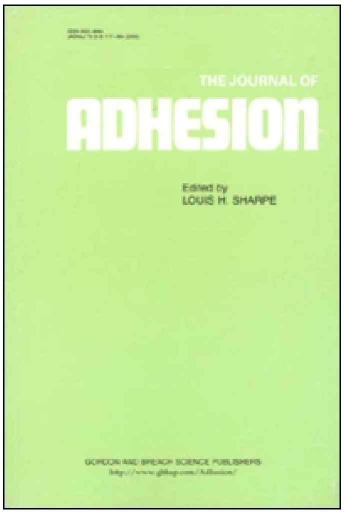


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion and Surface Analysis

D. M. Brewis[a]; G. W. Critchlow[a]
[a] Institute of Surface Science and Technology, University of Technology, Loughborough, Leics, UK

To cite this Article Brewis, D. M. and Critchlow, G. W.(1995) 'Adhesion and Surface Analysis', The Journal of Adhesion, 54: 1, 175 — 199
To link to this Article: DOI: 10.1080/00218469508014390
URL: http://dx.doi.org/10.1080/00218469508014390

J. Adhesion, 1995, Vol. 54, pp. 175–199
Reprints available directly from the publisher
Photocopying permitted by license only

Adhesion and Surface Analysis

D. M. BREWIS and G. W. CRITCHLOW

Institute of Surface Science and Technology, University of Technology, Loughborough, Leics LE11 3TU, UK

(Received August 8, 1994; in final form December 5, 1994)

In the last 25 years, surface sensitive analytical techniques have made a major contribution to our understanding of adhesion phenomena and problems. There are several areas where these techniques have provided important information including the identification of failure modes, the chemistry of a substrate before and after pretreatments, the stability of surfaces and interfaces, the identification of surface contaminants, the interaction across an interface and the nature of interphases. X-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES) and static secondary ion mass spectrometry (SSIMS) have proved to be especially useful. Many examples of the usefulness of these techniques are given.

KEY WORDS Auger electron spectroscopy (AES); contamination; interfaces; interphases; locus of failure; pretreatments; static secondary ion mass spectrometry (SSIMS); X-ray photoelectron spectroscopy (XPS or ESCA).

INTRODUCTION

Surface analysis can be defined as the direct chemical characterisation of the outermost few atomic layers on a solid surface. Surface analytical techniques may be extended to study thin solid films, for example anodic oxides, and buried interfaces. This information is clearly of vital importance in our understanding of adhesion phenomena and problems. Prior to 1970 direct chemical information from surfaces was unobtainable. However, in the early 1970s several techniques which could provide this information became available. Three surface analytical techniques have since proved to be of particular importance in the study of adhesion phenomena. These are Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS, also known as ESCA) and Static Secondary Ion Mass Spectrometry (SSIMS).

These techniques have provided key information on several different aspects of adhesion science and technology, namely: the identification of failure modes (loci of failure); effects of pretreatments on surface chemistry; the stability of pretreated surfaces; interactions across interfaces; identification of contamination and the nature of interphases. In this review, examples from these six areas are given. Adhesion studies have, of course, successfully utilised many techniques other than AES, XPS and SSIMS.

---

[*] One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

Other widely-used techniques include electron microscopy, contact angle measurements and infra-red analysis. The complementary nature of these techniques will be illustrated in some of the studies discussed below. The literature on the subject of this review is very extensive and it has been necessary to omit many excellent studies. However, our objective has been to demonstrate how surface analysis can assist the understanding of many aspects of adhesion.

A detailed consideration of AES, XPS and SSIMS may be found elsewhere.[1] However, a brief summary of these techniques and their abilities and limitations in relation to adhesion studies is given in Table I.

The depths quoted are typical values. For example, variations in sampling depth can be achieved with XPS by varying the take-off angles or by changing the anode material.

IDENTIFICATION OF FAILURE MODES

An adhesive joint can fail in several areas. Cohesive failure may occur in either of the substrates or in the adhesive. Interfacial failure may occur between the first substrate and the adhesive or between the second substrate and the adhesive (see section on Interphases).

In cases where adhesion is inadequate, it is critical to know where failure has occurred so that improvements in pretreatment, adhesive selection or joint design may be made. In some cases it is obvious where failure has occurred; for example, in a bonded wood structure failure often occurs deep within the wood. However, in many cases failure occurs very close to an interface. It is only with a highly surface-sensitive technique such as SSIMS that the true locus of failure may be determined.

Surface analytical techniques have frequently been used by the present authors to determine the locus of failure not only with bonded joints but also with printed and painted surfaces. However, as Sharpe[2a] has pointed out, care must be taken in these

TABLE I
Summary of information from, and limitations of, surface analytical techniques

Technique	Depth	Information	Limitations
AES	~ 3 nm	Quantitative elemental analysis. Depth profiling. Imaging. Limited information on oxidation states.	Possible beam damage, particularly with polymers. No information on hydrogen.
XPS	~ 3 nm	Quantitative elemental analysis. Chemical groups from high resolution spectra or derivitisation. Homogeneity or otherwise from angular variation studies. Depth profiling. Imaging.	No information on hydrogen.
SSIMS	2 monolayers	Molecular information from ion fragments. Imaging.	Not quantitative.

studies. If material is lost during the breaking of structures, erroneous conclusions may be made regarding the locus of failure.

Examining the surface chemistry of the two sides of a broken joint can be used to determine the cause of adhesion problems. Two examples are now given. In the first case, poor adhesion was sometimes observed when a polyimide film was bonded to copper foil with an epoxide adhesive.[3] XPS was used to elucidate the reason for the bonding problem. The chemistry of the two surfaces obtained from a peel test was examined. The results corresponding to both poor and good adhesion are given in Table II.

Consider first the results where poor adhesion occurred. Within experimental error, the analyses for the two surfaces were the same, indicating cohesive failure within an organic material. Likewise, where good adhesion was observed, cohesive failure is indicated. However, the percentages of nitrogen observed were very different. With the poor adhesion the nitrogen level was very similar to that observed for the polyimide, whereas with good adhesion the nitrogen level was very similar to that of the epoxide. There is a very strong probability that the poor adhesion was due to failure within a cohesively weak layer of polyimide, i.e. a layer inadequately polymerised.

In the second case, poor peel strength was observed between etched PTFE and polychloroprene which had been bonded with an epoxide.[3] The resultant two surfaces were examined using XPS and the results are shown in Table III.

The most interesting feature of the results is the high level of silicon on both surfaces and the low level of chlorine on the polychloroprene side; the polymer itself possesses 20 atom % chlorine excluding hydrogen which is not detected by XPS. These results are consistent with the presence of substantial quantities of a silicone. Such materials are widely used in the processing of polymers and are the cause of many adhesion problems. The presence of a silicone was confirmed using SSIMS (see section on Contamination).[4,5] The silicone probably originated during the production of the

TABLE II
XPS analyses of the surfaces produced when a polyimide-epoxide-copper laminate is separated by peeling

	Surface	Composition (atom %) C	 N	 O	Peel Strength
1.	Copper	74.8	9.3	15.9	Low
	PI	73.7	10.0	16.5	
2.	Copper	82.8	1.2	16.0	High
	PI	84.3	1.1	14.6	

TABLE III
XPS analyses of the surfaces produced when a polychloroprene-epoxide-etched PTFE laminate was separated by peeling

Surface	Composition (atom %) C	 N	 O	 Cl	 Si	 S
Polychloroprene side	83.6	–	8.8	0.5	6.5	0.6
PTFE side	80.5	1.5	9.7	–	7.6	0.7

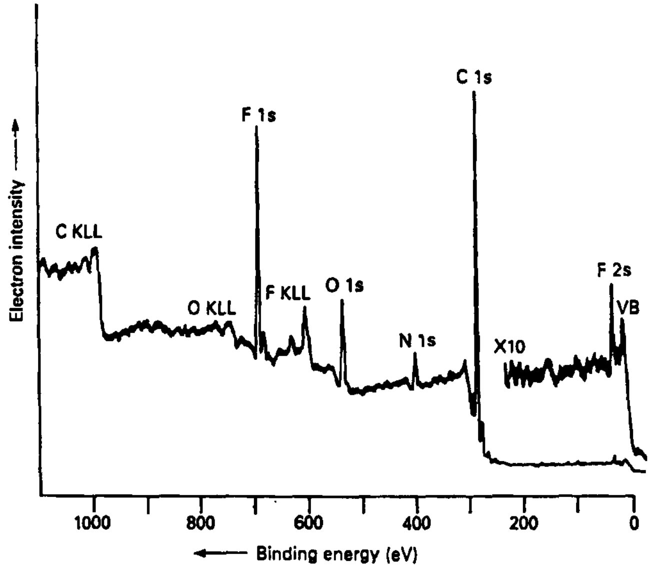


FIGURE 1 XPS survey (broad) scan of the surface of an epoxide adhesive cured in contact with PTFE. The PTFE film detached at a very low load but transfer of fluorinated material clearly occurred. Both core level and Auger peaks originating from the PTFE are apparent.[6] Reproduced with permission.

polychloroprene sheet. The nitrogen on the PTFE side probably originated from the epoxide adhesive.

The results shown in Figure 1 show the cohesive failure of a substrate, in this case PTFE.[6]

SIMS, in an imaging mode, has been used to study the locus of failure in CFRP.[6] An ion beam with 0.5 μm diameter was rastered over the fracture surface of a carbon fibre reinforced thermoplastic. The mass spectrometer was tuned to fragments of interest, especially $C_2H_2^-$ which is highly characteristic of the fibre surface. By detecting the $C_2H_2^-$ it was thus possible to identify areas of interfacial failure.

Failure near a metal-adhesive interface, but within the adhesive, is common. Mixed failure modes are also commonly observed with metal-metal bonded systems. For example, Watts and Dempster[7] observed this type of failure using seven different pretreatments for titanium. In this study, titanium adherends were treated using the following methods: grit blast; grit blast plus either silane or epoxide primer; grit blast plus either chromic acid or sodium hydroxide anodise; grit blast plus anodise plus epoxide primer. Joints were assembled using an epoxide adhesive in a Boeing wedge configuration; these were then exposed to 95% RH at 50°C. With all treatments, initial failure was visible within the adhesive. XPS was used to identify a switch in the locus of failure from one interface to the other. "Islands" of polymer were identified as present on the metal surfaces by changing the X-ray anode and hence the sampling depth. A transfer of TiO_2 onto the adhesive side of the failed joint was also observed by XPS.

Boerio and Ondrus[8] studied the locus of failure of iron and titanium, bonded with an epoxide adhesive, using XPS. They pretreated iron and titanium adherends with aqueous solutions of the primer γ-aminopropyltriethoxysilane (γ-APS). They then formed iron-epoxide and titanium-epoxide lap joints and exposed some of these to water at 60°C. Iron-epoxide lap joints prepared using γ-APS applied at pH 8.0 but not exposed to the hot water failed near the oxide-primer interface. Similar joints, but where γ-APS was applied at pH 10.4, failed partly within the adhesive. After exposure to water for seven days all the iron-epoxide joints failed in the primer near the primer-oxide interface but very little corrosion was observed. With no exposure to water, the titanium-epoxide joints failed partly within the adhesive and partly near the primer-oxide interface regardless of the pH when the primer was applied. However, when exposed to water for seven days, the locus of failure was near the primer-oxide interface. The authors concluded that the failure of the exposed joints was associated with hydrolysis of the primer rather than with extensive corrosion of the metals.

In some cases, and especially in the automotive industry, it is necessary to bond oily steels. Commercon and Wightman[9] used XPS, AES and Energy Dispersive X-ray Analysis (EDXA) to determine the locus of failure of joints formed by bonding oily automotive steels with two one-part epoxide adhesives. After bonding, the joints were exposed to water at 70°C for 7 days. After determining the joint strengths, the various failure surfaces were analysed. In the case of a galvanised cold-rolled steel, interfacial failure between the adhesive and metal occurred. With a zinc electroplated steel, failure occurred within the zinc layer.

An application of coating-to-substrate adhesion is given by Naem *et al.*[10] In this example, a combination of AES, SEM and EDXA was used to identify both the locus and cause of coating-to-substrate failure of ceramic coatings on high-speed steel. In scratch-adhesion tests, TiN demonstrated good adhesion with no flaking observed at the edge of scratch channels. In contrast, TiC and Al_2O_3 on a Ti-based interlayer did exhibit pre-critical load flaking. EDXA and SEM results from the Al_2O_3 coated system are given in Figure 2. EDXA and SEM results were obtained from all three systems. Results from the TiC-coated system showed that mixed failure occurred, with both Ti and Fe present in the EDXA images of the regions where flakes had been removed. EDXA images from the regions where flaking had occurred on the Al_2O_3 and Ti-base coated sample showed no aluminium present (see Figure 2(a)), but titanium could be observed (see (Figure 2 (b)). These images indicate failure in a region beneath the Al_2O_3 coating. AES depth profiles from all three systems are given in Figure 3 and from these results it is concluded that the good adhesion of TiN was associated with a $\sim 1\,\mu m$ substrate-to-coating diffusion zone, while TiC has poor adhesion associated with a thinner $\sim 0.4\,\mu m$ diffusion zone. In the TiC case, it is believed that the crack was initially formed at the interface; it then propagated through into the TiC. Al_2O_3 exhibited poor adhesion despite a thick diffusion zone. The presence of a cohesively weak Ti-based oxide in the interfacial region, as identified by AES, is the most likely explanation for this result.

CHEMISTRY BEFORE AND AFTER PRETREATMENT

It is very useful to determine the chemical changes that have been caused to surfaces by pretreatments to enhance adhesion. XPS has been especially useful in determining the chemical changes to polymers whereas XPS and AES have both been useful with metals.

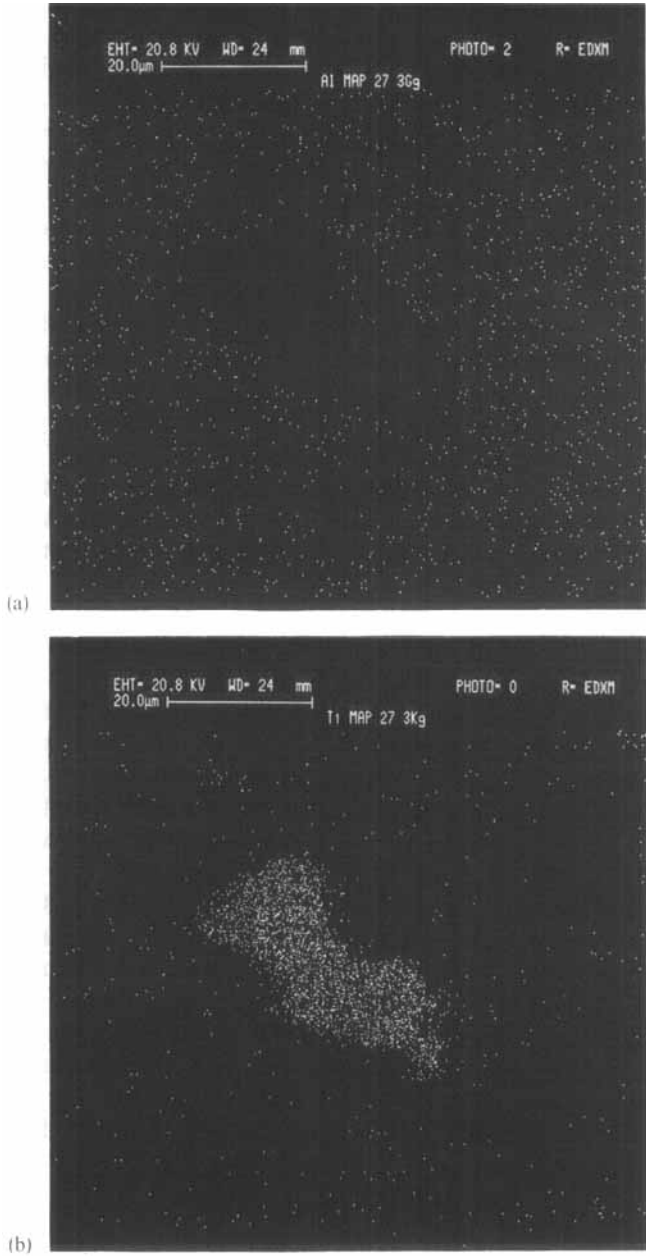


FIGURE 2 (a) Al Kα x-ray map of area shown in (c). (b) Ti Kα x-ray map of area shown in (c). (c) Scanning electron micrograph of flaking at the edge of scratch channel on multilayer Al_2O_3-coated PM HSS insert.[10]

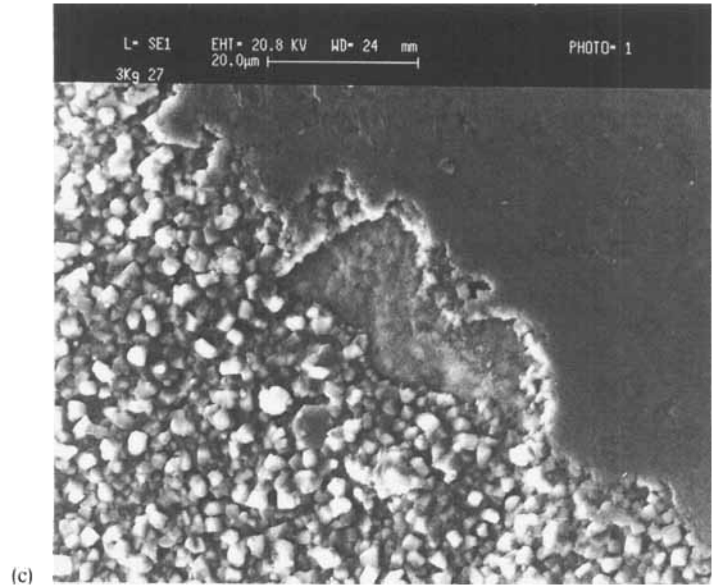


FIGURE 2 *(Continued.)*

One of the earliest studies of polymer pretreatments was by Briggs *et al.*[11] They studied the chromic acid treatment of polyolefins and some of the results are summarised in Table IV.

The results with polypropylene were of particular interest. Oxidation could readily be detected even with a very mild treatment. A previous study by Blais *et al.*[12] using reflection infrared analysis had failed to detect any chemical changes in PP and they concluded that the chromic acid enhanced adhesion by washing away a weak boundary layer. The reason reflection IR failed to detect any chemical changes was because the modified layer was very thin. By measuring the O1s:O2s ratio, and the O1s:C1s ratio as a function of take-off-angle, it was concluded that an equilibrium oxidised layer of less than 10 nm was rapidly formed.

In a recent study,[13] the effectiveness of a common commercial etchant with polytetrafluoroethylene PTFE and poly (vinyl fluoride) PVF was compared. These results are summarised in Table V.

It can be seen that PTFE was rapidly defluorinated and substantial quantities of oxygen were introduced into the surface. The radical anion in "Tetra Etch" is a very powerful reducing agent and the PTFE was rapidly defluorinated producing a highly active carbon. This rapidly reacted with oxygen, forming various functional groups. With PVF the chemical changes were much slower. After one hour little oxygen had been introduced but a large improvement in adhesion had occurred. It was concluded that the improvement in adhesion was mainly due to the elimination of a weak layer on the PVF.

There is good evidence that pretreatments such as the corona discharge method result in the formation of several different functional groups in a polymer surface. The identification and quantification of these groups may be carried out using XPS with two approaches. The first involves curve fitting of high resolution C1s spectra[14] and the second involves the use of derivitisation reactions. The latter approach requires the use of a series of reagents each of which reacts with only one functional group and which introduces a new element into the polymer surface. A wide range of derivitisation reagents is given in Reference 16. Where possible vapour phase reagents should be used, as solvents can cause molecular rearrangements at surfaces.

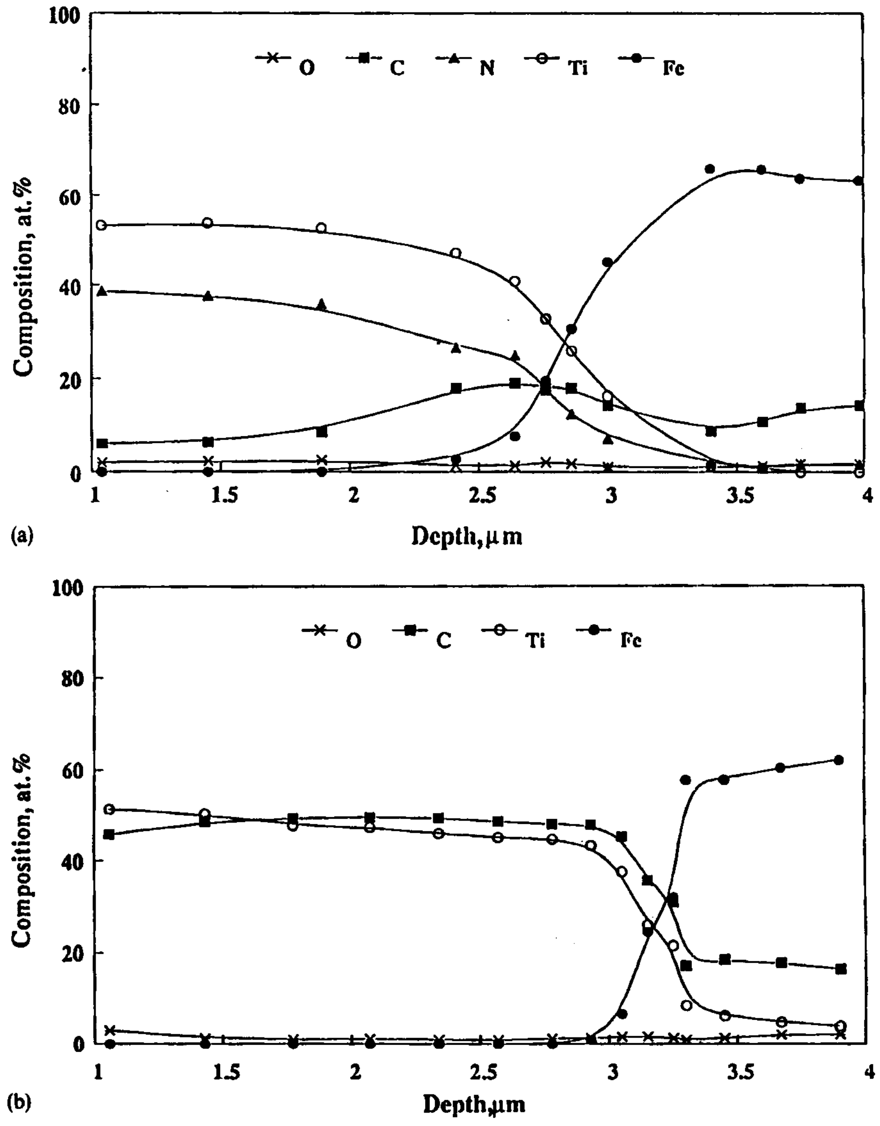


FIGURE 3 (a) AES depth profile through the coating and coating/substrate interface of a TiN-coated PM HSS insert. (b) AES depth profile through the coating and coating/substrate interface of a TiC-coated PM HSS insert. (c) AES depth profile through the Al_2O_3 coating and into the Ti-base pre-coating on a multilayer-coated PM HSS insert.[10]

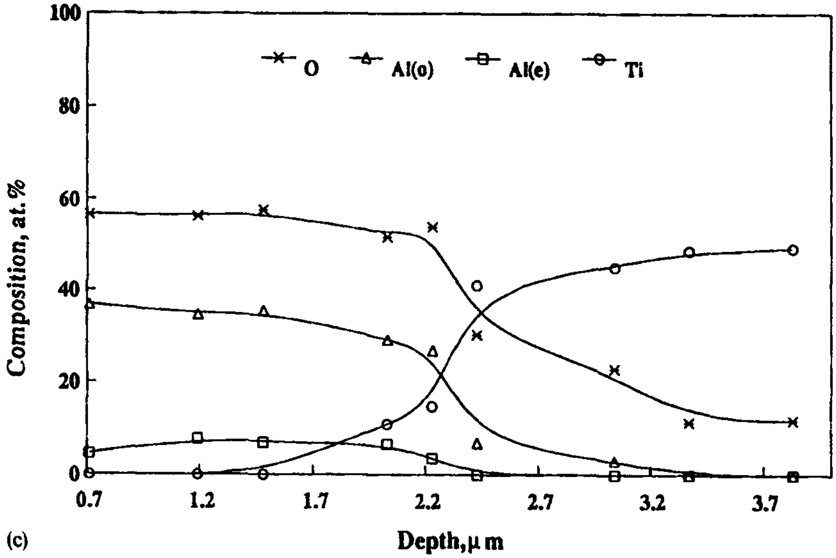


FIGURE 3 *(Continued.)*

TABLE IV

XPS data for chromic acid treated low density polyethylene LDPE and polypropylene PP

Polymer	Etching	condition	C	Composition (atom %) O	S	Ols: O2s[b]
LDPE	Acid B[a]	5 secs at 20°C	95.2	4.3	0.5	–
LDPE	Acid A	30 mins at 70°C	87.5	11.4	1.1	9.2
LDPE	Acid A	6 hrs at 70°C	81.7	16.7	1.6	9.9
PP	Acid B	5 secs at 20°C	96.1	3.6	0.3	35.9
PP	Acid A	1 min at 20°C	94.3	5.4	0.3	22.7
PP	Acid A	6 hrs at 70°C	94.8	4.9	0.3	13.7

[a] Acid A "normal" chromic-sulphuric acid ($K_2Cr_2O_7$:H_2O:H_2SO_4 = 7:12:150 (by weight); Acid B as Acid A but 1/100th concentration with respect to $K_2Cr_2O_7$

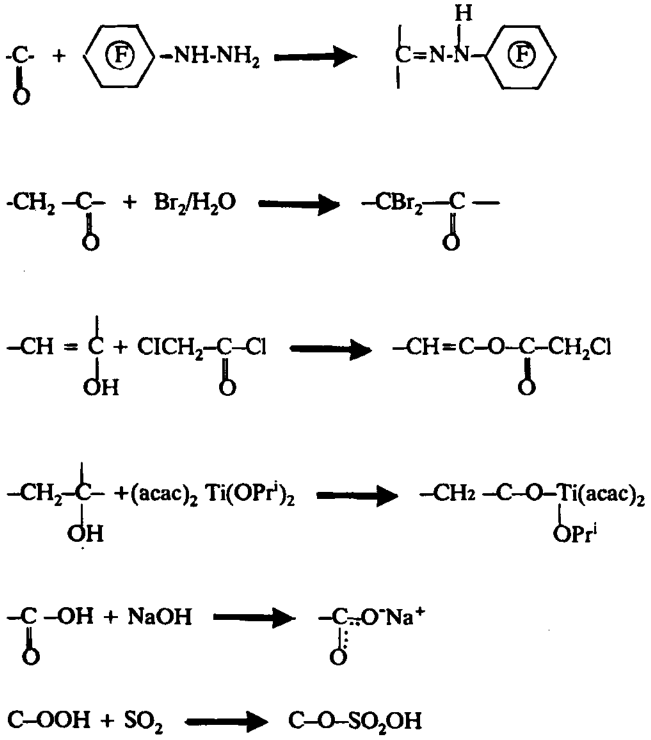
[b] For a homogeneous sample Ols:O2s ≈ 10

TABLE V

Effect of "Tetra Etch" treatment on PTFE and PVF

Polymer	Treatment	C	XPS (Atom %) F	O	Failure Load (N)
PTFE	none	38.4	61.6	–	420
PTFE	10 secs	87.6	0.8	11.6	4280
PTFE	1 min	82.2	0.9	16.9	4260
PVF	none	70.4	28.8	0.8	360
PVF	10 secs	72.4	26.7	0.9	800
PVF	1 min	75.4	23.0	1.6	2080
PVF	60 mins	87.3	11.4	1.3	3020

A good example of a derivitisation study is that by Briggs and Kendall[15] who examined the corona discharge treatment of LDPE. They used the reagents shown in Figure 4 to determine the concentrations of the various groups. The results, therefore, confirm that the corona treatment of polyolefins introduces a range of different oxygen-containing functional groups; these include hydroxyl, carbonyl and peroxide.



	Number of functional groups per original surface -CH_2-
> C=O	1.1×10^{-2}
$CH_2C=O$	5.3×10^{-3}
C-OH	6.0×10^{-3}
C-OH	1.5×10^{-2}
-COOH	1.1×10^{-2}
C-OOH	4.7×10^{-3}

FIGURE 4 Derivatisation reagents used to determine the concentrations of various groups introduced into the surface of low density polyethylene by a corona discharge treatment.[15]

By reducing the take-off angle of the photoelectrons, XPS becomes more surface sensitive, *i.e.* there is a greater contribution from the first few atomic layers. By varying the take-off angle, it is therefore possible to obtain information on the depth of chemical modification caused by a pretreatments. Jones[17] used XPS to compare two pretreatments for carbon fibres, namely: electrochemical treatment with aqueous ammonium bicarbonate solution and the use of a low power air plasma. By using angular variation studies it was shown that the plasma treatment only modified about 1 nm of the fibres whereas the electrochemical treatment modified a much greater depth. The concentration of functional groups at the surface was much higher with the plasma treatment.

In metals, a variety of techniques has been used to monitor the effects of, and also to optimise, a particular pretreatment process. Ditchek *et al.*[18] used AES and Scanning Transmission Electron Microscopy (STEM) to study the influence of a range of pretreatments on the Ti-6Al-4V alloy. The range of treatments investigated was: the standard and a modified phosphate-fluoride etches (P/F and MP/F); Dapcotreat; dry and liquid hone Pasa Jell; Turco 5578 etch; chromic acid anodise (CAA) and the alkaline hydrogen peroxide etch (AHP). In this study, STEM was used to provide information on the degree of micro- and macro-roughness, while AES was used to give information on surface chemistry and, in depth-profiling mode, to determine oxide thicknesses. A summary of the information obtained is given in Table VI.

The surface texture classification scheme applied to these surface is as follows: Group I adherends have thin oxides with little macro- or micro-roughness; Group II adherends all have a high degree of macro-roughness; Group III surfaces have porous oxides with a high degree of micro-roughness but with little macro-roughness.

To investigate the effects of these pretreatments on joint durability, these physicochemical data were correlated with bond durability results as measured by crack propagation. In these tests, samples were bonded with the FM 300 K/BR127 adhesive system. Results showed the performance of treatments was as follows:

MP/F < P/F < Dapcotreat < liquid and dry honed Pasa Jell < Turco 5578 < CAA and alkaline hydrogen peroxide etch.

TABLE VI
A summary of information given by AES and STEM on treated titanium alloy surfaces

Treatment	Oxide Thickness (nm)	Surface Texture Classification	Comments
P/F	20	I	F contamination.
MP/F	8	I	F contamination.
Dapcotreat	6	II	No apparent fine structure. Cr on surface.
Dry hone /Pasa Jell	10–20	II	Deformed surface with embedded Al_2O_3. F contamination.
Liquid hone /Pasa Jell	20	II	Embedded Al_2O_3. F contamination. Cr on surface.
Turco 5578	17.5	II	Fe containing particles on surface.
CAA 5V	40	III	Porous oxide with protruding whiskers. F contamination.
10V	80		
AHP	45–135	III	Porous oxide.

With these treatments P/F out-performed MP/F; this is, in part, explained by the increased oxide thickness on the P/F treated adherend. With the Group II adherends, although all four treatments produced similarly textured surfaces, Turco performed best while Dapcotreat gave the worst performance. Again, the increased thickness of the surface oxide could account for this effect. The presence of F on five of these surfaces is important since F would be expected to modify the surface oxide at high humidity.

With aluminium, Sun *et al.*[19] used AES, again combined with STEM, to study the phosphoric acid anodise (PAA) oxide on 2024-T3 alloy (composition > 91% Al, 4.4% Cu, 1.5% Mg and 0.6% Mn by weight). In this work, the limitations of AES and the complicating factors in the interpretation of AES depth-profiles are discussed. In particular, it is concluded that the porosity of the anodic film complicates the depth scale calibration, that surface roughness causes broadening of the metal-oxide interface and that oxide chemistry can be modified as a result of electron-beam exposure. In this instance, a reduction in the oxidation state of the P is observed with electron beam exposure time. Resultant depth profiles are given in Figure 5. These results show the presence of phosphate ions and a lack of Cu throughout the surface oxide. Cu is shown to accumulate at the oxide/metal interface. The absence of Cu in the oxide is considered to be beneficial from a galvanic corrosion point of view, while the presence of P might be considered beneficial, imparting a degree of oxide stability. Despite these complicating factors it is clear that AES, particularly when combined with STEM, can provide useful information on the physico-chemical effects of pretreatments.

SIMS has been used in its imaging mode by Treverton *et al.*[20] to demonstrate the direct association of aluminium and fluorine within chromate-phosphate films on aluminium. In this work, SEM, electron probe micro-analysis (EPMA) and XPS were also used to provide complementary information to the SIMS. By a combination of these techniques, a mechanism for the chemical and topographical development of such films could be determined.

STABILITY OF SURFACES

Briggs *et al.*, using XPS and contact angle measurements, showed a distinct ageing effect on a corona-treated poly (ethylene terephthalate) surface.[21] After a few days there were distinct changes in the C1s and O1s spectra. They also noted a substantial increase in water and formamide contact angles over a period of 10 days. The authors concluded that the treatment introduced phenolic and carboxylic acid groups into the surface. This was accompanied by much chain scission resulting in low molecular weight material. The ageing effect was due to the migration of some of the oxidised low molecular weight material towards the bulk of the polymer.

Another example where XPS demonstrated the instability of a treated polymer surface is given by O'Kell *et al.*[22] They treated polyethylene film with a low power nitrogen plasma and detected amines, imines and amides. Exposing the treated surfaces to air resulted in an increase in surface oxygen levels. This was attributed to short term hydrolysis of the amines and the gradual oxidation of polymer chains.

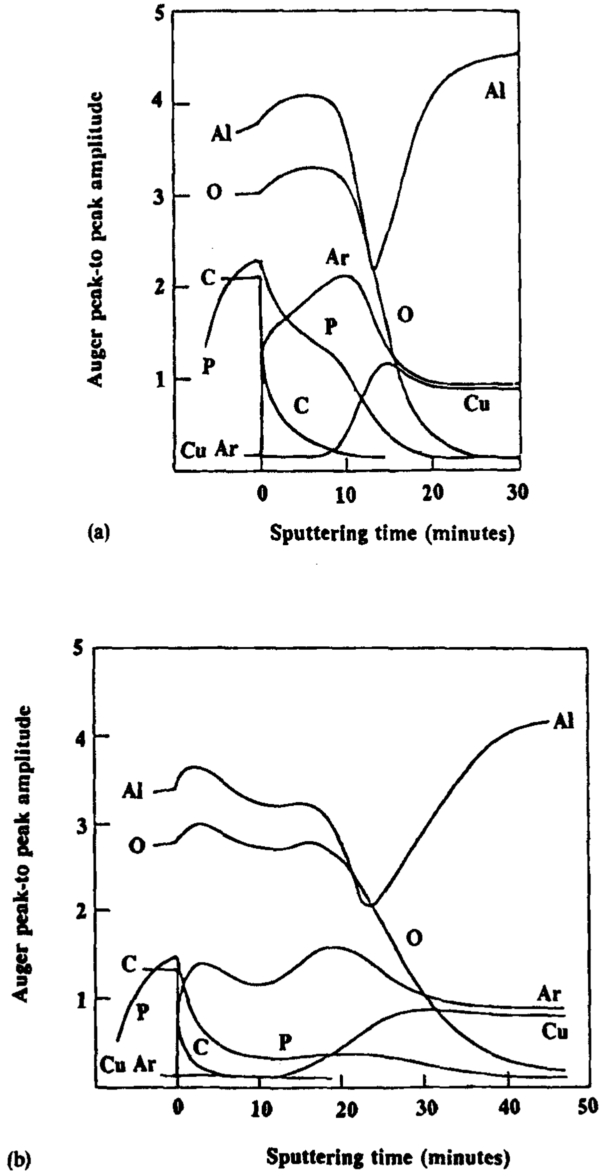
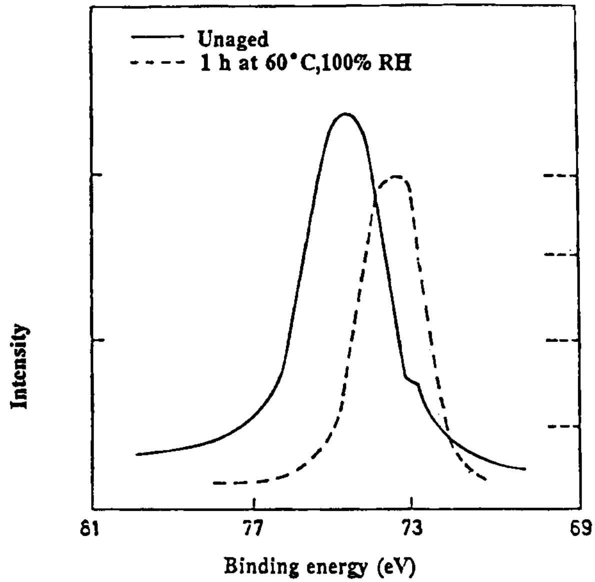
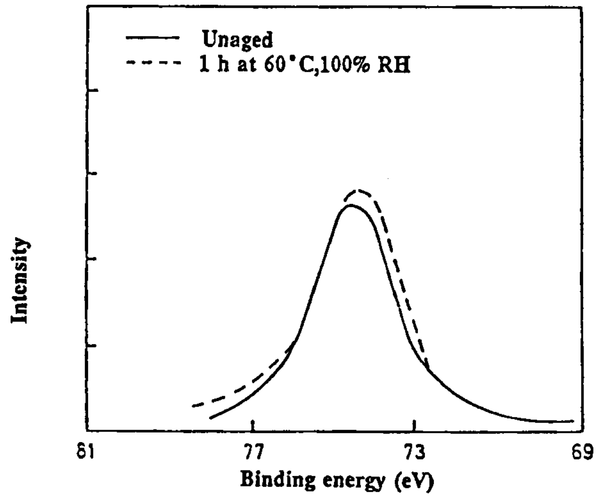


FIGURE 5 AES depth profiles through the PAA oxide on Al 2024 after anodisation times of (a) three minutes and (b) eight minutes.[19] Reproduced with permission.

The stability of a metal oxide is regarded as an important factor in determining the durability of a bonded metal structure to hot humid conditions. Noland,[23] using XPS, showed that the surface of aluminium was more stable after phosphoric acid anodising than after chromic acid etching (Figure 6). This is in line with the better durability provided by the former treatment.



(a) $H_2SO_4/Na_2Cr_2O_7$ etched



(b) Phosphoric acid anodise

FIGURE 6 (a) The Al 2p peak from an aluminium surface etched with chromic acid immediately after treatment and after ageing at 60°C and 100% RH for one hour. (b) The Al 2p peak from an aluminium surface anodised in phosphoric acid immediately after treatment and after ageing at 60°C and 100% RH for one hour. Reproduced with permission.[23]

In an extensive study, Smith[24] used a combination of AES, surface potential difference, ellipsometry, contact angles and photoelectron emission to investigate the stability of the FPL-etch to a number of environments. These results show that on aluminium 2024-T3 alloy the FPL-etch produces a clean, high energy surface with a thin oxide film. These features are retained if surfaces are stored in a contamination-free environment. However, exposure to gaseous environments is shown to produce low energy surfaces due to either adsorbed contamination or degradation of the surface oxide. A similar conclusion was obtained by Minford[25] using surface resistivity to monitor the modification of aluminium 1100 alloy surface chemistry as a function of environment and time. Results show that exposure to a laboratory ambient causes surface modification in a relatively short period of time compared with storage in a desiccator.

Scanning transmission electron microscopy (STEM) and XPS have been combined by Davis *et al.*[26] to identify a three-stage degradation mechanism for the PAA oxide on aluminium following exposure to a water vapour saturated atmosphere. In this work, XPS was used to monitor degradation in surface chemistry while variations in surface morphology were studied with STEM. For reference purposes a number of binding energy differences were determined for a range of Al-P compounds.

PAA anodised 2024-T3 surfaces were exposed to 100% RH at either 50 or 60°C. After various times, samples were removed from their ambient and analysed by XPS and STEM. STEM results show the pores in the PAA oxide to be nearly filled after 24 hours exposure to 50°C, 100% RH and a discrete overlayer of hydration product after 72 hours. The authors concluded, by comparing XPS data from exposed adherends with the known reference materials, that the initial PAA surface comprised mainly $AlPO_4$, which adsorbed water to expose Al_2O_3. In the next stage, this product hydrated to form AlOOH and, in the final stage, further hydration occurred to form $Al(OH)_3$.

Work carried out by Clearfield *et al.*[27] used AES and XPS to identify the cause of poor pull strengths on CAA-treated titanium alloy (Ti-6Al-4V) exposed to various environments prior to bonding with a RT-curing epoxide. A summary of their results is given in Table VII.

Of particular interest was the detrimental effect on the adherend exposed to vacuum at 400°C, since this temperature may be required for curing of a polyimide adhesive to this surface.

AES depth-profiles comparing surfaces as-anodised and after exposure to elevated temperatures are given in Figure 7. These results demonstrate the dissolution of the anodic oxide into the metal adherend. This mechanism is considered to create a mechanically weak, non-stoichiometric oxide. The exposure of "metallic" Ti at these temperatures is considered to facilitate carbide formation on the surface, as identified by XPS. Furthermore, there is the creation of an oxygen-rich embrittled zone in the

TABLE VII

A summary of results obtained in tensile tests on CAA-treated titanium alloy surfaces exposed to various environments

Exposure	Pull Strength (MPa)	Failure Mode
As anodised	9.2 ± 0.5	within adhesive
Vacuum at 400°C for 24 hours	< 0.7	within oxide
Air at 330°C for 160 hours	3.5	within adhesive and oxide
Air at 330°C for 1200 hours	< 0.7	within oxide

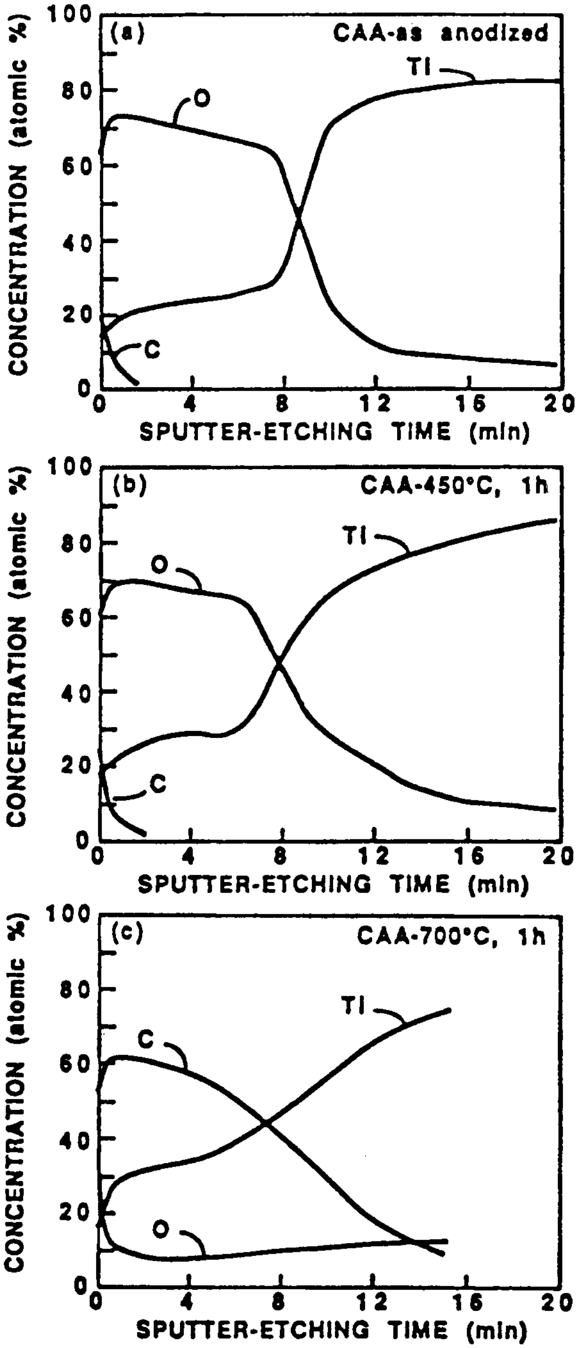


FIGURE 7 AES depth profiles of CAA-treated Ti-6Al-4V, (a) as-anodised, (b) after one hour in vacuum at 450°C and (c) after one hour in vacuum at 700°C. Reproduced with permission.[27]

near-surface region. Such modifications to the adherend are considered responsible for the poor joint performance after exposure to these conditions.

INTERFACIAL CHEMISTRY

Chemical bonding across an interface is clearly likely to optimise adhesion performance especially where resistance to water is concerned. The nature of the interaction across an interface is not usually known but it can range from weak dispersion forces to covalent bonds.

In-situ studies of interfaces may be made in some cases. In one study, Marcus *et al.*[28] used XPS to study the initial stages of aluminium deposition on polypropylene. From the appearance of new peaks in the Al2p and C1s region, the authors concluded that a chemical reaction between aluminium and polypropylene had occurred.

SSIMS has been used to obtain evidence of chemical bonding across an interface.[29] In a study of the durability of mild steel bonded with an epoxide, it was found that γ-glycidoxypropyltrimethoxysilane gave a substantial improvement compared with the unprimed metal. On the other hand, two other primers resulted in worse durability than the control (Figure 8). Static SIMS of mild steel primed with the effective silane revealed the presence of a fragment of mass 100 and this was attributed to $FeOSi^+$. It

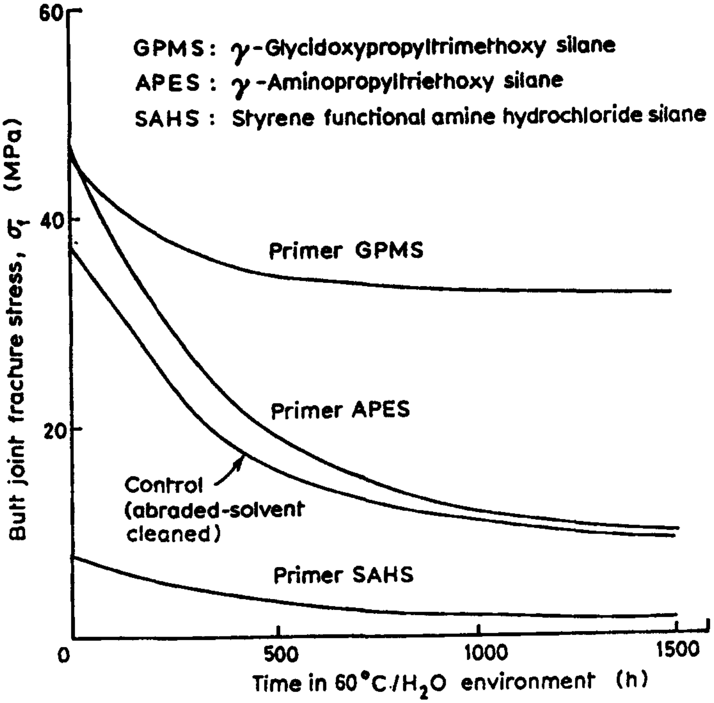


FIGURE 8 Durability study of mild steel joints bonded with an epoxide adhesive.[29] Reproduced with permission.

was concluded that a chemical bond had been formed between the silane and the iron oxide, and that this was the reason for the enhanced durability.

Van Ooij[30] has described methods by which the two sides of polymer-metal interfaces may be examined. For example, an organic coating may be removed from a metal by swelling in an organic solvent. After drying, the two surfaces may then be examined by XPS, SSIMS and other techniques. Metal substrates can sometimes be dissolved selectively. Thin steel sheets can be dissolved in a saturated solution of iodine in methanol leaving exposed iron oxide which may be studied by AES and other techniques. Aluminium and zinc together with their oxides will dissolve in aqueous sodium hydroxide, thus permitting the study of the corresponding polymer surfaces, *e.g.* using XPS or SSIMS.

Van Ooij has made many detailed studies of the polymer-metal interface with particular emphasis on tyre-cord adhesion and the adhesion of paints to metals. A number of these studies using XPS and AES are given in Reference 30. A more recent study used time-of-flight SIMS (TOFSIMS) to study the paint-metal interface.[31]

CONTAMINATION

Contaminants on polymers, metals and other substrates can severely reduce the level of adhesion. Problems with organic contaminants are widespread. Such contaminants include processing aids, additives which have migrated to the surface of a polymer, organic molecules adsorbed from the atmosphere and oils deposited during handling.

XPS can provide useful information on contamination, *e.g.* from the carbon level on acid-etched aluminium. However, SSIMS is especially useful in identifying contaminants and two examples are now given.

The first example is provided by silicones which are widely used as processing aids in the polymer industry. However, transfer of a silicone to a polymer, *e.g.* from a mould, can have a highly detrimental effect on adhesion. The most commonly-used silicone, polydimethylsiloxane or dimethylsilicone, has a very characteristic positive ion spectrum (Figure 9).[4] Silicone contamination is, therefore, readily detected. Furthermore, detection can be made even at low concentrations.

The second example is the identification of a lubricant in a polyurethane.[5] The upper spectrum in Figure 10 was obtained from "Pellethane" which is a commercial polyurethane. However, the fragments at 282 and 310 are not characteristic of a PU. Briggs[5] found that the lubricant ethylene bisstearamide had a very similar positive ion spectrum to "Pellethane", again showing major peaks at 282 and 310 (Figure 10). The masses of 282 and 310 would be produced by scission of the CH_2—NH bond.

McNamara *et al.*[32] used XPS and STEM to study the influence of handling freshly-prepared FPL-etched and PAA surfaces. Surfaces were exposed to handling with bare fingers, vinyl gloves and Kraft paper. An indication of the relative levels of surface contamination is given in Table VIII. The percentage contamination of each surface was determined using STEM at low magnification (x1000).

The high C:O ratios on both FPL and PAA surfaces after finger handling shows this to contaminate both surfaces badly. In contrast, the relatively low values, ~2, show

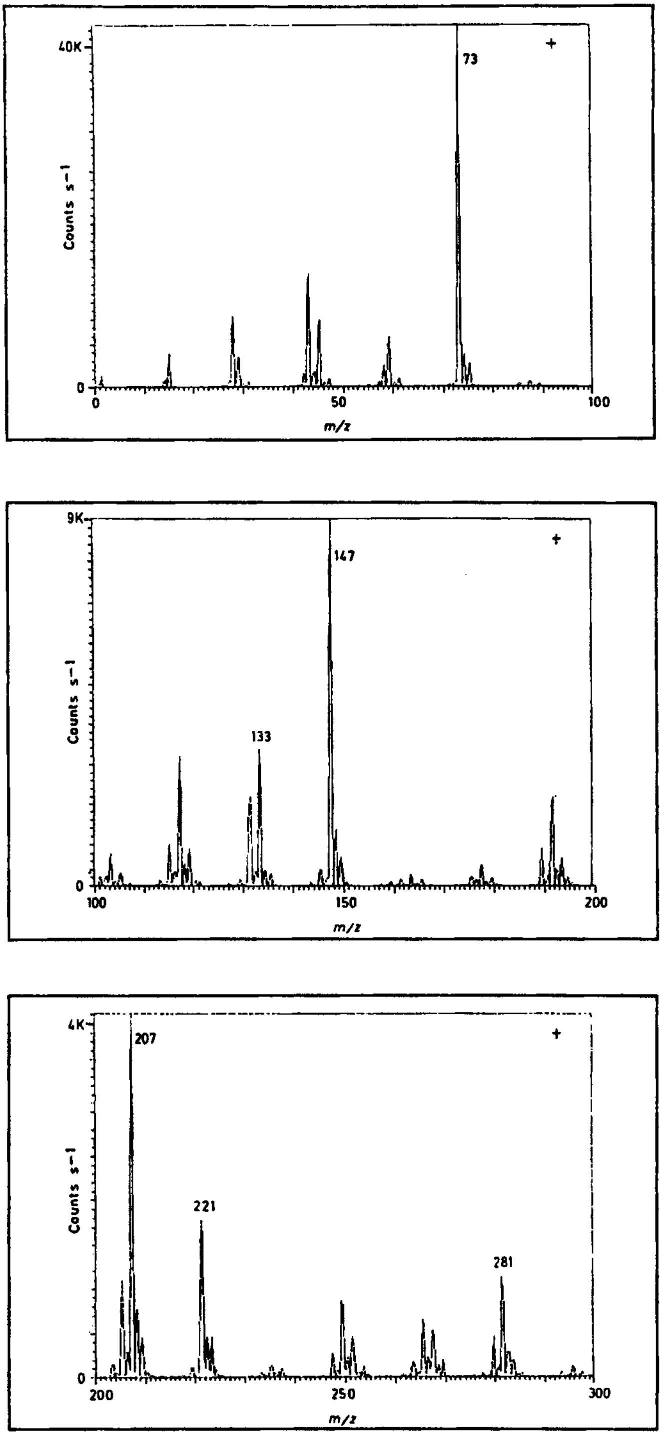


FIGURE 9 Positive SIMS spectrum of dimethylsiloxane showing characteristic major peaks at 73, 147, 133, 207, 221 and 281. Reproduced with permission.[4]

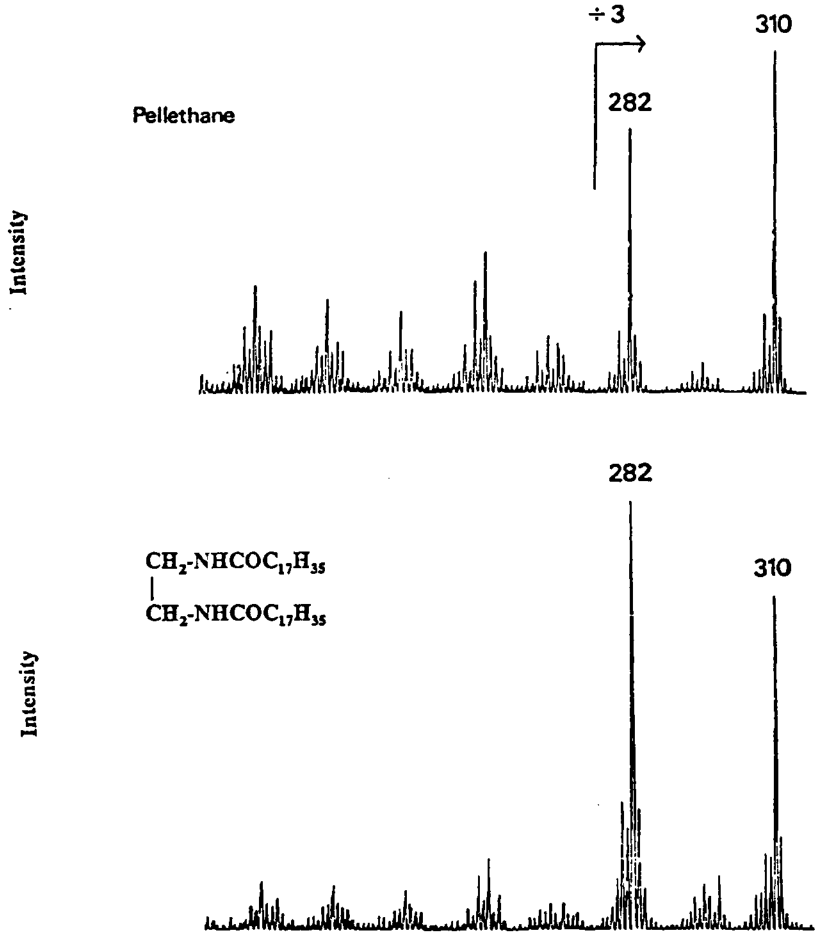


FIGURE 10 Part of the positive ion spectrum of (a) the polyurethane "Pellethane" and (b) ethylene bisstearamide.[5] Reproduced with permission.

TABLE VIII
Ratio of C:O XPS peak heights and percentage of contaminated area, as determined by STEM, on deliberately-handled FPL and PAA surfaces

	FPL		PAA	
	XPS	STEM	XPS	STEM
Finger	8.8	80%	4.5	80%
Vinyl Glove	5.2	50%	2.8	30%
Kraft Paper	1.9	20%	2.5	20%

that although some contamination occurs as a consequence of handling with Kraft paper this is less severe than handling by fingers or vinyl gloves. STEM of contaminated FPL and PAA surfaces showed that the underlying oxide structures can remain intact beneath the contaminating layer. However, although contamination can occur without accompanying damage to the underlying oxide, it is possible that the all-important fine structure on these surfaces can be filled by contamination.

In contrast to this, Chen *et al.*[33] used STEM, XPS and AES to identify a change in surface morphology caused by surface contamination. In this work, the effect of fluorine contamination was studied on the FPL-etched 2024-T3 alloy surface. A correlation was made between surface fluorine concentrations and joint strengths measured by climbing drum peel, as indicated in Figure 11.

AES depth profiling on both good and bad surfaces showed similar surface and sub-surface compositions (Figure 12), the only difference being the high levels of F present at the surface of the bad sample. STEM showed the poor bonding surface to be devoid of the small protruding fibrils present on the as-prepared surface. It was concluded that the fibrils responsible for micro-mechanical interlocking, and hence good adhesion, are removed by exposure to a combination of fluorine and high humidity (*e.g.* 2 hours 80% RH).

INTERPHASES

Sharp[2b] has pointed out that there is a transition between, for example, the bulk of a metal substrate and the bulk of an adhesive to which it is bonded, *i.e.* there is a transitional zone which he termed an interphase. There is clear evidence that such interphases exist and much detailed information has been provided on these regions especially by AES and XPS.

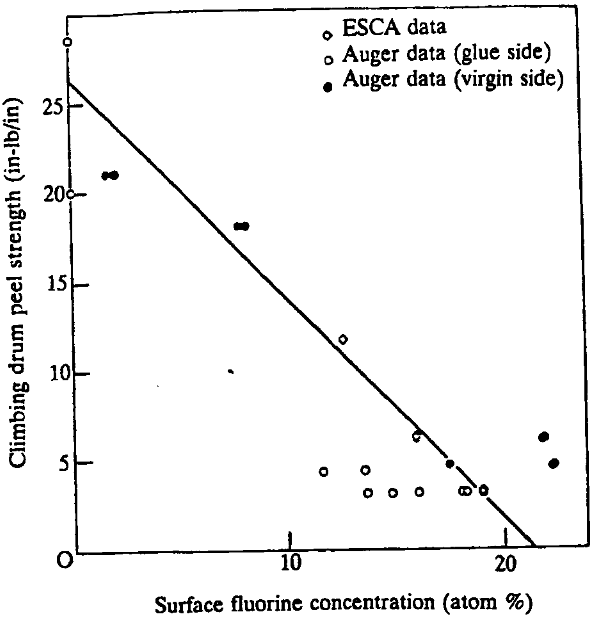


FIGURE 11 Correlation between peel strength and surface fluorine concentration.[33] Reproduced with permission.

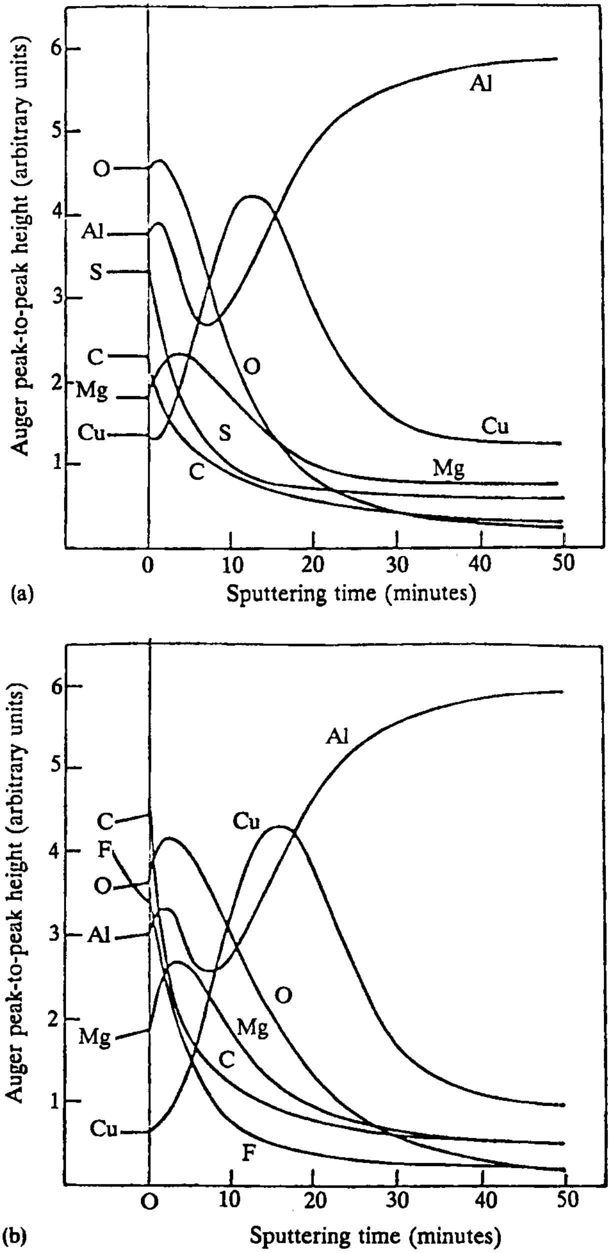


FIGURE 12 AES depth profiles through the surface oxides on (a) a "good" bonding surface and (b) a "poor" bonding surface.[33] Reproduced with permission.

The non-uniformity of substrates themselves may be studied using a variety of approaches.

With polymers, the degree of uniformity in the first few nanometres may be studied using XPS. The most usual approach is to vary the electron take-off angle and determine the effect of this on the elemental composition obtained. If the chemistry of the polymer is uniform within the sampling depth ($\sim 3\lambda$ where λ is the attenuation length of the electrons), there will be no change in the elemental analysis with changes in take-off angle. However, if an element is more concentrated in the first 1–2 nm then an angular effect will be apparent.[34] Such angular take-off effects have been observed not only with contaminants but also with pretreatments.[11]

The variation in the near-surface regions of a corona treated polypropylene is shown by some work of Strobel *et al.*[35] Of particular interest are the results shown in Table IX. The as-treated material shows no angular variation effect. Therefore, oxygen is uniformly distributed within the XPS sampling depth of a few nanometres. The treated film was washed with water and the weight loss determined. This was equivalent to about 150 nm of material. The washed film showed a distinct angular effect indicating a higher degree of oxidation near the surface. To summarise, the treatment produced a relatively thick layer of heavily oxidised, low molecular weight material and only a thin layer of oxidised, high MW polymer.

Another method of assessing the chemical uniformity of a polymer within the first few nanometres is to measure the relative intensities of different core levels of the same element with substantially different kinetic energies. For a chemically homogeneous polymer this ratio has a particular value. If the element is concentrated in a layer thinner than 3λ max, where λ corresponds to the higher KE, then this ratio will be greater. For example, the O1s:O2s ratio was used to show[11] that only a very thin layer (<10 nm) of PP was modified with chromic acid (see Table IV).

With metals, depth profiling using AES has been very widely used.[18,19] In one example,[36] AES was used to identify more clearly where failure had occurred in a metal-epoxide joint. Anodised aluminium 5251 alloy was bonded with a single-part epoxide. After exposure and subsequent fracturing, AES results from the surface on both faces indicated that failure was cohesive within the epoxide. Depth profiling carried out on the shiny side of the joint indicated that, although high levels of carbon were present on the immediate surface, aluminium oxide produced by the pretreatment could be observed just below this. No metallics, but mainly carbon, could be observed in a depth profile on the counterface. These results enabled the locus of failure to be identified as being within the adhesive, but, close to the polymer-metal oxide boundary region.

TABLE IX

XPS data for polypropylene treated with a corona (17 J cm^{-2}) at 5% RH·O:C atomic ratios as a function of electron take-off angle

Unwashed			Washed		
18°	38°	68°	18°	38°	68°
0.23	0.23	0.21	0.12	0.08	0.06

DISCUSSION

There can be no doubt that AES, XPS, and SSIMS have made major contributions to our undetstanding of adhesion phenomena and problems, although many other techniques have made useful contributions both in isolation and in conjuction with AES, XPS and SSIMS.[37]

Other techniques of particular note are: infra-red analysis; contact angle measurement and electron microscopy. The latter has been the most widely used technique to study surface topography, oxide growth mechanisms and failure analysis. Recently, atomic force microscopy has been used to provide additional information complementary to electron microscopy.[38]

This review has been limited to the electron spectroscopies and ion spectrometry but the major contribution of infra-red analysis to adhesion studies should not be overlooked. A brief search in just one journal revealed a number of important studies including: the characterisation of pretreated aluminium surfaces;[39] the ingress of water into aluminium joints;[40] interactions between ethlene copolymers and aluminium;[41] degradation inhibitors and adhesion promoters for polyimide films on copper substrates[42] and the structure of silanes adsorbed onto aluminium and titanium.[43]

Although these other techniques provide much useful information, a knowledge of the chemistry of the first few atomic layers is often essential. As far as adhesion studies are concerned, AES, XPS and SSIMS have been paramount in providing this information.

The three analytical methods are largely complementary. XPS can provide a quantitative elemental analysis of most solid surfaces. By curve fitting of narrow scan spectra or the use of derivatisation reactions it is possible to obtain quantitative information on the chemical groups present in a polymeric surface, *e.g.* after a pretreatment. Auger also provides quantitative elemental analysis of surfaces but is not usually suitable for characterisation of polymers due to excessive beam damage and sample charging. However, the technique is especially useful for the depth profiling of metals and inorganic materials. SSIMS is even more surface sensitive than AES or XPS and provides more molecular information than the other two techniques. It is possible, in some cases, to identify specific organic compounds on surfaces. However, SSIMS is not quantitative and it is, therefore, of particular value when used in conjunction with XPS.

Despite their great contribution to adhesion studies, some caution is required. Firstly, the three techniques all use ultra-high vacuums. Small molecules which were originally present on a surface may be lost before the analysis is carried out. Clearly, this could lead to misleading results. Changes may occur between breaking an adhesive joint and analysing the surfaces. This is especially true where metals are involved, although many spectrometers have facilities for breaking joints *in-situ*. Another problem is that critical material from a joint may be lost during its destruction.[2a] Furthermore, the limitations of these techniques should be borne in mind when interpreting analytical data. Perhaps the most care is required in AES, where difficulties associated with quantification and depth scale calibration, and the possibility of electron or ion-beam damage to materials, complicate full interpretation of data.

Despite the great increase in our understanding of adhesion phenomena over the last 20 years, there is still much to learn. With improved performance from AES, XPS, SSIMS and other techniques, and with the increasing number of scientists interested in adhesion, even more dramatic progress is likely in the next 20 years.

References

1. *Practical Surface Analysis*, Vols. 1 and 2, 2nd edn., D. Briggs and M. P. Seah, Eds. (John Wiley & Sons, Chichester, 1990).
2. (a) L. H. Sharpe, *J. Adhesion*, **29**, 1 (1989); (b) *J. Adhesion*, **4**, 51 (1972).
3. D. M. Brewis, unpublished data.
4. *Handbook of Static Secondary Ion Mass Spectrometry*, D. Briggs, A. Brown and J. C. Vickerman, Eds. (John Wiley & Sons, Chichester, 1989), p. 50.
5. D. Briggs, *Surf. Interface Anal.*, **9**, 391 (1986).
6. D. Briggs in *Industrial Adhesion Problems*, D. M. Brewis and D. Briggs, Eds. (Orbital Press, Oxford, 1985), Chapter 2.
7. J. F. Watts and B. R. Dempster, *Surf. Interface Anal.*, **19**, 115 (1992).
8. F. J. Boerio and D. J. Ondrus, *J. Adhesion*, **22**, 1 (1987).
9. P. Commercon and J. P. Wightman, *J. Adhesion*, **22**, 13 (1987).
10. Z. Naem, A. B. Smith, M. Lamehchi and G. W. Critchlow, *Surf. Interface Anal.*, **20**, 352 (1993).
11. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mat. Sci*, **11**, 270 (1976).
12. P. Blais, D. J. Carlsson, G. W. Csullog and D. M. Wiles, *J. Colloid Int. Sci.*, **47**(3), 636 (1974).
13. I. Mathieson, D. M. Brewis, I. Sutherland and R. A. Cayless, *J. Adhesion*, **46**, 49 (1994).
14. C. M. G. Carlsson and G. Ström, *Surf. Interface Anal*, **17**, 511 (1991).
15. D. Briggs and C. R. Kendall, *Int. J. Adh. & Adh.*, **2**, 13 (1982).
16. D. Briggs in *Practical Surface Analysis* Vol. 1., 2nd edn., D. Briggs and M. P. Seah, Eds. (John Wiley & Sons, Chichester, 1990), Chapter 9.
17. C. Jones, *Carbon*, **27**(3), 487 (1989).
18. B. M. Ditchek, K. R. Breen, T. S. Sun and J. D. Venables, *Proc. 12th SAMPE Tech. Conf.*, October 1980, p. 882.
19. T. S. Sun, D. K. McNamara, J. S. Ahearn, J. M. Chen, B. M. Ditchek and J. D. Venables, *Applications of Surface Science*, **5**, 406 (1980).
20. J. A. Treverton, M. P. Armour and A. Bosland, *Corros. Sci.*, **33**(9), 1411 (1992).
21. D. Briggs, D. G. Rance, C. R. Kendall and A. R. Blythe, *Polymer*, **21**, 895 (1980).
22. S. O'Kell, T. Henshaw, G. Farrow, M. Aindow and C. Jones, *Surf. Interface Anal.*, in press.
23. J. S. Noland in *Adhesion Science and Technology*, Vol. 9A, L-H Lee, Ed. (Plenum Press, New York, 1975), p. 413.
24. T. Smith, *J. Appl. Poly. Sci.*, **32**, 37 (1977).
25. J. D. Minford, *Adhesives Age*, **21**(3), 17 (1978).
26. G. D. Davis, T. S. Sun, J. S. Ahearn and J. D. Venables, *J. Mat. Sci.*, **17**, 1807 (1982).
27. H. M. Clearfield, D. K. Shaffer, S. L. Vandoren and J. S. Ahearn, *J. Adhesion*, **29**, 81 (1989).
28. P. Marcus, C. Hinnen, D. Imbert and J. M. Siffre, *Surf. Interface Anal.*, **19**, 127 (1992).
29. M. Gettings and A. J. Kinloch, *J. Mat. Sci.*, **12**, 2511 (1977).
30. W. J. van Ooij, in *Industrial Adhesion Problems*, D. M. Brewis and D. Briggs, Eds. (Orbital Press, Oxford, 1985), Chapter 4.
31. W. J. van Ooij, *Surf. Interface Anal.*, **19**, 101 (1992).
32. D. K. McNamara, J. D. Venables, T. S. Sun and J. M. Chen, *11th SAMPE Tech. Conf.*, November 1979, p. 740.
33. J. M. Chen, T. S. Sun, J. D. Venables and R. Hopping, *SAMPE J.*, July-August 1978, p. 22.
34. D. Briggs in *Surface Analysis and Pretreatment of Plastic and Metals*, D. M. Brewis, Ed. (Applied Science Publishers, London 1982), Chapter 4.
35. M. Strobel, C. Dunatov, J. M. Strobel, C. S. Lyons, J. Perron and C. Morgan, *J. Adhesion Sci. Technol.*, 3(5), 321 (1989).
36. G. W. Critchlow and A. Maddison, *Surf. Interface Anal.*, **17**, 539 (1991).
37. MTS Technical Report 2, Project 4, *Characterisation of Surface Condition*; programme funded by the Department of Trade and Industry, September 1993.
38. F. Creuzet, G. Ryschenkow and H. Arribart, *J. Adhesion*, **40**, 15 (1992).
39. F. Fondeur and J. L. Koenig, *J. Adhesion*, **40**, 189 (1993).
40. F. Fondeur and J. L. Koenig, *J. Adhesion*, **43**, 263 (1993).
41. L. Ulrén, T. Hjertberg and H. Ishida, *J. Adhesion*, **31**, 117 (1990).
42. H. Ishida and K. Kelly, *J. Adhesion*, **36**, 177 (1991).
43. F. J. Boerio, C. A. Gosselin, R. G. Dillingham and H. W. Liu, *J. Adhesion*, **13**, 159 (1981).