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The contributions of surface analysis to adhesion research

John F. Watts
Surrey Materials Institute and School of Engineering, University of Surrey, Guildford, Surrey GU2 7XH, UK.
E-mail: j.watts@surrey.ac.uk

Introduction

The last four decades have seen a tremendous growth in the application of surface analysis methods in fields as diverse as metallurgy, corrosion, catalysis, polymer technology and microelectronics, to name but a few. One area that has benefited enormously from these techniques is the field of adhesion science; in other words the reasons why materials stick to each other! Before justifying this statement, a few words about surface analysis methodologies are in order. Techniques which provide a surface-specific chemical analysis are often based around electron or ion spectroscopies and, although there are many such techniques, the ones which are most widely used and most commercially developed are X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These techniques are fully described in recent text books,[1–3] and the intention is not to describe them in any detail in this article, merely to pick up on important points relevant to adhesion science as required. Suffice to say at this point that the techniques use X-ray photons (XPS), a finely focussed electron beam (AES) or a beam of monoatomic or polyatomic ions (ToF-SIMS) to yield an analysis by electron spectroscopy (XPS and AES) or mass spectrometry (ToF-SIMS) that emanates from the outer few nanometres of the solid sample under examination. This is particularly useful in the examination of commercial formulations that contain low concentrations of small molecules. Such molecules may segregate as very thin layers at interfaces to enhance adhesion or act in a deleterious manner to bring about failure.

It is this surface sensitivity that makes these techniques so attractive to the adhesion scientist, as the forces responsible for adhesion in, for instance a structural adhesive bond in an aircraft, operate at only very short length scales, typically of the order of 1 nm. Thus, in principle, surface analysis should be able to identify the chemistry at an interface that is responsible for adhesion, and in the most advantageous cases reverse engineer the interphase chemistry in order to provide insight into the required durability, toughness and so forth in the component. Approaching the interphase region is an extremely complex procedure, but examples of how this can be achieved will be given in a later section of this article. If one was to survey the applications of surface analysis in adhesion research it would be clear that there are three specific areas in which XPS, AES and ToF-SIMS have been applied. First, there is the examination of a substrate surface prior to bonding or coating and the correlation of its surface chemistry with subsequent performance. Second, the forensic analysis of the failure of interfaces of adhesive bonds, organic coatings or polymer matrix composites can tell one much about the cause of failure and sometimes indicate the bonding mechanism itself. Finally, there is the use of surface analysis to understand the molecular mechanisms of adhesion. In a recent review the author of this article described the latter category as the holy grail of adhesion research, as it points the way to the control of interface chemistry to obtain specific properties.[4] In the following sections examples are provided of the manner in which surface analysis can be used in order to help advance our understanding of adhesion phenomena.

Control of surface characteristics prior to bonding

One of the most basic requirements for a good bond between a substrate and an adhesive is that the substrate is free from contamination that may interfere with the formation of a good bond between the substrate and the mobile organic phase. An interesting example of the manner in which XPS can be of use in such a situation is the following case history, taken from the aerospace industry, relating to the bonding of composite surfaces which had been protected following manufacture by the use of peel ply release films. These films are removed immediately prior to bonding; easy removal is facilitated by the presence of low surface energy release agents, in this case based on fluorocarbon chemistry. Although they allow the easy removal of peel plies any residual release agent remaining on the bonding surface will obviously compromise the integrity of the adhesive bond. The data of Figure 1 show the relationship between the concentration of release agent remaining on the surface, following various cleaning regimes, prior to bonding against, on the left-hand side (LHS) axis, the relative strength of the bond fabricated from components cleaned in this manner. The right-hand side (RHS) axis indicates how the failure interface passes through the adhesive when there is no release agent present and gives rise to a strong joint but as the amount of release agent increases so the joint strength falls and the failure interface passes to the adhesive/substrate
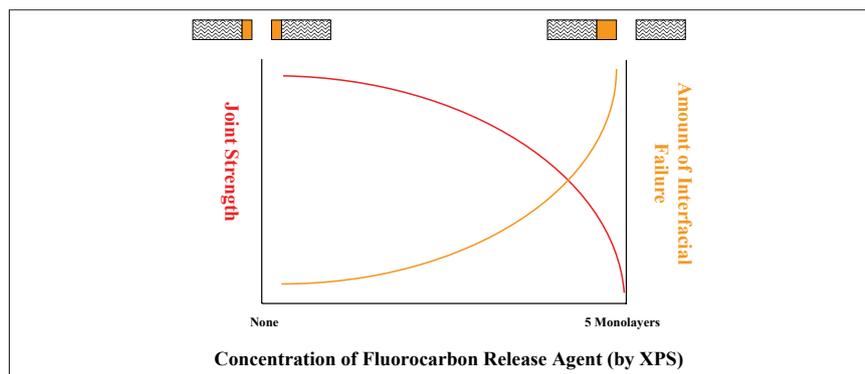
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Figure 1. Correlation between residual release agent on a composite bonding surface and joint strength (LHS axis). As the strength reduces so the locus of failure changes from a cohesive failure in the adhesive (RHS axis and upper left schematic) to an interfacial failure between composite and adhesive (upper right schematic).
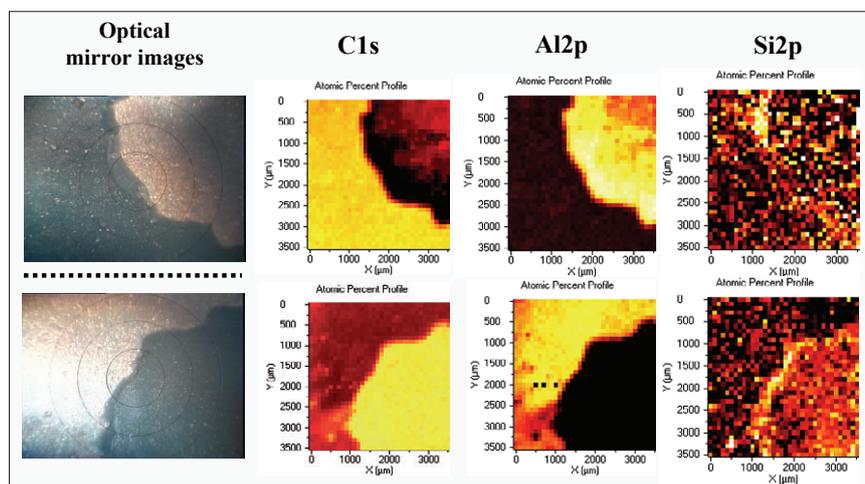

Figure 2. XPS images of the fracture surfaces taken from adhesively bonded aluminium using a structural epoxy adhesive with an addition of 1% organosilane adhesion promoter. (Courtesy of Dr M.-L. Abel, University of Surrey.)

interface. Although this is all very intuitive, it was not until the advent of XPS that it was possible to design a quality control process based on the amount of release agent remaining rather than the detailed specification of the cleaning process itself.

Forensic analysis of failure interfaces

As indicated above, the locus of failure often provides a clue to the chemical nature of the failure and any shortcoming in the production process. The XPS images of Figure 2 are taken from the failure surfaces of a failed adhesive joint tested in a wedge cleavage geometry (Boeing Wedge Test). This work is part of an ongoing programme to investigate the mode of action of organosilane adhesion promoters when incorporated into the formulation of a commercial structural adhesive. These images were acquired by recording small area (100 µm diameter X-ray spot size) XPS spectra and rastering the specimen stage of the spectrometer over a 3 × 3 mm area in steps of 120 µm. Once the data set of high-resolution spectra and an XPS survey spectra at each pixel point has been acquired, retrospective images of the type displayed in Figure 2 can be constructed. Figure 2 shows the complementary mirror image interfacial failure surfaces, correlation between the coloured chemical maps and the optical images of the failure surfaces (LHS of Figure 2) allows the failure to be characterised as interfacial with complementary carbon and aluminium images being

seen. The carbon images show that there are very small amounts of carbon on the metallic substrate after failure and that it is not uniform. In a similar vein, the silicon maps show that residues of the organosilane adhesion promoter are seen in one part of the failure but the other apparently show no adhesion promoter. The reason for this is not clear but one possibility is segregation occurring in the adhesive following application. As a full set of XPS spectra are available at each pixel point, it is possible to process the data using conventional XPS procedures to yield compositional maps, contour lines of thin layers such as metal oxides or (as in this example) residual organic overlayers on metallic surfaces and so forth. The spatial resolution of this example is not high but the best attainable in this mode of operation is c. 15 µm.

The presence of vanishingly thin layers of a single component of a multicomponent formulation at a substrate surface is not unusual, although they can be very difficult to track down, as the following example of the failure of a UV cured paint coating on galvanised steel will show. The coating in question showed good dry adhesion but as soon as it was exposed to moisture, adhesion loss quickly occurred. XPS spectra, this time in the standard area integrating mode of approximately 10 mm^2, from the uncoated galvanised steel substrate and the steel and coating interfacial failure surfaces are shown in Figure 3.[5] Superficially the XPS survey spectra of the bare steel [Figure 3(a)] and the steel failure surface [Figure 3(b)] look very similar, indeed the carbon concentration on the failure surface is actually lower than on the bare steel, but on the failure surface a small amount of fluorine is seen (F1s at c. 686 eV). The chromium is the result of a Cr(VI) surface treatment and the aluminium is an addition made to the zinc bath to prevent the formation of a brittle Fe–Zn intermetallic. The coating failures surface [Figure 3(c)] shows no sign of fluorine, but there is evidence of the presence of chlorine. The radcure coating formulation includes a cure initiator, part of which is a phosphorus hexafluoride anionic component. The fluorine on the metal surface is diagnos-
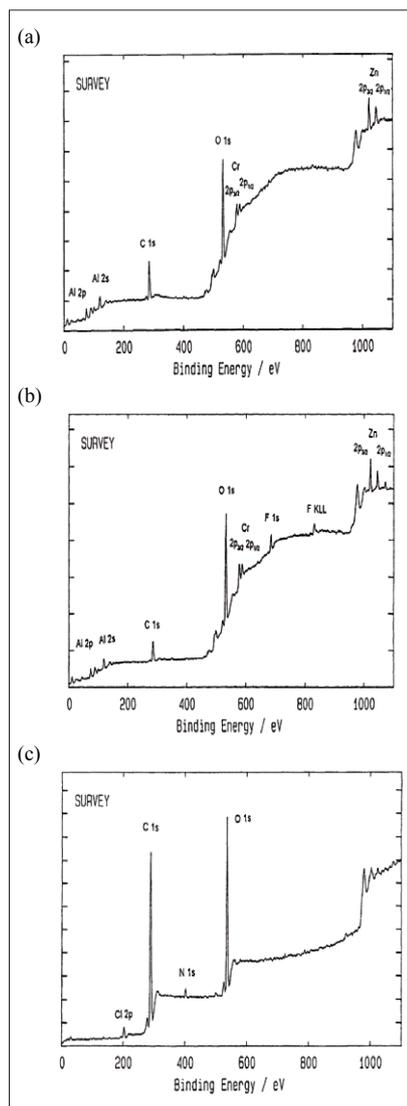
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Figure 3. The failure of a radcure coating applied to galvanised steel. (a) uncoated steel, (b) steel interfacial failure surface, (b) coating interfacial failure surface.

tic of this component and ToF-SIMS indicated a high concentration of this ion in the negative SIMS spectrum. The reason for failure thus becomes clear; the anionic part of the cure package has diffused to the interface to form a segregated layer and the interface between this and the paint film itself is very susceptible to hydrodynamic displacement. The solution to the problem was to reduce the amount of curing agent in the formulation; the mechanical properties of the film were not affected but the adhesion in damp conditions was improved dramatically.
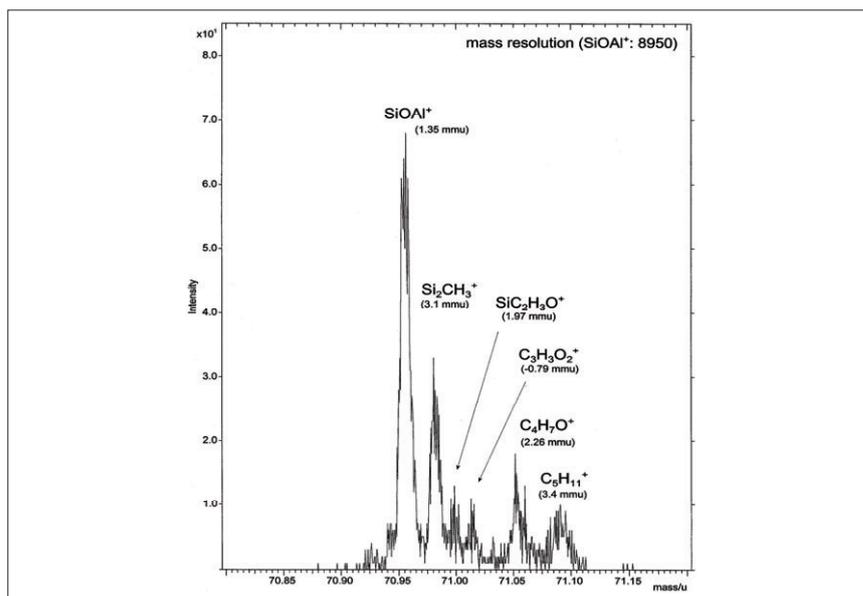

Figure 4. High-resolution positive ToF-SIMS spectrum of aluminium treated with an organosilane adhesion promoter. N.B. Total width of spectrum is *c.* 0.3 u.

Direct examination of interface chemistry

Although it is relatively straightforward to examine failure interfaces in the manner described above, and this may tell us a great deal about the causes of adhesion failure, it will not necessarily provide information regarding the nature of the interfacial chemistry of adhesion. With the current requirement to reduce Cr(VI) emissions, there has been much effort to identify an environmentally friendly pretreatment for the adhesive bonding of aluminium for aerospace applications. One strong candidate is the family of adhesion promoters based on organosilane chemistry and surface analysis has proved to be extremely useful in identifying the manner in which such molecules interact with aluminium surfaces to provide a durable bond. Figure 4 shows high-resolution positive ToF-SIMS spectra of an aluminium surface treated with an organosilane [γ glycidoxypropyl trimethoxysilane (GPS)] primer. The intense peak at $m/z = 70.9521\,u^6$ is assigned to the fragment $AlOSi^+$ and is related to the formation of a covalent bond between the silane and the aluminium surface which occurs in the manner shown in Structure 1.

The alternative to using an adhesion promoter as a primer pretreatment is to incorporate the organosilane into the product formulation. Such a product may be a paint or an adhesive, but care must be taken in extrapolating the results obtained with a primer to the inclusion of the same organosilane in a formulation. Although GPS reacts in the manner described above with aluminium when used as a primer, when added to a formulation this specific interaction is not observed in the ToF-SIMS spectra of the fracture surface. A different silane, γ aminopropyl triethoxysilane (APS), when tested in a high relative humidity, does show the presence of the diagnostic $AlOSi^+$ ion on the failure surfaces as shown in Figure 5.

In recent years a number of methods have been developed in the author's laboratory to prepare specimens to probe the interface chemistry directly.[4] One method that shows much promise is the use of a histological microtome to cut ultra-low angled cross-sections through polymer–polymer and polymer–metal foil interfaces. The general principle relies on the use of specially manufactured angle blocks which enable a cut to be taken almost parallel to the specimen surface. By "almost parallel" an angle of between 0.003° and 2.0° can be chosen by using blocks with out of parallel surfaces in the range of 25 μm to

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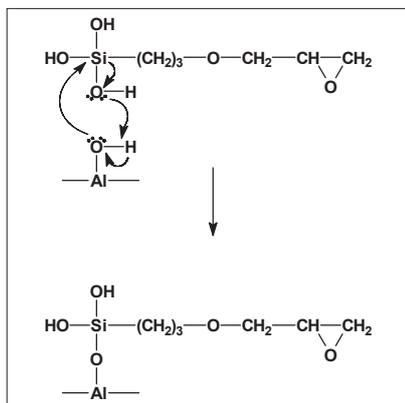
Structure 1

about 1 mm. By using small spot XPS or ToF-SIMS on the sample it is possible to reconstruct a depth profile with a depth resolution of better than 10 nm.[7] An example of this type of work is featured in the false colour ToF-SIMS image of Figure 6. The specimen is a duplex organic coating of a poly(vinylidene fluoride) (PVdF) topcoat applied over a poly(urethane) (PU) primer. The field of view is 500 × 500 μm and the taper has been cut at 0.03°, which means the difference in height between the top and bottom of the field of view is about 250 nm. The false colour image allows the regions of PU (green) to be clearly identified; the characteristic ions of the PVdF region are identified in red but as there is also an acrylic copolymer added to the formulation (blue) the PVdF appears beige. The
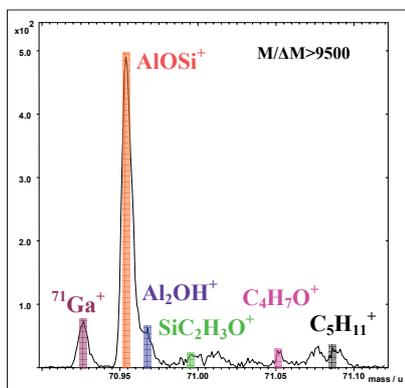
Figure 6. Negative ToF-SIMS image of an ultra-low angle microtome section of a PVdF/PU paint film. The field of view is 500 μm which corresponds to a height difference of 250 nm from top to bottom. The ions used to construct this false colour image were: poly(urethane) $m/z = 66$ u: $C_3H_2N_2^-$, poly(vinylidene fluoride) $m/z = 19$ u: F^-, acrylic copolymer $m/z = 85$ u: $C_4H_5O_2^-$. The blue band clearly identifies the segregation of the acrylic copolymer to the interface between PVdF and PU layers. The presence of this component in the PVdF film gives characteristic beige colouration to this layer. (Courtesy of Dr S.J. Hinder, University of Surrey.)

important observation from this image is the segregation of a layer of acrylic (seen as a blue band across the middle of the micrograph) between the two layers of paint. The purpose of this component in the PVdF topcoat is to enhance adhesion to the primer and it clearly achieves this aim by the formation of a layer some 50 nm thick between the two paints.[8]

Conclusions

It is hoped that this brief article has demonstrated the important role that surface analysis has to play in adhesion research. The examples used have featured XPS and ToF-SIMS as these methods are readily applicable to polymers, and the segregation of small molecules to interfaces, which will invariably be an important component when adhesives and organic coatings are concerned! AES, although not specifically mentioned in this article, has an important role to play in the analysis of metallic substrates prior to bonding or the analysis of the metal interfacial surface of a failure at high spatial resolution.[9]

Figure 5. Positive ToF-SIMS spectra taken from the metal failure surface of adhesively bonded aluminium. The epoxy adhesive used contained 0.5% APS in the formulation. (Courtesy of Dr M.-L. Abel, University of Surrey.)
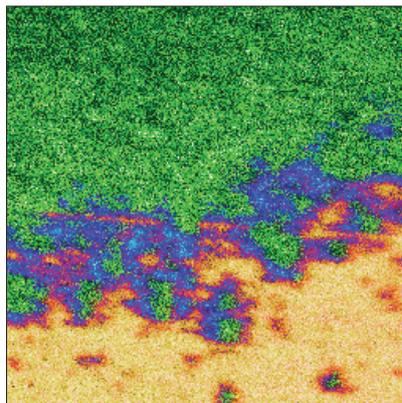
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