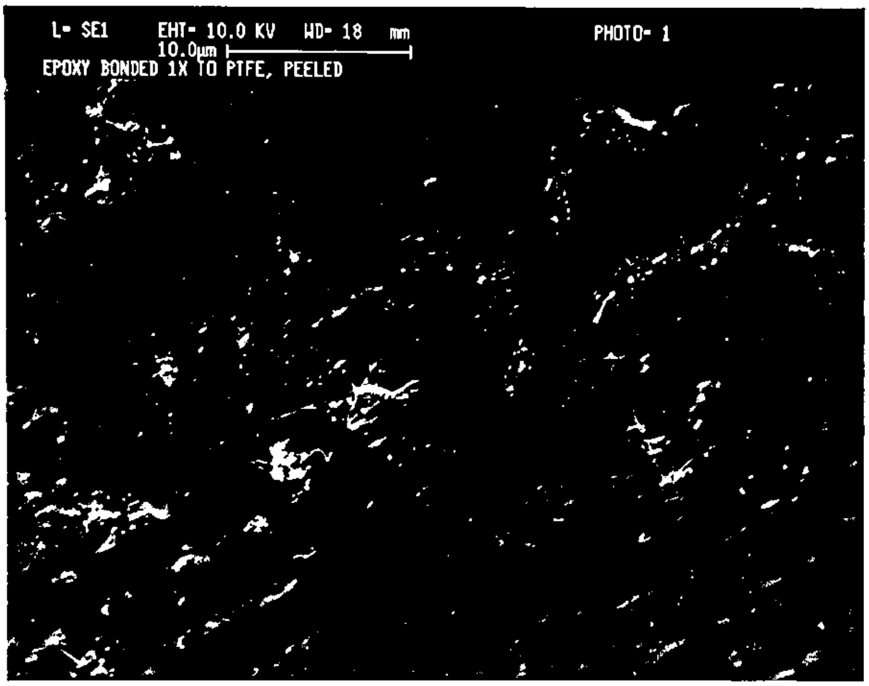


Figure 3.17 Micrograph of epoxy side of an adhesive joint to PTFE (first bond)



The following micrographs are PTFE after it has been bonded 9 and 20 times, and epoxy after it had been bonded to PTFE that have undergone 20 bonds.

Figure 3.18 PTFE after it had been bonded 9 times

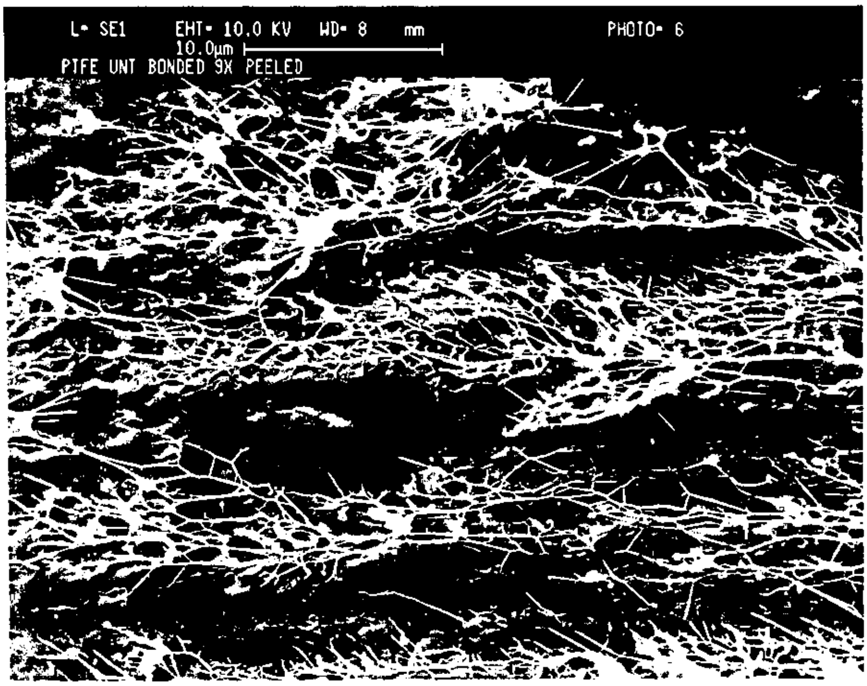


Figure 3.19 PTFE after it had been bonded 20 times

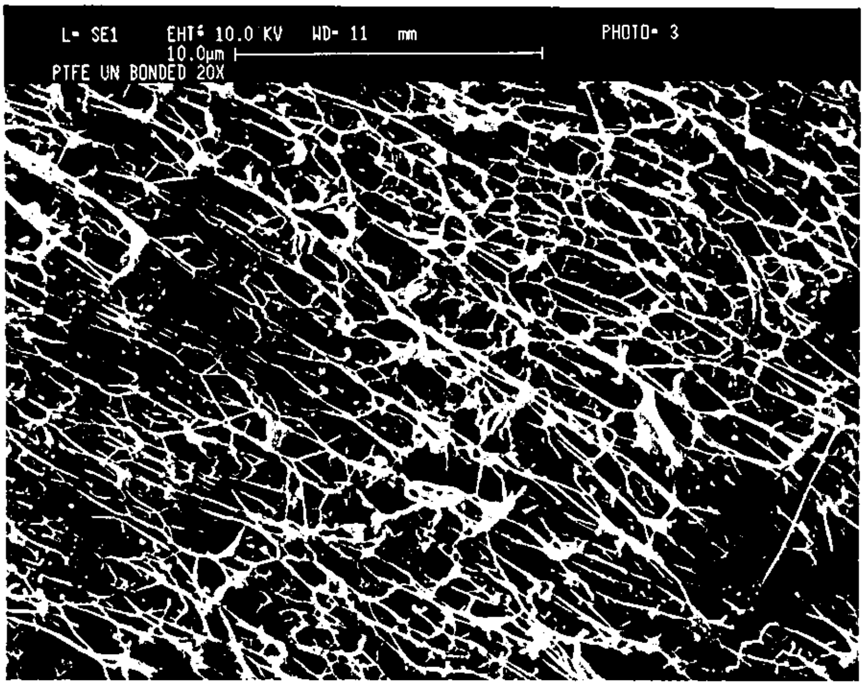
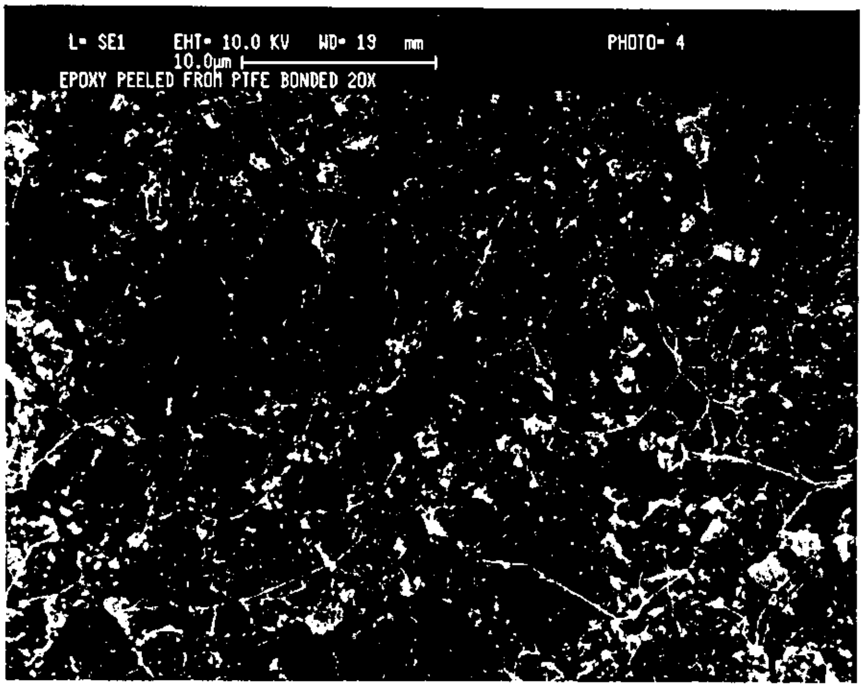
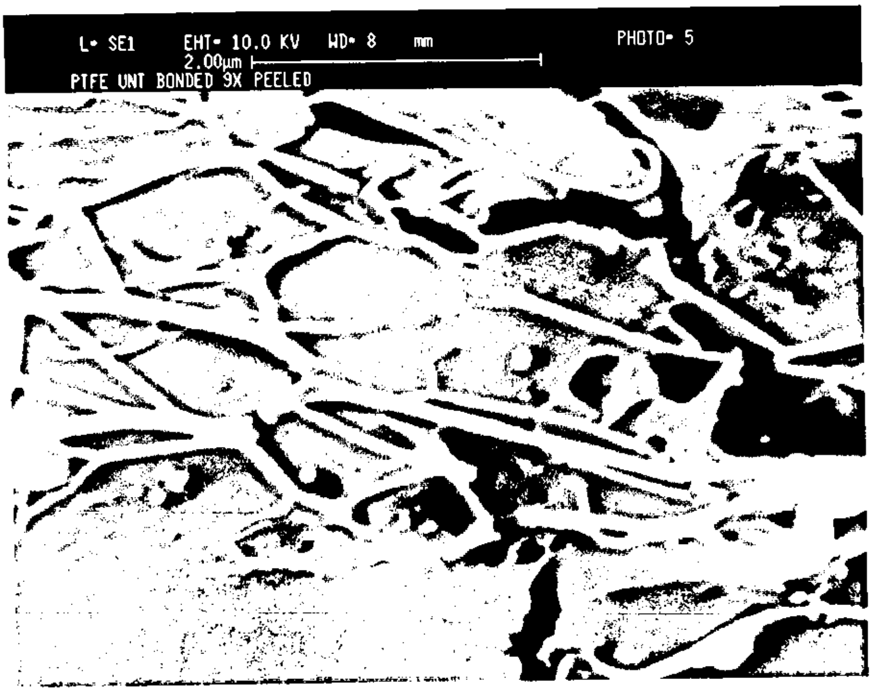


Figure 3.20 Epoxy side of an adhesive joint with PTFE that had been bonded 20 times



Both the PTFE and epoxy looked very different after the PTFE had been repeatedly bonded. The PTFE had an increasing amount of fibrous material; a micrograph at higher magnification shows clearly that these emerged from the porous bulk (Figure 3.21).

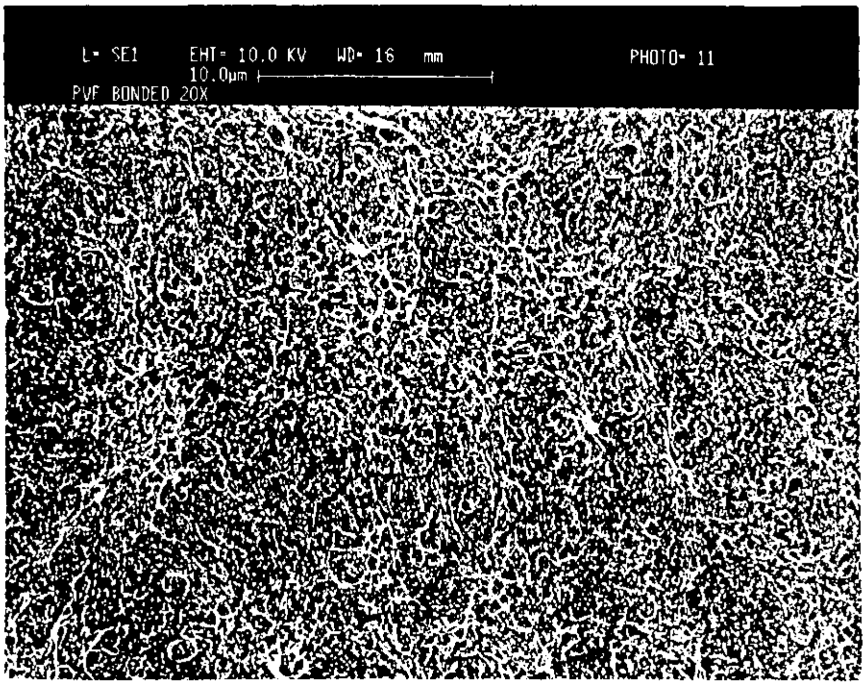
Figure 3.21 **PTFE after it had been bonded 9 times**



The epoxy surfaces also displayed fibrous material. However, XPS of the epoxy surface showed that the background after the F1s peak fell slightly. This is indicative of a higher concentration of fluorine in the near surface region, suggesting a thin layer of fluorine containing material compare Figure 3.13 with Figure 3.1 as an example. The F2s/F1s ratio was 0.03 in Figure 3.13.

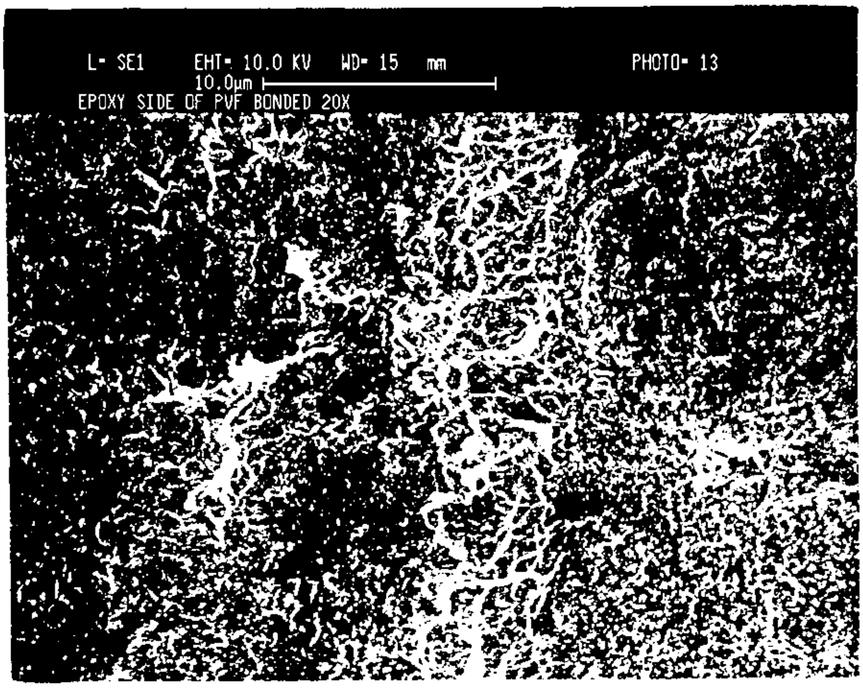
Considering now PVF, the topography changed after many bonds (Figure 3.22).

Figure 3.22 **Micrograph of PVF after 20 bonds**



Plastic deformation of the substrate was apparent after 20 bondings. The surface composition of the PVF surface after 20 bondings was C - 70.1%, O - 1.7% and F - 28.1% i.e. no N. Figure 3.23 shows the micrograph of the epoxy side of the PVF after 20 bondings.

Figure 3.23 **Micrograph of epoxy side of joint containing PVF bonded 20 times**



The XPS spectra of epoxy surfaces that had been bonded to PVF 10 and 20 times all display a falling background intensity to the higher binding side of the F1s peak (the F peak on the epoxy to 5 times bonded sample was too small to distinguish this phenomena). As with PTFE this suggests a thin layer of transferred fluorine-containing material on the epoxy adhesive.

3.2 'Tetra-Etch'

3.2.1 Comparison of 'Tetra-Etch' and sodium naphthalenide treated PTFE.

Treatment of PTFE with 'Tetra-Etch' and sodium naphthalenide solution caused the normally white substrate to become blackened very rapidly. A typical broad scan XPS spectrum of 'Tetra-Etch' treated PTFE is shown below. (Figure 3.24)

Figure 3.24 **Broad scan XPS spectrum of PTFE treated with 'Tetra-Etch' for 2 seconds**

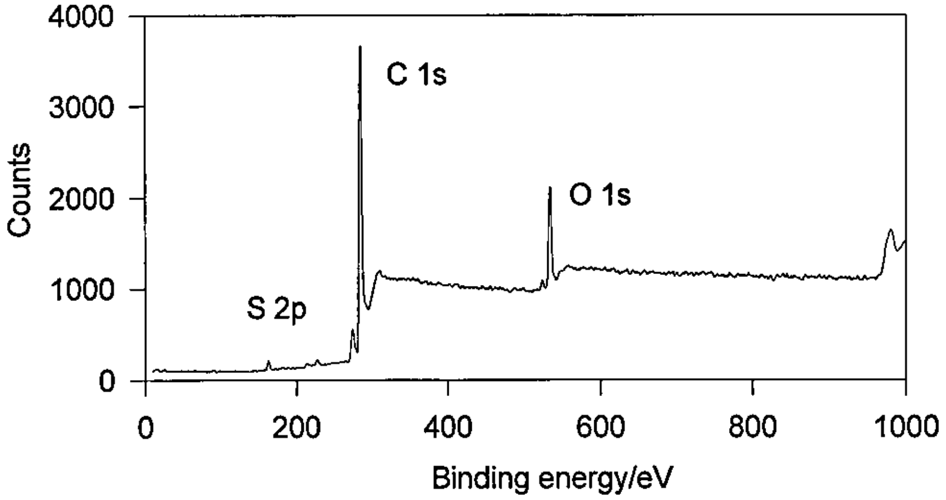


Table 3.5 shows the surface composition changes and the reduction in water contact angle as a result of the treatments and the effect on joint strength.

Table 3.5 Comparison of PTFE treated with 'Tetra-Etch' and sodium naphthalenide solution.

Treatment	Failure load/N	SD	Bond strength /MPa	water contact angles/°			XPS /atom %		
				Adv.	Rec.	Hyst.	C	F	O
None	420	88	2.1	124	94	30	34.7	65.3	-
'Tetra-Etch' 1 min	4260	246	21.3	69	11	58	82.1	0.9	16.9
Naphthalenide 1 min	4280	115	21.4	78	28	50	87.1	0.4	12.4
Naphthalenide 1 min + UV 7 h	1540	-	7.7	134	84	50	41.4	42.5	11.2*
'Tetra-Etch' + Na/hypochlorite	1880	148	9.4	144#	140	4	33.4	65.2	1.4

Key: SD = Standard deviation
Adv = Advancing
Rec = Receding
Hyst = Hysteresis

* also 4.9% impurities

\# It was very difficult to get the drop to rest on the sample. The extremely hydrophobic surface caused the drop to remain on the syringe needle.

The adhesion of PTFE was increased ten fold after a 1 minute 'Tetra-Etch' or sodium naphthalenide treatment. The advancing water contact angle was reduced by around 50 degrees for both treatments and the hysteresis was increased to an average of 54 degrees from 30 degrees. XPS results show almost complete defluorination of the near surface region and that a substantial amount of oxygen was incorporated.

'Tetra-Etch' and sodium naphthalenide treatments produced very similar results on PTFE bond strength, water contact angle and XPS results. However, in some cases XPS showed traces of sulphur (generally less than 1 %) on 'Tetra-Etch' treated PTFE. The binding energy of the S 2p peak in the XPS spectrum was 163 eV; it is therefore, not likely to be present in a high oxidation state. It was assumed that this was part of an additive or an impurity in the manufactured solution.

Table 3.5 also shows the effect of ultra-violet (UV) radiation on sodium naphthalenide treated PTFE. After irradiation the characteristic black coloration was removed and the water contact angle was restored to near the untreated value; hysteresis however remained high. The chemical composition of the surface however, did not reflect that of untreated; substantial oxygen was observed and the amount of fluorine was less than untreated. The failure load of the irradiated sample was 4 times that of untreated PTFE.

Hypochlorite solution (bleech) also removed the black treated region on the PTFE surface; it resulted in a much less contaminated surface than the UV post-treated sample. A very small amount of oxygen remained but adhesion was about 4.5 times that of untreated. It is interesting to note the apparently low hysteresis. This is discussed in section 4.4.1

3.2.2 Washing procedure after 'Tetra-Etch' treatment.

Note should be made briefly on the washing procedure after 'Tetra-Etch' treatment. Three different washings were carried out after treating PTFE with 'Tetra-Etch' (see Section 2.3.1 for details). The bond strength was unaffected by these procedures whereas the water wettability was significantly different, see Table 3.6.

Table 3.6 The effect of washing procedure on water contact angles and surface composition for PTFE treated with 'Tetra-Etch'

Treatment	Washing method	Water contact angles /°			XPS /atom %		
		Adv.	Rec.	Hyst.	C	F	O
untreated	-	124	94	30	34.7	65.3	-
Tetra-Etch. 1 min	A	48	0	48	78.0	6.0	13.6*
"	B	65	0	65	80.9	1.9	16.1*
"	C	79	12	67	82.4	2.5	14.2*

Key: A: Hot water, acetone, (x2)
B: Hot water + detergent, acetone (x2) recommended by 'Gore & Associates'
C: Methanol, hot water, methanol (x2)
* Sulphur present about 1 %
Adv = Advancing
Rec = Receding
Hyst = Hysteresis

Wash C was chosen as the procedure for this project because after storage of the samples there was no naphthalene odour detected in the containers, unlike samples washed according to the other methods.

3.2.3 Comparison of 'Tetra-Etch' treatment on different fluoropolymers.

Table 3.7 shows that 'Tetra-Etch' was an effective pretreatment for PTFE, PVF and PVdF.

Table 3.7 Effect of treatment time on failure load, water contact angle, and surface composition for PTFE[a], PVF[a] and PVdF[b] treated with 'Tetra-Etch'.

Polymer	Treatment time	colour	Failure load/N	SD	BS /MPa	θ adv/°	XPS /atom %			
							C	F	O	S
PTFE	none	white	420	88	2.1	118	34.7	65.3	-	-
	2 secs	brown	3660	152	18.3	79	88.0	-	10.6	1.4
	10 secs	"	4270	277	21.4	64	87.0	0.8	11.6	0.6
	30 secs	"	4100	137	20.5	68	87.5	0.8	10.6	1.1
	1 min	"	4260	246	21.3	69	82.2	0.9	16.9	-
	10 mins	"	4440	89	22.2	71	85.3	3.8	10.1	0.8
	30 mins	black	4160	207	20.8	72	84.6	5.5	9.1	0.8
	1 h	"	4460	251	22.3	73	88.8	2.7	8.6	-
PVF	none	colourless	350	70	1.8	78	70.4	28.8	0.8	-
	2 secs	"	720	110	3.6	77	71.6	27.9	0.5	-
	10 secs	"	800	100	4.0	78	72.4	26.7	0.9	-
	30 secs	"	1000	100	5.0	81	74.2	21.4	4.4	-
	1 min	"	2080	221	10.4	84	75.4	23.0	1.6	-
	10 mins	"	3180	168	15.9	87	84.3	15.0	0.8	-
	30 mins	"	2680	386	13.4	89	86.7	12.1	1.2	-
	1 h	"	3020	298	15.1	91	87.3	11.4	1.3	

Key: BS = Bond strength
SD = Standard deviation
br = brown

a: bonded with epoxy adhesive
b: bonded with cyanoacrylate adhesive
adv = advancing contact angle

Table 3.7 is continued over....

Table 3.7... .....continued **Effect of treatment time on failure load, water contact angle, and surface composition for PTFE[a], PVF[a] and PVdF[b] treated with 'Tetra-Etch'.**

Polymer	Treatment time	colour	Failure load/N	SD	BS /MPa	XPS /atom % C	F	O	S
PVdF	none	colourless	1580	356	7.9	51.5	48.5	-	-
	10 secs	"	2930	1062	14.7	70.0	20.1	9.9	-
	1 min	faint br	2450	915	12.3	71.4	17.7	10.9	-
	10 mins	"	3560	952	17.8	74.0	14.0	12.0	-
	30 mins	"	3740	373	18.7	72.4	14.8	12.7	-
	1 h	"	2940	293	14.7	70.9	16.1	13.0	-

Key: BS = Bond strength
SD = Standard deviation
br = brown

a: bonded with epoxy adhesive
b: bonded with cyanoacrylate adhesive
adv = advancing angle

PVF was also treated in THF alone (3 hours at 60°C) as a control. The bond failure load was 540N after immersion which is only slightly greater than untreated.

The modification of PTFE was rapid and the chemical changes were in agreement with similar studies outlined in chapter 1 (Section 1.4.4). A large increase in adhesion (10X) was observed when it was bonded with epoxy adhesive; the surface was also severely roughened by the treatment as seen by SEM (Figures 3.25 and 3.26).

Figure 3.25 Micrograph of untreated PTFE

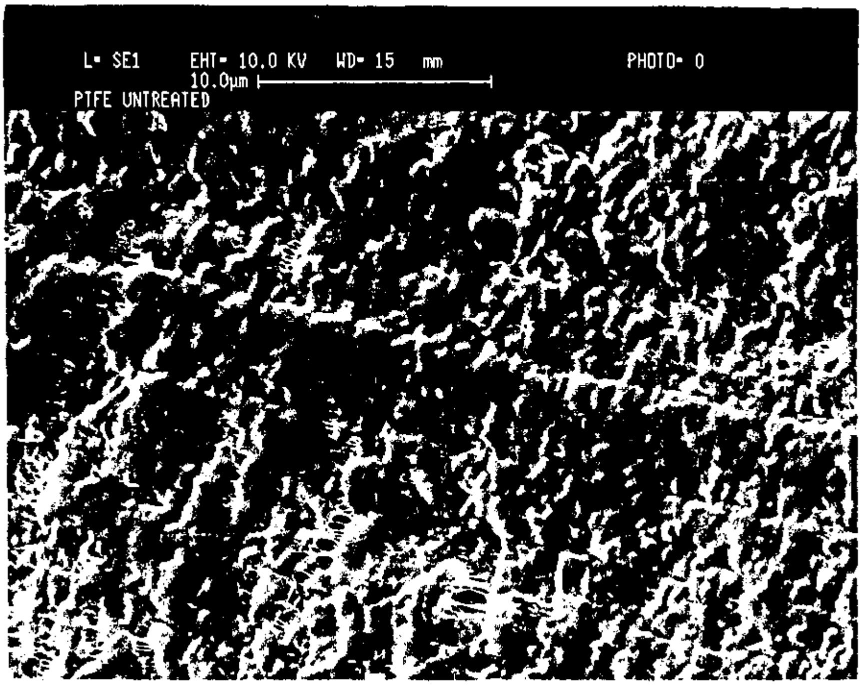
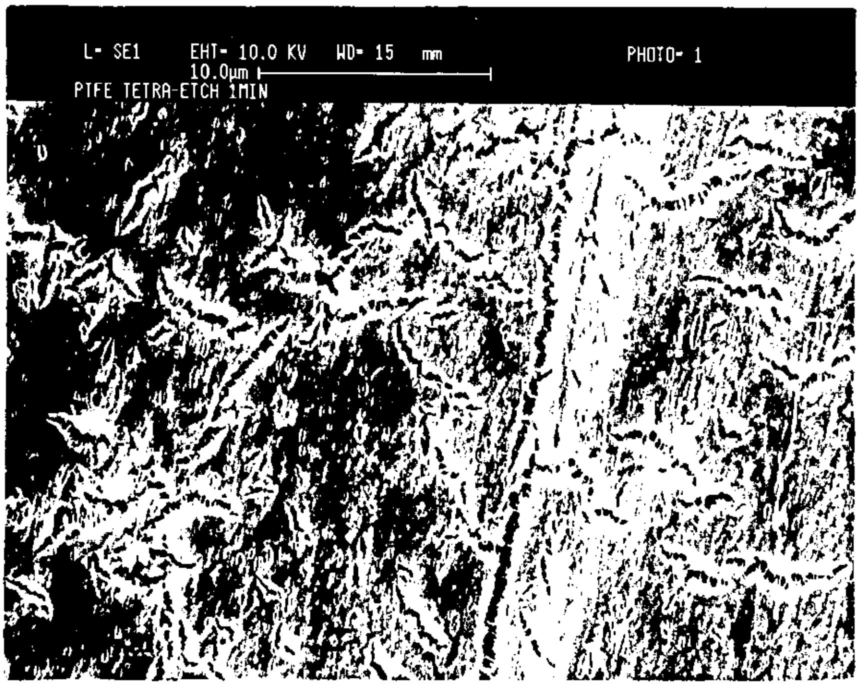


Figure 3.26 Micrograph of PTFE after treatment with 'Tetra-Etch' for 1 minute.



Wettability of the PTFE surface after treatment with 'Tetra-Etch' was increased as shown by a rapid initial decrease in water contact angle. The treatment of PVF however, was slower and the chemical changes were much less marked. After one hour the fluorine level on the PVF had fallen to half that of untreated and the oxygen incorporation was very slight. There was no change in coloration of the treated PVF samples as in PTFE. However, the adhesion was high (9X that of untreated after 10 mins treatment)

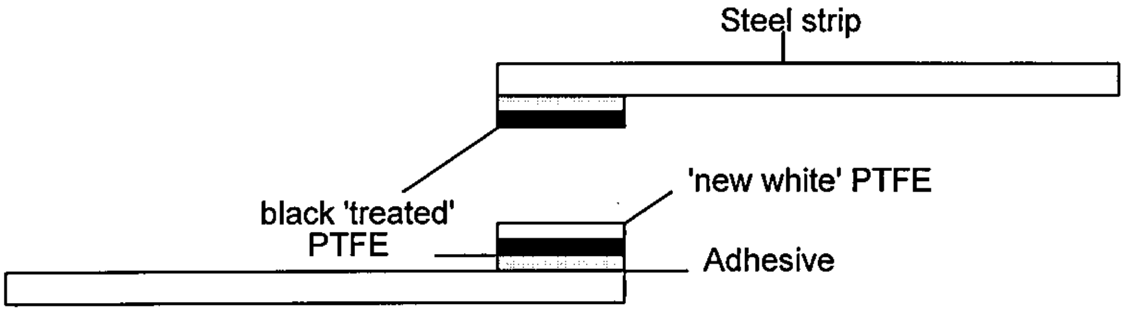
It is interesting to note that the advancing water contact angle on 'Tetra-Etch' treated PVF gradually increaseed over the range of treatments, from 78° to 91°. This was not associated with a change in roughness; a sample treated for one hour did not show any topographical changes.

'Tetra-Etch' treatment of PVdF produced a slight discoloration of the material and gave a 2.2X increase in adhesion using a cyanoacrylate adhesive; however, the value with untreated was relatively high as compared with PTFE and PVF. The changes in chemical composition of PVdF after treatment with 'Tetra-Etch' were intermediate to those of PVF and PTFE; there was significant, but not total defluorination, and a large incorporation of oxygen. There was no topography change observed with SEM.

3.2.4 Locus of failure

Examination by eye, of a failed joint comprising of PTFE treated with 'Tetra-Etch' showed apparent cohesive failure within the PTFE bulk. Figure 3.27 is a schematic showing where the apparent failure occurs. Failure was not always at just one interface as shown in the figure; this is given for simplicity.

Figure 3.27 **A schematic of a debonded joint of PTFE treated with 'Tetra-Etch'**



The two epoxy surfaces apparently had the characteristic black 'treated' PTFE adhered to them, with 'new white' PTFE exposed between them, suggesting failure at the boundary of untreated and treated material. To clarify the locus of failure, XPS examination of the failed joint were carried out. Table 3.8 shows the results; side 1 was originally an epoxy side, side 2 was the 'new white' PTFE.

Table 3.8 **Elemental composition of failed joint surfaces from 'Tetra-Etch' treated PTFE.**

Polymer	Side	XPS /atom%			
		C	F	O	N
PTFE	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 and 'Tetra-Etch' treated and there is no nitrogen apparent on the surface that was originally epoxy.

3.2.5 Derivatisation of PTFE treated with 'Tetra-Etch'.

Figure 3.28 is a high resolution XPS C1s spectrum from PTFE treated with 'Tetra-Etch' for one minute. The peaks due to oxygenated carbon are seen to the higher binding energy side of the hydrocarbon peak. Figures 3.29 is an ATR-FTIR spectrum of the same sample compared with untreated PTFE showing that at least some of the oxygen is present as carbonyl (1714 cm^{-1}). The peaks between 1560 and 1650 cm^{-1} are assigned to double bonds.

Figure 3.28 C1s region of PTFE treated with 'Tetra-Etch' for one minute

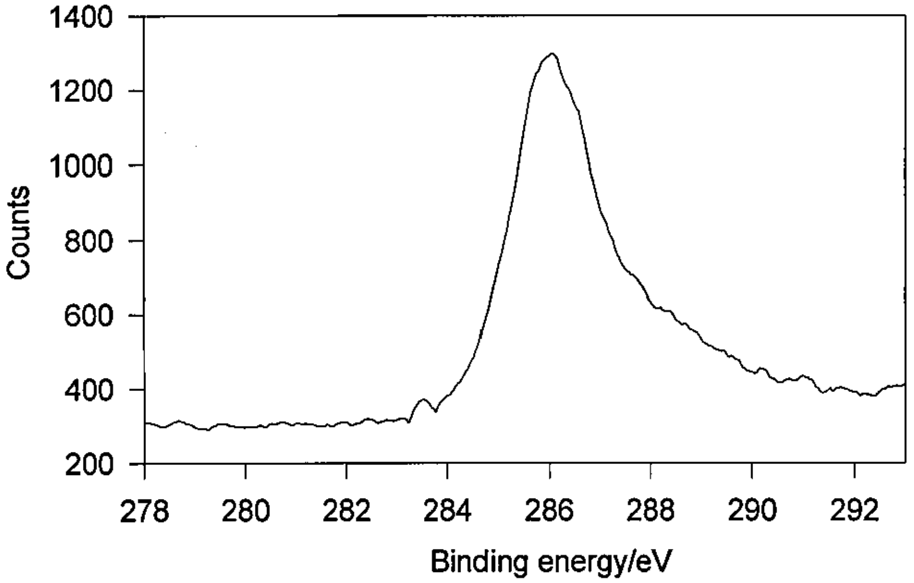
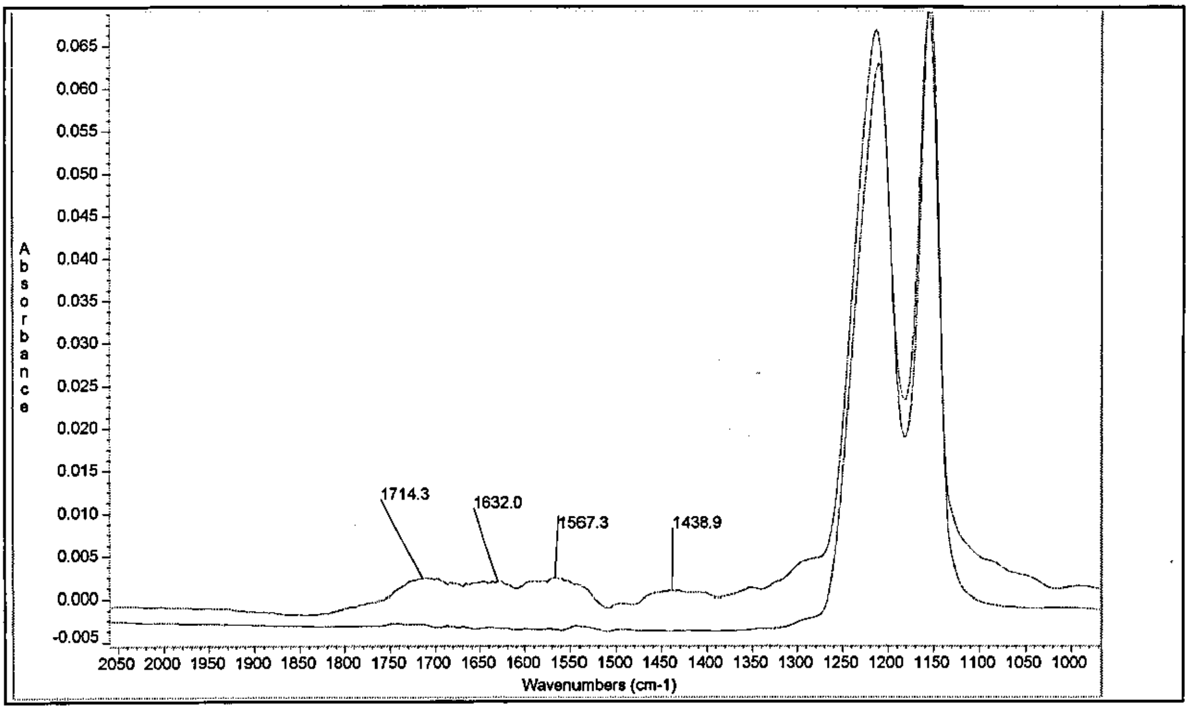
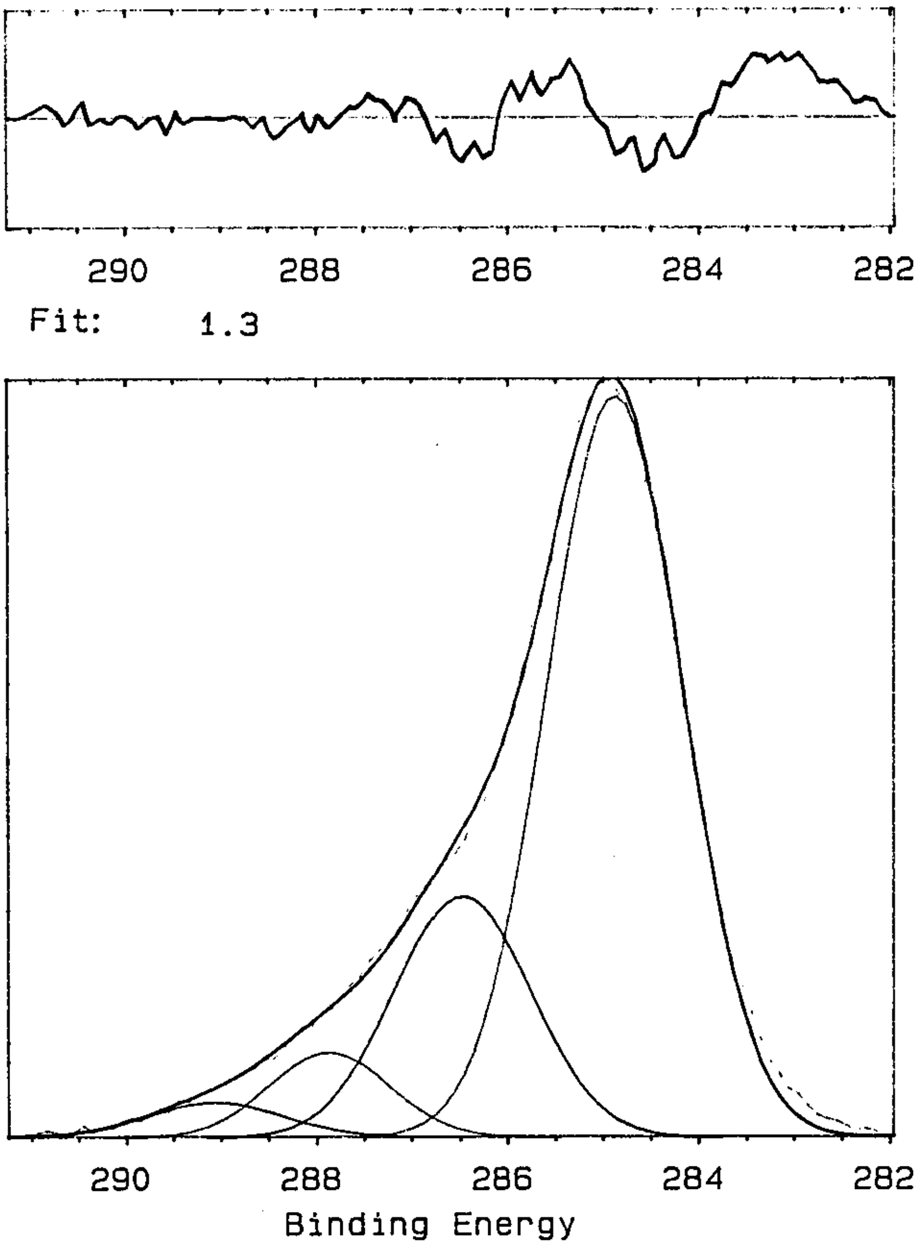


Figure 3.29 **ATR-FTIR spectrum of PTFE treated with 'Tetra-Etch' for one minute (a), compared with untreated (b)**



An estimate of the proportions of particular oxygen containing species was carried out via curve fitting of a high resolution C1s scan XPS spectrum from a sample of PTFE treated with 'Tetra-Etch' for one minute. This was done at BP, Sunbury-on-Thames. Figure 3.30 displays the C1s peak to which 4 peaks have been fitted. The four peaks shifts were chosen to correspond to C-C/C-H, C-O-C/C-OH, C=O and O-C=O. They were given a freedom of 2 eV. The peak shapes were Gaussian, and a straight line background subtraction was carried out. The total surface composition of the same sample was determined to be 76.4% C and 23.6% O.

Figure 3.30 A curve fitted XPS C1s narrow scan spectrum of PTFE treated with 'Tetra-Etch' for 1 minute



The areas of the four curves were:

C-C/C-H	67.9
C-O-C/C-OH	22.0
C=O	6.9
O-C=O	3.2

It is noted that this is just one possible estimation of the groups contained within this C1s spectrum. The use of curve fitting will be discussed in Section 4.4.1

In order to establish the chemical environment of the oxygen present in 'Tetra-Etch' treated PTFE more rigorously, gas phase derivatisation reactions were carried out. Carboxylic acid groups were tagged with trifluoroethanol (TFE), hydroxyl groups with trifluoroacetic anhydride (TFAA) and carbon-carbon double bonds were reacted with bromine in the dark. Tables 3.9 to 3.11 display the results

Table 3.9 **Derivatisation of OH groups with TFAA on 'Tetra-Etch' treated PTFE**

Element	Before tag/%	After tag/%	Original OH/%
C	82.2	69.2	3.4
F	0.9	10.1	
O	16.9	20.7	

Reaction was near to 100% complete; demonstrated from the standard polymer, PVA which gave 85% reaction.

Table 3.10 Derivatisation of COOH groups with TFE on 'Tetra-Etch' treated PTFE

Element	Before tag/%	After tag/%	Original COOH/%
C	83.6	80.4	1.3
F	1.1	3.8	
O	13.9	15.9	
S	1.4	0.0	

In this case polyacrylic acid was the standard polymer; it showed 50% reaction.

Table 3.11 Bromination of C=C groups on 'Tetra-Etch' treated PTFE

Element	Before bromination /%	After bromination/%
C	83.2	69.4
F	1.0	2.9
O	14.1	18.6
S	1.7	-
Br	-	9.2

From Table 11 it can be said that there is 1 bromine for every 8 carbon atoms on the derivatised sample or 1 double bond per 16 carbons on the original 'Tetra Etch' treated PTFE surface.

3.3 Flame

3.3.1 Comparison of flame treatment on different fluoropolymers

Flame treatment of PTFE and PVF was carried out at two different flame contact times. Table 3.12 shows the different surface effects as a result of the treatment and the values of bond strength.

Table 3.12 Surface composition, failure loads and water contact angles for flame treated PVF and PTFE

Polymer	Treatment /seconds	Failure load/N	SD	BS /MPa	XPS C	/atom F	% O	water contact angles/° Adv.	Rec.	Hyst.
PVF	none	350	70	1.8	70.4	28.2	0.8	78	65	13
	0.04	3040	378	15.2	68.7	27.9	3.4	73	45	28
	0.06	3230	126	16.2	67.6	28.0	4.4	69	42	27
PTFE	none	420	88	2.1	38.4	61.6	-	124	94	30
	0.04	85	65	0.4	34.0	66.0	-	131	93	38
	0.06	98	99	0.5	-	-	-	132	95	37

Key: BS = Bond strength
SD = Standard deviation
Adv = Advancing
Rec = Receding
Hyst = Hysteresis

In the case of PVF an average 9 fold improvement in bond strength was achieved with a flame contact time of 0.04 and 0.06 secs. There was an increase in wettability with respect to water and an increase in hysteresis; SEM indicated no topographical changes to account for this.

The XPS results showed no significant defluorination of the PVF; however, a significant amount of oxygen was incorporated.

Flame treatment, under the conditions used in this work reduced the bond strength of PTFE. Water contact angles were increased slightly indicating a less wettable surface than untreated. XPS results show a small change in the C:F ratio but no oxidation.

3.3.2 Aging and washing of flame treated PVF

Flame treated PVF samples (0.06 second flame contact time) were kept in clean jars. At appropriate time intervals a sample was removed and the surface energy was measured. The results are presented in Table 3.13.

Table 3.13 Advancing water contact angles and surface energy estimations of aged flame treated PVF (0.06s treatment time)

Age	Advancing water contact angle/°	γ_s^p /mJ m^{-2}	γ_s^d /mJ m^{-2}	γ /mJ m^{-2}
untreated	76	6.2	31.0	37.2
Initial - 30 minutes	65	15.7	24.1	39.8
1 day	74	10.0	25.7	35.7
6 days	76	7.6	28.3	35.9
5 weeks	72	9.6	28.1	37.7
16 weeks	74	8.4	28.9	37.3

Key: γ_s^p = Polar component to surface energy
γ_s^d = Dispersion component to surface energy
γ_s = Total surface energy

After 1 and 6 days aging the polar component of surface energy of a treated sample was reduced. Aging for longer than 6 days did not result in any further surface energy change. The total surface energy of the samples aged for long periods were the same as that of untreated.

The surface tension of the liquids used for measuring the surface energy of solids were recorded before and after the immersion of a flame treated PVF sample. This was repeated for untreated PVF. The results are given in Table 3.14

Table 3.14 Surface tension of test liquids before and after immersion of polymer samples

Liquid	γ before immersion	γ after immersion of untreated PVF	γ before immersion	γ after immersion of flamed PVF
Water	72.0	71.9	72.3	72.5
Ethandiol	49.2	49.3	49.3	49.3
DMSO	44.3	44.4	44.4	44.6
DMF	37.4	37.6	37.6	37.5

Key: 'γ' surface tension (units are $mN\ m^{-1}$)

Immersion of untreated or flame treated PVF did not effect the surface tension of the measuring liquids.

3.4 Plasma

3.4.1 Comparison of different plasmas on PTFE and PVF

A number of plasma treatments were carried out on PTFE and PVF under the same conditions. Batches of samples were treated on the same day. Specimens treated with a hydrogen plasma were carried out at a later date in the project along with the shorter treatment time experiments. The plasma's effectiveness at improving adhesion and causing surface changes was investigated (Table 3.15). Joint testing and XPS analysis was carried out at BP, Sunbury-on-Thames except §. XPS quantification was done via the standard broad scans; the conditions are outlined in Section 2.4.4 An X-ray power of 50 Watts, (5 mA and 10 kV) was used.

Table 3.15 Comparison of different plasmas on the pretreatment of PTFE and PVF for 1 minute at 100 Watts.

Polymer + plasma	Failure load/N	SD	BS /MPa	water contact angle adv./°	XPS C	/atom F	% O
PVF							
None	487	136	2.4	78	69.8	29.6	0.6
Argon*	4060	119	20.3	53	71.3	11.0	17.7
Oxygen	3410	323	17.1	54	66.3	21.3	12.4
Air	3090	353	15.5	62	66.8	25.2	8.0
Nitrogen	2720	425	13.6	61	68.5	25.1	5.8
Hydrogen§	1530	186	7.7	-	70.8	28.1	1.1
PTFE							
None	140	52	0.7	118	33.4	66.6	-
Argon*	460	95	2.3	102	32.9	65.9	1.2
Oxygen	330	78	1.7	114			
Air	190	138	1.0	112	33.6	66.2	0.2
Nitrogen	190	84	1.0	118			
Hydrogen§	Broke before test				34.2	65.8	-

For key see over:

Key: BS = Bond strength
SD = Standard deviation
* 70 Watts were used in this treatment
§ Analysis carried out at LUT

For both PVF or PTFE, an argon plasma was the most effective at improving the adhesion under these conditions. Considering first PVF, an argon plasma resulted in the biggest reduction in water contact angle, most defluorination and the greatest amount of oxygen incorporation. PTFE was less readily treated than PVF; surface chemical changes were minimal for all the plasmas. An argon plasma resulted in a slightly more wettable surface and the most adhesion improvement. The bond strength was increased 3.3 fold by a 1 minute argon plasma.

3.4.2 Variation of treatment time on certain plasma treatments of PVF

On one occasion the time of treatment for an argon plasma (power = 100 Watts) was varied over the range of one second to one minute on PVF. One second was probably the lowest measurable time possible with the plasma equipment used. The analysis was carried out using instruments at LUT. XPS broad scan conditions are outlined in chapter Section 2.4.4. An X-ray anode power of 100 Watts (10 mA, 10 kV) was used. Table 3.16 shows the adhesion and XPS results.

Table 3.16 Joint strengths and surface compositions of PVF treated with an argon plasma (100 Watts).

Time	Failure Load/N	SD	BS /MPa	XPS C	/atom F	% O
None	350	70	1.8	71.4	28.1	0.5
1 second	3310	202	16.6	68.8	29.0	2.2
5 seconds				70.1	26.2	3.7
15 seconds				68.9	24.2	6.9
30 seconds	3310	175	16.6	68.4	23.6	8.0
45 seconds				68.7	22.8	8.5
1 minute	4025	307	20.1	68.7	22.2	9.1

Adhesion improvement was very rapid; after just one second there was a 9 X increase in joint strength. About 2 % of oxygen had been introduced into the surface but there was no defluorination. As the treatment time was increased beyond one second the adhesion level increased only a further 20 % (Figure 3.31); material failure was starting to occur at these joint strengths. However, oxygen incorporation increased more steadily for the duration up to 1 minute and was accompanied by a drop in fluorine concentration at a similar rate (Figure 3.32).

Figure 3.31 Failure load and oxygen concentration for PVF treated with an argon plasma for various exposure times (□ = oxygen concentration, ● = Failure load)

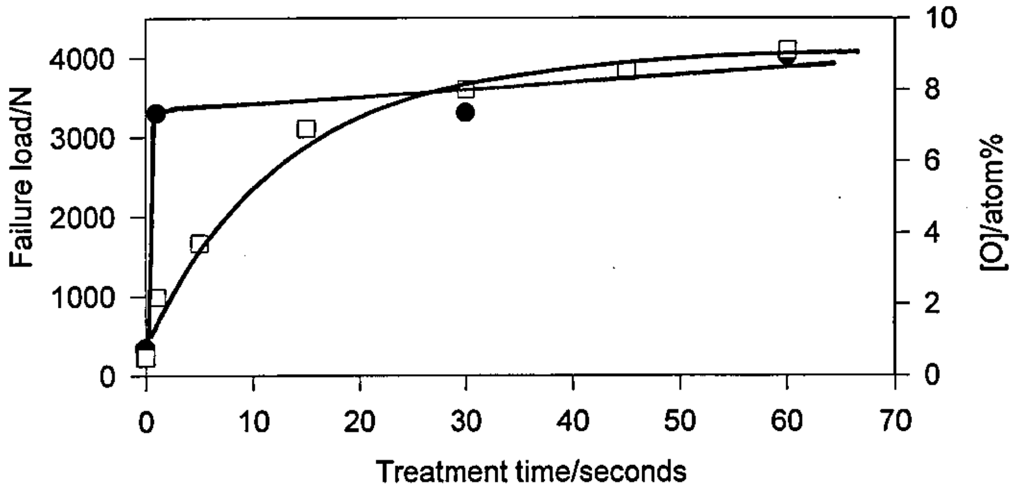
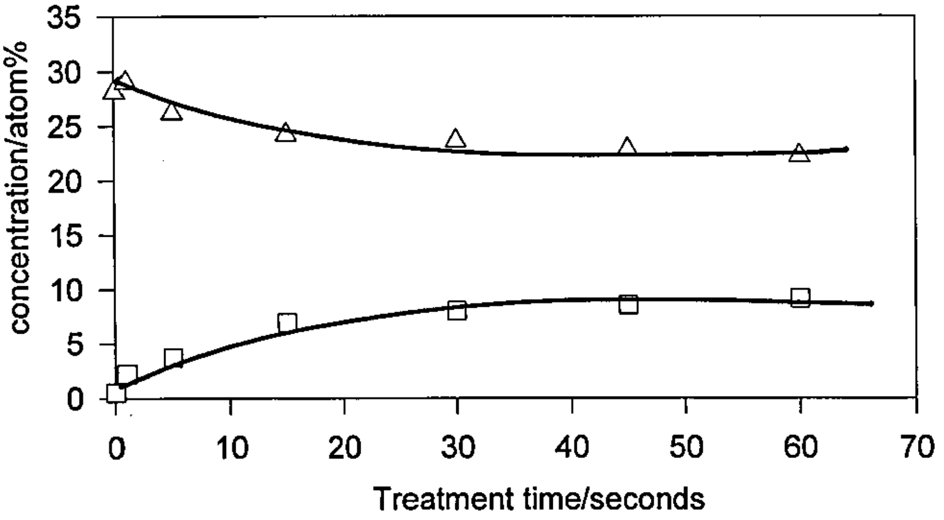


Figure 3.32 Fluorine and oxygen concentration for PVF treated with an argon plasma for various exposure times (Δ = Fluorine concentration, □ = oxygen concentration)



A similar trend was observed for PVF treated with an oxygen plasma (Table 3.17).

Table 3.17 Joint strengths and surface compositions of PVF treated with an oxygen (100 Watts).

Time	Failure	SD	BS	XPS	/atom	%
	Load/N		/MPa	C	F	O
None	350	70	1.8	71.4	28.1	0.5
1 second	3080	130	15.4	67.6	29.3	3.1
5 seconds				67.5	25.6	6.9
15 seconds				68.2	25.1	6.7
30 seconds	3030	148	15.2	67.6	24.9	7.7
45 seconds				67.0	24.4	8.6
1 minute	2910	85	14.6	66.4	22.8	10.8

Key: BS = Bond strength
SD = Standard deviation

A gradual increase in oxygen incorporation and defluorination was observed as time of treatment increased but the highest failure load of a joint was reached after just 1 second.

On an other occasion PVF was exposed to a range of longer treatment times with an argon plasma. This time joint strength measurements and XPS was carried out at BP. An X-ray anode power of 50 Watts, (5 mA, 10 kV) was used. Table 3.18 displays the results.

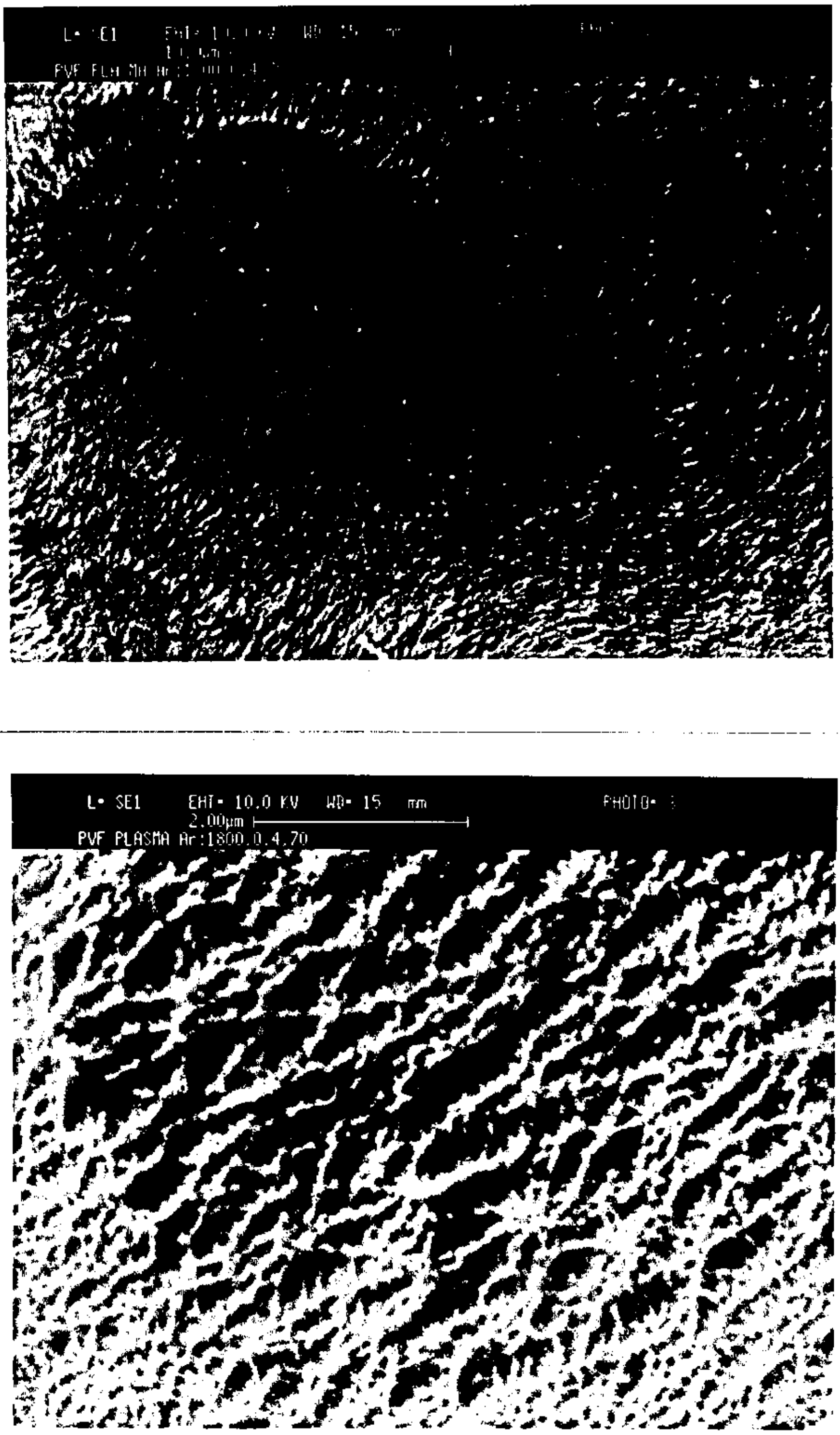
Table 3.18 Argon plasma treatment of PVF for long periods and its effect on joint strength and composition.

Time	Failure load/N	SD	BS /MPa	XPS C	/atom F	% O
None	350	70	1.8	69.8	29.6	0.6
5 seconds	3890	187	19.4	72.8	15.7	11.5
1 minute	4060		20.3	69.1	19.4	11.5
5 minutes				72.7	13.4	13.9
30 minutes*	4540#	106	22.7	78.0	10.1	11.9

Key: BS = Bond strength
SD = Standard deviation
* sample was discoloured after treatment.
\# failure within the polymer

A joint strength of 13 times that of untreated was reached after 30 minutes. The oxygen concentration was similar over the range of treatment times but the fluorine level continued to fall throughout the longer exposures. The value fell to one third of that of untreated after 30 minutes. For the 30 minute sample a change in topography was observed using SEM. (Figure 3.33). Pitting of the surface was evident.

Figure 3.33 Micrographs at two different magnifications showing the topography of PVF after a 30 minute argon plasma treatment.



It is clear that when comparing certain results of Table 3.15 and 3.17 there are variations in the surface compositions for similar conditions on the two separate occasions. For a 5 second treatment, the following compositions were observed on two different occasions:

	C	F	O
From Table 3.17	72.8	15.7	11.5
From Table 3.15	70.1	26.2	3.7

The compositions did not affect the bond strengths dramatically. It may be noted here that the former results (Table 3.15) were carried out at a later date to those in Table 3.17 and the plasma instrument had recently undergone a complete service and thorough cleaning operation. Base pressures had been improved from 0.030 Torr before cleaning to <0.001 Torr.

A specimen of PVF was treated for 1 minute in an argon plasma using 60 watts. Water advancing contact angles were measured at BP at various time intervals after treatment. In an aging period of up to 1 day there was no change in wettability. After 10 days the water contact had increased from 50 to 60 degrees compared with an untreated value of 78°.

3.4.3 Hydrogen plasma treatment of PVF

A broad range of treatment times was carried out on one day for hydrogen plasma treatment of PVF (Table 3.19). Bond testing and XPS analysis was carried out at LUT with an X-ray anode power of 100 watts (10 mA 10 kV).

Table 3.19 Joint strength and surface composition of hydrogen plasma treated PVF.

Treatment	Failure load/N	SD	BS /MPa	XPS	/atom	%
				C	F	O
none	350	70	1.8	71.4	28.1	0.5
1 second	500	141	2.5	69.5	30.1	0.4
10 seconds	1020	160	5.1	69.6	29.6	0.8
1 minute	1530	186	7.7	70.8	28.1	1.1
10 minutes	2360	288	11.8	82.0	16.1	1.9
1 hour	388			79.1	19.2	1.7

Key: BS = Bond strength
SD = Standard deviation

Oxygen incorporation was slight, reaching levels of just 2 %. Defluorination was more significant, the fluorine concentration falling to nearly half of that characteristic of the original surface. Bond strength increased to 6.5 times that of untreated.

3.4.4 Argon and Oxygen plasma treatment of PTFE

The adhesion of PTFE was improved by treatment with argon or oxygen plasmas. Tables 3.20 and 3.21 show the chemical compositions of the treated surfaces and their water wettability, and corresponding failure loads. The results are given in separate tables as the treatments were carried out on different occasions. Bond testing and XPS were carried out at BP using the standard broad scan conditions and an X-ray anode power of 50 Watts (5 mA, 10 kV).

Table 3.20 The effect on adhesion, surface composition and water contact angle when PTFE was treated with an argon plasma (60 Watts) for different treatment times.

Time	Failure Load/N	SD	BS /MPa	XPS C	/atom F	% O	Adv. /°
None	202	0.7	1.0	30.3	69.7	-	124
1 min	1340	172	6.7	42.1	53.4	4.5	103
5 mins	1390	156	7.0	33.1	65.3	1.6	116
30 mins	1850	36	9.3	33.5	65.6	0.9	119
1 hour	1780	130	8.9	32.8	67.0	0.2	114

Key: BS = Bond strength Adv = Advancing water contact angle
SD = Standard deviation

Table 3.21 The effect on adhesion, surface composition and water contact angle when PTFE was treated with an oxygen plasma (100 watts) for different treatment times.

Time	Failure Load/N	SD	BS /MPa	XPS C	/atom F	% O	Adv. /°
1 min	1080	231	5.4	34.4	65.6	-	116
5 mins	1440	101	7.2	33.6	66.2	0.2	118
30 mins	630	364	3.2	34.0	65.2	0.5	135
1 hour	Broke before test			34.5	65.5	-	
*Ar 1min 60 W	1344	183	6.7	33.4	63.9	2.7	*

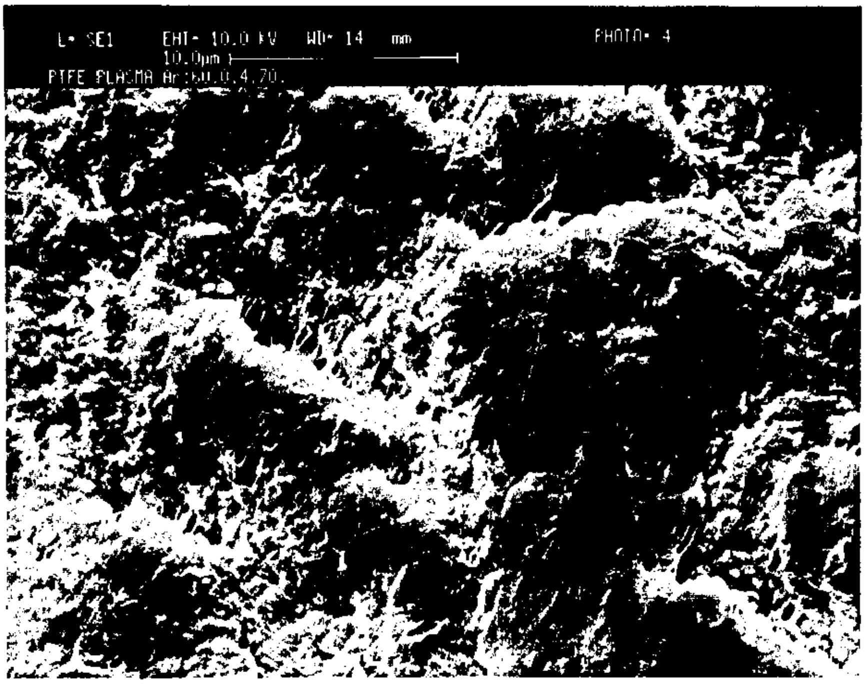
Key: BS = Bond strength SD = Standard deviation

* This sample was plasma treated and analysed on this occasion to assess the consistency of the plasma results. No significant difference in bond strength was observed (see Table 3.20) but chemical compositions were different.

The treatments did not incorporate much oxygen and as treatment time with argon increased, the level was less. However, an argon plasma improved the adhesion of PTFE up to 9x that of untreated. The maximum improvement with the oxygen plasma was 7x the untreated value after 5 minutes treatment. Greater treatment times e.g. 1 hour in an oxygen plasma resulted in a surface devoid of oxygen detected at the surface.

A micrograph of PTFE treated with an argon plasma for 1 hour is shown below (Figure 3.34) the surface appears to be very porous and raised.

Figure 3.34 **Micrograph of PTFE after treatment with an argon plasma for 1 hour.**



3.4.5 Hydrogen plasma treatment of PTFE

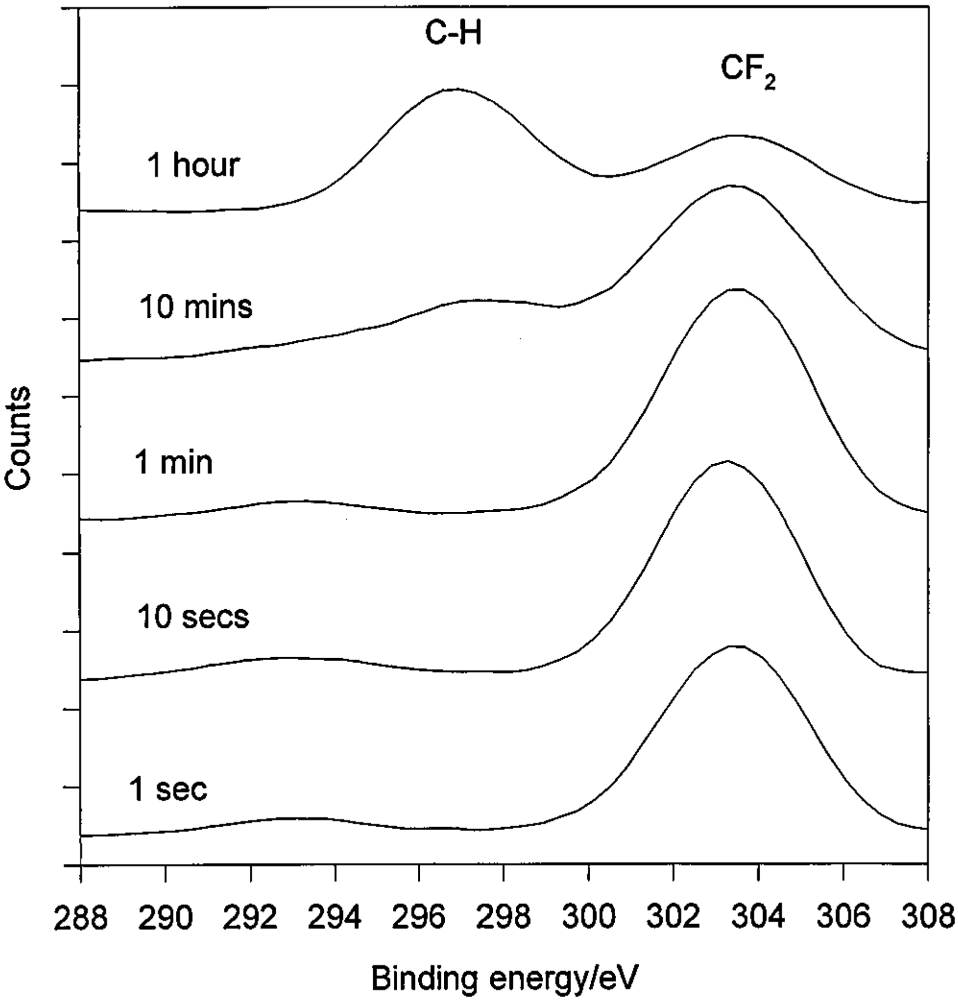
Treatment times of one second up to 1 hour were employed for the treatment of PTFE with a hydrogen plasma at 100 watts. XPS analysis was carried out at LUT using an X-ray anode power of 50 Watts (5 mA, 10 kV). Table 3.22 displays the results.

Table 3.22 **XPS results for PTFE treated with a hydrogen plasma**

Treatment time	Surface composition /atom%			
	C	F	O	N
None	34.1	65.9	-	-
1 sec	34.9	65.1	-	-
10 sec	35.9	63.2	-	0.8
1 min	34.2	65.8	-	-
10 mins	41.0	59.0	-	-
1 hour	80.6	18.8	0.6	-

There was a large reduction in F at the surface over the 1 hour period with virtually no oxygen incorporation. The loss of fluorinated species is shown clearly in the C 1s spectra in Figure 3.35 with the concurrent rise in C-H species.

Figure 3.35 C 1s peaks for PTFE treated with a hydrogen plasma for various times



These spectra were not obtained under high resolution conditions.

3.5 Group I hydroxides

3.5.1 Treatment of PVF

Comparison of different Group I hydroxides

Treatment of PVF with LiOH, NaOH and KOH at the same concentration (5M) and time (2 hours) was carried out at two different temperatures (56 and 80°C) for comparison (Table 3.23). An X-ray anode power of 10 mA and 10 kV was used for all XPS analysis of PVF samples treated with Group I hydroxides.

Table 3.23 Comparison of the surface compositional and adhesion effects of treatment of PVF with Group I hydroxides (5M for 2 hours)

Hydroxide & temp	Failure load/N	SD	BS /MPa	XPS / atom%			
				C	F	O	Zn
None	350	70	1.8	71.4	28.1	0.5	-
56°C							
LiOH	223	52	1.1	69.0	28.0	3.0	-
NaOH	570	84	2.9	69.3	28.0	2.7	-
KOH	460	72	2.3	69.5	25.8	4.5	0.1
80°C							
LiOH	650	41	3.3	72.0	20.7	7.1	0.2
NaOH	660	164	3.3	74.3	15.1	10.0	0.5
KOH	720	88	3.6	74.1	17.6	7.7	0.6

Key: BS = Bond strength
SD = Standard deviation

At the higher temperature of 80°C the bond strengths of all the Group I hydroxide treated samples were similar. A substantial amount of oxygen was present and defluorination had occurred. At 56°C, defluorination only occurred on treatment with KOH, but oxygen was present at significant levels for all three treatments. At 56°C the LiOH appeared less effective at adhesion improvement, compared with KOH and NaOH. However, even the NaOH and KOH treatments at this temperature resulted in bond strengths less than double that of untreated PVF. Hereafter KOH was used as the main reagent for investigations.

Note: Up to this point in the present study zinc or tin had not been found on the surface of any other treated or untreated specimen. Hence it was thought that the zinc observed on surfaces treated with Group I hydroxides was a contaminant within the solid reagent. Attempts were made to remove the zinc from the surface using acid washing but this proved unsuccessful. The contamination however, was traced to the container in which the methanol, used in the final rinse after treatment, was stored (see Appendix A). The most contamination was found on PVdF samples hence the treatments were repeated using different methanol. All of the PVF samples were not repeated due to time constraints but adhesion levels of the samples were not significantly affected by the presence of the zinc.

Variation of concentration and temperature on the treatment of PVF with aqueous KOH.

Preliminary experiments using aqueous KOH at 56°C and 80°C as a pretreatment for PVF did not give large improvements in adhesion despite significant changes in surface chemistry. Hence different conditions were investigated. The first variable to be examined was concentration (Table 3.24).

Table 3.24 **The effect of concentration on the adhesion and surface composition of aqueous KOH (2 hours, 80°C) treated PVF**

Concentration	Failure load/N	SD	BS /MPa	XPS / atom % C	F	O	Zn
Untreated	350	70	1.8	69.5	29.4	1.0	-
5 M	700	141	3.5	74.1	17.6	7.7	0.6
10 M	1150	129	5.8				
15 M	3040	152	15.2	72.1	17.3	9.6	1.0

Key: BS = Bond strength
SD = Standard deviation

An 8.5 fold increase in bond strength, compared with that of untreated, was observed by using a 15 M solution. At 10 M the increase was 3 times that of untreated and just double when the concentration was 5 M. The surface compositions of PVF after treatment with either 5 M or 15 M were very similar, i.e. the fluorine level fell to nearly half the untreated value and a substantial amount of oxygen was present (around 8 %).

A concentration of 15 M was then used for further experiments; this time varying the temperature of the solution. Treatment was carried out for just one minute except at the highest temperature where the time was also extended to 30 minutes. For some of the more severe treatments the PVF changed colour from no colour to brown; this was recorded see Table 3.25.

Table 3.25 The effect of solution temperature on the surface composition and bondability of PVF treated with aqueous KOH solution (15 M, 1 minute).

Temperature / °C	colour	XPS / atom%				Failure load/N	SD	BS /MPa
		C	F	O	Zn			
Untreated	none	69.5	29.4	1.0	-	350	70	1.8
80	none	68.4	29.9	1.7	-	2900	250	14.5
100	none	68.8	29.0	2.0	0.2			
120	none	73.3	18.5	7.6	0.6			
140	faint br	75.6	10.5	12.7	1.2	3100	283	15.5
140 for 30 minutes	brown	80.6	1.0	17.6	0.8	4330	249	21.7

Key: BS = Bond strength SD = Standard deviation br = Brown

The bond strength increase resulting from an aqueous KOH solution at 15 M, 80°C and just one minute was very similar to the equivalent treatment for two hours (see Table 3.24) i.e. they both resulted in about an 8 fold increase on the untreated value (failure loads were 2900N and 3040N respectively). However, surface compositions were different; the level of oxygen being lower for the one minute sample.

Increasing the temperature from 80 to 140°C, for a fixed treatment time of 1 minute, did not improve the adhesion of the PVF beyond the value obtained at 80°C.(i.e. 8 X that of untreated) However, the fluorine concentration on the sample surface was much reduced and oxygen levels increased as the temperature increased . At 140°C (the highest temperature possible at this concentration before the solution boiled) a one minute treatment time caused the PVF to become slightly coloured, when the treatment was extended to 30 minutes the film was distinctly brown and XPS results showed an almost completely defluorinated surface. The longer treatment time at 140°C increased the adhesion level to 12 times that of untreated.

Comparison of aqueous and alcoholic KOH treatments

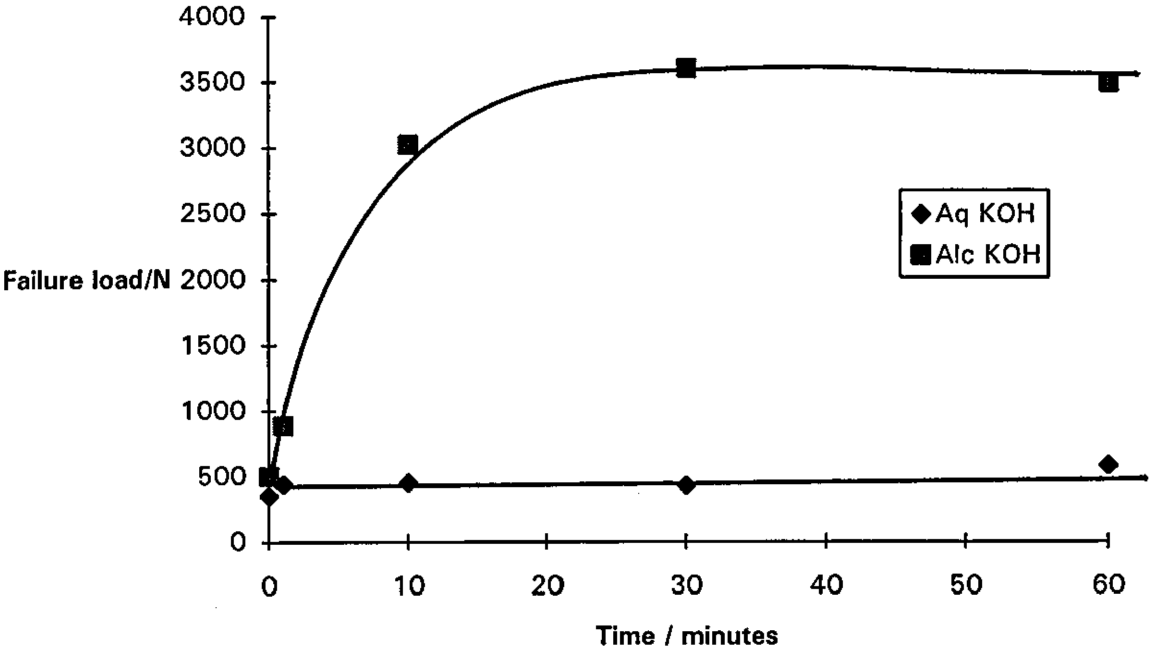
The solubility of KOH in an alcoholic solution was much less than the solubility in water alone. Hence a maximum concentration of 5 M was used for comparing alcoholic (95% ethanol, 5% water) and aqueous solutions. Treatment of PVF was carried out at 80°C for various times (Table 3.26). Figure 3.36 displays a comparison of the effect of aqueous and alcoholic KOH treatments of PVF on joint failure load.

Table 3.26 Comparison of surface compositions and adhesion level of PVF treated with aqueous and alcoholic KOH solutions (5M, 80°C)

Time	colour	Failure load/N	SD	BS /MPa	XPS / atom %					
					C	F	O	Zn	Sn	K
Aqueous										
0	None	350	70	1.8	69.5	29.4	1.0	-	-	-
1 min	None	440	160	2.2	71.2	27.9	0.9	-	-	-
10 mins	None	450	0	2.3	69.6	28.0	2.4	-	-	-
30 mins	None	430	50	2.2	71.4	23.6	4.6	0.2	0.1	-
1 hour	None	580	115	2.9	72.6	20.1	6.6	0.6	-	-
Alcoholic										
0	None	350	70	1.8	69.5	29.4	1.0	-	-	-
10 secs	None	500	115	2.5	74.5	24.9	0.6	-	-	-
30 secs	None	530	126	2.7	68.6	29.6	1.8	-	-	-
1 min	Faint br	890	85	4.5	68.8	28.6	1.1	0.3	-	1.2
10 mins	Faint br	3020	192	15.1	68.9	27.9	2.1	0.2	0.1	0.8
30 mins	Light br	3600	200	18.0	68.8	23.7	4.8	0.3	0.2	2.2
1 hour	brown	3490	85	17.5	70.3	21.7	6.2	0.3	0.1	1.4

Key: BS = Bond strength
SD = Standard deviation
br = Brown

Figure 3.36 **Bond strength improvement of PVF using alcoholic KOH compared with an aqueous solution (5M, 80°C).**

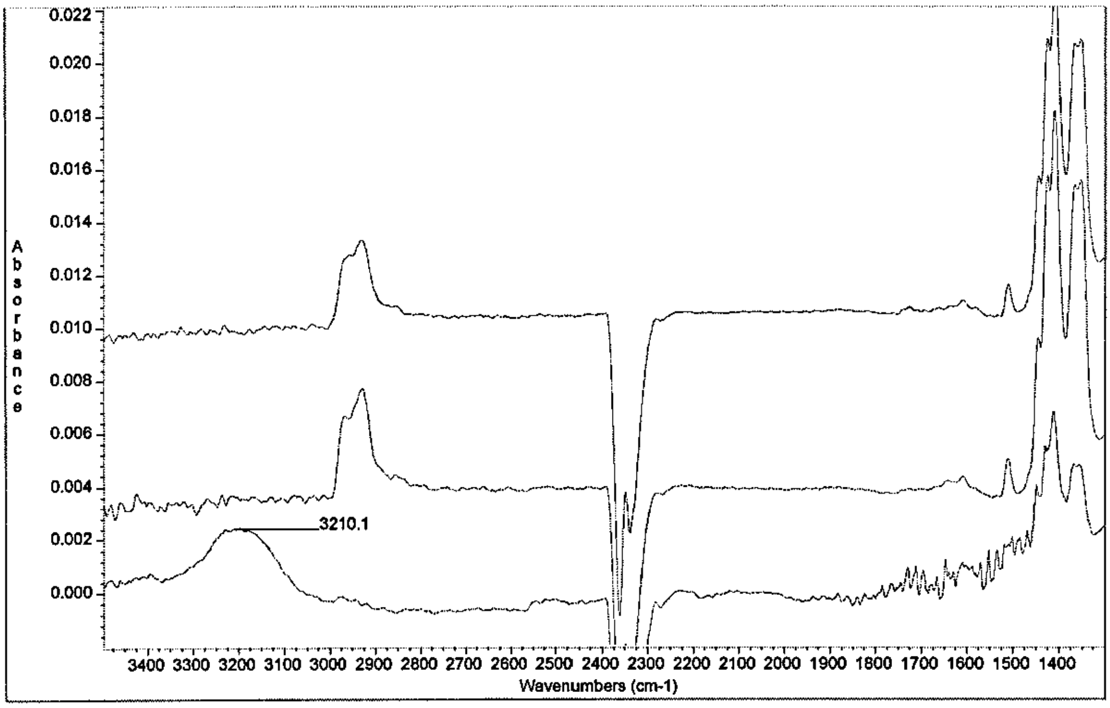


An alcoholic KOH solution (5 M 80°C) was able to improve the joint strength level of PVF by 2.5 times that of untreated after 1 minute. Over a treatment time range of 10 seconds to one hour the adhesion level increased then remained at a value of around 3500 N, which was equivalent to 7 times that of untreated. The PVF film became more coloured as it remained in the solution. In comparison, an equivalent aqueous KOH treatment did not change the colour of the film nor did it even double the adhesion level of PVF after one hour.

Chemical compositions of the surfaces of PVF treated with alcoholic and aqueous KOH were fairly similar under comparable conditions. As treatment time was increased both treatments resulted in more oxygen on the PVF and less fluorine. However, an alcoholic KOH treatment resulted in the presence of potassium in the PVF surface unlike an aqueous solution.

Figures 3.37 and 3.38 are ATR-FTIR spectra of aqueous and alcoholic treated PVF respectively treated under comparable conditions. Each figure displays an untreated spectrum, a spectrum recorded using a KRS prism and one obtained using a Ge prism.

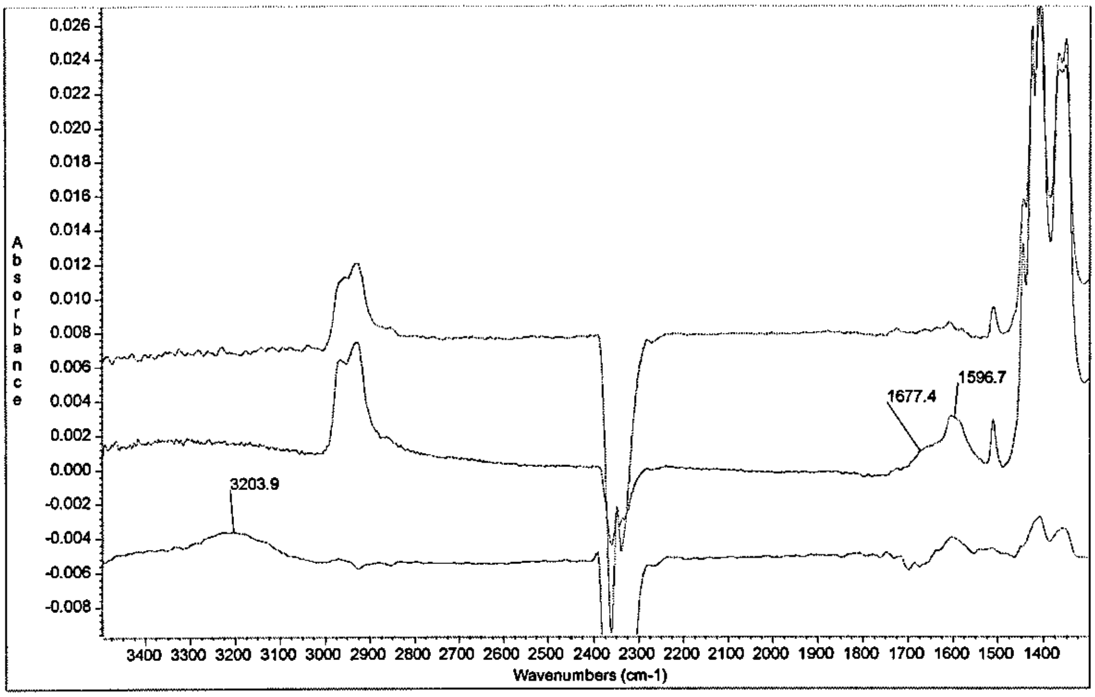
Figure 3.37 ATR-FTIR spectra of untreated PVF and 5M aqueous KOH treated PVF at 80°C for 1 hr



Key: A = Untreated PVF - KRS at 50°
B = Treated PVF - KRS crystal at 50°
C = Treated PVF - Ge crystal at 45°

The more surface specific spectrum obtained with the Ge crystal shows a large OH band at around 3200 cm^{-1} and a reduction in the CF bands in the fingerprint region around 1400cm^{-1}. There was no significant difference between the untreated and treated spectrum taken with a KRS crystal.

Figure 3.38 ATR-FTIR spectra of untreated PVF and 5M alcoholic KOH treated PVF at 80°C for 1 hr



Key: A = Untreated PVF - KRS at 50°
B = Treated PVF - KRS crystal at 60°
C = Treated PVF - Ge crystal at 45°

The spectrum from the Ge crystal shows OH groups at 3200 cm^{-1} and no CH bands at 2900 cm^{-1}. At greater depth, with the KRS crystal absorbances due C=C are seen between 1500 and 1700 cm^{-1}.

The use of tetrabutylammonium bromide (TBAB) to improve the effectiveness of aqueous KOH solutions to pretreat PVF.

A) Addition of TBAB at two different temperatures

A small amount (0.03g) of tetrabutylammonium bromide, TBAB was added to 50 ml of an aqueous KOH solution (5M). PVF was immersed in the solution at two different temperatures, 23 and 80°C. Table 3.27 has the adhesion test results and the surface compositions of the treated film.

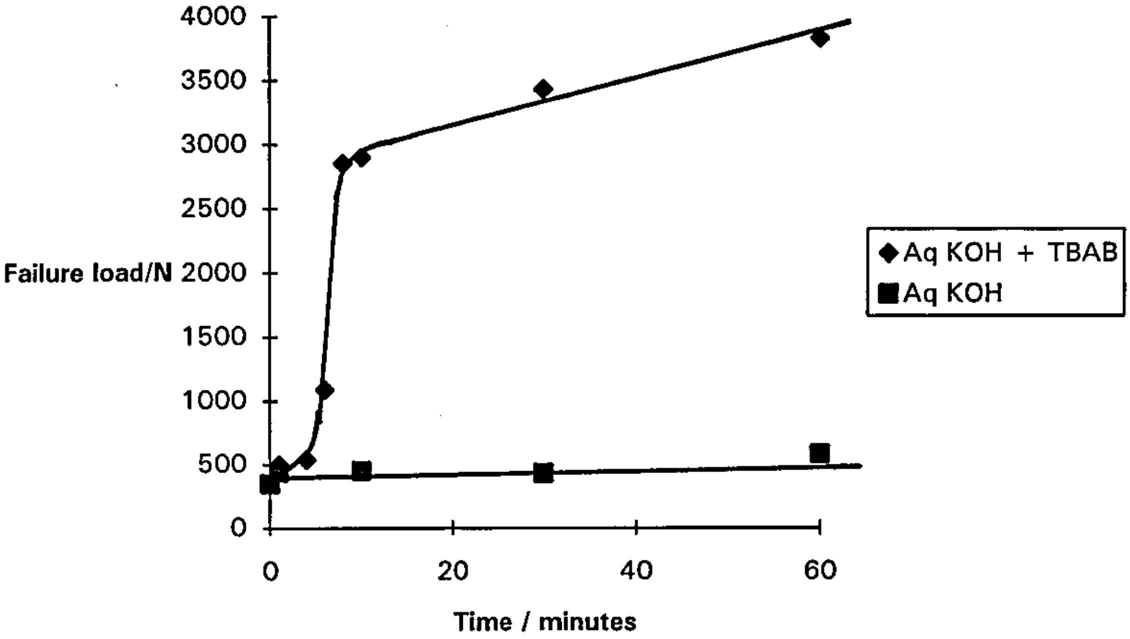
Table 3.27 The effect of 0.03g of TBAB per 50 ml of 5M aqueous KOH on the pretreatment of PVF at different temperatures

Time & Temp	colour	Failure load/N	SD	BS /MPa	XPS / atom % C	F	O	Zn	Sn
Untreated	None	350	70	1.8	69.5	29.4	1.0	-	-
23°C									
10 secs	None	475	29	2.4	69.1	30.0	0.9	-	-
1 min	None	460	111	2.3	69.7	29.6	0.8	-	-
1 hour	None	438	75	2.2	68.6	29.9	1.5	-	-
80°C									
10 secs	None	520	179	2.6	70.4	29.0	0.6	-	-
30 secs	None	480	84	2.4	70.3	29.1	0.6	-	-
1 min	None	500	173	2.5	70.0	28.7	1.3	-	-
4 mins	None	540	114	2.7	70.5	28.1	1.5	-	-
6 mins	Faint br	1090	213	5.5	70.7	28.1	1.3	-	-
8 mins	Faint br	2850	360	14.3	71.7	26.5	1.8	-	-
10 mins	Faint br	2900	141	14.5	70.5	27.3	1.8	0.3	0.1
30 mins	Light br	3430	282	17.2	71.0	24.1	4.2	0.5	0.2
1 hour	Brown	3830	96	19.2	70.7	21.9	6.4	0.7	0.3

Key: BS = Bond strength
SD = Standard deviation
br = Brown

Addition of TBAB to the KOH solution at 23°C was ineffective at improving its effectiveness as a pretreatment. However, at 80°C there were significant effects on the bond strength of the PVF. Figure 3.39 compares the bond strength of aqueous KOH treated PVF with aqueous KOH + 0.03g of TBAB per 50 ml of solution.

Figure 3.39 **Bond strength vs. time for PVF treated with 5M aqueous KOH and 5M aqueous KOH + 0.03g of TBAB per 50 ml of KOH solution at 80°C**



B) Increasing the amount of TBAB

The amount of TBAB was increased by a factor of three to 0.15g and PVF was treated over a similar time range. The bond strength results and surface compositions for aqueous KOH treatments with no TBAB and 0.03g or 0.15g of TBAB are shown in full in Table 3.28 and then Figure 3.40 displays the comparison graphically.

Table 3.28 The effect of different amounts of TBAB in solution on the treatment of PVF with 5M aqueous KOH solution at 80°C

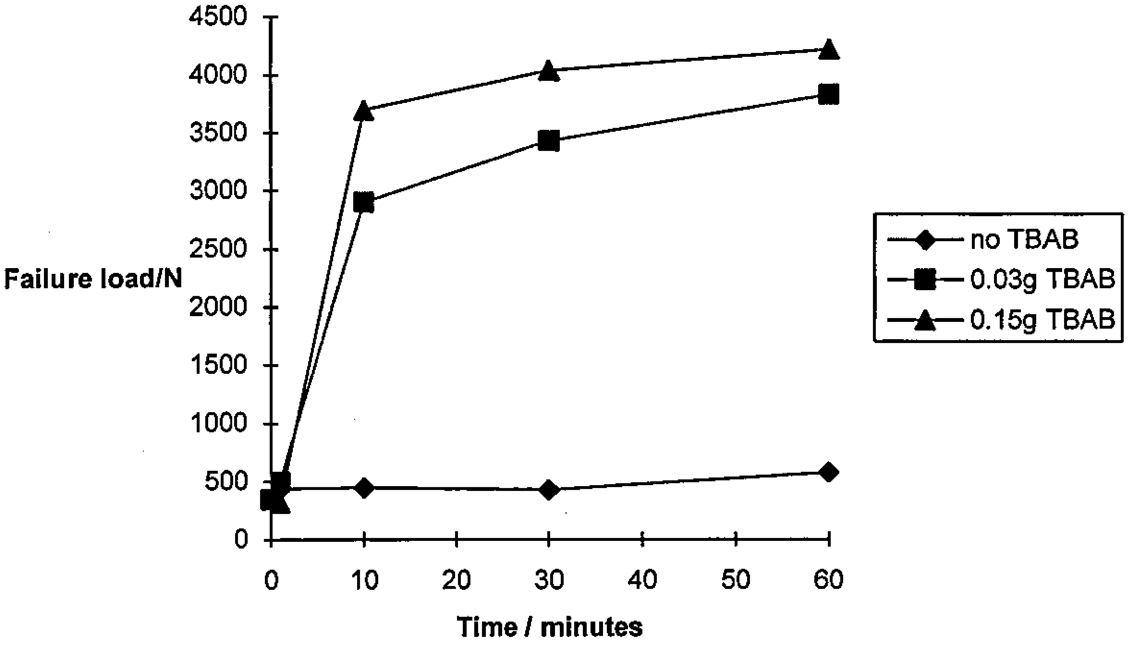
TBAB /g*	Time /mins	Colour	Failure load/N	SD	BS /MPa	XPS /Atom%			
						C	F	O	Zn+Sn
0	0	none	350	70	1.8	70.4	28.8	0.8	-
	1	"	440	160	2.2	71.2	27.9	0.9	-
	10	"	450	0	2.3	69.6	28.0	2.4	-
	30	"	430	50	2.2	71.5	23.6	4.6	0.3
	60	"	580	115	2.9	72.7	20.1	6.6	0.6
0.03	1	none	500	173	2.5	70.0	28.7	1.3	-
	10	faint br	2900	141	14.5	70.5	27.3	1.8	0.4
	30	light br	3430	282	17.2	71.0	24.1	4.2	0.7
	60	brown	3830	96	19.2	70.7	21.9	6.4	1.0
0.15	1	none	320	29	1.6	73.4	23.9	1.6	1.1
	10	light br	3700	0	18.5	73.6	20.9	4.9	0.6
	30	brown	4040 MF	89	20.2	73.4	18.3	7.5	0.8
	60	dark br	4220 MF	157	21.1	74.9	20.2	4.3	0.6

Key: BS = Bond strength
SD = Standard deviation
MF = material failure
br = brown
*TBAB concentration is g in 50 ml of hydroxide solution.

It is interesting to note that surface compositions for each treatment time were very similar for all three conditions despite very different failure loads of the adhesive joints. At failure loads greater than around 4000N material failure was evident by viewing the debonded joint by eye. Cohesive failure was confirmed by the use of ESCALAB 220i at BP the surface compositions of two small complementary areas of a debonded joint. The compositions for a debonded sample that had been treated with 5M aqueous KOH containing 0.15g of TBAB per 50 ml of solution at 80°C for 1 hour were as follows:

	C /atom%	F /atom%	O /atom%
Side A.......	72.4	2.6	25.1
Side B.......	72.5	2.4	25.1

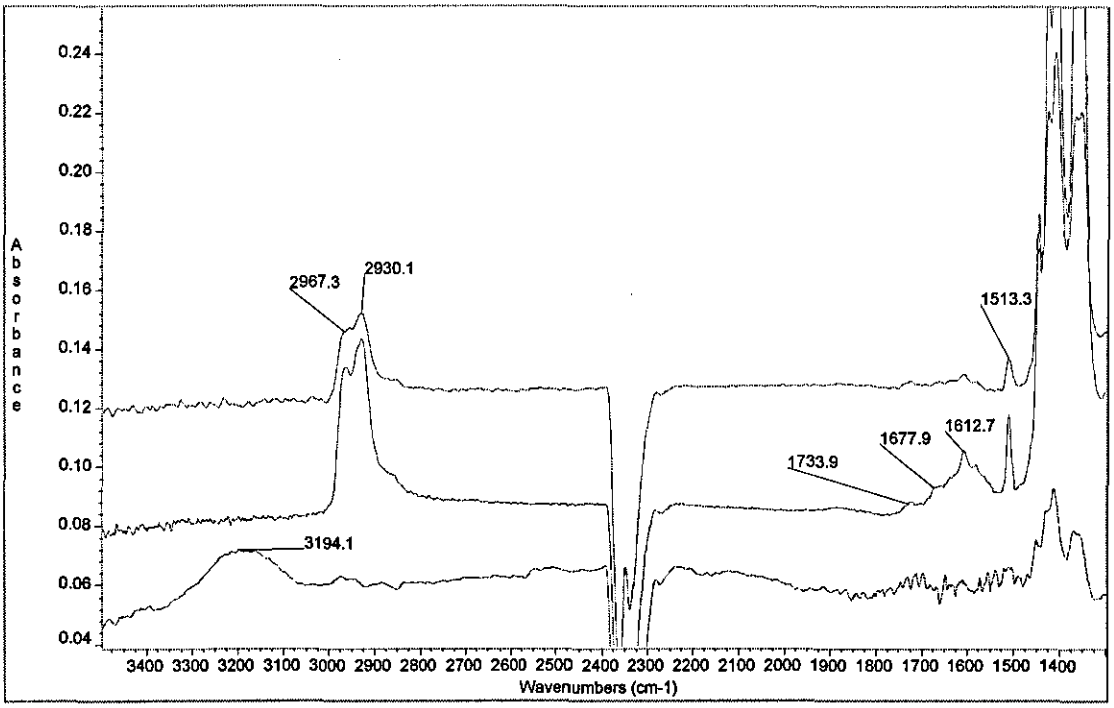
Figure 3.40 Bond strength vs time for PVF for different levels of TBAB per 50 ml of a 5M aqueous solution of KOH.



Increasing the concentration of TBAB to 0.15g in 50 ml raises the adhesion level of PVF to levels where the failure is cohesive in the polymer; for this reason the concentration was not increased any further

Figure 3.41 shows the ATR-FTIR analysis at two different depths, of PVF treated with aqueous KOH plus TBAB.

Figure 3.41 **ATR-FTIR spectra of untreated PVF and PVF treated with 5M aqueous KOH containing 0.15g of TBAB per 50 ml of solution at 80°C for 1 hr**



Key: A = Untreated PVF - KRS at 50°
B = Treated PVF - KRS crystal at 50°
C = Treated PVF - Ge crystal at 45°

There are OH bands at the surface 3200 cm^{-1} (Ge crystal) and C=C bands deeper in the material 1600s cm^{-1} (KRS crystal) There may also be some evidence of C=O adsorptions at 1733 cm^{-1}.

C) The effect of temperature on the effectiveness of an aqueous KOH solution containing TBAB to pretreat PVF.

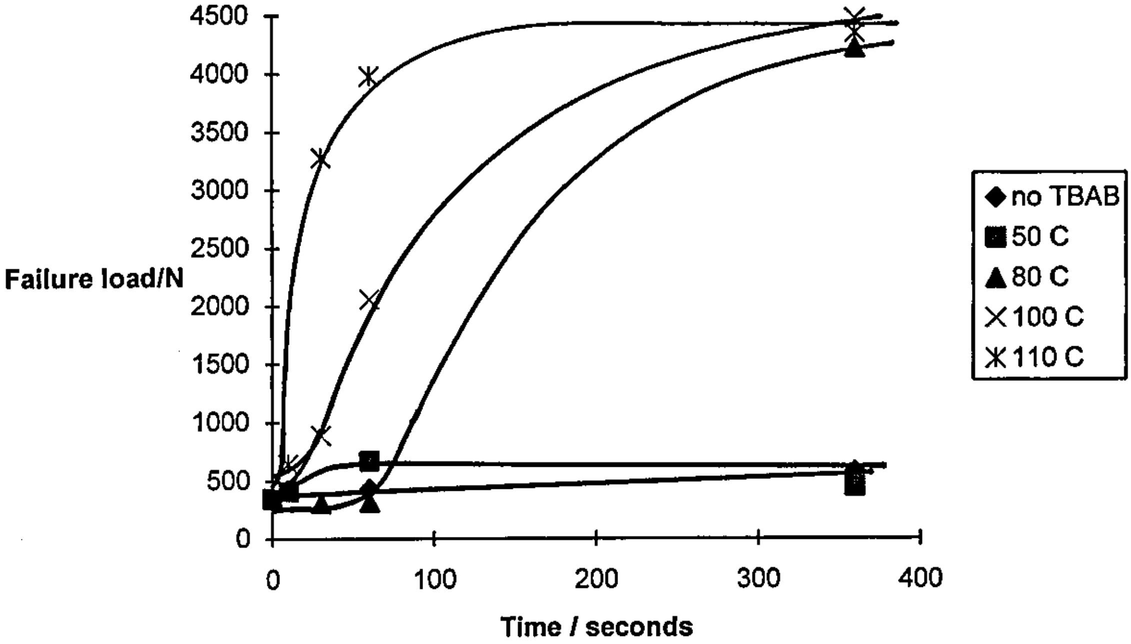
The addition of TBAB to a 5 M aqueous KOH solution at 80 °C had proved to be very effective at achieving the equivalent level of adhesion that had previously only been obtained with much higher concentrations and temperatures and longer times. An experiment on the effect of temperature on a solution containing TBAB was carried out to see if the rate of increase of adhesion level could be further increased so that it was comparable to say, 'Tetra-Etch' treatment of PTFE. Table 3.29 shows the details of adhesion tests and some surface compositions but the results are better seen graphically in Figure 3.42.

Table 3.29 Effect of temperature on the treatment of PVF using 5M aqueous KOH + 0.15g TBAB per 50 ml of solution.

Temp /°C	Time	Failure load/N	SD	BS /MPa
50	10 secs	410	76	2.1
	1 min	670	76	3.4
	1 hour	450	141	2.3
80	10 secs	430	177	2.2
	30 secs	310	115	1.6
	1 min	320	29	1.6
	1 hour	4220 MF	157	21.1
100	30 secs	890	114	4.5
	1 min	2060	746	10.3
	1 hour	4470 MF	58	22.4
110 (boiling)	10 secs	650	265	3.3
	30 secs	3280	171	16.4
	1 min	3980 MF	171	19.9
	1 hour	4350 MF	129	21.8

Key: BS = Bond strength
SD = Standard deviation
MF = Material failure

Figure 3.42 **The effect of temperature on bond strength of PVF treated with 5M aqueous KOH with 0.15g of TBAB per 50 ml vs. time**



Increasing the temperature of the solution above a certain level improved the adhesion. 110°C was the highest temperature reached before the solution boiled.

Addition of TBAB to alcoholic KOH

An alcoholic KOH solution was much more effective than an equivalent aqueous solution at increasing the bond strength of PVF. For completeness the effect of adding TBAB to an alcoholic solution was explored. Table 3.30 shows the results.

Table 3.30 Surface composition and bond strengths of PVF treated with 5M alcoholic KOH + TBAB per 50 ml of solution.

TBAB /g	Time	Failure Load/N	SD	BS MPa	XPS / atom %					
					C	F	O	Zn	Sn	K
0	0	350	70	1.8	69.5	29.4	1.0	-	-	-
	10 secs	500	115	2.5	74.5	24.9	0.6	-	-	-
	30 secs	530	126	2.7	68.6	29.6	1.8	-	-	-
	1 min	890	85	4.5	68.8	28.6	1.1	0.3	-	-
	10 mins	3020	192	15.1	68.9	27.9	2.1	0.2	0.1	0.8
	30 mins	3600	200	18.0	68.8	23.7	4.8	0.3	0.2	2.2
	1 hour	3490	85	17.5	70.3	21.7	6.2	0.3	0.1	1.4
0.03	10 secs	350	50	1.8	68.2	28.2	28.7	1.5	0.1	1.5
	30 secs	400	50	2.0	67.3	30.4	2.0	-	0.2	-
	1 min	450	129	2.3	67.9	29.1	2.6	-	0.4	-
	2 mins	1020	216	5.1						
	5 mins	3100	200	15.5						
	10 mins	3260	118	16.3	69.2	27.3	3.3	0.2	-	-
	30 mins	3500	238	17.5	70.3	24.3	5.0	0.3	0.2	-
	1 hour	3740	202	18.7	74.4	19.3	5.7	0.5	0.1	-

Key: BS = Bond strength
SD = Standard deviation

The TBAB had little effect on the adhesion level or the surface composition of treated PVF.

3.5.2 Treatment of PVdF

As outlined in Section 3.1.1 it was decided that PVdF be bonded with a cyanoacrylate adhesive which gave poor bond strength in order to explore the effectiveness of pretreatments to enhance adhesion. The effectiveness of KOH solutions are discussed in this section.

Comparison of aqueous KOH, alcoholic KOH and aqueous KOH containing TBAB.

PVdF was treated with 5M solutions at 80°C; treatment time was varied. PVdF was treated with aqueous KOH with and without TBAB, and with an alcoholic KOH solution. Adhesive joints were made up using cyanoacrylate adhesive and surface compositions were obtained using XPS. Table 3.31 shows the results for different treatment times.

Table 3.31 The effect on adhesion level and surface composition for various KOH treatments of PVdF

Treatment	Colour	Failure load/N	SD	BS /MPa	XPS	/ atom	%
					C	F	O
None	None	1300	294	6.5	51.0	49.0	-
Aq KOH (5M 80°C)							
10 secs	None	4120	135	20.6			
30 secs	None	4040	261	20.2	52.7	45.7	1.6
1 min	faint br	4010	699	20.1	53.9	43.1	3.0
10 min	faint br	4560	723	22.8	58.0	37.0	5.0
1 hr	light br	4320	286	21.6	62.0	28.9	9.1
Aq KOH + TBAB 0.15g# (5M 80°C)							
10 secs	light br	4250	250	21.3	62.0	28.4	9.6
30 secs	light br	3940	241	19.7	63.1	24.4	12.5
1 min	brown	4860	152	24.3	69.7	16.7	13.6
10 min	brown	4430	222	22.2	74.6	9.9	15.5
1 hr	dark br	4740	297	23.7	77.7	4.3	16.8 *
Alc KOH (5M 80°C)							
10 secs	light br	4150	129	20.8	59.3	34.7	6.0
1min	brown	4630	330	23.2	62.2	27.5	10.3
5 mins	dark br	4340	329	21.7	65.7	21.7	12.6
10 min	black	4150	71	20.8	67.0	18.7	14.3
1 hour	black	3230	472	16.2	74.0	8.9	17.1

Key: BS = Bond strength
SD = Standard deviation
br = Brown
* N 0.7 and Na 0.5 atom % were also present

\# TBAB per 50 ml of solution

Debonded joints viewed with an optical microscope showed evidence of failure between the adhesive and the metal at values greater than approximately 4400 N (a metal-adhesive-metal joint failed at 4370 N). These bond strengths were reached after 1 minute in the case of aqueous plus TBAB and alcoholic treated, and after 10 minutes for an aqueous treatment. For this reason it was not possible to say if longer treatment times were beneficial for improving adhesion. The bond strengths obtained were very similar for all three treatments under similar conditions. After just 10 seconds all three treatments resulted in a near 4 fold increase in adhesion.

Differences in surface composition of samples treated with the different solutions were evident. All three treatments resulted in a loss of fluorine from the surface but the effect was greater with an aqueous KOH solution containing TBAB and an alcoholic KOH solution. An average reduction of 88% of fluorine occurred after one hour with the latter treatments, compared with just 40 % reduction with an aqueous KOH solution. Oxygen incorporation was high for aqueous KOH containing TBAB and alcoholic solutions (~17%) and substantial for treatment with an aqueous solution ~9%). Nitrogen was present on a sample treated with aqueous KOH containing TBAB.

ATR-FTIR of PVdF treated with the 3 types of KOH solution are given in Figures 3.43-3.45. In each case an untreated PVdF spectrum is included on the graphs for comparison.

Figure 3.43 ATR-FTIR spectra of untreated (a), and aq KOH treated PVdF (15M, 80°C, 2 hours) (b), KRS prism, 60°

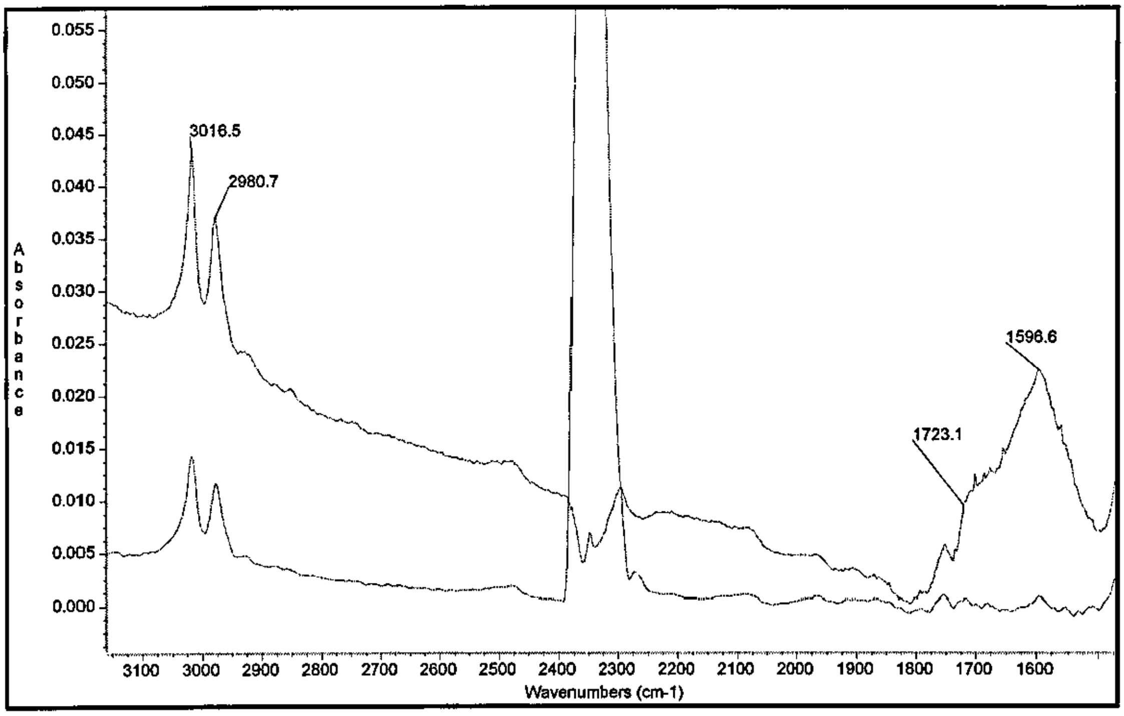


Figure 3.44 ATR-FTIR spectra of untreated (a), and aq KOH treated 'PVdF + TBAB' (5M, 80°C, 1 hour) (b), Ge prism, 45°

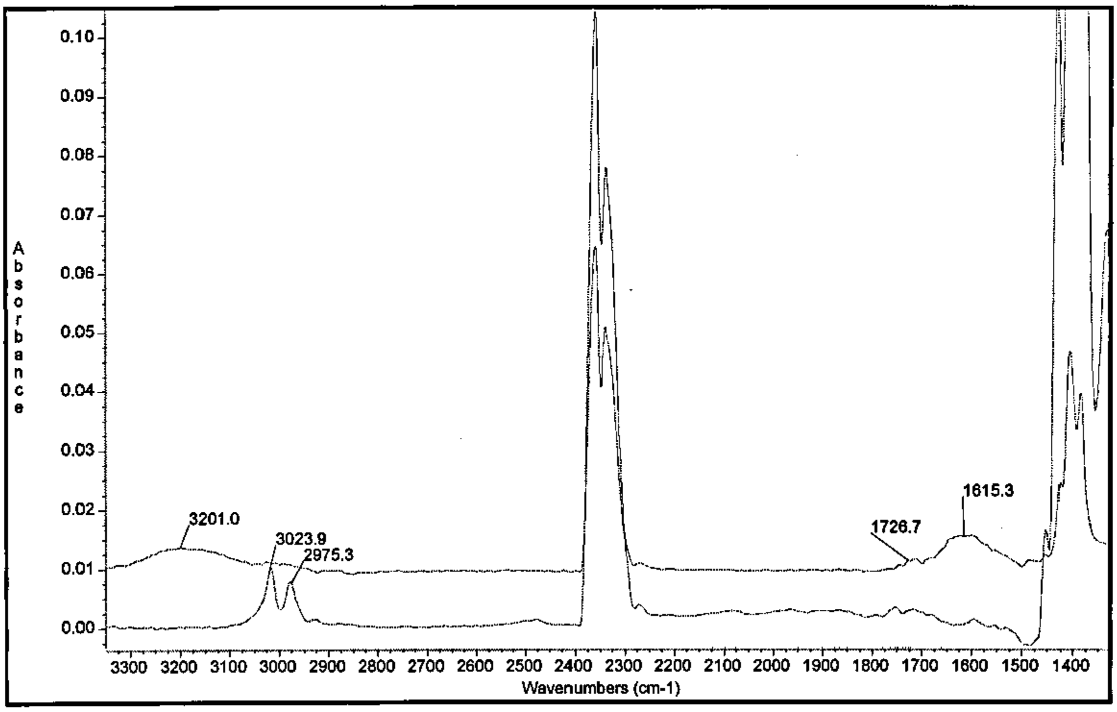
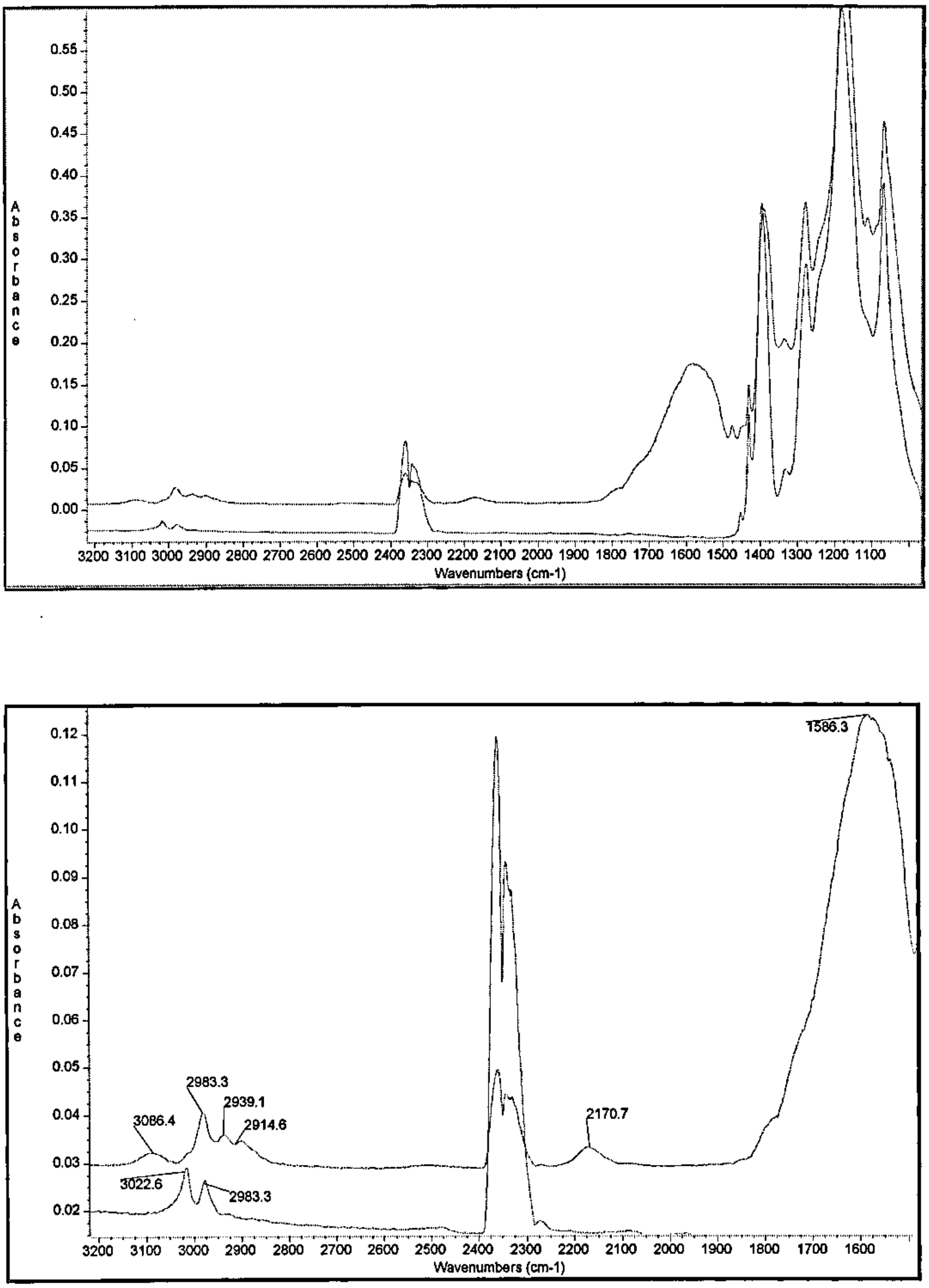


Figure 3.45 ATR-FTIR spectra of untreated (a), and alcoholic KOH treated PVdF (5M, 90°C, 30 minutes) (b), KRS prism, 60°; on two different scales



A summary of the functional groups observed as a result of the treatments is as follows:

		Group and wavenumber:
Aqueous + TBAB	5M, 80°C, 1 hr	C=O 1726
		C=C 1615*
		O-H 3201*
Aqueous	15M, 80°C, 2hr	C=O 1723
		C=C 1596
Alcoholic	5M, 90°C, 30 mins	C=O 1700-1800
		C=C 1500-1700
		C=C 2170
		CH change 2914-3086

* alternatively these bands could be due to adsorbed water.

Investigations into the mechanism of TBAB in KOH solutions for treatment of PVF and PVdF

A) The action of a solution of TBAB on its own

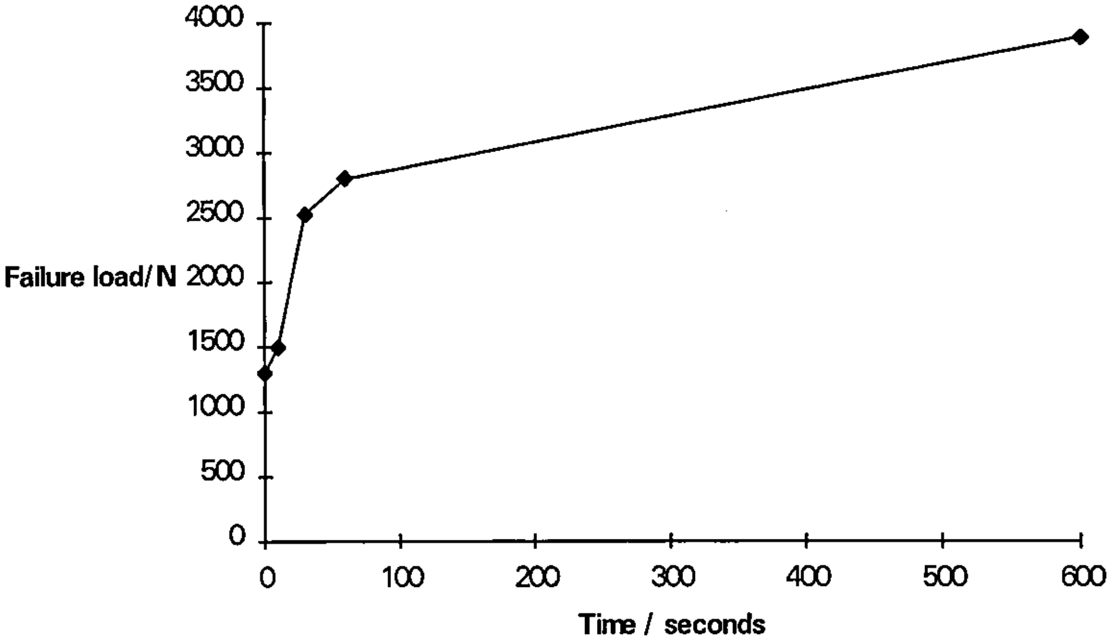
PVdF and PVF were immersed in water at 80°C that contained 0.15g of TBAB per 50 ml for a range of times, they were washed with water then methanol before drying. Adhesion tests were carried out and surface compositions of the PVF and PVdF were determined with XPS. The results for PVdF are shown in Table 3.32 and Figure 3.46.

Table 3.32 **Treatment of PVdF with an aqueous solution of TBAB (0.15g in 50 ml) at 80°C.**

Time	Failure load/N	SD	BS /MPa	XPS C	/ atom F	% O
0	1300	294	6.5	51.0	49.0	-
10 secs	1500	200	7.5	51.7	48.0	0.3
30 secs	2530	666	12.7	52.8	46.9	0.3
1 min	2800	100	14.0	51.7	47.7	0.6
10 mins	3900	361	19.5	50.6	49.4	-
1 hr	3070	839	15.4	52.8	46.0	1.2

There was no surface composition change or improvement in bond strength in the PVF samples.

Figure 3.46 **Failure load of PVdF joints against time of treatment with a solution of TBAB (0.15g in 50ml of water) at 80°C**



Clearly adhesion increased as the film remained in the solution (the value for 1 hour is not included in the graph so that the shorter term effect is seen more clearly). Little chemical change was observed with XPS. A small amount of oxygen was incorporated but no significant defluorination occurred.

A control, comprising of immersion of PVdF in water at 80°C for 1 hour was carried out, bonded and its load to failure compared with an as received sample.

As received	1580 N	SD = 356
Water 80°C, 1hr & MeOH washed	1930 N	SD = 551

Within the standard deviation limits these values were not significantly different. Therefore, the presence of TBAB brought about some modification of the PVdF surface to improve its adhesion.

B) Treatment of PVF with solutions of TBAB and KOH separately

Dias and McCarthy[100] suggested that the role of phase transfer agents in similar systems to this work was that of a wetting agent. Other common wetting agents were investigated in this present study replacing the TBAB in an aqueous solution of KOH. Some household detergent ('Fairy Liquid') was added to a 5 M aqueous KOH solution; unfortunately the detergent would not go into solution. However, Decon 90 (pH 11) was more successful; although it was not possible judge how much dissolved. A sample of PVF was placed in this mixture at 80°C for 10 mins. The resulting joint failure load was 420 (SD = 76) which was not any significant improvement on untreated (350 N).

Another possibility for the role of TBAB proposed in this study was that it might aid dissolution of low molecular weight species present as a weak cohesive layer on the surface of the untreated material or produced by the reaction with KOH. To investigate this, PVF was treated with solutions of TBAB and KOH independently. A sample of PVF was treated with a 5 M KOH solution at 80°C for 1 hour and washed. Then it was immersed in a solution of TBAB (0.15g in 50 ml of water) at 80°C for 1 hour, washed and analysed. Neutracon was also tried in the place of TBAB. Below is a summary of the results:

KOH then TBAB - Failure load = 660 (SD 182)
KOH then Neutracon - Failure load = 390 (SD 103)

i.e. TBAB used after a KOH treatment did not enhance the adhesion of PVF any more than the value for just KOH treatment and Neutracon appears to have a detrimental effect on adhesion level.

A series of experiments were carried out using solutions of KOH and TBAB in different orders The results are give in Table 3.33

Table 3.33 Combinations of KOH (5M, 80°C, 1 hour) and TBAB (0.15g in 50ml water, 80°C, 1 hour) treatments of PVF

Exp No.	Treatment	Failure load/N	SD	BS MPa	XPS C	/atom F	% O
	Untreated	350	70	1.8	70.4	28.8	0.8
1	KOH (water) TBAB (water + MeOH)	660	182	3.3			
2	TBAB (water) KOH (water + MeOH)	350	108	1.8	75.0	18.3	6.8
3	TBAB only	340	55	1.7	70.0	28.4	1.6
4	KOH only	670		3.4	75.7	16.5	7.6

Key: BS = Bond strength
SD = Standard deviation
( )details in brackets indicate the type of wash carried out after treatment

C) Treatment of PVdF with solutions of TBAB and KOH separately.

Some PVdF samples were also treated first, with KOH (5M, 80°C, 1 hour), washed with water, then a TBAB solution (0.15g in 50 ml of water, 80°C, 1 hour) and visa versa: TBAB solution then KOH solution. Table 3.34 compares bond strengths and surface compositions of various treatments.

Table 3.34 Combinations of KOH (5M, 80°C, 1 hour) and TBAB (0.15g in 50ml water, 80°C, 1 hour) treatments of PVdF

Exp No.	Treatment	Failure load/N	SD	BS /MPa	XPS C	/atom F	% O
	Untreated	1300	294	6.5	51.0	49.0	-
1	KOH (water) TBAB (water + MeOH)	4190	207	21.0			
2	TBAB (water) KOH (water + MeOH)	2880	698	14.4	66.6	15.6	17.3*
3	TBAB (water + MeOH) KOH (water + MeOH)	4420	319	22.1	64.9	19.7	15.4
4	TBAB only	3070	839	15.4	52.8	46.0	1.2
5	KOH only	4320	286	21.6	62.0	28.9	9.1

Key: BS = Bond strength
SD = Standard deviation
* Na was present as an impurity at 0.5 %
( ) details in brackets indicate the type of wash carried out after treatment

Treatment of PVdF with TBAB followed by KOH with just a water wash in between (experiment 2) gave a similar bond strength value as that of treatment with TBAB alone (4), i.e. less than an aqueous KOH treatment on its own (5). However, when the film was washed with water and then methanol in between the TBAB and the KOH treatments (3) then the bond strength value was as high as that with just aqueous KOH (5). The surface compositions were roughly the same for both washing procedures. Treating with KOH first then TBAB (1) did not produce a bond strength any higher than that of KOH alone (5). It must be noted that, as mentioned earlier, the strength of the adhesive/metal interface may be a limiting factor in these experiments.

In the cases of both PVdF and PVF, the high adhesion level obtained when TBAB was used in conjunction with KOH was not achieved when the reagents were used separately, in whatever order.

3.6 Amine treatments

As outlined earlier PVdF was observed to have some reaction with the epoxy adhesive used in this project. A cyanoacrylate adhesive was used for joint strength measurements and samples of PVdF were immersed in the amine hardener HV100 under different conditions (Table 3.35). The PVdF become yellow in colour after treatment

Table 3.35 **HV100 Amine treatment of PVdF**

Conditions	Failure load/N	SD	BS MPa	XPS/atom%			
				C	F	O	N
Untreated	1300	294	6.5	51.0	49.0	-	-
2 hours @ 70°C	5310	239	26.7	63.5	32.6	1.6	2.3
Overnight @ 23°C	3850	370	19.3	57.0	40.9	1.1	1.0

Key: BS = Bond strength
SD = Standard deviation

The presence of N is an indication of a reaction having taken place at the PVdF surface.

The same experiment was carried out on PVF; Table 3.36 displays the XPS results. Adhesion tests were not carried out as the adhesion of cyanoacrylate to the untreated PVF was very good (Table 3.1). A small amount of Nitrogen was detected.

Table 3.36 **HV100 Amine treatment of PVF**

Conditions	XPS/atom%			
	C	F	O	N
Untreated	70.4	28.8	0.8	
2 hours @ 70°C	71.6	27.3	0.6	0.5
Overnight @ 23°C	69.2	28.8	1.0	0.6

Chapter 4

Discussion

4.1 Introduction

In general it is more difficult to achieve good adhesion to polymers than to metals. However, some polymers like poly (ethylene terephthalate) (PET) and polyamides may require only a solvent wipe or perhaps abrasion to give reasonable adhesion levels. Polyolefins and fluoropolymers generally require some other form of pretreatment before suitable bond strengths are achieved. In light of the theories of adhesion, given in Chapter 1.3 the poor adhesion of these materials may arise from the following.

i) Lack of functionality in their chemical structure which could result in:

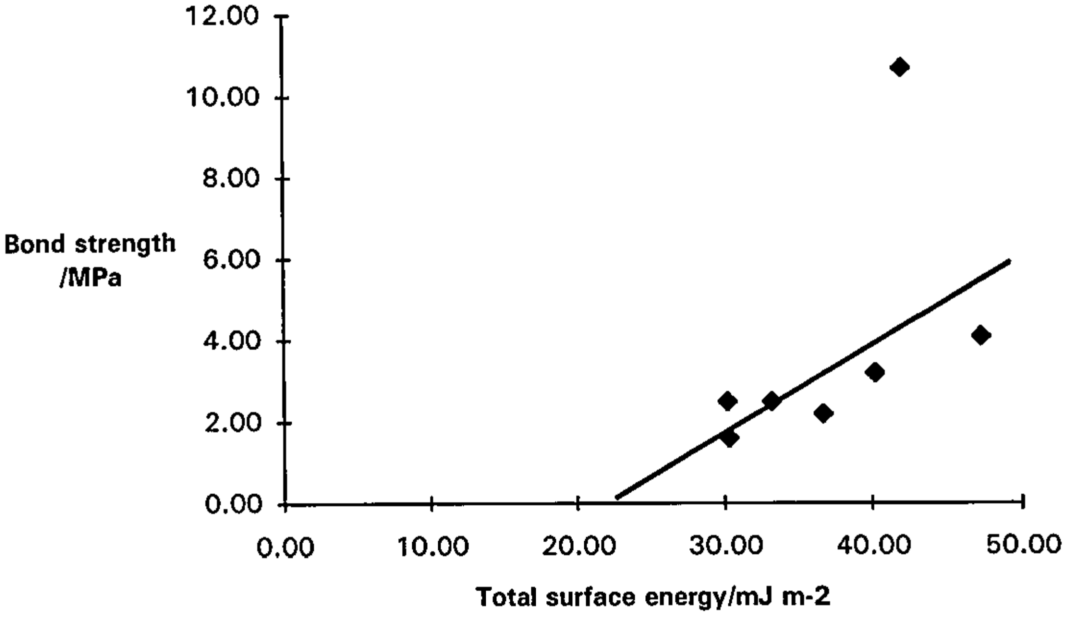
a) Poor wetting of the adhesive on the substrate.

b) Weak interactions across the interface. The importance of specific interactions has been shown for a polyolefin surface modified chemically by corona discharge treatment[101]. Briggs *et al*[101] showed the importance of hydrogen bonding through enolic OH groups in autohesion using derivatisation techniques and XPS. In the same study, the adhesion of a nitrocellulose-based ink to corona discharge treated PE was shown to be facilitated by enolic OH. A more recent example of the role of specific interactions in adhesion is given by Sheng *et al*[102]. PP was treated with a flame which incorporated OH functional groups. The adhesion was good with epoxy adhesive and Polyurethane (PU) paint. However, when the OH groups were derivatised with TFAA for quantification the adhesion to epoxy remained high but was reduced with PU paint. This demonstrates the importance of OH groups for strong interactions with PU.

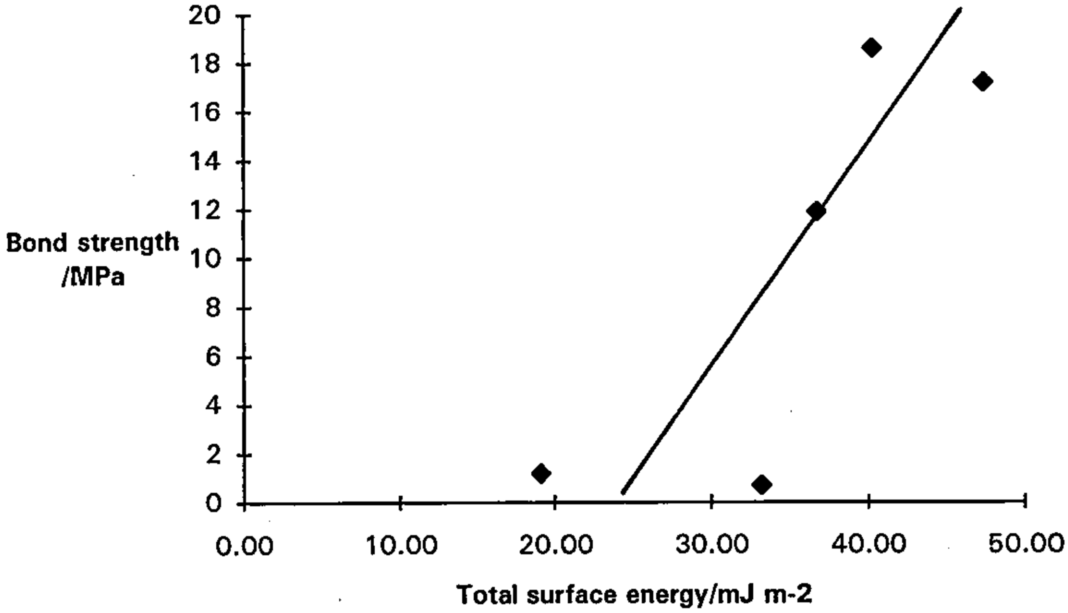
Wetting can be assessed by measuring the surface energy of a sample. In several studies there has been a good overall correlation between surface energy and bond strength. The results are presented in Figure 4.1a, 4.1b and 4.1c.

Figure 4.1 **A graph showing the general trend of increasing bond strength with increasing surface energy for polymeric materials**

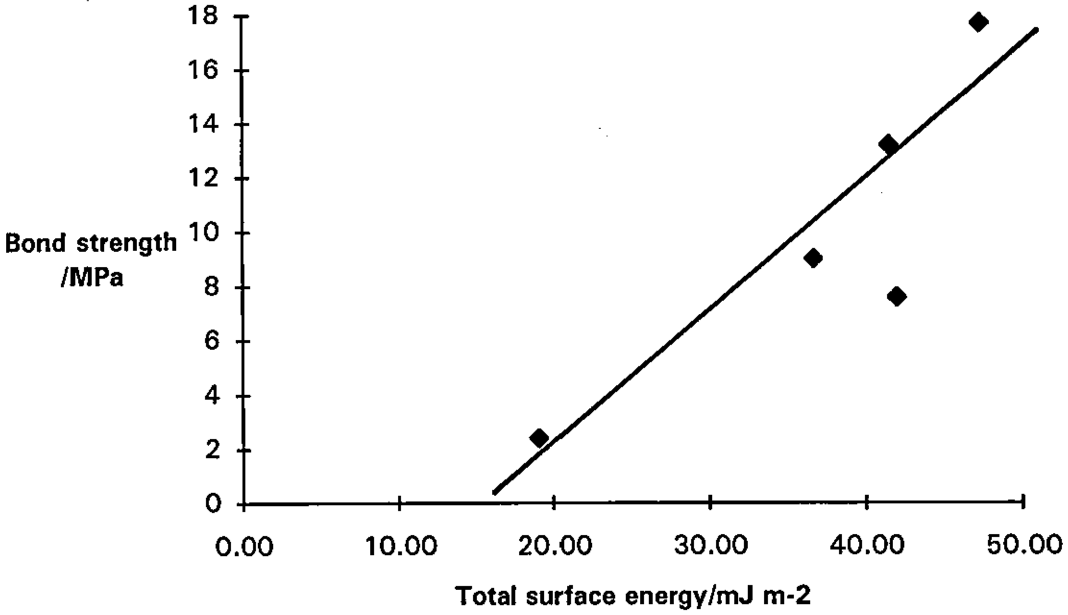
4.1a Ref 103



4.1b Ref 104



4.1c Ref 105



ii). The presence of weakly cohesive material on the polymer surface may result in a weak boundary layer on bonding.

Understanding the reasons for adhesion improvement brought about by particular pretreatments is made difficult because the pretreatment may improve adhesion in three ways concurrently: introduce functionality, remove potential weak boundary layers and bring about a favourable topography. Within this discussion the various mechanisms will be considered for the pretreatments studied and where possible, suggestions will be made regarding the dominant effect.

4.2 Bonded untreated fluoropolymers

It has been shown by Briggs *et al*[106] that a region of low cohesive strength exists on PTFE. XPS showed that fluorinated material was transferred from PTFE to an epoxy adhesive at a low load. Similar experiments in the present work showed the same result for PTFE and PVF. Therefore, it is suggested that there is a region of weakly held fluorinated material on the PTFE and PVF used in this work resulting in a weak boundary layer when bonded to epoxy. However, as will be discussed below, with PVdF transfer of fluorinated material occurred at a higher failure load. It is also suggested that under certain conditions a weak boundary layer may not exist with PVF.

Simple washing experiments were carried out on PVF with an aim to remove the weakly cohesive material. PVF was washed in methanol and trichlorotrifluoroethane separately (see below Table 3.2). Surface compositions were unchanged indicating no chemical reaction due to the washing. The adhesion to the washed material was not improved, clearly the weak layer was not removed. It might be anticipated that the solubility of fluorinated material would be very poor in methanol but better in trichlortrifluoroethane. However, the molecular weight of the layer may also be a limiting factor.

In work prior to this study Brewis[104] bonded untreated PVF with the same epoxy adhesive used in this work; high joint strengths were obtained. The value was 11.9 MPa for a butt test compared with 1.8 MPa for a lap shear test in this work (Table 3.1). These values may be compared because with other polymers similar values were obtained with the two tests. Clearly, when two different batches of PVF bonded with the same adhesive give such different joint strengths, the most likely cause for the poor adhesion is a weak boundary layer in one case. It is reasonable to expect high joint strengths with untreated PVF considering the fairly high polar component of surface energy. A value of 6.2 mJ m^{-2} was measured in this work (section 3.1.1). Table 1.3 displays a reference value of 5.4 mJ m^{-2}. This would enable good wetting of a polar adhesive and the potential for polar interactions with the adhesive.

When the PVF used in this work was bonded with a cyanoacrylate adhesive good adhesion was obtained; the bond strength was 17.5 MPa (Table 3.1). This means that the weakly held surface material, seen to transfer to epoxy adhesive, was absorbed by the cyanoacrylate adhesive.

Levine *et al.*[105] report a joint strength of PVF to epoxy of 9.1 MPa. The epoxy, Epon 828[a], was cured with diethylenetriamine (DETA). Yet Hall *et al*[103] report a value of 1.9 MPa when PVF was bonded with Epon 828 cured with Versamid 140[b]. Again differences in the cohesive strength of the surface regions are likely to be the reason for the differences in joint strength.

In the case of PVdF, Schonhorn[107] has pointed out an additional complication. Schonhorn showed variations in bond strengths on a single batch of PVdF when it was bonded with epoxy resins cured with different amines. He concluded that some amine curing agents have the potential to chemically react with the fluoropolymer before gelation of the adhesive. The speed of the adhesive curing reaction, the curing conditions and the nature of the amine may influence whether a reaction with the polymer would take place. For example, when untreated PVdF was bonded with Epon 828 cured with triethylene tetramine (TETA) or with diethylaminopropylamine (DEAPA) at room temperature the bond strength was low (2 MPa). When the two adhesive systems were cured at 80°C, the DETA cured bond still gave a bond strength of 2 MPa, whereas the DEAPA cured system resulted in a bond strength of 13 MPa. He suggested that both the amines in isolation will have the potential to react with the PVdF surface, like a chemical pretreatment. However, when used in conjunction with the Epon 828, the DETA which is highly reactive does not have enough time prior to gelation to bring about surface modification whereas the slower reacting DEAPA has sufficient time to

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[a] Reaction product of epichlorhydrin and bisphenol A.

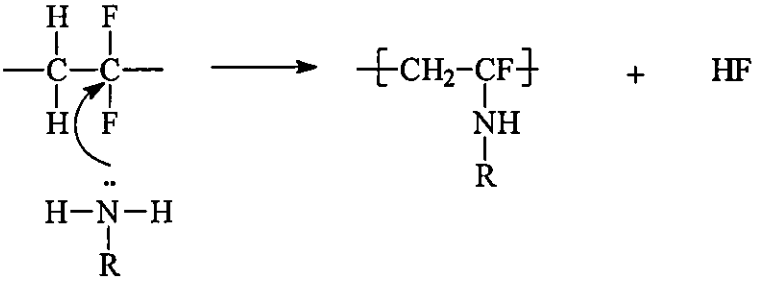
[b] A polyamide-polyamine manufactured by General Mills, Inc.

modify the PVdF and so enable strong adhesive joints on curing. A higher temperature was necessary to enable reaction of DEAPA with the PVdF.

Schonhorn expanded his study and used these two amines in isolation as pretreatments for PVdF. He bonded the treated samples with Epon 828 cured with Jefferamine T-403 (a polyetheramine containing three amine groups which gave low bond strengths (5 MPa) with untreated PVdF when cured between room temperature and 140°C). Pretreatment at room temperature for up to 24 hours resulted in an improvement in bond strength with the DETA (15 MPa) but only slightly with DEAPA. However when the PVdF was treated with DEAPA at 70°C the bond strength was around 17 MPa. The higher reactivity of DETA causes it to be a better pretreatment in isolation at lower temperatures, but its reactivity with epoxy resin when used as an adhesive precludes polymer modification prior to solidification of the epoxy. The surface modification of PVdF brought about by reaction with DEAPA was facilitated by increased temperature.

Schonhorn included transmission infrared spectra of untreated PVdF, DETA and PVdF-DETA composite reacted for 16 hours at 70°C. Comparing the spectra showed that the primary amine bands of the DETA were replaced by secondary amide bands in the reacted spectrum arising from a defluorination reaction. It is possible for the secondary amine to react further with PVdF to produce an imine structure

Results in this work show that when PVdF was bonded with epoxy AV100/HV100, cured at room temperature for 24 hours the bond strength was 6.5 MPa (Table 3.1). When the cure profile was 70°C for 2 hours the bond strength was in excess of 32 MPa. In fact, the bond failed at the adhesive-metal interface. The similarity between these results and Schonhorn's observations above suggested there may be some reaction between PVdF and the adhesive used in this work. Schonhorn's experiments were repeated; PVdF was immersed in the amine hardener, HV100 for either 70°C for 2 hours or overnight at room temperature then washed (section 2.3.4). Modification of the PVdF was evident from a yellowing of the material and the introduction of nitrogen and oxygen into the surface at both temperatures (Table 3.36). The adhesion of the treated surface to cyanoacrylate was increased from 6.5 MPa (untreated) to 26.7 MPa (treated at 70°C, Table 3.36). Reaction at 70°C rather than room temperature gave a more pronounced surface modification. The precise formulation and reactivity of the hardener was not known except it was a polyaminoamide. It is quite probable that the reactivity was such as to allow sufficient time for reaction between the hardener and the PVdF before gelation when used as an adhesive hardener with AV100, i.e. similar to the DEAPA/Epon 828 system described by Schonhorn. In general terms the following reaction may take place.



The observation of 1.6 atom% O and 2.3 atom% N in the XPS spectrum of HV100 treated PVdF at 70°C for 2 hours (Table 3.35) is consistent with the amide group contained in R in the above scheme. Further reactions with amino groups and dehydrofluorination would lead to the production of imines. Crosslinking would occur if there were 3 replaceable hydrogen atoms in the amine hardener. There are therefore, two mechanisms by which the amine treatment might enhance adhesion: the introduction of chemical groups which would improve wetting and specific interactions with an adhesive, and the strengthening of relatively weak surface material through crosslinking.

The above two mechanisms can also be invoked when untreated PVdF is bonded to epoxy at two different temperatures. The adhesion level when PVdF was bonded to epoxy at room temperature, and bonded with cyanoacrylate was fairly low. However, it was significantly greater than the level achieved when untreated PTFE and PVF were bonded with epoxy (70°C) so may not be regarded as possessing a 'classical WBL'. It can be said to have relatively weak surface material as substantial fluorinated material is transferred to epoxy at relatively low failure loads. It is likely, that when untreated PVdF is bonded with epoxy at 70°C a combination of mechanisms is occurring. Absorption of these relatively weak layers by the epoxy may be facilitated by the higher temperature. In addition, the HV100 component may be chemically modifying the PVdF, as described above, producing a mechanically stronger surface and one containing groups that the adhesive can chemically bond to, so producing the very high joint strengths. When PVdF was bonded with epoxy at the lower temperature of 23°C the energy of reaction is not sufficient to bring about surface modification.

The question is posed then, why PVF does not exhibit such high bond strengths with the same epoxy and hardener which has the same potential for reaction between hardener and PVF. The lower bond strengths obtained with PVF may be explained by its lower reactivity towards amines. This is due to the smaller positive charge on the carbon atom bonded to the fluorine atom. It was also possible that the region of low cohesive strength on the PVF was chemically modified by the HV100 but the new species were still present in a mechanically weak layer that was not able to be absorbed into the adhesive due to poor solubility or molecular weight. Table 3.36 presents XPS results from PVF treated with HV100; a small amount of N and O are introduced in to the surface showing a reaction has taken place. In addition, the amount of crosslinking reactions may not be sufficient to strengthen the mechanically weak layer. It could also be due to the thickness of the weak layer. As mentioned above adhesion of PVF to cyanoacrylate is very high; weak cohesive material must be absorbed completely in the adhesive resulting in no weak boundary layer.

It can be seen from the results in this work that for PVF and PVdF, removal of weak boundary layers and a correct choice of adhesive may be all that is necessary to obtain good adhesion. However, untreated PTFE will not react with amines except possibly at high temperatures and solubility in epoxies and cyanoacrylate will be very low due to the non-polar nature of fully fluorinated polymers. Nonetheless, the next section discusses how removing the potential weak boundary layer on PTFE can achieve some improvement.

4.3 Multiple bonding of untreated fluoropolymers

Having shown the transfer of fluorinated material at low loads for PTFE, PVdF and PVF (Table 3.2), specimens were repeatedly bonded and separated to determine whether high joint strengths could be achieved without chemically modifying the polymers[108]. After one bonding the PTFE surface, viewed with SEM (Figure 3.16), was very similar to an unbonded sample . The epoxy adhesive side showed a replica of the surface with no visible evidence of fluorinated material (Figure 3.17). XPS however, indicated 16.9 atom % fluorine on the epoxy surface (Table 3.3), and a falling background to the high binding energy side of the F1s peak in Figure 3.13 suggests that the fluorinated material was present as a thin layer. Further, the F2s/F1s ratio in Figure 3.13 was 0.03. For a homogeneous layer of fluorine containing material the ratio would have been 0.05. After the PTFE had been bonded 20 times there was visible evidence on both the PTFE (Figure 3.19) and epoxy (Figure 3.20) of fluorinated material in the form of fibres. The fibres emerged from the PTFE bulk (Figure 3.21) and appeared to result from plastic deformation of the surface region. The bond strength of the 10 times bonded sample was more than double than that bonded once (Table 3.4). It is likely that the first few bondings removed weakly held fluorinated material, the new surface was then cohesively strong enough to resist separation and bring about plastic deformation of certain regions; some of the fibres remained on the epoxy (Figure 3.20). The presence of the fibres on the PTFE means topographical effects on adhesion cannot be ruled out; however, no change in adhesion was observed when the quantity of the fibres was increased in samples bonded 10 times and 20 times (Table 3.4).

PVF behaved in a similar way to PTFE. After 1 bonding adhesion was poor with transfer of material only seen in XPS (Table 3.4). After 10 bonds the adhesion was increased 3 fold and 4 fold after 20 bonds. It is more likely that the resulting change in topography after 20 bonds (Figure 3.23) affected the increased between 10 and 20 bonds. However, as in the case of PTFE there had been a change in the cohesive strength of the surface from when material was removed easily, to when material was held more strongly to the bulk, with the resulting in plastic deformation.

Multiple bonding experiments were not carried out on PVdF but Figure 3.15 shows that 12.2 atom% fluorine was transferred to epoxy cured at room temperature at a relatively low load of 1290 N (Table 3.3). The F2s/F1s ratio on the XPS spectrum of the debonded epoxy was 0.03 indicating a thin layer of fluorine containing material.

In summary, it has been shown that weakly cohesive material can be removed from the surface of PTFE and so improve its bond strength to a moderate degree. To achieve good adhesion it is likely that removing WBLs is insufficient. A pretreatment that enhances adhesion to PTFE must incorporate removal or strengthening of this region as part of the mechanism. Though, if high adhesion is obtained it is not likely to be the predominant factor. For PVF a more substantial improvement in adhesion was obtained by just removing potential weak boundary layers and these are likely to be the main reason for the poor adhesion obtained with this polymer in the present study.

4.4 Pretreatment of fluoropolymers

4.4.1 'Tetra-Etch'

In agreement with other authors (Dwight & Riggs[60]) treatment of PTFE with 'Tetra-Etch' caused almost complete defluorination of the surface and introduced substantial amounts of oxygen. Adhesion improvement was very rapid; a ten fold increase was obtained after just 10 seconds (Table 3.7). The treatment also caused roughening of the surface (Figure 3.26). It is likely that three factors contributed to the adhesion improvement: removal of weakly cohesive material, favourable topography and introduction of functionality that improved the wettability and interactions with the adhesive.

Figure 3.27 shows a schematic of where apparent failure was in a debonded 'Tetra-Etch' treated joint. The 'black' treated surface appeared to be attached to the adhesive suggesting failure at the boundary between untreated and treated. However, XPS showed there was no clear interface between the bulk PTFE and the 'black' treated PTFE (Table 3.8). When debonded joints were examined with XPS, both sides gave similar compositions, both contained carbon, fluorine and oxygen. The side that had originally been the epoxy showed no nitrogen suggesting the possibility of a thick layer (in XPS terms) of modified fluoropolymer. The C/F ratio on this surface was ~ 1 and there was around 6% oxygen. The original PTFE side had slightly more carbon than fluorine and 6% oxygen. Defluorination and oxygen incorporation was not uniform into the sample producing an interphasial region between the outermost surface and bulk PTFE.

High resolution XPS on the C1s region of a sample of PTFE treated with 'Tetra-Etch' showed the oxygen functionality (Figure 3.28). A C1s spectrum obtained from the ESCALAB instrument at BP was curve fitted with four peaks (Figure 3.30). Note is made here of the limitation of curve fitting in isolation. The C1s spectrum being considered (Figure 3.28 and 3.30) was clearly comprised of a number of unknown chemical groups. The shoulder to the higher binding energy side was broad and no specific peaks were resolved. The signal:noise ratio was not good enough for reliable deconvolution. Hence, four of perhaps the most likely oxygen containing functionalities were chosen to be represented (many other types of functionality could be expected). The curve fitting software is such that any number of peaks and degrees of freedom for peak position or peak width could have been chosen; this highlights that in a case of a mostly unknown sample one has to decide on a likely answer and not regard curve fitting as a means to rigorously identifying chemical groups. If data are such that deconvolution routines could result in better resolved peaks, a greater confidence could be given to the fits and areas produced from curve fitting software.

Considering again the 'Tetra-Etch' treated PTFE sample (Figure 3.30), curve fitted data estimated that 27% of the surface composition was oxygen and an estimation that 2.4% of the surface carbons may be as O-C=O. Derivatisation of a sample of PTFE treated with 'Tetra-Etch' was carried out for a more rigorous method to measure the amount of particular chemical species at the surface. It was found that the treated surface contained 3.4 % OH and 1.3 % COOH (Tables 3.8 and 3.9) which is less COOH than estimated by curve fitting. This may be due to the curve fit having contributions from other species and/or incomplete reaction of the TFE. The two derivatisation reaction results accounts for 6.0 atom% of the total surface oxygen. Therefore, there was approximately 17 atom% oxygen as other species such as carbonyl, ether etc. The presence of certain functional groups may be of primary importance in the adhesion of this surface to epoxy through specific interactions. This will be referred to in the 'Further work' section of this thesis.

The presence of C=O was confirmed with ATR-FTIR; a peak around 1710 cm^{-1} is seen in Figure 3.29. The bands around 1500-1650 cm^{-1} are most likely to be due to conjugated double bonds rather than $COO^{-}Na^{+}$ as no sodium was detected in XPS. Derivatisation reactions with bromine in the dark confirmed the presence of C=C. It was found that there was one double bond per 16 carbon atoms (Table 3.11).

When PTFE was treated with 'Tetra-Etch' for different times (Table 3.6) the bond strength was increased after a matter of seconds. The adhesion level remained high for treatment times of one hour. The surface chemical modification however, varied over the different durations. It was observed that after 30 and 60 minutes of treatment the surface contained more fluorine and less oxygen than sample treated for shorter times. This will be discussed in the section describing the mechanism of 'Tetra-Etch'

Irradiation of the treated surface with UV light or immersion in sodium hypochlorite solution removed the black coloration on the treated PTFE and the surface hydrophobicity was restored (Table 3.5). However, the adhesion level did not fall to that of untreated but was around 4 times that of untreated. In this case poor water wettability did not mean poor adhesion. The hydrophobicity of the UV irradiated sample was not reflected in the XPS results which indicated oxygen levels of around 11%. There are different possible explanations. XPS samples from a depth of up to 10 nm, whereas contact angles are representative of the very surface, so it is possible that the oxygenated species were oriented away from the surface in order to minimise surface energy. Alternatively, the high water contact angle may be due to high roughness and not lack of polar species. XPS indicated the presence of impurities on the UV irradiated surface however; these did not result in a weak boundary layer but were likely to have been dissolved in the adhesive. The presence of oxygenated species, absence of a WBL and a very rough surface may all have been important in the attainment of reasonable adhesion levels.

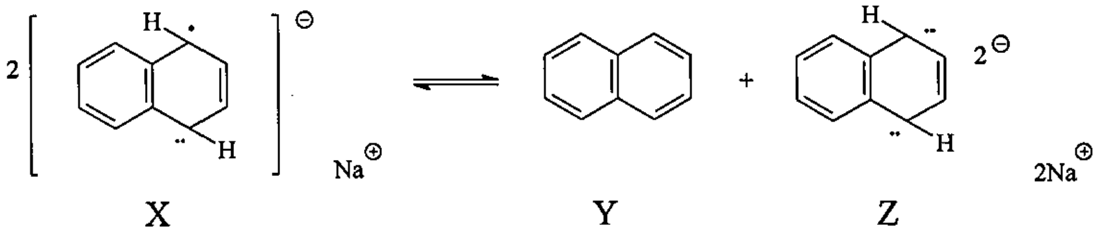
The sodium hypochlorite treated sample was extremely hydrophobic (Table 3.5), such that it was difficult to get the drop to leave the metal syringe and rest on the PTFE. The hysteresis was very low, yet SEM showed a highly rough surface.

This behaviour can arise from a 'composite' surface[109]. When a surface is so rough that the liquid cannot wet into the crevices then the drop has both solid and air interfaces beneath it; this is said to be a 'composite' surface. Morra *et al*[110] reported such behaviour on PTFE treated extensively with an oxygen plasma. The bond strength of the hypochlorite treated sample was 4 times that of untreated. It is possible that the adhesive was able to wet the highly rough PTFE surface. Good contact and the absence of a weak boundary layer may account for the improved adhesion. However, XPS showed there was 1.4 atom% of oxygen present at the surface (Table 3.5); even this small amount of oxygen seen in XPS may increase the interactions at the interface enough to significantly affect the adhesion level.

Gribbin[108] has carried out research on the reduction of PTFE surfaces which included reaction with sodium naphthalenide. He proposed that the surface morphology of the PTFE determined the effectiveness of the reducing solution. He concluded that crystalline regions were more easily reduced by the naphthalenide solution. No experimentation into levels of crystallinity was carried out on the PTFE within this work. However, as outlined in section 1.2.1 skived PTFE film will have a partially oriented and partially crystalline structure and as such was easily reduced.

In considering the mechanisms by which the 'Tetra-Etch' chemically modifies the surface of these fluoropolymers it will be taken that the radical anion from sodium naphthalenide is the reactive species.

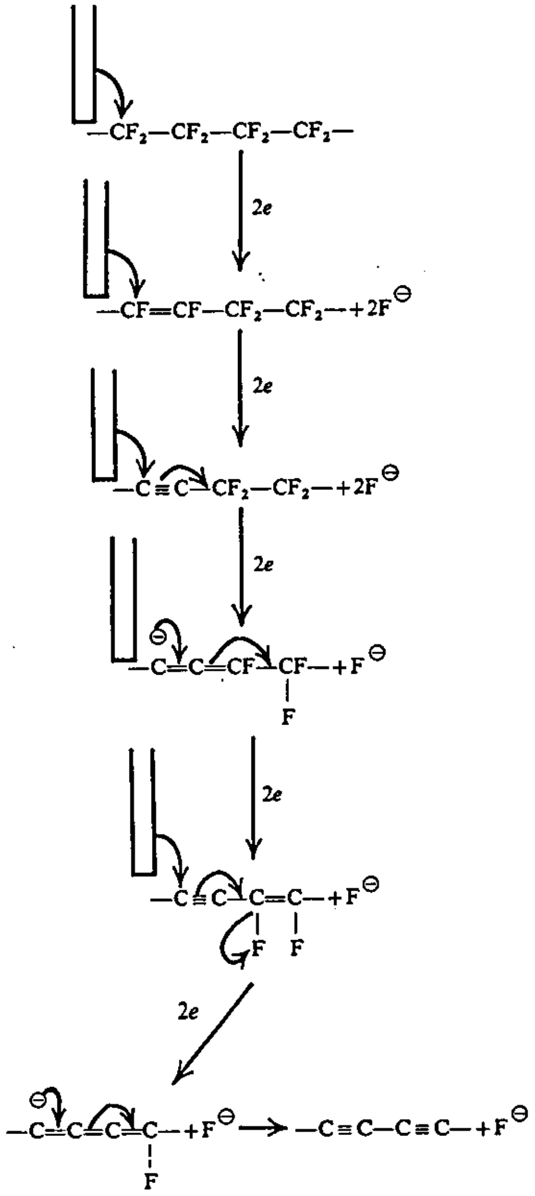
The radical anion exists in equilibrium with the corresponding dianion according to the following scheme:



The species X is a powerful reducing agent and will react with the positive carbon sites in the PTFE causing rapid defluorination via electron transfer.

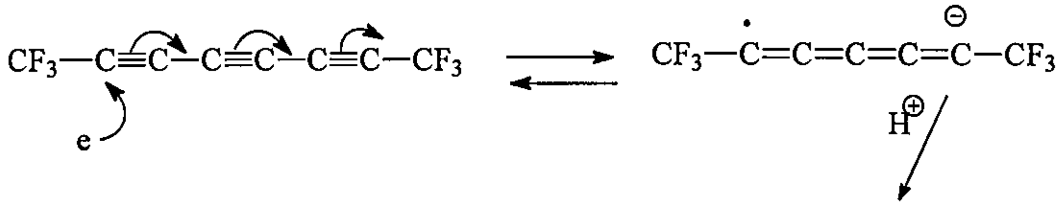
A similar mechanism was proposed by Dahm[111] for an electrochemical initiated reduction of PTFE. The scheme is included here showing the electron transfer mechanism and the resulting reduced carbon chain.

Figure 4.2 Electron transfer mechanism for the reduction of PTFE[111]



The resultant carbon chain will be extremely reactive and oxygen from the solvent or the atmosphere will produce specific functionalities in the carbon chain including >C=O, COOH, C=C and others.

A possible explanation of the observation of less defluorination and oxygen on a PTFE sample treated with 'Tetra-Etch' for longer periods (Table 3.7) is as follows. A polyacetylinic chain formed from the reaction could undergo further reduction as shown in the scheme below. The anion could then pick up a proton; this site would then be less likely to be oxidised.

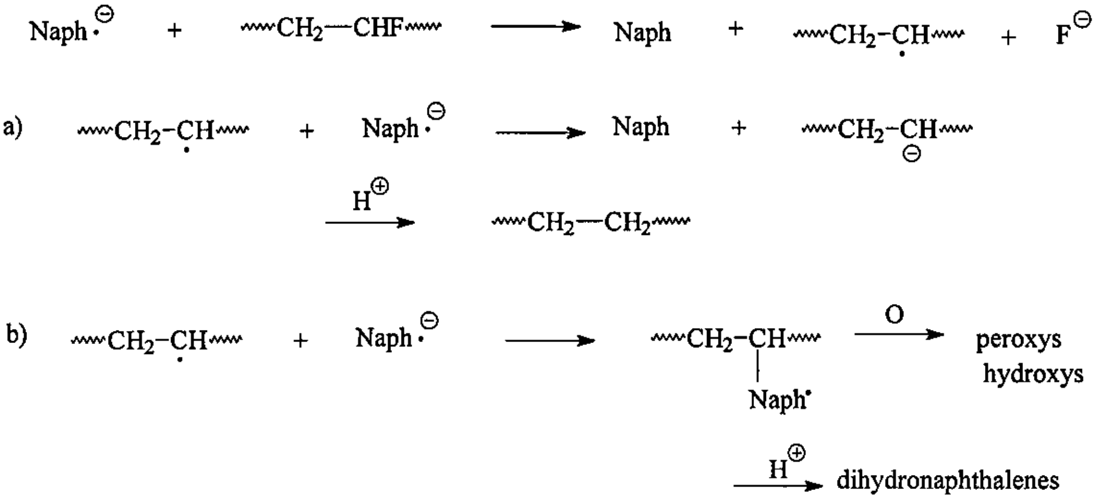


This electron transfer mechanism for the reduction of PTFE has been accepted[111]. However, the mechanism of reaction of this radical anion with PVF has not been considered before and there are different reaction possibilities.

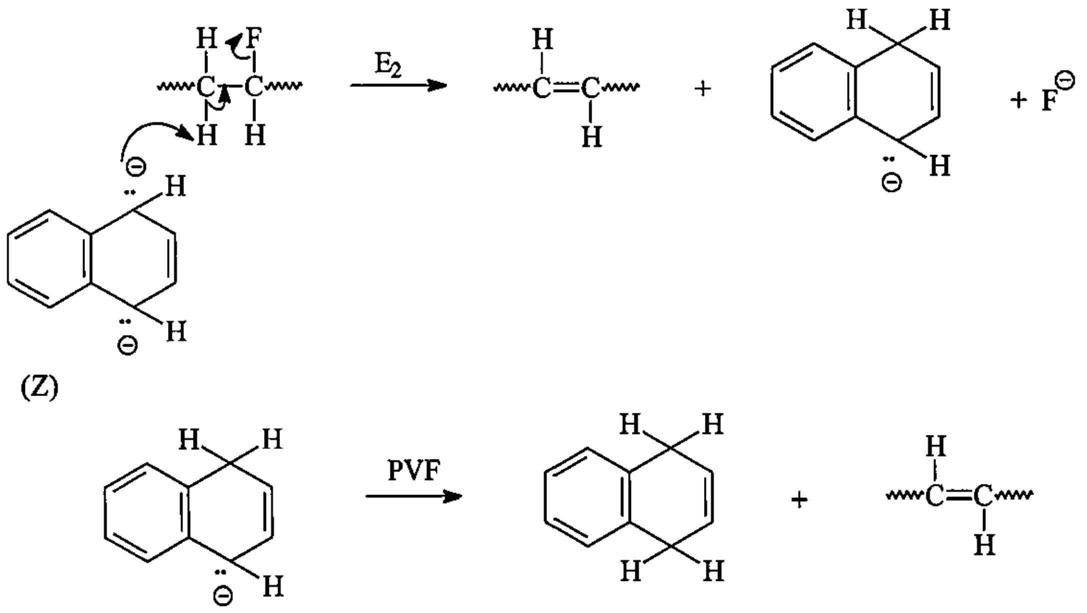
Treatment of PVF with 'Tetra-Etch' was slower than for PTFE; the bond strength reached its maximum after 10 minutes rather than 10 seconds in the case of PTFE and no discoloration occurred on the PVF.

If a reductive mechanism via electron transfer is considered for PVF, like that described above for PTFE, it may be expected that the positive carbon site in PVF would be less reactive towards a reducing agent having only one electron withdrawing fluorine attached to it. Also the reduction could not proceed along the chain in the 'unzipping' type mechanism as in PTFE because the fluorines are not adjacent to one another. These factors, in simple terms may account for the slower and less complete reaction of the 'Tetra-Etch' with PVF.

More specifically, in a study on electrochemical reduction by the naphthalenide radical anion of some alkyl halides[112] it was shown that the reduction of a C-F bond is less likely than a C-Cl bond with these agents. An electron transfer mechanism has been established for a reaction between PVC solution and sodium naphthalenide; the solution changed colour from the characteristic dark green colour of the radical anion to brown and the PVC blackened[113]. If this is applied to PVF then the following scheme may apply:



Alternatively the naphthalenide radical anion may also act as a base. In the scheme on page 167 species Z, the dianion is a very powerful base. The following elimination reaction between PVF and the dianion could occur:



In both the electron transfer or base promoted dehydrofluorination of PVF the reactions result in a defluorination without oxygen incorporation with the exception of scheme b) in the electron transfer process where it is proposed that oxygen could, at this point be introduced. The origin of the oxygen would most likely be from the washing procedures. These schemes correspond well with the experimental observations. XPS detects significant defluorination after longer treatment times but very little oxygen incorporation (Table 3.7). It is not clear however, whether the electron transfer mechanism or elimination was predominant. The defluorination is likely to reduce the polarity of the surface and may account for the small water contact angle increase after the longer treatment time (Table 3.7). There were no topographical changes as observed by SEM. From these factors wettability or roughening were not responsible for the increase in adhesion. It seems more probable that removal of a weakly cohesive region is the explanation. This could occur by crosslinking (possible via scheme (b) in the electron transfer mechanism) or by increased compatibility of the PVF with the adhesive when defluorination had occurred resulting in absorption by the adhesive.

'Tetra-Etch' improved the bond strength of PVdF to nearly double after 10 seconds (Table 3.7). Within the standard deviation of the results this is around the maximum level achieved.

The same mechanisms for the action of the naphthalenide radical anion may be considered for PVdF. As such, it would be expected that

1. PVdF should be a better electron acceptor, increasing the probability of electron transfer mechanisms. This would account for the intermediate rate of chemical modification of PVdF compared to PTFE and PVF.

2. PVdF should undergo elimination reactions more readily than PVF and could lead to the formation of carbon-carbon triple bonds.

These arguments are strengthened by the evidence of more defluorination on PVdF than PVF in the early stages. More oxygen is incorporated than with PVF which may be due to the possibility of ketone formation. The amount of fluorine decreased as the treatment time increased up to 10 minutes, where it was less than one third of the original. It is also likely that the discoloration of the PVdF after greater than one minute immersion in the solution is due to conjugated carbon double bonds produced as a result of the elimination mechanism.

Introduction of oxygen functionality and removal of moderately weak cohesive surface material are likely to be responsible for the improvement in adhesion with PVdF.

4.4.2 Flame

The adhesion of PVF was increased by a factor of 9 on treatment with flame. Around 4 % oxygen was introduced by the treatment (Table 3.12). Water contact angles reflected this increased surface polarity by resulting in a reduction in advancing and receding angles. The receding angle showed a larger reduction which is consistent with the suggestion of Good[114] that the receding angle is representative of high surface energy regions of a heterogeneous substrate. This is the most likely explanation for the increased hysteresis, as SEM did not revel any roughening of the PVF on flame treatment.

In contrast to the previous treatment discussed i.e. 'Tetra-Etch' where chemical modification of the PVF was largely defluorination and only slight oxygen incorporation, the flame treatment of PVF resulted in little or no defluorination. Oxygen functionality must therefore have been introduced through the rupture of C-H or C-C bonds. This is reasonable considering the effectiveness of flame to pretreat polyolefins. Briggs[115] outlines several possibilities for the mechanism of surface modification of polyolefins with flame. There is the possibility of thermal oxidation, which is a free radical process, or when it is considered that a flame is also a plasma, many different energetic species e.g. free radicals, atomic oxygen, electrons etc. are present and free radical oxidation with addition of oxygen and other species like nitrogen may occur.

It may be assumed that the above oxidation processes are likely in the case of PVF. Reaction at C-F sites apparently did not occur within the time of treatment used in this work.

Introduced functionality and removal of weakly cohesive material are likely to be responsible for the improved adhesion; regarding the latter, introduction of oxygen will increase the compatibility with the epoxy adhesive. In addition ablation of the surface may be occurring

Although the contact angle hysteresis was fairly high after flame treatment of PVF, surface energy measurements were carried out for an aging experiment (Table 3.13). Initially after treatment the total surface energy was raised from 37.2 mJ m^{-2} to 39.8 mJ m^{-2}. The advancing water contact angle reflects this by reducing from 76 to 65°.

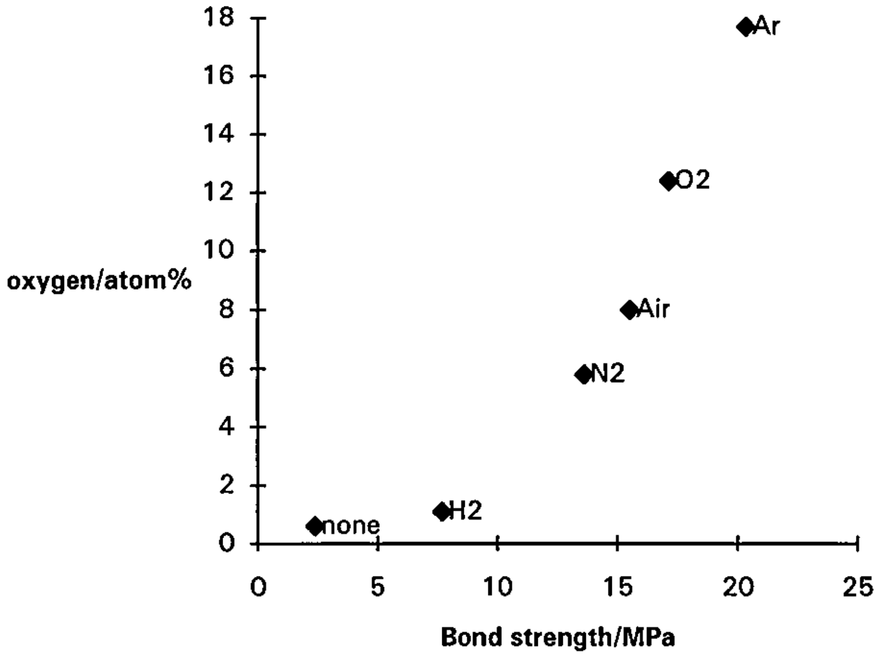
After one day the polar component of surface energy was reduced, the overall surface energy fell and the advancing angle increased. The polar component continued to fall to 7.6 mJ m^{-2} after 6 days without a change in the total surface energy. No further changes were observed over a 16 week period. It is possible that the high surface energy components on the surface were sufficiently mobile to reorient away from the surface to minimise surface energy. Investigating this suggestion it was questioned as to whether or not these possibly mobile components could be removed by washing. Samples of freshly treated flame PVF were washed in each of the liquids used in the surface energy measurement, whose surface tensions were measured before and after immersion (Table 3.13). Any components removed from the PVF may have altered the surface tension of the liquid. No changes were observed. This served to give credibility to the surface energy measurements in the aging experiment.

PTFE was not chemically modified by the flame treatment under the conditions used in this work (Table 3.12). Considering the lack of modification of PVF at C-F sites this was maybe to be expected. The bond strength results show a small loss of adhesion. This is probably due to chain scission resulting in more weak cohesive material. Alternatively heat induced migration of LMWM to the surface may have occurred.

4.4.3 Plasma

When PVF was treated with different plasmas for 1 minute each there was a general trend that bond strength increases with oxygen incorporation see Figure 4.1. (values from Table 3.15)

Figure 4.1 **Relationship between oxygen concentration and bond strength for various plasma treatments of PVF**



It was shown in section 4.3 that reasonable bond strengths could be achieved with PVF on removal of weakly cohesive material. Most plasmas may also be effective at removing weakly cohesive material through ablation or crosslinking. However, in comparison to 'Tetra-Etch' or multiple bonding, a larger incorporation of functionality was achieved with plasma treatment of PVF resulting in higher levels of adhesion. The exception is treatment with a hydrogen plasma: a lower bond strength, as compared to 'Tetra-Etch' treatment, is achieved with similar levels of oxygen.

'Tetra -Etch................................15.9 MPa with 0.8 %O
H_2...7.7 MPa with 1.1 % O

It is possible that a region of relatively low cohesive strength remained even after hydrogen plasma treatment. No information is available regarding the nature of the oxygen-containing functionalities in the two cases and this could also account for the differences in bond strength.

Adhesion of PVF was improved by a factor of 9 after an argon and oxygen plasma treatment (Tables 3.16 and 3.17 respectively) and this was achieved after the shortest practical treatment time of one second. For a short exposure to an argon plasma there was no defluorination but oxygen was incorporated; modification had therefore taken place at C-H or C-C sites. Increasing the treatment time to one minute for an argon plasma resulted in a further 20 % increase in bond strength; at this stage the debonded joints were beginning to show some material failure. Fluorine was reduced by 20 % after one minute and oxygen was increased four fold on the value at 1 second (Figure 3.32). An oxygen plasma resulted in very similar chemical modification over the treatment range of one minute (Table 3.17); the only difference being the adhesion level remained constant over this range. Comparing the surface composition and adhesion of oxygen and argon plasma treatments for up to one minute suggests that good adhesion can be obtained with a certain level of chemical modification; further modification may or may not give a further increase, depending on the type of plasma. It may be that argon was more effective at crosslinking the surface[11] and this is the cause of the higher adhesion for similar conditions.

On another occasion, PVF was exposed to an argon plasma for longer treatment times (Table 3.18). After 5 seconds and up to 30 minutes the level of oxygen incorporation remained constant at around 11 atom percent while the fluorine was depleted by 50 % after 5 seconds and 66 % after 30 minutes. The bond strength was consistently high over this range; the 30 minute sample was slightly greater than the shorter times. After a treatment time of 30 minutes the sample failed cohesively at around 4500 N. SEM of the 30 minute sample showed pitting of the surface (Figure 3.33). The increased roughness may account for the additional bond strength; however, the ultimate strength of the material was a limiting factor.

A discoloration of this sample suggested excess chemical modification and the possibility of conjugated double bond formation which is consistent with the loss of fluorine and constant oxygen levels over this range of treatment times.

Results in Tables 3.16 and 3.18 for argon plasma treated PVF show that chemical compositions were not consistent on separate occasions. However, the resulting bond strength was little affected by these compositional differences. This underlines the observation that, for this particular plasma, in the absence of weak boundary layers some functionality is advantageous for high adhesion but increasing the amount of oxygen further is not necessarily beneficial. The most reasonable explanation for the discrepancies in surface composition for the same conditions could be as a result of components from within the plasma equipment. Various gases, monomers and materials had been used in the plasma chamber leading to inevitable contamination (base pressure reading was not less than 0.03 Torr) prior to the results in Table 3.17. The shorter treatment time samples were carried out just after the instrument had been cleaned and a base pressure of < 0.001 Torr was reached. Less oxygen was incorporated into the PVF samples, for the same conditions, on the occasion after servicing and was more likely to have originated from oxygen in the residual gas in the chamber and on exposure to atmosphere rather than contamination from instrument walls and connectors.

Hydrogen plasma is the least effective plasma at improving the bond strength of PVF (Table 3.19). Hydrogen atoms will act as good radical scavengers and deactivate free radicals without introducing any polarity. Indeed, oxygen incorporation was much less than with other plasmas. In line with other observations, hydrogen plasma is effective at producing a certain improvement in bond strength (about 7 fold) with fairly low levels of oxygen; the most likely reason being the combination of removal of weak cohesive layers and the introduction of some oxygen functionality. Table 3.19 also shows that the bond strength value for a one hour hydrogen plasma treatment fell to that of untreated. This 'over-treatment' is most likely due to chain scission predominating over crosslinking reactions leading to the reformation of a mechanically weak surface.

The bond strength of PTFE was improved up to 9 fold with an argon plasma (Table 3.20). After a one minute treatment around 5 % oxygen was incorporated. The level of oxygen decreased as the treatment time was increased whereas, the bond strength increased to a plateau after about 30 minutes. Clearly functionality was not the primary reason for improved adhesion. Ablation of low molecular weight material was the most probable cause of adhesion improvement. It was likely that after a one minute treatment when the chemical modification was significant the functionality was associated with the low molecular weight material and was not absorbed into the adhesive and therefore still resulted in a weak boundary layer. At longer treatment times the regions of low cohesive strength may become broken down into small volatile molecules such as CO_2, and H_2O exposing underlying PTFE. The composition of the PTFE after 1 hour treatment was similar to untreated PTFE. It may be that the weak boundary layer was completely removed and that bulk PTFE was in fact difficult to chemically modify with plasma. The bond strength however, showed that a reasonable increase in adhesion can be achieved by simply removing potential weak boundary layers.

An oxygen plasma treatment of PTFE resulted in very little oxygen incorporation (Table 3.21). A maximum of 7 times improvement in bond strength was achieved with a 5 minute treatment. At a longer exposure of 30 minutes the chemical composition is similar but the bond strength is much reduced, falling to 3 times that of untreated. The most likely reason is a physical effect. SEM shows a raised up surface (Figure 3.34). This may account for the rise in water contact angle. Excess chain scission may produce more low molecular weight species than are removed resulting in a weak boundary layer.

Up to a one minute treatment, hydrogen plasma of PTFE results in little change in chemistry whereas after one hour there were major changes in surface composition (Table 3.22). The growth of the C-H against the loss of C-F is seen in the XPS C1s region (Figure 3.35). Radicals formed by rupture of C-C and C-F bonds react mainly with hydrogen rather than oxygen.

4.4.4 Group I hydroxides

PVF

The treatment of PVF with aqueous KOH solution gave increases in bond strengths which varied greatly depending on the conditions used. As expected, joint strength increased with increasing treatment time, temperature and solution concentration.

It is interesting to note that the surface composition of untreated PVF and a sample treated at 80°C for 1 minute with 15 M KOH was very similar (Table 3.25). The oxygen concentration had increased by only 0.7 % of the total surface composition. Yet, this yielded an 8 fold increase in bond strength. It is likely that removal of weakly cohesive material at the surface of the PVF was the major factor in the observed adhesion improvement, with some possible contribution from the oxygen functionality.

When the solution temperature was increased (Table 3.25) the amount of oxygen incorporated into the PVF increased and the fluorine concentration decreased over the temperature range. However, adhesion improvement remained constant for different temperatures for a fixed treatment time. As with certain plasma treatments of PVF it is concluded that a certain degree of functionality may be necessary for high adhesion levels but a further increase in functionality may not necessarily be advantageous.

In an experiment where solution molarity was varied and time and temperature were fixed (Table 3.24) there was a particularly interesting feature. Here it was observed that where chemical compositions were similar for a 5M or 15M treated sample i.e. significant oxygen incorporation and defluorination, adhesion was only very good for the 15M treated sample; at 5M the increase in joint strength was 2 fold whereas at 15 M it was more than 8 fold. The most reasonable explanation for the lack of good adhesion despite large chemical modification in the sample treated with 5M KOH would be that the oxidised species were located in the weakly cohesive regions at the surface. In a 15M solution, the dissolution of weak oxidised material was rapid whereas, after the same period at 5M the weak oxidised material was not completely dissolved.

There are two possible reactions for the treatment of PVF with aqueous KOH if, the polymer molecule is regarded as a type of alkyl halide. Nucleophilic substitution that results in the replacement of halide by an OH group is one possibility. In the case of PVF, F would be the leaving group which is the least easily displaced compared with the other halides. However, there is evidence of OH groups and the reduction of the CF fingerprint (around 1400cm^{-1}) from the ATR-FTIR spectra of aqueous KOH treated PVF using a 5M solution at 80°C for 1 hour (Figure 3.37). The broad OH band (around 3200 cm^{-1}) was only visible on the spectrum obtained using a Ge prism in the analysis. It is not fully understood why such a large OH band is not visible in the KRS spectrum. One suggestion is that optical contact of the sample with the prism was a lot poorer with the Ge prism (which is harder than the KRS) resulting in greater surface sensitivity. This would suggest that the modification was in the near surface region. XPS results in Table 3.26 show that for this sample 6.6 atom % oxygen was introduced and the fluorine level fell by 32%.

The OH$^-$ group in KOH can also act as a base leading to an elimination reaction; HF can be removed leaving an unsaturated C=C bond. Under the more extreme reaction conditions e.g. 1 and 30 minutes treatment with 15M aqueous KOH at 140° C the samples became discoloured (Table 3.25). This suggested the presence of conjugated double bonds. XPS results shown in the same table showed there was a large reduction in fluorine on the 1 minute sample; the 30 minute treated sample was almost completely defluorinated hence, elimination reactions are likely to be prominent under these conditions. Although infrared and derivatisation reactions with bromine were not carried out on these particular aqueous KOH treated samples, evidence of C=C was found on similarly discoloured samples.

To study the influence of the solvent in which the reaction was carried out, aqueous and alcoholic solutions of KOH were compared (Table 3.26). Molarity and temperature were kept constant and due to the poor solubility of KOH in alcohol the molarity had to be just 5 M. Previous experiments had shown that at this molarity and temperature (80°C), little adhesion improvement was achieved with aqueous KOH. However, an alcoholic solution under similar conditions had a much greater effect on adhesion level. A plateau of ~ 18 MPa was reached after 10 minutes i.e. a 10 fold improvement compared with an equivalent aqueous treatment which did not even double the bond strength level. The most striking feature of this comparative experiment was, although the bond strengths were so different for equivalent treatment conditions, the surface compositions were very similar (Table 3.26). ATR-FTIR however, revealed different chemical groups on the alcoholic KOH treated sample. Figure 3.38C shows that in the near surface region (spectrum using Ge prism) of a sample treated with 5M alcoholic KOH at 80°C for 1 hour, there was an OH band at 3200 cm^{-1} and no CH bands around 3000cm^{-1}. Sampling deeper with the KRS prism (Figure 3.38B) resulted in a spectrum with no OH band but at least 2 new peaks at around 1600 and 1670 cm^{-1}. These are most likely to be due to conjugated double bonds from the observation of discoloration of samples treated under these conditions. This would lead to the conclusion that the predominant reaction mechanism was elimination. However, at least some of the absorbances at around 1600 cm^{-1} may be due to COO^-. This is reasonable as a small amount of potassium is detected by XPS on a similar sample (Table 3.26) that could be present as the salt of a carboxylic acid.

The greater effectiveness of alcoholic KOH solution to enhance adhesion over aqueous may be due to better solubility of weak oxidised material in the alcoholic solution. Alternatively, the greater depth of modification and different chemical groups available for specific interactions may be the primary factor.

The addition of small amounts of tetrabutylammonium bromide, TBAB to aqueous KOH at certain temperatures had a dramatic effect on the ability of the aqueous solution to treat PVF for good adhesion.

The observations of the action of TBAB in aqueous KOH were complex and may be summarised as follows:

1. At 23°C TBAB did not make the KOH any more effective at increasing the bond strength of PVF (Table 3.27).

2. A solution of 0.03g of TBAB in 50 ml of 5M aqueous KOH was used to treat PVF at 80°C (Table 3.27). Adhesion increased 10 fold after 1 hour compared with 5 fold without the TBAB. The chemical composition of the surfaces were similar to that with just aqueous KOH. The TBAB facilitated removal of weak oxidised material.

3. A higher concentration of TBAB i.e. 0.15g in 50ml of aqueous KOH solution, resulted in higher adhesion levels (Table 3.28 and Figure 3.40). Samples treated for longer than 30 minutes failed cohesively within the PVF (see above Figure 3.40).

4. Treatment with 5M aqueous KOH containing 0.15g of TBAB per 50 ml (Table 3.29 and Figure 3.42) showed a marked temperature effect; for example after 30 seconds at 80°C there was no significant change in bond strength but after 30 seconds at 110°C there was a 9 fold increase.

5. At treatment times of greater than 10 minutes the PVF became discoloured suggesting the presence of conjugated double bonds (Table 3.28). FTIR supports this; bands are visible the 1600 - 1700cm^{-1} range on a spectrum obtained from the KRS prism (Figure 3.41B)

6. FTIR also shows evidence of OH groups at 3200 cm^{-1} and possibly carbonyls at 1730cm^{-1} (Figure 3.41).

In general terms the effectiveness of TBAB in KOH solution to enhance adhesion was temperature and concentration dependant. The mechanism of TBAB will be discussed in a separate section.

PVdF

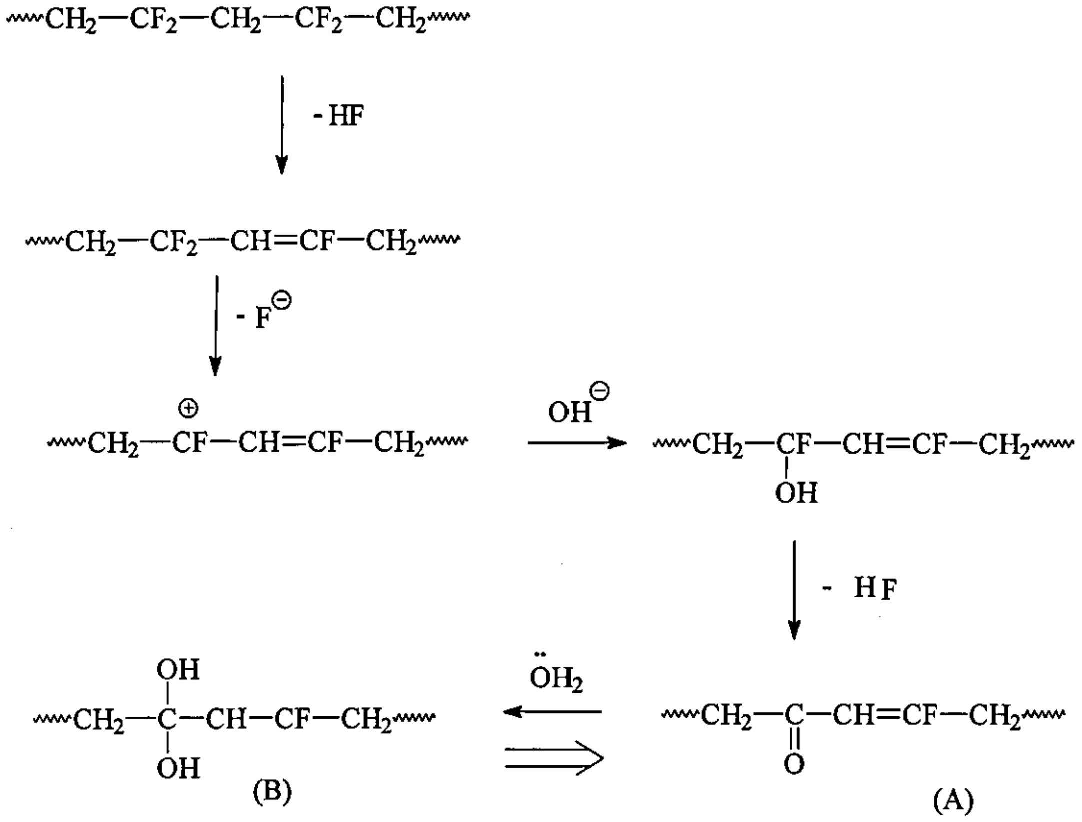
The treatment of PVdF with aqueous KOH, alcoholic KOH or aqueous KOH plus TBAB gave similar adhesion improvement for all conditions used (Table 3.31). This was due to the rapid increase in joint strength and the limit of the adhesive bonding system; most of the joints failed at the metal/adhesive interphase region thus limiting the potential of the treatment. The effect of the treatments were much more rapid than with PVF; for 5M solutions near maximum joint strengths were obtained after only 10 seconds. A treatment time of typically 30 minutes was required to reach a maximum bond strength with PVF under similar conditions.

In contrast to PVF however, there were differences in the surface compositions of PVdF treated with the different reagents. Alcoholic and 'aqueous plus TBAB' treatments incorporated more oxygen than aqueous treatments, and 'aqueous plus

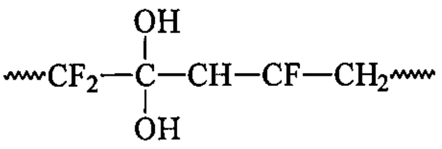
TBAB' treatments resulted in the most defluorination (Table 3.31). A summary of the relevant groups observed in FTIR (Figures 4.43 - 4.45) are as follows:

Aqueous + TBAB	5M, 80°C, 1 hr	C=O, C=C, O-H
Aqueous	15M, 80°C, 2hr	C=O, C=C
Alcoholic	5M, 90°C, 30 mins	C=O,C≡C, C=C CH change

Nuecleophilic substitution reactions are unlikely to occur with PVdF as it would be sterically hindered. Elimination reactions may occur according to the following scheme:



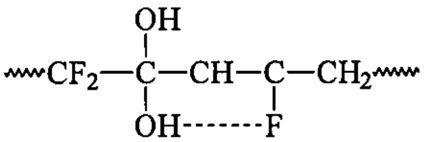
Species (A) will predominate if the polymer chain is as represented. However, if the polymer repeat units are not all head-tail-head-tail, species (B) with CF_2 replacing a CH_2 is more likely i.e.:



$$\sim CF_2-C(OH)_2-CH-CF-CH_2\sim$$

(C)

This species is further stabilised by intramolecular hydrogen bonding in a 5 members ring:



$$\sim\sim CF_2-\overset{OH}{\underset{OH\cdots\cdots\cdots}{C}}-CH-\underset{F}{C}-CH_2\sim\sim$$

Two dehydrofluorination processes at the first stage in the previous scheme would lead to the formation of carbon-carbon triple bonds.

FTIR data supports the schemes proposed above. There are no OH bands visible in both the alcoholic and aqueous KOH treated PVdF (Figures 4.43 and 4.45). There is a small broad OH band in a sample treated with aqueous KOH plus TBAB that could be arise from species C. All three figures show carbonyls (1720 cm^{-1}) and double bonds (1600 cm^{-1}). The alcoholic KOH treatment appears to facilitate two dehydrofluorination stages in the reaction as the band at 2170 cm^{-1} is assigned to carbon-carbon triple bonds (Figure 3.44). The changed environment of C-Hs is seen in the new peaks round 2900-3100 cm^{-1}.

TBAB

Compounds like tetrabutylammonium bromide, TBAB are used in organic synthesis as phase transfer catalysts; they draw an insoluble reagent, like an inorganic compound, into an organic phase for reaction. For example, in an aqueous solution of KOH the OH^- will be surrounded by the water molecules because of the $\delta+$ on the H atoms (weak hydrogen bond interaction). But, on addition of the TBAB the Bu_4N^+ species which has a much stronger positive charge than water, solvates the OH^-. The butyl end of the molecule is compatible with organic molecules thus bringing the OH^- in contact for reaction.

It has been proposed by Dias and MacCarthy[100] in their work on PVdF and aqueous KOH containing tetramethylammonium hydroxide, that PVdF can be regarded as the 'organic phase' of a reaction and the OH^- from KOH is the inorganic reagent. The butyl groups will dissolve in, or 'plastisize' the PVdF and bring the OH^- in close proximity to the substrate for reaction.

Experimentally with respect to PVF, the presence of TBAB in aqueous KOH solution increased the adhesion of the substrate compared with aqueous KOH alone under similar conditions (Figure 3.39); the chemical composition of the 'KOH + TBAB' treated substrate however, was similar to a KOH treated material (Table 3.26 and 3.27). In both cases it is clear that chemical modification of the surface had taken place. However, it is possible that in the TBAB case, the tetrabutylamonium ion surrounding the OH^- plastisized the weak cohesive regions of the PVF surface enabling reaction at the surface and deeper into the weak region. This might have enabled complete removal of the weak surface material revealing fresh, stronger bulk that was subsequently treated. In a KOH solution without TBAB, reaction would have occurred more slowly at the surface with less penetration into the weak layer; without removal of weak cohesive material poor bond strength remained. In both cases the compositions of the surface would have been similar.

There is a complicating factor for a solution of TBAB in KOH. At 80°C and in the presence KOH the TBAB is able to undergo a Hofmann degradation forming butene and a tertiary amine:

$$Bu_4N^{\oplus}\,Br^{\ominus} + OH^{\ominus} \longrightarrow Bu_3\ddot{N} + CH_3{-}CH_2{-}CH{=}CH_2 + Br^{\ominus} + H_2O$$

The tributylamine has the potential to react with the fluoropolymer via nucleophilic substitution. XPS did not detect any nitrogen on the surface of a 'KOH plus TBAB' treated PVF or PVdF samples accept after 1hour with PVdF; it may be that this reaction is occurring but, the amount of nitrogen may be below the detection limit of the XPS instrument.

Heat alone may enable Hofmann degradation of the TBAB; in fact on occasion at higher temperatures and higher TBAB concentration an inmiscible layer likely to be butene was evident. A solution containing 0.15g of TBAB in 50ml of water without KOH was heated to 80°C and samples of PVF or PVdF were immersed for 1 hour (Table 3.32). There was no surface composition change or improvement in bond strength with PVF as a result of immersion. PVdF however, showed a gradual bond strength improvement over 1 hour and a small amount of oxygen was introduced in the surface indicating a possible reaction on the surface. It will be discussed later that the subsequent washing of samples after treatment may be important; it is possible that the oxygen had originated from the washing stage.

When PVdF was treated with a solution of KOH plus TBAB (Table 3.31), in contrast to PVF, the surface composition of the PVdF after this treatment was different to a sample that had been treated with just KOH. The TBAB facilitated more oxygen incorporation and more defluorination. It may be that the action of TBAB on reaction was simply a kinetic effect. The fact that more reagent is brought into contact with the substrate means there was more surface modification within a given time. As mentioned earlier the adhesion levels were high for both treatment solutions.

To investigate further the mechanism of 'KOH plus TBAB' to enhance adhesion, a series of experiments using KOH and TBAB separately and in different orders were carried out (Table 3.33 and 3.34). The aim was to determine if the action of TBAB was simply scouring away treated weak cohesive material. A sample of PVF was treated first with aqueous KOH solution and then with a solution of TBAB in water (both were carried out at 80°C); refer to Table 3.33 experiment 1. The bond strength of this sample was no greater than one treated with KOH on its own (experiment 4). A single treatment with just TBAB (experiment 3) gave no improvement in bond strength compared with untreated and experiment 2 showed that a TBAB treatment subsequently followed with a KOH treatment gave the same value. It may be that the TBAB on its own plastisizes the PVF's weak cohesive layer without reaction and is not removed with just water. The subsequent KOH treatment only treated a weak cohesive layer giving no bond strength improvement.

When these experiments were carried out on PVdF a further interesting feature emerged (Table 3.34). As in previous treatments KOH only (experiment 5), gave a good bond strength. A KOH treatment followed by a TBAB treatment (experiment 1) also gave the same adhesion value. It was pointed out earlier that this value was limit of the adhesive system hence; no additional information was available from this experiment. However, comparing experiment 2 and 3 where TBAB was used first and then a KOH solution, a difference in adhesion level was observed when methanol was used in the washing procedure after the TBAB treatment (experiment 3). Without an intermediate methanol wash the bond strength was lower than the other treatments (experiment 2) and comparable with TBAB on its own (experiment

4). It is suggested that the action of TBAB on PVdF was to plastisize and react with the surface. It was not clear how the relatively weak material was present at the surface i.e. whether as a continuous layer or as patches. This plastisized layer was removable with methanol leaving a strong surface, but not with water. On subsequent immersion in KOH the strongly cohesive surface became treated and gave a good bond strength. The water washed sample resulted in a treated but mechanically weak layer.

The above experiments underlined the theory that with PVF, TBAB was not simply acting as a surface scourer on its own but that it enabled removal of weak material through enhanced penetration of the OH^- into the surface. With PVdF, the TBAB allowed more of the surface to be modified thus increasing its reactivity to the adhesive However, it was necessary to remove TBAB by washing to prevent reintroduction of a WBL.

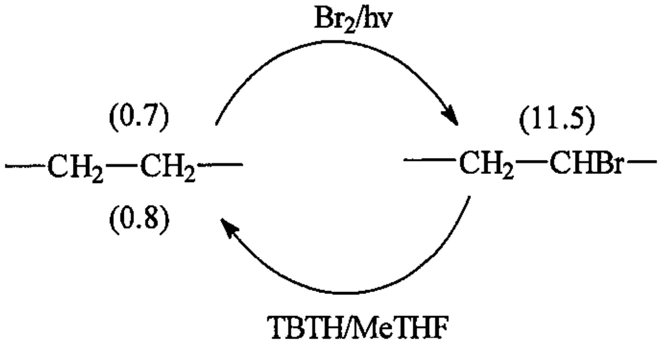
4.1 General discussion

Understanding of adhesion to polymers must include a consideration of wetting, surface chemistry, topography and the cohesive strength of the surface regions of a substrate.

As far as polyolefins are concerned, studies by Brewis, Briggs *et al*[116-118]. support the view that pretreatments usually increase adhesion by introduction of functionality rather than the removal of potential weak boundary layers, WBLs. Although in some cases it may also be necessary for the pretreatment to remove contaminants such as mould release agents.

In general, it was found that the degree of adhesion increased as the level of chemical modification increased[119].

In one study, HDPE was brominated and then reduced back to HDPE with tributyltin hydride[120]. After bromination the adhesion was much higher but it reverted back to the untreated value when the reverse reaction was carried out.



Values in brackets are lap shear joint strengths in MPa.

This is strong support for the view that it is sufficient to introduce functional groups into polyolefins for good adhesion.

The present study has shown that adhesion to fluoropolymers is more complex than to polyolefins. In particular, there are definite regions of low cohesive strength at the surfaces of PTFE and PVF, and a relatively weak layer on PVdF.

With PTFE it was possible to get reasonable increases in adhesion without significant changes in surface composition. This was found to be the case with the multibonding experiment and in some plasma treatments. However, it was only possible to obtain large increases in adhesion with major chemical modification.

With PVF, removal of potential WBLs either with the multibonding experiment or 'Tetra-Etch', without significant chemical changes lead to much larger increases in adhesion than with PTFE. This is in line with the fact that PVF is quite polar whereas PTFE is non-polar. The fact that Brewis[104] obtained much higher bond strengths with untreated PVF and the same adhesive, confirms that the batch used in the present study contained a region of low cohesive strength at the surface. Again, the high bond strengths between a cyanoacrylate adhesive and untreated PVF indicates that a potential weak boundary layer can be absorbed by a suitable adhesive.

Major chemical modification did not necessarily result in large increases in adhesion. It was found that when PVF was treated with aqueous KOH under standard conditions, major chemical changes occurred, including the introduction of substantial quantities of oxygen, but the adhesion remained poor. In other words the weakly cohesive layer was not completely absorbed by the adhesive.

PVdF showed a complicating feature in that the main adhesive used in this study reacted with the untreated PVdF. It is therefore not possible to make a direct comparison in terms of potential WBLs with PTFE and PVF.

The facts relating to weak boundary layers may be summarised as follows:

	Little or no chemical modification	Major chemical change
PTFE:	Moderate improvement in adhesion (multibonding and some plasma).	High adhesion ('Tetra-Etch).
PVdF:	untreated has moderate adhesion.	High adhesion ('Tetra-Etch', KOH).
PVF:	Large increases in adhesion can be obtained ('Tetra-Etch') or using cyanoacrylate adhesive.	Usually high adhesion (plasma, flame, some KOH) but some circumstances can be poor (some KOH).

In terms of reactivity PTFE responded much more rapidly than PVF or PVdF towards 'Tetra-Etch'. On the contrary, PVF was more easily modified than PTFE by plasma. With Group I hydroxides PVdF reacted more readily than PVF whereas PTFE was unaffected.

Conclusions

PTFE

1. Multiple bonding of PTFE in this work showed that moderate improvement in adhesion could be achieved without surface chemical modification. Improvement in adhesion was brought about by the removal of weakly cohesive material that normally resulted in a weak boundary layer, WBL.

2. For high adhesion to PTFE it was necessary for a pretreatment to bring about major chemical change at the surface.

PVF

3. There exists, on the PVF used in this study, a potential weak boundary layer. On removal, large increases in adhesion were observed.

4. Removal of cohesively weak surface material on PVF was proposed to be the primary action of 'Tetra-Etch' to improve the adhesion. Likewise multiple bonding of PVF resulted in good adhesion by removing the potential weak boundary layer.

5. A weak boundary layer did not result when as-received PVF was bonded with cyanoacrylate adhesive, due to absorption of the weakly cohesive material into the adhesive.

6. Significant oxidation of the surface of PVF did not always result in high adhesion. Plasma and flame treatments introduced sufficient polar functionality to enable the adhesive to absorb the potential WBL. However, with some Group I hydroxide solution treatments the surface was significantly oxidised but there remained a mechanically weak underlying layer which was not absorbed into the adhesive when bonded.

PVdF

7. In comparison to the potential WBLs on PTFE and PVF, PVdF had a relatively strong surface. High adhesion was obtained with the introduction of oxygen functionality by 'Tetra-Etch' and potassium hydroxide treatments.

8. The extremely good adhesion of PVdF and epoxy adhesive cured at 70°C was due to reaction of the amine hardener with the PVdF prior to gelation of the adhesive.

Mechanisms of pretreatments

9. In contrast to PTFE where 'Tetra-Etch' produces chemical modification via an electron transfer mechanism, PVF may be primarily susceptible to base promoted dehydrofluorination by the reactive species in 'Tetra-Etch'. As such, double bond formation was the most significant functionality introduced.

10. PVdF is more reactive towards 'Tetra-Etch' than PVF. This is in line with its chemical structure and the above mechanisms.

11. Hydrogen plasma treatment of PVF and PTFE showed that the hydrogen atoms reacted more readily with the surfaces of the substrates than with oxygen resulting in a lack of polar functional groups.

12. Group I hydroxide solution treatments of PVF resulted in chemical modification through nucleophilic substitution or base elimination reactions. For PVdF elimination reactions were more likely.

13. The presence of tetrabutylammonium bromide, TBAB in aqueous KOH greatly increased the effectiveness in promoting the adhesion of PVF, and gave greater chemical modification of PVdF. The TBAB enabled the hydroxide ions to make closer contact with the fluoropolymers.

Further work

This work has presented results and proposals on the mechanisms of several pretreatments to improve the adhesion of three quite different fluoropolymers. There are a number of areas arising from the findings in this report that warrant further investigation; these are outlined below:

- The role of specific interactions in the adhesion between each fluoropolymer and adhesive. In particular, further chemical derivatisation of functional groups on the treated surfaces and rebonding to observed the effect of removing particular species.

- The use of different adhesives on the treated and untreated fluoropolymers to investigate specific interactions. Fluorinated adhesives could be used to investigate the solubility of surface material in an adhesive.

- To investigate more fully the removal of weak cohesive fluorinated species in the PVF-'Tetra-Etch' or PVF-NaOH systems using GCMS (Gas chromatography - mass spectrometry) of the reaction solutions. Model perfluorinated compounds would be necessary for this work.

- The role of surface morphology on the susceptibility of PVF and PVdF to 'Tetra-Etch' treatment.

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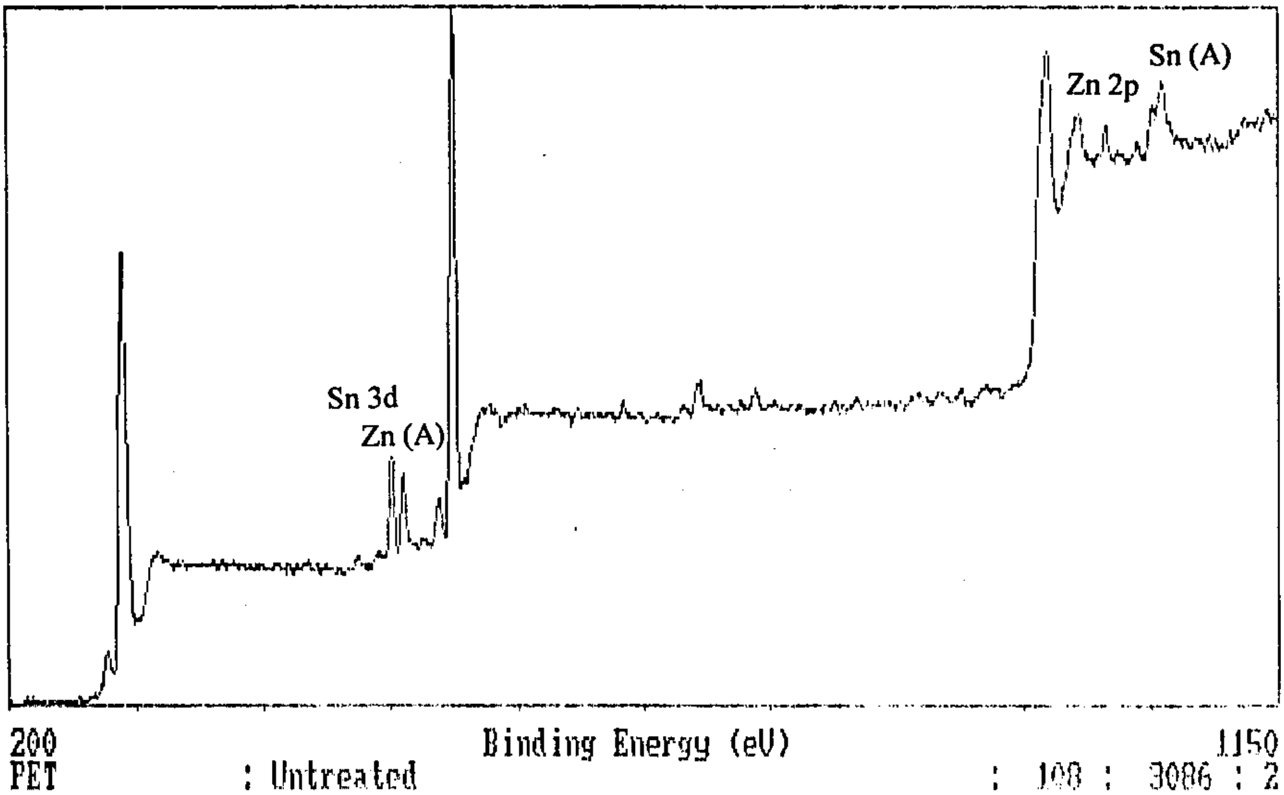
Appendix A

Origin of Zn on KOH treated samples

Samples of PET were washed in 'high purity' (Romil) methanol that had been contained in either a bottle or a drum. the surface compositions of the PET after drying are given below. The spectrum of the drum MeOH washed sample is included:

	C	O	Zn	Sn
Bottle MeOH	72.5	26.4	0.2	0.9
Drum MeOH	74.7	25.3	0.0	0.0



Appendix B

Calculation of 'penetration depth' of Ge and KRS prisms used in FTIR-ATR studies.

An example of the calculation of 'penetration depth' in ATR is given below.

Prism	Ge	
Prism refractive index	4.01	n_p
Angle of prism end	60°	θ_p
Substrate refractive index	PVF 1.46	n_s
Wavenumber	3200 cm^{-1}	(OH band)
Angle of incidence of beam at entrance to prism	45°	θ_a

First the angle of incidence of the beam on the inside of the prism 'θ' is calculated according to equation (16) in the text.

$$\theta = \theta_a - \sin^{-1}\left[\frac{\sin(\theta_a - \theta_p)}{n_p}\right] \quad ....(16)$$

i.e.

$$\theta = 45 - \sin^{-1}\left[\frac{\sin(45-60)}{4.01}\right]$$

$$\theta = 48.7°$$

The wavelength of the radiation in the prism is calculated as:

$$\lambda_1 = \frac{\lambda}{n_p}$$

whereλ is the wavelength of the radiation in vacuum

i.e.

$$\lambda = \frac{{}^{1}\!/_{3200x10^{2}}}{4.01}$$
$$\lambda = 7.79x10^{-7}m$$

Then d_p is calculated according to the Harrick equation (equation 15 in the text)

$$d_p = \frac{\lambda_1}{2\pi\left[\sin^2\theta - \left(\frac{n_s}{n_p}\right)^2\right]^{½}} \quad \text{..................(15)}$$

i.e.

$$d_p = \frac{7.79x10^{-7}}{2x\pi x\left[\sin^2 48.7 - \left(\frac{1.46}{4.01}\right)^2\right]^{½}}$$
$$d_p = \frac{7.79x10^{-7}}{4.13}$$
$$d_p = 1.87x10^{-7}$$
$$d_p = 0.18\mu m$$

A summary of the refractive indices of prisms and substrate used in this study are given below:

Ge prism	- Refractive index	4.01
Ge prism	- angle of prism end face	60°
KRS prism	- Refractive index	2.38
KRS prism	- angle of prism end face	45°
PTFE	- refractive index	1.35
PVF	- refractive index	1.46
PVdF	- refractive index	1.42