New Tools for Adhesion Science - Surface Pretreatment and Analysis

Thursday 8th December 1994
IoMat, Adhesives Group Seminar
Thursday 8th December 1994
at
Society of Chemical Industry
15 Belgrave Square, London

New Tools for Adhesion Science - Surface Pretreatment and Analysis

9.45: Registration

10.15: The Use of Surface Analytical Techniques in the Development of Pretreatments for Improved Adhesive Durability to Steel and Zinc Substrates: DL Perry [Consultant]

10.45: Pretreatment of Polymers to Enhance Adhesion: DM Brewis [Institute of Surface Science and Technology, University of Technology, Loughborough]

11.15: Coffee

11.40: The Role of Electron Microscopy in the Study of Adhesion to Aluminium Surfaces: JA Bishopp [Ciba Composites] and GE Thompson [UMIST - Corrosion and Protection Centre]

12.10: The Use of Scanning Probe Microscopy for Mapping Surface Topography: J Leckenby [J.K. Instruments Ltd]

12.40: Lunch

14.00: Measurement of Adhesive/Adherend Interlayer Properties using Acoustic Microscopy: P Cawley, AJ Kinloch, [Imperial College of Science, Technology and Medicine], Z Sklar and GAD Briggs [University of Oxford]


15.00: Tea

15.30: Recent Developments in the Application of XPS to Adhesion Science: JF Watts [University of Surrey]

15.50: Time-of-Flight SIMS in Surface Analysis - The Current Situation and Opportunities for the Future using High-Resolution TofSIMS: A Swift and A Paul [CSMA Ltd]
The Use of Surface Analytical Techniques in the Development of Pre-treatments for Improved Adhesive Durability to Steel and Zinc Substrates

D L Perry

The pre-treatment of "difficult to bond" materials such as many plastics, and the development of good durability in bonding to metals, are recognised as areas of technology where interfacial science has a determining role. The application of surface analytical techniques to adhesion science has played an important role in the development of our understanding of some of the key factors involved. However, much greater progress is required if we are to get to the stage where we can design the surface chemistry required for good and durable adhesive bonds on all types of substrate. Some of this progress may be awaiting the development of new techniques for the study of complex (and buried) interfaces.

This presentation will describe the various ways in which surface analysis techniques can be used to optimise surface treatments; including the identification of the chemistry of the surfaces to be bonded, identification of failure mechanisms and the monitoring of pre-treatment chemistry. Examples will be drawn from studies of epoxy bonding to steel and zinc-coated steel. Locus of failure studies showed that the stability of the surface metal oxide and the bonding of this oxide to the adhesive were the two weak links in a bond after extended exposure to water at a temperature of 50C. It will be shown how strengthening both of these weak links simultaneously with different surface pre-treatments, to stabilise the oxide and to improve interfacial chemical bonding, improved the durability of the bonds very significantly. The way that surface analysis was used in the development and optimisation of these techniques will be described. However, it will be clear that the improvement is based as much on empirical advances as on improved fundamental understanding.

The presentation will be concluded with a discussion of some new advances in surface analysis; particularly the recent developments in surface imaging techniques. It will be shown how these should enable our understanding of surface pre-treatment technology to be improved and assist the development of improved surface treatments for enhanced adhesion and environmental durability.

DLL 28.11.94
Good adhesion to polymers is required not only in adhesive bonding but also in printing, painting, metallisation and certain other technologies. Untreated polyolefins and fully fluorinated polymers are especially difficult to adhere to but other polymers cause problems from time to time. A wide range of pretreatments is available; these range from grit blasting to the use of plasmas. In some cases the underlying chemistry of a polymer is favourable to good adhesion but the surface consists of a contaminant such as a release agent. In such cases, a solvent or mechanical method may be sufficient to remove this weak layer and produce a good surface for bonding. In other cases, as with polyolefins, it is necessary to chemically modify the surface to achieve good adhesion.

One of the most widely used methods is the corona discharge treatment. This has been used to enhance the adhesion of print to plastic films since about 1950. A high voltage is used to break down air into atoms, ions, electrons and activated molecules, i.e. to form a plasma which can react with the polymer surface. A typical commercial pretreatment of polypropylene would introduce 7 atomic percent of oxygen into the first few nanometres of the surface. The oxygen is in the form of several different chemical groups. The nature and concentrations of these groups may be determined using X-ray photoelectron spectroscopy either by derivitisation reactions or by curve fitting.

The effectiveness of the corona treatment can decrease with time, probably due to the inversion of polar groups towards the bulk of the polymer. This inversion can be demonstrated by measuring water contact angles as a function of ageing time. A high level of corona treatment will lead to the formation of a substantial quantity of low MW material which is water soluble.

The flame treatment has been used with polyolefins in thick sections, as with plastic bottles, since about 1950. Again substantial oxidation of the polymer surface takes place. The main variables which affect the degree of oxidation are the air:gas ratio, the total gas glow, the distance between the flame and polymer and the treatment time. The method is effective with other polymers containing CH₂ groups such as nylon-type plastics.

The two methods used commercially for fully fluorinated polymers such as PTFE are sodium in liquid ammonia and sodium naphthalenide in tetrahydrofuran. These
reagents are both very powerful reducing agents. They rapidly defluorinate the polymers, producing a highly active carbon which in turn reacts rapidly with oxygen to produce various oxygen-containing groups. Partially fluorinated polymers respond much more slowly to these reagents and can be more effectively treated with a low pressure plasma, a flame or a corona discharge.

To conclude, a wide range of pretreatment for polymers is available. Some of these simply remove contaminants whereas others introduce new functionality. X-ray photoelectron spectroscopy has been especially useful in increasing our knowledge of the chemical changes caused by pretreatments.

28 November 1994
The Role of Electron Microscopy in the Study of Adhesion to Aluminium Substrates

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The analysis of the bondline in structural aluminium joints is taken as an example to illustrate how electron microscopy can be used to gain a new insight into the phenomenon of adhesion. Scanning electron microscopy and transmission electron microscopy of ultramicrotomed sections has been used to characterize the adherend surfaces generated by the pretreatment processes prior to bonding. It is shown how a simple extension of these techniques can be used to analyse and characterize the interfacial and interphasial morphologies of the bonded joint both before and after exposure to 'hot/wet' environments. Results have shown that the importance of the so-called mechanical interlocking phenomenon is related to the durability resistance of the joint rather than enhancement of the 'dry-state' mechanical properties. It is also concluded that the formation of the voluminous hydrated alumina at the interface occurs post-rupture and is not a prima facie cause. From the observed interphasial morphologies a hypothesis is advanced to explain the effect of various pretreatments on joint durability. Other analytical techniques, such as 'parallel' sections, AES, XPS and electron energy-loss spectroscopy (EELS), are discussed and it is shown how these methods can be used, not only to confirm the interphasial structures but also to generate new data in their own right.

A greater understanding, therefore, of the effect of adhesive theology, environmental exposure, adherend composition and pretreatment on the interface between adhesive and adherend, can be obtained using these techniques.

INTRODUCTION

Over the past 30 years, much theoretical work has been carried out in an attempt to analyse the adhesive bond and hence determine the mechanisms of adhesion. Current theories include those of Zisman,¹ where intimate wetting of the adherend by the adhesive is required not only to facilitate the formation of any covalent bonds between adherend and adhesive but also to allow intermolecular attraction forces (Van der Waals, London dispersion, etc.) to come into play.

Other hypotheses concern the disappearance of a definite interface between adhesive and substrate with the formation of the so-called inter-penetrating networks of the diffusion theory,²,³ acid–base interactions across the interface⁴ and the electrostatic theories of Derjaguin.⁵ For the latter, electron transfer on contact between adhesive and adherend results in the formation of a double layer of electrical charge; adhesion is due to the attractive forces across this double layer.

Couples, to a greater or lesser extent, with all these theories is that of 'mechanical' adhesion;⁶ the adhesive fills and forms round surface discontinuities in the substrate and then, on hardening, forms a strong mechanical key, 'locking' the two substrates together.

The various mechanisms proposed have been formulated largely through examination of model adhesive systems, generally on 'real' substrates, coupled with an in-depth study of the physicochemical properties and thermodynamics of the adhesive, the adherend and the adhesive/adherend interface. Such analyses, of necessity, only consider a maximum distance of ~1 nm across that interface. Thus, whilst giving an insight into the actual mechanisms of adhesion, such examinations do not yield much information about the way in which an adhesive will perform within a load-bearing bonded structure. Nor, at the other end of the scale, does simple visual inspection of a bonded and/or ruptured joint yield many useful data.

Hence, the ability to view the joint, particularly after rupture, close to the original interface between adhesive and substrate has represented a significant advance.

Nowadays the use of scanning electron microscopy (SEM) has become well established for examining both the surface of an adherend and the adhesive fracture surface within the ruptured joint, but the information gained concerning the substrate surface and, more particularly, the actual interface is not sufficient to yield an in-depth characterization of the system.

Following the work by Wood and Thompson at UMIST, which led to improved ultramicrotomy techniques⁷ where 5–45 nm thick slices can be taken through the adhesive joint—perpendicular to the bondline—and then examined by transmission electron microscopy (TEM), the possibility of making a direct examination of the adhesive/adherend interface and interphasial regions has become a reality.⁸–¹⁰

THE ADHESIVE JOINT

The range of substrates that the Adhesives Industry requires to be bonded is vast: wood, glass, plastics, metal, rubber, composite materials (e.g. CFRP, GLARE, registered trademark of Structural Laminates), etc. The work reported here has concentrated on one of the most commonly encountered materials when bonding structural (i.e. load-bearing) components—namely aluminium.

Alclad 2024-T3 (Table 1), a material much used in the aerospace industry and having something of a reputation of being difficult to bond, is the substrate employed, unless other indicated. However, as will be
Table 1. Percentage composition of aluminium and aluminium–lithium alloys

<table>
<thead>
<tr>
<th>Element</th>
<th>BA 8090C-T3</th>
<th>Core 2024-T3</th>
<th>Cladding 8090C-T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.86–1.36</td>
<td>3.80–4.90</td>
<td>0.10 max</td>
</tr>
<tr>
<td>Lithium</td>
<td>2.28–2.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.89–0.90</td>
<td>1.20–1.80</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.30–0.90</td>
<td>0.05 max</td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>0.13–0.17</td>
<td>0.50 max</td>
<td>0.70 max</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.04–0.06</td>
<td>0.50 max</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>0.10 max</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>0.25 max</td>
<td>0.10 max</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>0.15 max</td>
<td>0.03 max</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>0.06 max</td>
<td>0.03 max</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

seen, using these analytical techniques with other alloys, such as those based on aluminium–lithium, is very straightforward and allows a direct comparison between adherends to take place.

When bonding structural components, the adherends are usually pretreated to ensure that the adhesive is applied to a clean, stable surface to enable as effective a bond as possible to develop. However, economic and end-use considerations often mean that a less-than-optimum form of pretreatment, and occasionally none, is used. The most common forms of pretreatment for aluminium are:

1. Mechanical abrasion using Scotchbrite® or wire wool.
2. Shot-blasting using an alumina 'grit'.
3. Potassium dichromate/sulphuric acid pickling (CSA) to DTD 915B.11
4. Phosphoric acid anodizing (PAA) to BAC 5555.12
5. Chromic acid anodizing (CAA) to DEF STAN 03-24/2.13

After pretreatment, the adhesive—in this case an experimental, toughened epoxy film adhesive curing at 120 °C and supported with a knitted nylon 6 carrier—is applied to the dry substrate and the bond is formed by application of pressure (~300 kPa) and temperature for the requisite time (in this case, 60 min at cure temperature).

PREPARATION OF SPECIMENS FOR MICROSCOPY

A series of standard floating roller peel panels14 were bonded with the adhesive described above, the aluminium substrates having been subjected to the above pretreatments. Peel specimens were then submitted to increasing loads, applied at a cross-head speed of 50 mm min⁻¹. Samples from the unbonded substrate area and the adhesive rupture surfaces were cut out, sputter coated with gold and examined using an ISI DS-130 scanning electron microscope. Selected areas from the adhesive rupture surfaces and from the essentially unstressed, unruptured area of the bond—well in advance of the crack tip—were mounted and prepared for ultramicrotomy in the usual manner.7 Specimens 5–45 nm thick were cut, using a Dupont Sorval or Rei-

Figure 1. Scanning electron micrograph of a shot-blasted Alclad 2024-T3 substrate.

SUBSTRATE AND FRACTURE SURFACE EXAMINATION BY SCANNING ELECTRON MICROSCOPE

Simple, high-resolution SEM examination of the pretreated but unbonded substrate can reveal enough structure to characterize the 'mechanically' pretreated substrates.

During pretreatment, although the weak air-formed film is removed, the aluminium cladding is partially cut open to produce a highly convoluted, rough surface to which a significant amount of aluminium detritus is still loosely attached (Fig. 1). Such features are likely to act as potential areas of failure initiation in the bonded joint, particularly when exposed to harsh environments.

Scanning electron microscopy examination of the chemically pretreated substrates reveals the expected surface configurations but, owing to some masking by the gold coating, very few data relative to their true morphologies. Figure 2, for CAA pretreatment, is

Figure 2. Scanning electron micrograph of a chromic acid anodized Alclad 2024-T3 substrate.
Typical. Full characterization of these pretreatments is, therefore, difficult, if not impossible.

Similarly, SEM examination of the adhesive fracture surfaces generated on peel testing shows the same paucity of novel information. Again, it is the joints prepared using abraded substrates that are most revealing; poor adhesion and air-blistering through the adhesive layer is evident on all specimens examined (Fig. 3).

Turning to the chemically pretreated specimens, the expected fracture morphology for toughened epoxies is evident (Fig. 4). However, Fig. 5 shows the first real difference to be seen. Post-rupture cracks through the oxide film, formed by chromic acid anodizing, can be clearly identified. These are not seen on either of the other forms of chemical pretreatment.

Certainly, TEM of replicates could have been employed to characterize all substrate surfaces, but it is only of limited use here as both the surface topography and morphology have to be analysed. 'End-on' examination of fractured substrates has, indeed, yielded much useful information concerning film structure but it is the use of the ultramicrotomy/TEM technique that appears to be ideal and yields the data sought. Further, by its vary nature, it not only allows characterization of the substrate to be made but that of the adhesive/adherend interface and interphasial regions, at the same time.

INTERFACIAL AND INTERPHASIAL ANALYSIS

Figures 6–10 immediately show how powerful a tool ultramicrotomy/TEM is for surface and interfacial/interphasial analysis.

Figure 6 permits one hypothesis to be formulated for the presence of blisters in the glue-line of mechanically...
pretreated joints; the surface prepared is too convoluted. As the adhesive melts and flows during its cure cycle, the air trapped between adhesive and adherend should be displaced to allow the substrate to be fully wetted. Here, because of the high degree of convolutions, not all the air has been displaced. This has left voids and, consequently, microscopic areas of either no contact or point-contact between adhesive and adherend. With a film adhesive such as that used here, therefore, mechanical keying of the adhesive into the adherend is not a significant factor when abraded substrates are used. The potential weakening effect of loosely bound surface detritus is also shown in this figure, as is the presence of a subsurface fracture that is possibly induced by the method of pretreatment itself.

All the above would indicate low failure loads for such adhesive joints, and this is indeed seen in Fig. 14.

The chemically pretreated substrates reveal three very different morphologies:
(1) CSA: ostensibly finely-spaced ~30 nm high whis-
kers that appear to be well wetted and penetrated by the adhesive (Fig. 7).

(2) PAA: a porous 0.5–0.8 μm thick oxide film is present (Fig. 8). Surface roughness is enhanced due to film material collapse during anodizing (caused by progressive thinning of the cell material adjacent to the pore wall). The degree of convolution, however, is some orders of magnitude less than for abraded surfaces, which can be seen with the naked eye. The adhesive not only wets the surface well, filling the revealed surface cavities, but also penetrates into the depths of the pore to form the ‘microcomposite’ interphasial structure postulated by Davies and Moths.

(3) CAA: a porous 2.0–4.0 μm thick oxide film is present (Fig. 9). The original surface roughness is not significantly enhanced by the anodizing process and essentially mirrors the initial surface topography. Although the adhesive wets this surface well, there is no obvious deep penetration of the oxide pores by the adhesive; this is confirmed by Auger spectroscopy. Whilst this casts significant doubt over the theories of mechanical interlocking with CAA adherends, it does go some way to explain the fracture patterns seen by SEM examination (Fig. 5). When a truly planar interface exists, it is easier for the locus of failure to be in the interphasial region than in the bulk of the adhesive matrix.

It is worthwhile, at this point, to consider briefly other characterizations that this technique can accomplish. The first is the possibility of comparing the effect of the same pretreatments on different substrates. Here, the surfaces prepared by chemically pretreating the aluminium–lithium alloy BA 8090C-T3 can, very simply, be compared with those already discussed on Alclad 2024-T3.

Apart from a slightly less efficient formation of the anodic film layer owing to the alloying elements present (Table 1), the overall morphologies and interfacial and interphasial structures are remarkably similar (Fig. 10). However, when differences do arise these can be readily classified by this technique: Fig. 11 is a typical example, where the aluminium–lithium substrate has pitted, probably due to the dissolution, during the pretreatment process, of the lithium that has been transported to the surface during alloy preparation.

By careful control of sampling conditions, etc., other data can easily be generated—such as the rate of growth and change in morphology of the anodic film with time (Fig. 12).

The use of a typical corrosion-inhibiting adhesive primer on the adherend surface can, likewise, be evaluated and characterized; the technique is even powerful enough to examine the interface between the primer and the structural adhesive (Fig. 13).

**ANALYSIS OF THE EFFECT OF ENVIRONMENTAL EXPOSURE**

Having established the usefulness and versatility of the technique, it was a small step to use this approach to attempt to analyse the effect of exposing the adhesive joint to ‘hot/wet’ conditions—in this case, exposure to a relative humidity of > 85% at 70 °C.

Peel specimens were exposed to this environment for periods of 30, 60 and 90 days. On removal from the environmental chamber, the joints were wiped down to remove surface water and were then tested to destruction under ambient conditions. That exposure to such an environment has a severe effect on the bond can be readily seen from the results of the peel tests after the critical first 30 days of exposure (Fig. 14), as well as from visual examination of the rupture surface after testing.

Much has been postulated about the presence of hydrated alumina species at the interface of the environmentally exposed joint. The argument has always been whether the hydrated alumina species seen on the ruptured surface of the bond were formed prior to or post-testing. For the first time it has proved possible to examine the interface directly and look for typical evidence of transformation, i.e. swelling of the oxide layer.
Figure 13. Transmission electron micrograph of a section through a primed joint showing the diffuse interface between adhesive and primer.

or the actual appearance of the pseudoboehmite structure of hydrated alumina.

Under standard chemical pretreatment and exposure conditions, no such evidence has been found. Figure 15 is typical and can be compared directly with Fig. 8, where no environmental exposure has taken place. The transformation that is possible in the oxide film can be simulated by boiling the pretreated substrate in water (Fig. 16): this confirms the findings of other workers.16,19

From the characterization already made, it is fairly simple to explain the performance of the joint using abraded substrates; water can be transmitted to the interface through the included voids and disruption of the bond can readily take place. However, it is clear that a much more subtle mechanism must operate in the case of the chemically pretreated systems, as no significant interfacial disruption can be seen in the micrographs obtained.

Since it has been shown that the oxide film is well wetted by the adhesive, there can be no such easy route for water to pass to the interface, the dominant diffusion path almost certainly being through the resin matrix. The water ingress, once at the interface, may wet the adherend surface and porous structure comprising the anodic film morphology better than the adhesive matrix already in place; the extent to which the oxide pores are wetted by water will be dependent on the degree of adhesive penetration into those pores. In such cases, the wetting of the alumina material may be sufficient, per se, for bond deterioration by significantly reducing the Van der Waal forces, etc. across the interface. If not, then a subtle transformation of the adjacent alumina film to Al(OH)₃, at a rate dependent on the exposure conditions, must be considered.

Speculating further, in situations where the pore volume is not penetrated substantially by the adhesive,

Figure 14. Graph of peel strength versus exposure time (>85% relative humidity at 70 °C) for various substrate pretreatments.

Figure 15. Transmission electron micrograph of a section through a phosphoric acid anodized bonded joint that has been environmentally exposed for 90 days; no oxide transformation or interfacial damage is visible.

Figure 16. Transmission electron micrograph of a section through a chromic acid anodized Alclad 2024-T3 substrate; swelling/ transformation of the oxide film, caused by forced hydration of the surface, can be clearly seen.
(i.e. following CAA), wetting of the pore surface and possible build-up of water and other potentially damaging species within the pore (either direct from the environment or dissolved out of the cured adhesive matrix, as shown, for example, by Brockann \textit{et al.}\textsuperscript{20} can also be contemplated; a ready transformation of the alumina to hydrated material would be anticipated. Transformation is expected to proceed by moisture penetration of the cell material surrounding the pore, developing a disaggregated alumina zone behind which dissolution and reprecipitation occur.

This disruption of the alumina cell, with precipitation of relatively voluminous hydrated material, could contribute significantly to the undermining of the film surface and hence lead to bond deterioration, as postulated by Venables and Davies.\textsuperscript{21} Further, should moisture gain access to the pore volume, then direct passage to the metal via flaws in the substrate is a distinct possibility. Once in contact with the metal, water, assisted by damaging species (e.g. chloride ions, etc.), can enhance corrosion of the substrate, thus undermining the alumina film. Considering the situation where the adhesive substantially penetrates the porous morphology, any undermining of the alumina (through hydration proceeding into the cell walls) or corrosion of the metal is likely to be significantly delayed.

However, in the present study, where durability has been assessed by exposure to relatively high humidity, visual examination of the adhesive fracture surface shows no strong evidence for failure through the alumina film and hence crack propagation should proceed along, or close to, the interface, with intermittent diversions into the immediate adjacent bulk of the adhesive matrix; a hypothesis supported by Kinlock \textit{et al.}\textsuperscript{16,22} Further, as voluminous hydrated alumina has not been found in the interfacial area not ruptured by peel testing, the degree of any surface transformation does not, therefore, have to be extensive in order to cause potentially severe bond degradation. That severe bond degradation does exist is evidenced by the peel strengths.

As the adhesive, metal adherends, cure cycle and operators have, essentially, been kept constant, the differences revealed in the resistance to the environmental attack by the bonded specimens, prepared using chemical pretreatments (Fig. 14), must be due to the pretreatments themselves. Before these differences can be fully explained, however, the moisture diffusion path, the factors affecting the rate of diffusion and the alumina/moisture reaction must be more fully understood.

One major pointer does already exist. As opposed to PAA and CSA surfaces, those produced in chromic acid, although possessing a porous morphology, reveal a macroscopic planar surface in intimate contact with the adhesive but with little pore penetration. The outer regions of the PAA film, particularly, comprise both a coarse and a fine cavity-like structure due to film collapse. These areas are readily wetted by the adhesive, which also occupies a significant fraction of the internal film volume. Thus, for such anodic films, the moisture diffusion paths are considerably extended when compared with those for CAA films.

Considering the PAA adherends, the presence of bound, absorbed and adsorbed phosphates could well mask potential hydration sites, slowing down the damages aging transformation to hydrated alumina. However, even in the presence of these phosphates, if hydration does eventually proceed in the outer regions of the anodic film then the transformed areas will be almost fully enveloped by adhesive. In other words, no distinct, weak interphase can develop parallel to the aluminium substrate surface. In addition, any later corrosion processes in the metal itself are also likely to be delayed because of the penetration of the adhesive into the pores.

It is important to note, though, that there are certain conditions where the effect of environmental attack can be seen pre-rupture. Figure 17 shows what can happen to the interface should moisture and an FeAl\textsubscript{3} intermetallic inclusion come into contact; disruption of the oxide film will take place. However, the intermetallic has to be at, or very close to, the interface for such an effect to occur. Attack, therefore, is restricted to CSA-pretreated adherends where the oxide film is not thick enough to ensure the required separation. Naturally, the abraded substrates will also meet this criterion and similar interfacial disruption is, indeed, also seen in these joints.

\section*{USE OF RELATED TECHNIQUES}

In isolation, the use of SEM and ultramicrotomy/TEM techniques had probably yielded as much information as could be expected. It was, therefore, important to augment this approach with other analytical methods that would give a better three-dimensional resolution of the interphasial regions as well as yielding chemical information concerning the interphase and the bulk.

\section*{TRANSMISSION ELECTRON MICROSCOPY OF \textquoteleft PARALLEL\textquoteleft SECTION}

By its very nature, examination of sections taken through the joint gives very little spatial resolution. If, however, sections are produced by ultramicrotoming
parallel to the surface plane or, better still, if a shallow-angle section is taken, not only is this situation remedied but also some degree of depth profiling can be achieved.

Not only do such sections (Figs 18 and 19) confirm the cell shapes previously proposed for each form of pretreatment but they also reinforce the argument concerning the degree of pore penetration by the adhesive; Fig. 19 (CAA adherends) shows only a very low incidence of adhesive penetration. In Fig. 18 (PAA adherends) the lack of obvious deformation of the organic material under the electron beam gives a very good indication that the adhesive which has penetrated the pores is probably in a cross-linked state.

Carrying out the same technique on specimens that have been exposed to a full 90-days of 'hot/wet' conditions has confirmed that no clearly evident degradation of the 'oxide' film, by hydration, has occurred.

**X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)/AUGER ELECTRON SPECTROSCOPY (AES)**

The first stage of this examination was to perform a ball-cratering depth profile through the fracture surface (peeling face) of a ruptured joint; the joint had been exposed, before test, to the 'hot/wet' environment for 90 days. The adhesive matrix and 'oxide' film so exposed was then probed using an Auger linescan. However, heavy carbon contamination obscured any peaks that might have been associated with hydration products in the interphasial region.

An initial XPS analysis of the same fracture surface showed a very small aluminium peak in relation to the carbon peak. This would support the hypothesis that the locus of failure is close to the interface but generally in the interphasial region associated with the adhesive matrix. Analysis of the C 1s carbon peak shows that a shift has taken place over the immersion period. Deconvolution techniques indicate an increase in C—O bonds. X-ray photoelectron spectroscopy therefore, should prove to be a further powerful technique to augment the original electron microscopy studies, yielding important information concerning the interphasial hydration of the adhesive matrix.

**ELECTRON ENERGY-LOSS SPECTROSCOPY (EELS)**

Early work has shown that this technique could prove to be the most important and powerful of all, to augment the ultramicrotomy/TEM approaches.

Ultramicrotomed sections, again taken through the bonded joint, have been submitted to EELS analysis to identify the distribution of aluminium, oxygen, carbon, phosphorus and chromium throughout the section; each analysis run is specific to one of the elements. The concentration of the element under analysis is represented on a grey scale; black indicates the absence of the element and this changes through various shades of grey to a white level as the concentration increases. The initial results are sufficiently positive to allow conclusions to be drawn as to the presence of these elements. These results again confirm the penetration of the 'oxide' film by the adhesive (carbon analysis) for PAA adherends and show only isolated domains of adhesive within the film produced by CAA (carbon analysis, Fig. 20). These areas of penetration, though, are not sufficiently large, or great enough in number, to extend the effective interface or to create the postulated 'microcomposite' structure.

The technique has also been used to confirm that PAA leads to some bound phosphorus in the 'oxide' film (phosphorus analysis, Fig. 21) whereas no such distribution of chromium exists on CAA.
Figure 20. Electron energy-loss spectroscopy analysis for carbon in a section through a chromic acid anodized bonded joint; isolated areas of minimal penetration into the pores can be seen.

**FUTURE TECHNIQUES**

Extended electron energy-loss fine structure (EXELFS) and laser resonance techniques will be used to examine any chemical bonding taking place across the interface.

**CONCLUSIONS**

1. The use of SEM together with ultramicrotomy coupled with a TEM examination is an extremely powerful tool both to characterize and to aid in the analysis of the substrate surface morphology and the interfacial and interphasial regions of bonded joints.

2. For good wetting of the adherend, and hence good adhesive strength levels, chemically pretreated substrates appear essential. The surface convolutions and loosely bound detritus, produced by mechanical abrasion, lead to low levels of intimate contact, weak interfacial layers and stress-cracking in the adherend; all contribute to poor bond strength.

3. The needle-like oxide morphology formed on pickled substrates and the rough, porous anodic oxide layer grown on phosphoric acid appear to be well penetrated by the adhesive. Although porous, the CAA film does not appear to be significantly penetrated by adhesive and, hence, in this case, enhancement of bond strength by mechanical interlocking can be neglected.

4. The morphologically characterized pseudoboehmite form of hydrated alumina appears to be formed only after the bonded specimen is tested to destruction and hence is not thought to be the cause of environmental failure per se.

5. Environmental attack appears either to disrupt the physicochemical bonds across the interface or to undermine the interface itself, rather than weakening the adhesive matrix.

6. Penetration of the adhesive into the depths of the oxide film is important in that it effectively increases the length of the interface at the same time as eliminating a true planar boundary between adhesive and adherend. Thus, for pickled and PAA adherends, once water reaches the interface, there is no continuous passage for moisture between adhesive and adherend—effectively hindering any possible bond disruption. Should transformation of the alumina film to its hydrated form take place, then any area attacked will be isolated by the surrounding adhesive. Both will limit the development of a continuous, weak interface or even interphase.

7. If water can reach the surface film/metal interface, through flaws or by means of intermetallic sites, then corrosion is feasible, unless limited by the presence of primer. The result again would be an undermining of the pre-developed 'oxide' films. This would be particularly relevant where the developed film is relatively thin, i.e. on pickled adherends.

8. Spatial and depth profiling using ultramicrotomed sections has confirmed the postulated pore shape associated with the various pretreatments as well as penetration, by the adhesive, into the film produced by CSA and PAA pretreatment but not into that produced by CAA.

9. X-ray photoelectron spectroscopy analysis has indicated that the locus of failure is, indeed, very close to the interface. Some change in matrix chemistry has been detected—increase in C—O content on exposure of the joint to 'hot/wet' conditions.

10. Early indications from EELS analysis show how powerful a tool this technique could be.

Figure 21. Electron energy-loss spectroscopy analysis for phosphorus in a section through a phosphoric acid anodized bonded joint (poor quality); bound phosphorus in the 'oxide' film can just be discerned.
REFERENCES

The Use of Scanning Probe Microscopy for Mapping Surface Topography

(J N Leckenby & A J Murray, J K Instruments Limited *)

Introduction:

In 1986, Binnig and Rohrer were awarded the Nobel Prize in Physics for their discovery of the scanning tunnelling microscope(1). This was the birth of a series of techniques which has become an exciting new area of analytical science - the field of scanning probe microscopy (SPM). Since then, the field of SPM has developed into a broad family of techniques enabling surface scientists to reach a better understanding of the surface topography of their particular material. Whether they be working with a polymer, a semiconductor or a biomaterial, the field of SPM has opened up a whole new range of ways to study the surface of a material and it's properties.

SPM is defined generically as follows: a technique that involves the movement of a probe across a surface to generate an image representative of a specific physical property of the surface under study.

Early studies using STM involved the measurement of the current generated when a sample, held at a given potential, was scanned by a very sharp tip (usually a wire made from tungsten or platinum/iridium). The resulting tunnelling current could be related to the topography of the surface of the material. The technique was particularly exciting because it enabled the scientist to look at the atomic spatial positions of a material.

Much of the early work was performed under ultra high vacuum conditions. The attraction of the technique today is that the user may now work in air or even liquid.

The restriction of STM is that the material under study had to be conducting. Thus, the true arrival of the family of techniques known as SPM came with the discovery of atomic force microscopy (AFM) by Binnig et al (2) which did not require a conducting surface and hence opened up the ability to image the topography of all surfaces, conducting or otherwise. Using the measurement of the response of a tip with respect to the surface of a material (repulsive or attractive), it has become possible...
to follow the changes in topography of a sample with respect to a wide range of changes in physical condition, e.g. in air, in liquid, under charge, in a magnetic field, under changing electrochemistry. The full family of SPM techniques is growing continually and is one which is destined to become one of the mainstream analytical techniques in the coming years. In this paper, a description of SPM will be given and this will then be applied to a series of practical examples where the technique has been used to help understand the mechanism of certain physical and dimensional changes of a material.

Within AFM, it is important to understand that there are different modes of imaging possible depending on how far above the surface the user is making the measurements (3). This may also be dependent on the sample being studied - whether it is a hard or soft material.

The basic AFM mode of operation is known as the contact or DC mode. Here, the tip is held a few angstroms above the surface. Interaction between the surface and the tip is caused by repulsive forces. This mode may be used to study most materials and is the simplest method of operation of AFM.

An alternative method of measurement is known as the non-contact or attractive mode. In such measurements, the tip is held some tens of angstroms above the surface and is oscillated at a frequency above its natural resonant frequency. Such a method is recommended in the study of soft materials such as biological and certain polymeric specimens. The downside of this method is a loss in lateral resolution as compared to the contact mode.

What is a scanning probe microscope?

Three values differentiate SPM from all other types of microscopy:

* extremely high resolution
* three dimensional magnification
* operation in a diverse range of environments

Traditional microscopy has given quantitative measurements of distances in two dimensions, usually in a plane perpendicular to...
the focusing optics, e.g. scanning electron microscopy. However, SPM enables the user to work in three dimensions with the added bonus of depth of field studies.

Key to the construction of an SPM system is the use of piezoelectric materials. These are electromechanical transducers that undergo a change in physical dimensions when activated by a voltage source. This capability enables the control of motion down to fractions of an angstrom.

The STM comprises an x,y,z piezoelectric scanner, a sensor for measuring the tunnelling current, feedback electronics for controlling the z piezo ceramic and electronics for rastering the x and y piezoelectric ceramics. A computer completes the system for control, image acquisition, storage and processing.

The atomic force microscope is similar to the STM with the exception of the sensing device. The sensor in the AFM uses a laser beam that deflects off a small cantilever onto a multi-section photodetector. When the tip is rastered across the surface of the sample, repulsive or attractive interactions between the tip and the surface cause the cantilever to move up or down. This results in a change in the light falling on each section of the photodetector. In turn, this provides a feedback signal for controlling the z piezoelectric ceramic which is used for the calculation of the z height topographic information.

Experimental considerations

Sample preparation for an SPM experiment is usually minimal. Dependent on the design of the instrument, the user may study a small sample, e.g. 10mm x 10mm x 2mm mounted using double sided tape. If the sample is much larger, there are instruments designed to be placed directly on top of the sample (4). Such flexibility enables a broad range of samples to be studied in a wide range of environments.

One of the most important considerations for the user is the choice of tip or probe used in the study. In STM, probes may be made from wire such as tungsten or platinum/iridium. While preparation of such tips may be made by just cutting the wire with a pair of wire snips, the best tips are usually prepared using a chemical etching process.

cont/...
In AFM, the field of tip technology is growing very rapidly. The tips used in the majority of work are made from silicon nitride. Typically, these are pyramidal in shape, the pyramid having a base and height of 4 microns with a point of less than 500 angstroms. However, for the study of certain materials, tips with a higher aspect ratio are required. Such tips may be grown onto the silicon nitride pyramid in an SEM, electron beam deposition producing a carbon-like material giving a tip of less than 100 angstroms at the end of a two micron long finger. More recently, ion-milled tips of similar dimension have started to become available.

Another material being used for tips is silicon. Being stiffer than silicon nitride, silicon tips are better suited to measurements in the non-contact mode where the user may choose cantilevers of different stiffness dependent on the type of sample being studied. Silicon tips are also used as the core of the new range of coated tips introduced for techniques such as magnetic and electrical force measurements where cobalt and platinum respectively may be put down in a very thin layer on the silicon.

Silicon tips are being used in the growth area of force distance curve measurements where quantitative information on the interaction of a tip with a surface may be studied.

Applications of SPM

It is next to impossible to place limitations on the use of SPM. Resolution is such that it may be used to study the surface topography of materials to a level of a few angstroms. The paper will show a range of the myriad of applications being studied using SPM. The majority of the images to be shown will have been made in air or in liquid highlighting the relative ease of sample preparation and the range of materials which may be imaged. Examples will include semiconductor and polymer studies as well as taking a look at some biological applications. With the subject of adhesion being one of the driving forces behind this meeting, examples will also be given as to how the AFM may be used to quantify binding forces between species.
Conclusions

The range of applications and new techniques is growing monthly as evidenced by the continuing increase in publications on the subject. Whereas ten years ago, all instruments were home-built, off-the-shelf systems are now readily available. One of the newest commercial techniques is the scanning near-field optical microscope (6,7) which offers optical resolution beyond the diffraction limit and the potential of chemical information when combined with spectroscopy studies (8). Then, there is the scanning thermal microscope...the list goes on. The techniques of SPM are here to stay and grow much further in the coming years.

References:


3) AFM Imaging Modes, TopoMetrix Corporation publication, 5-0293-002 (1993)


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MEASUREMENT OF ADHESIVE-ADHEREND INTERLAYER PROPERTIES USING ACOUSTIC MICROSCOPY

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INTRODUCTION

There is considerable uncertainty about the mechanism of adhesive bonding and, in particular, the changes occurring during environmental attack which greatly reduce the bond strength [1]. This lack of understanding hampers the development of better adhesive systems and also makes the development of non-destructive evaluation methods very difficult since it is not certain what properties should ideally be measured.

The standard surface pre-treatments used on aluminium adherends in aerospace applications produce a honeycomb-like oxide structure on the adherend surface, and the adhesive (or primer if one is used) penetrates some distance into the honeycomb cells, the depth of penetration depending on the pre-treatment used and on the viscosity of the primer or adhesive. The overall thickness of this 'interlayer' between the bulk adhesive (or primer) and the bulk adherend in a typical aluminium-epoxy joint is typically only of the order of 1µm and, even over this distance, its properties may be a function of depth depending on the adhesive penetration and the honeycomb structure. It is therefore extremely difficult to measure the mechanical properties of the interlayer.

Recent developments in acoustic microscopy have made it possible to carry out accurate wave velocity measurements at frequencies up to 1 GHz where the wavelength approaches 1 µm, the velocity being obtained by Fourier analysis of the V(z) curve [2]. If these measurements could be carried out on samples with the complex structure found in the interlayer of adhesive joints, it would be possible to measure the velocity of a surface wave whose energy is predominantly contained within the interlayer. This opens up the possibility of measuring the properties of the interlayers produced by different surface preparations, and also of monitoring the changes which occur during environmental attack.

Most previous quantitative acoustic microscopy of multi-layer systems has been done at frequencies around 200-400 MHz, and has been limited to relatively simple, low attenuation systems such as gold plated silicon wafers (see, for example, [3,4]). It was therefore necessary to demonstrate that satisfactory measurements could be obtained on the much more complex structures found in adhesive joints where a honeycomb oxide structure is partially penetrated by an attenuative polymer (the adhesive or primer). In order to do this, tests have
been carried out using 225, 820 and 980 MHz centre frequency lenses on plain, polished aluminium, polished aluminium coated with thin layers of polymer, anodised aluminium and anodised aluminium coated with polymer. This preliminary study is reported here.

EXPERIMENTS

An aluminium/lithium alloy (8090) was used as the substrate for the experiments. Quantitative Acoustic Microscopy (QAM) requires a good surface finish, ideally with local flatness to within a tenth of a wavelength, or about 0.3 µm at 1 GHz. It was therefore necessary to polish the aluminium prior to measurement.

For the initial experiments on coated samples, it was desirable to use specimens coated with a small, well controlled thickness of polymer. This was most easily achieved by spin coating PMMA onto a polished aluminium substrate, rather than by attempting to bond a very thin layer of adhesive to the substrate. Various concentrations of PMMA dissolved in toluene were therefore spin coated onto polished aluminium substrates. Adhesion to the substrate was not found to be a problem, and the resultant coating was reasonably uniform, with PMMA concentrations of 3% and 10% yielding coating thicknesses of approximately 0.2 and 1 µm respectively, as measured by optical spectrophotometry.

The anodised specimens were produced by phosphoric acid anodisation (PAA) of polished aluminium substrates, the thickness on the samples used in this investigation being approximately 0.2 µm. The thickness was determined by taper polishing, and checked by examining the cross-section in a scanning electron microscope.

Measurements were taken using three different acoustic lenses, with centre frequencies of 225, 820 and 980 MHz. The 225 MHz lens had a cylindrical cavity, while the other two lenses had spherical cavities. When using the higher frequency lenses it was necessary to heat the water used as couplant to about 50°C, in order to reduce the attenuation. Twenty five measurements were made at each frequency over a small area of the surface, and this enabled an assessment of the accuracy at each frequency, as well as giving an indication of the scatter due to the inhomogeneity of the samples.

RESULTS

General

It had initially been thought that the highly inhomogeneous nature of the oxide might preclude acoustic measurements, but it was found that good quality V(z)s were easily obtainable between 225 and 980 MHz. A second potential source of difficulty, namely the attenuative nature of the PMMA coating, was not significant for the thicknesses of coating employed. Figs 1a, 1b, 1c, 1d, 1e and 1f show V(z) curves obtained with the 225 MHz lens for polished aluminium, anodised aluminium, polished aluminium coated with a 0.2 µm layer of PMMA, polished aluminium coated with a 1.0 µm layer of PMMA, anodised aluminium coated with a 0.2 µm thick layer of PMMA and anodised aluminium coated with a 1.0 µm thick layer of PMMA respectively. Fig 2 shows the corresponding results obtained with the 980 MHz lens. The signal-noise ratio is much poorer on the V(z) curves at 980 MHz, but satisfactory analysis could still be carried out.

There are two main qualitative differences in the raw data between the various specimens. The first is a difference in the periodicity of the oscillations near focus: the oscillations are associated with various types of acoustic wave propagating along the surface, and a change in the periodicity represents a change in the velocity of the wave. This effect is small for most of the specimens, and not easily detectable by eye. The second difference is much more striking, and may be seen by comparing the V(z)s at 225 MHz obtained on aluminium coated with 0.2 µm and 1 µm layers of PMMA (Figs 1c and 1d). A second mode with a larger periodicity begins to dominate the V(z), particularly at higher negative defocus. This mode is called a pseudo-Sezawa wave, and is characteristic of certain coating-substrate combinations. The pseudo-Sezawa wave is highly dispersive, and QAM is therefore extremely sensitive to changes in the thickness or elastic constants of the layer when this mode is strongly excited.
Fig. 3 shows the velocities of the mode closest to focus, i.e. the Rayleigh type mode, obtained at 25 points within a 4 mm² area for the polished aluminium and a 1 mm² area for the anodised materials. One reason for the scatter in velocity is the polycrystalline nature of the substrate. At 225 MHz, the insonified area averages over approximately 10 grains at average values of defocus. When the frequency is increased to 980 MHz, the insonified area is comparable to that of a single grain. This indicates the sensitivity of the technique, since the error at each individual point is usually much smaller than the overall scatter. Aluminium is only weakly anisotropic, and any effects due to texture are not noticeable for this orientation of 8090. Summaries of the Rayleigh type mode velocities measured at each frequency are presented in Table 1. The scatter in velocity is quite high for some of the materials, and this can result from surface roughness, weak excitation of the SAW, or non-uniformities in the layer thickness. These effects are discussed in more detail in the next section. It would be expected that the Rayleigh wave on the polished aluminium sample would be non-dispersive, so the velocities at 225, 820 and 980 MHz would be the same. The difference between the measured velocities at 225 MHz and the two higher frequencies exceeds the estimated error bounds due to random effects and appears to be due to a small systematic difference between the measurements made with the three lenses.

Errors in QAM

The best figures quoted for line-focus beam acoustic microscopy at 225 MHz are a relative error of 0.01% and an absolute accuracy of 0.05% in the velocity [5]. Such figures
Figure 2. \( V(z) \) curves at 980 MHz on different samples.

Table 1. Summary of measured SAW velocities. (The quoted errors refer to the scatter across the material, and do not include systematic errors in the analysis.)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>SAW velocity (m/s)</th>
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<tbody>
<tr>
<td></td>
<td>@ 225 MHz</td>
</tr>
<tr>
<td>Polished Al (8090)</td>
<td>3225 ± 5</td>
</tr>
<tr>
<td>Polished Al + 0.2 µm PMMA</td>
<td>3215 ± 5</td>
</tr>
<tr>
<td>Polished Al + 1.0 µm PMMA</td>
<td>3140 ± 25</td>
</tr>
<tr>
<td>Anodised Al</td>
<td>3205 ± 10</td>
</tr>
<tr>
<td>Anodised Al + 0.2 µm PMMA</td>
<td>3175 ± 10</td>
</tr>
<tr>
<td>Anodised Al + 1.0 µm PMMA</td>
<td>3060 ± 25</td>
</tr>
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</table>
apply only to ideal single crystal materials, and the errors are considerably higher for the inhomogeneous materials studied here. One cause of increased error is surface roughness. Li [6] has calculated the effect of periodic surface roughness on Rayleigh wave velocities as measured at 225 MHz in the LFB acoustic microscope. He found that the change in velocity from that for a smooth surface varied from 0.2% for a height/period ratio of 0.1 with 1 µm period, to 3% for a height/period ratio of 0.3 with 3 µm period.

A second cause for increased errors is inhomogeneity, since this increases scatter in the near surface region. In mild cases, the predominant effect is to increase the attenuation of the SAW. If the attenuation is sufficient to reduce the number of oscillations to two or three, then the errors in the estimation of the velocity from the Fourier analysis can become as high as a few percent. A similar effect can arise when more than one mode is present in the V(z). An example is shown in Fig 1f, where the Rayleigh-type mode, i.e. the mode closest to focus, is not the predominant mode at 225 MHz. Only two or three oscillations associated with this weakly excited mode are present in the V(z), and this can lead to large systematic errors in the analysis as mentioned. Although it is possible to correct for the peak position in the FFT of a highly attenuated sinusoid [4], this is again only really effective on reasonably homogeneous materials.

Table 2. Estimated standard deviations in velocity for V(z) analysis on polished aluminium.

<table>
<thead>
<tr>
<th></th>
<th>Frequency (MHz)</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>225</td>
<td>820</td>
<td>980</td>
<td></td>
</tr>
<tr>
<td>Relative error at a single point (m/s)</td>
<td>2.0 (0.06%)</td>
<td>10 (0.3%)</td>
<td>8 (0.25%)</td>
<td></td>
</tr>
<tr>
<td>Absolute accuracy (m/s)</td>
<td>10 (0.3%)</td>
<td>40 (1.2%)</td>
<td>30 (0.9%)</td>
<td></td>
</tr>
<tr>
<td>Scatter along specimen (m/s)</td>
<td>3.5 (0.1%)</td>
<td>15 (0.5%)</td>
<td>18 (0.6%)</td>
<td></td>
</tr>
</tbody>
</table>
The difficulties with inhomogeneity and roughness tend to increase as the frequency is increased, and there are two reasons for this. Firstly, the wavelength is decreased, and secondly, a smaller area is insonified by the acoustic lens, since the focal length of the lens must be reduced owing to higher attenuation in the water at high frequencies. The shorter focal length means that less negative defocus is available. This in turn can result in fewer oscillations being available, which decreases the accuracy of the analysis. Particularly at high frequencies, the combination of two modes, roughness and inhomogeneity can make the $V(z)$ extremely difficult to interpret. An indication of the errors for the Rayleigh mode obtained in tests on the plain, polished aluminium sample is given in Table 2.

The relative error in Table 2 refers to a series of 25 $V(z)$s taken at the same point on the specimen. At high frequencies, the values are considerably greater than at 225 MHz since the measurements themselves are considerably noisier, and a smaller range of negative defocus is available. The absolute accuracy refers to uncertainty in the analysis for a single $V(z)$, and has been estimated by conducting the analysis using windows of different shapes [7], and over different regions of the $V(z)$. Temperature effects and differences between the lenses, which might result in an offset in the velocity are not included in these figures. The accuracy is lower at 820 MHz than at 980 MHz because the range of negative defocus is the same for both lenses, and hence fewer oscillations are available for analysis at 820 MHz. The scatter has been estimated by taking 25 $V(z)$s in an area of 4 mm$^2$, and is higher at high frequencies since averaging is only over one or two grains for any single measurement, and reflections from grain boundaries are more significant. All the figures in Table 2 are approximately two to three times higher than on a more uniform material such as glass.

PMMA on polished aluminium

The aluminium substrate and PMMA coating were modelled as isotropic materials using literature values for the elastic constants and density. The calculated SAW dispersion is shown by the solid and dashed lines in Fig 4, whilst the measured velocities are marked by crosses, circles and squares for frequencies of 225 MHz, 820 MHz and 980 MHz respectively.

The pseudo-Sezawa mode in Fig 4 begins with a predominantly longitudinal polarisation, and is excited fairly weakly. However, the shear vertical component increases quickly with increasing frequency or thickness, so it becomes strongly excited in the acoustic microscope. The measurements agree well with the calculated dispersion curve, although measurements at intermediate frequencies would help greatly to fill the curves out. At higher thicknesses and frequencies, there are a large number of available modes, and a $V(z)$ calculated from the reflectance function will probably provide the easiest method of determining which mode is excited most strongly.

Anodised aluminium

Fig 5 shows the measured velocities on the plain and anodised samples, together with predictions for different levels of porosity made using the model described by Wang and Rokhlin [8] and also used by Cawley and Pialucha [9,10]. The curve labelled A was obtained using the properties which were found to fit best to the properties of a 43 µm thick sulphuric acid anodised (SAA) oxide layer [10]. The measured velocities at 820 and 980 MHz have been reduced by 25 and 50 m/s respectively in order to remove the apparent systematic error discussed above, so making the results with the three lenses the same on the plain, polished sample (the zero frequency-thickness points). The large error bars in the frequency-thickness direction for the measurements on the anodised sample are due to uncertainties in the thickness of the oxide layer which varied from its average 0.2 µm in the region of grain boundaries.

It can be seen that the measured velocities are not consistent with any of the calculated curves. However, the predictions as a function of porosity were made using cell wall properties corresponding to pure, fully compacted alumina, whereas the cell wall material formed during anodisation is more likely to be a relatively open array of amorphous alumina.
Figure 4. SAW dispersion curves for PMMA coatings on polished aluminium.

Figure 5. SAW dispersion curves for anodised aluminium. Measured results are for oxide thickness 0.2 μm.

microcrystallites, permeated by molecular water and with the surfaces of the crystallites carrying hydroxyl ions or groups [11]. The material is also likely to contain as much as 12-15% by weight of acid anions. Some discrepancy with the predictions would also be expected since the model assumes that the oxide cell structure is uniform with all the cells oriented normal to the interface. However, this is unlikely to be the case [11]. It is therefore
not surprising that the acoustic measurements do not give good agreement with the calculations. The measurements also do not correspond to the predictions using the properties measured on an SAA oxide layer. However, the SAA layer on which the earlier results were obtained was 43 μm thick compared with the 0.2 μm thick layer tested here, and phosphoric, rather than sulphuric, acid anodisation was employed in the current tests. The morphology and composition of the oxide layers can vary significantly with the anodisation conditions [12], so good agreement with the earlier work would not necessarily be expected. It is proposed to obtain high resolution transmission electron micrographs of the oxide layer in order to obtain more information about its morphology, and also to test a variety of oxide layers formed under different conditions. It should be noted that the oxide layer tested here was only 0.2 μm thick, compared with the industry standard 0.6 μm thickness for PAA surface treatment and 3.5 μm for CAA (chromic acid anodisation). Larger changes in velocity would be expected with these thicker layers.

CONCLUSIONS

Quantitative acoustic microscopy has been used to measure surface wave velocities on polished and anodised aluminium substrates, both with and without PMMA coatings spun onto the surface. Good quality V(z)s were obtained at frequencies between 225 and 980 MHz, and demonstrated the sensitivity of the technique to the presence of a 0.2 μm oxide layer and a 1.0 μm PMMA coating. It was thought to begin with that the anodised surface might be too rough or the PMMA coating too attenuative for successful measurement at 980 MHz, but neither of these effects has proved problematic. The highly dispersive nature of the pseudo-Sezawa mode excited on some of the coatings means that QAM is extremely sensitive to small changes in the material parameters.

Good agreement has been obtained between the SAW dispersion measured on the PMMA coated aluminium, and that calculated by a simple isotropic layer model. Work on predicting the dispersion behaviour on the anodised aluminium is at an early stage, more information about the morphology and composition of the oxide layer being required. This study is continuing and it is hoped to present more results at future meetings.

REFERENCES

One of the overriding aims of adhesion science is to understand and exploit the relationships that exist between the microscopic nature of an interface and its macroscopic properties. Such a fundamental understanding requires knowledge of the molecular structure and orientation of the adsorbed overlayer molecules, a description of their chemical bonding to the surface and the detailed geometric characteristics of the adsorption site at an atomic level. One surface analytical technique that is extremely powerful for elucidating such details is vibrational spectroscopy. In this talk, the potential of IR spectroscopy and Electron Energy Loss Spectroscopy (EELS) in understanding many fundamental aspects of adhesion will be reviewed. In particular, results will be presented on model interfaces representing the action of epoxy resins and novolak resins on metallic and oxidised surfaces. In each case, the performance of state-of-the-art instruments in providing detailed molecular information at submonolayer, monolayer and multilayer coverages will be demonstrated.
Recent Developments in the Application of XPS to Adhesion Science

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Over the last two decades X-ray photoelectron spectroscopy (XPS) has become the surface analytical method of choice for use in adhesion science investigations. This position is a result of the ability of XPS to provide a quantitative surface chemical analysis from virtually all materials. In depth information can be obtained in a non-destructive manner for layer thicknesses of up to about 5nm, and for metallic and inorganic materials XPS may be used in conjunction with inert ion sputtering to produce chemical compositional profiles to depths of up to 1μm.

As a result of this versatility XPS is routinely used to determine contamination levels on substrates prior to bonding, the exact locus of separation from failed joints, the segregation of aggressive species and minor components of the adhesive formulation to the locus of failure and the orientation of molecules at that point. In short a great deal can be said about the failure characteristics of an adhesive joint by the judicious application of XPS to "mirror" specimens taken from both sides of the failure surface.

In order to fully understand the failure mechanism of an adhesive joint or organic coating following environmental exposure it is helpful to have information regarding the interphase chemistry of the joint prior to failure. Acquiring such analytical information is not straightforward as the interphase region between metal oxide and polymer will necessarily be buried between many micrometres (or even millimetres!) of material. There are various methods that have been developed at the University of Surrey to approach this region and they include dissolution of the polymer or inorganic phase, in-situ taper section followed by XPS and the deposition of ultra-thin layers which enable the interphase chemistry to be probed directly. Examples of these methodologies will be provided and an indication of the quality of data attainable given.

In recent years there have been two major developments in XPS instrumentation which have had a great impact on the application of XPS to adhesion science: the introduction of imaging XPS (iXPS) and the commercialisation of a monochromated photon source based on a high power rotating X-ray anode. The latter when combined with a very high transmission electron energy analyser provides an electron spectrometer with the potential for both extremely high spectral resolution and very good counting statistics.

The advent of iXPS has enabled mixed mode fracture surfaces to be examined by XPS in a meaningful manner and areas of residual polymer can now be identified explicitly
in the XPS image. Of perhaps more importance is the ability to produce chemical images based on the XPS chemical shift phenomenon; this is probably the more daunting task as the manufacturers are driving towards ever smaller image resolution (at present around 1µm) rather than concentrate on optimum chemical resolution. Examples will be provided that indicate the potential of this approach for surface microanalysis using XPS.

In the analysis of the adhesives applied to insulating substrates (such as alumina which is widely used in the microelectronics industry) there is sometimes the possibility that chemical information present in the XPS spectrum may be masked by vertical differential charging. This can be overcome by the use of a monochromated X-ray source and the management of surface charge by the use of an electron flood gun. This enables the chemical information to be extracted quite readily. As some polymers are sensitive to X-radiation there is often a well-defined time window within which the XPS analysis must be acquired. The advent of high transmission analysers has enabled meaningful studies to be made of such materials, this is of particular importance when there are thin layers of a polymer remaining on a substrate after failure. Illustrations will be provided of these aspects of XPS with examples taken from studies of photocured resins used in the microelectronics industry.

The correlation of XPS data with other analytical results can often be beneficial. In recent work angle resolved XPS of thin (1-2nm) overlayers has been confirmed by the use of computer chemistry methods. XPS was able to identify the composition of the organic material at the failure interface, whilst computer modelling showed that the overlayer thickness was consistent with the most energetically favourable orientation of a monolayer of a minor component of the formulation, which had segregated to the interface prior to cure. Reformulation of the product without the minor component lead to improved durability and a rather different locus of failure.

In conclusion there are many facets of XPS which provide invaluable analytical data to the adhesion scientist. Most of these require careful interpretation of the XPS data, careful design of the XPS experiment and much ingenuity in the manner in which the specimen is presented for analysis. In a busy analytical laboratory it is perhaps not surprising that such opportunities are often missed as they all require analyst's time and instrument time: both are which are a valuable and expensive resource!

JFW
1.12.94
Time-of-Flight SIMS in Surface Analysis
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In secondary ion mass spectrometry (SIMS), a sample surface is bombarded with a primary beam of energetic particles, normally ions. This results in the emission of a range of secondary particles, including positively and negatively charged atomic and molecular species. These secondary ions are subsequently mass analysed to provide elemental and detailed chemical structure information.

SIMS using mass analysis by the Time-of-Flight method involves the use of a primary ion beam which is pulsed to produce packets of primary ions. These primary ion packets, of nanoseconds duration (typically 1 - 50 ns), bombard the sample surface and generate packets of secondary ions at a well-defined point in time. These secondary ions are then accelerated to the same kinetic energy (several keV) into the analyser. Secondary ions of different mass-to-charge ratio will have different velocities and will spread out in time. Their flight times through the analyser to the time-sensitive detector are measured to produce a mass spectrum. It should be noted that ToF-SIMS analyses of insulating materials are facilitated by using pulsed electron flooding in order to compensate for sample charging.

ToF-SIMS is characterised by a number of features which renders it particularly suitable for the study of organic and polymer surfaces. Firstly, the practical mass range is m/z 0 - 10,000. This capability can, for example, be exploited for the analyses of polymer and co-polymer structures and, in some cases, can also be used to provide molecular weight information. It is important to note that whilst this practical mass range capability exists, most polymeric systems do not yield ions above m/z 2000 and, indeed, the effective information range is often restricted to m/z 0 - 1000. In the case of discrete organic molecules, the detection of secondary ions above their molecular weight(s) are not expected unless, for example, such molecules are complexed with other species.

ToF-SIMS is generally characterised by good analytical sensitivity which derives, in part, from the high instrumental transmission and quasi-simultaneous detection of secondary ions in the ToF-SIMS experiment.
The sensitivity, however, is highly dependent upon the elemental, cluster and/or molecular secondary ion yield(s) associated with each of the species present in the sample under study.

The advent of high mass resolution (up to $M/\Delta M = 10,000$), one of the more recent developments (in practical terms, for both conductors and insulating materials), realises the full potential of ToF-SIMS as a surface mass spectrometry. This capability 'resolves' the problem of overlapping peaks of secondary ions with the same nominal mass and translates into the level of accurate mass measurement which is necessary for the identification of secondary ion signals. High mass resolution is also important in terms of the analytical sensitivity which is achievable for many elemental and molecular species. The practical detection limits of such species are often restricted by mass overlap.

In addition to mass spectra, it is possible to obtain chemical images by scanning a highly focussed primary ion beam over a selected area of the sample and collecting the secondary ions at each point. This form of chemical mapping can be carried out for both elemental and molecular species. Features of scanning ToF-SIMS include the ability to acquire a large number of chemical images simultaneously and the facility to integrate a number of secondary ion signals into each image. More recently, the capability of spectrum-per-point analysis has been developed whereby, for a given sample area, the spectrum at each pixel point (e. g. a 256 x 256 array) is acquired and stored. Chemical maps and selected area spectra can then be generated retrospectively.

An important feature of ToF-SIMS is that analyses can normally be carried out under experimental conditions which are effectively non-damaging (static) to the sample surface under study. This corresponds to the use of very low primary ion doses in the ToF-SIMS experiment, and is clearly an essential requirement for the characterisation of organic and polymeric materials which are rather sensitive to damage by ion bombardment. Finally, in its static mode, the ToF-SIMS technique is very surface specific with a sampling depth of only 1-2 monolayers.

The capabilities of ToF-SIMS as a surface mass spectrometry for the characterisation of organic and polymer surfaces will be illustrated by recent studies in the areas of adhesives and coatings.