Interfacial Chemistry and Adhesion Phenomena: How to Analyse and How to Optimise

John F Watts

Department of Mechanical Engineering Sciences
The Role of Surface Analysis in Adhesion Studies

- Assessing surface characteristics (cleaning/pretreatment)
- Forensic analysis of failed joints, coatings etc.
- Fundamental studies of adhesion
  - Sectioning of real systems
  - XPS and ToF-SIMS of thin films
  - Adsorption isotherms
The Problem Faced by the Analyst

- ARXPS $d \sim 10\text{nm}$
- X-ray spectroscopies $d \sim 200\text{nm}$
- RBS $d \sim 1\mu\text{m}$

![Diagram showing the interface region between the substrate and the adhesive or coating, with depths indicated in micrometers (\(\mu\text{m}\)) and millimeters (mm).]
Obtaining analytical information from intact interfaces is very difficult.

Carrying out *in-situ* experiments within the spectrometer can be useful but only rarely is the interphase chemistry exposed in this manner.

TEM/PEELS Cross-Sections

PAA treated joint  
bright interface  

PAA + primer joint  
diffuse interphase  

**Epoxy + GPS/Aluminium Joint**

**Fig. 2.** Composite image of the cross-section of a sample containing 1% (w/w) of APS showing the aluminium/adhesive interface from several TEM images.

**Fig. 3.** EELS spectrum of the core loss region of the oxygen K edge along the aluminium oxide layer for a sample containing 0.5% (w/w) of APS.

**Fig. 5.** Graph representing the relative oxygen content over the oxide layer for the various APS concentrations, obtained from EELS spectra. At 0.5% APS, the oxygen profile is bi-lobar, whilst at 1% and 2% the oxygen concentration has only one maximum, near the silane and near the Al respectively.

Oxide Stripping + Depth Profiling

Chemical removal of metal substrate, depth profiling of oxide *in situ* by ion sputtering. Interphase can then be analysed directly.

Iron 2p3/2 spectrum showing Fe(II) component at interface. Oxide is entirely Fe(III).
Ultra Low Angle Microtomy

Angle Sectioning Block

- $12 \times 12 \times 7 \text{ mm}^3$
- $+ 25 \mu m = 0.03^\circ$
- $+ 50 \mu m = 0.07^\circ$
- $+ 100 \mu m = 0.15^\circ$
- $+ 200 \mu m = 0.33^\circ$
Depth resolution attainable depends on the taper angle and the size of the analytical probe. In XPS small area XPS in the range 15 - 500 μm, for ToF-SIMS < 1 μm

<table>
<thead>
<tr>
<th>XPS spot size/μm</th>
<th>ULAM taper angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

XPS Line Scan Along Taper

PVdF Topcoat on Polyurethane Primer

- X-ray Spot = 15µm
- Step Size = 18 µm

Atomic %

PVdF

Polyurethane

Depth / um

Fluorine

Nitrogen

F: ΔZ = 50 nm

N: ΔZ = 27 nm

13nm
ToF-SIMS Line scan

Positive ToF-SIMS image, characteristic ion of the primer formulation

500 µm - 128 pixels

For each of the 128 rows
Pixel depth = f(cutting angle)
Stitched Images: Two Coat System

Large scale overview of the interface and species migration

Topcoat

Primer

Negative ToF-SIMS images: 8 (500 µm x 500 µm) squares
Line Scan : Species Segregation

Characteristic fragment of the topcoat

Characteristic fragment of a primer component

Line scan

500 µm - 128 pixels
ToF-SIMS of ULAM Section

FoV is 500 µm

Polyurethane ions

(a) \( m/z = 149: \ C_8H_5O_3^+ \)
(b) \( m/z = 26: \ CN^- \)
(c) \( m/z = 59: \ C_3H_4F^+ \)
(d) \( m/z = 19: \ F^- \)

PVdF ions

ToF-SIMS Anions from Images

Point 2: Bulk Polyurethane

Point 1: Bulk PVdF

www.surrey.ac.uk
ToF-SIMS at Interface

Point 3: PU and PVdF at Interface

PCA on Positive Spectra from Interfacial Region to Identify Those that are not Characteristic of PVdF or PU

www.surrey.ac.uk
A negative ion ToF-SIMS mass spectra of the pure acrylic co-resin component of the PVdF topcoat formulation in the mass range 30-200 m/z.
ToF-SIMS Images of Acrylic Ions

Negative Ion Mass Selected Images

(a) \( m/z = 31: \text{CH}_3\text{O}^- \)
(b) \( m/z = 55: \text{C}_3\text{H}_3\text{O}^- \)
(c) \( m/z = 71: \text{C}_3\text{H}_3\text{O}_2^- \)
(d) \( m/z = 85: \text{C}_4\text{H}_5\text{O}_2^- \)
(e) \( m/z = 87: \text{C}_4\text{H}_7\text{O}_2^- \)
(f) \( m/z = 141: \text{C}_9\text{H}_{13}\text{O}_4^- \)
Coil Coating: Adhesion Promoter

Red: Top coat
Green: Primer
Blue: HDGS

ULAM

25 μm

500 μm
128 pixels = 16 strips x 8 pixels

8 pixels = 15.6 μm
1.08 μm
α = 2°

RoI: Region of Interest

Approximately same area is used for XPS line scan.

Recording Relative Intensity (RI) for each specific fragment

Convert RoI to Depth

RI vs. RoI

RI vs. Depth

Depth profile of a various fragments obtained by reconstruction of SIMS spectra across the top coat/primer/metal area from 16 regions of interest.

www.surrey.ac.uk
The region associated with the primer layer can be determined considering the change in the elements concentration:

- Analysis point at a depth of ~18 µm where the concentration of carbon starts to decrease.
- Analysis point at a depth of ~25µm where Zn signal is observed to become more intense.

Having Characterised all the individual components present in the formulation, it can be concluded that nitrogen is associated with the adhesion promoter molecule.

Changes in C, O, Zn, Co and N elemental concentration traversing a ULAM taper which has exposed the buried topcoat/primer/metal substrate interfaces of the sample with higher concentration of adhesion promoter.
Correlative Surface Analysis:

**XPS and ToF-SIMS**

- Adhesion promoter segregates to the primer surface when added to the primer formulation at the higher concentration.
- Adsorption studies on this molecule proves that there is no chemical interaction between the metal substrate and adhesion promoter molecule.
- The concentration of the adhesion promoter at the higher level is beyond the critical miscibility limit of the primer and the adhesion promoter is rejected from the formulation towards the outer surface.

Depth profile of the fragments originating from the adhesion promoter molecule obtained by reconstruction of SIMS spectra across the metal/primer/topcoat area from 16 regions of interest. The intensity of molecular ion reaches the maximum intensity at the primer/topcoat interface (the intensity of the molecular ion has been multiplied by 50).
The Thin Film Approach

10’s μm - mm

100’s μm - mm

Adhesive or Coating

Interface Region

Substrate

thin (< 2 nm film on substrate)

select sample from the plateau region of the adsorption isotherm
PMMA on Oxidised Metals

S R Leadley, J F Watts, J Adhes, 60, 175, (1997)
Polymer Conformation

PMMA on Oxidized Si and Al

Organosilane Adhesion Promoters

Molecular Dynamics Models of:
(a) Epoxy
(b) Amino
(c) Vinyl

www.surrey.ac.uk
The intense SiOAl\(^+\) peak is indicative of a covalent bond between the aluminium oxide and the organosilane adhesion promoter.
Specific Interactions
Flame Treatment Used for Many Years
Flame Treatment of Automotive Polypropylene
Example XPS Spectra

XPS spectra for Sample A untreated (lower) and treated (upper).
As Received PP Samples

The Surface Analysis Laboratory

![Graph showing binding energy distribution for Sample B, Sample C, Sample A, and Sample D. Peaks for C1s and O1s are visible.](www.surrey.ac.uk)
Mono XPS Valence Band

characteristic of pendant methyl group
XPS/Cluster Profiling

The Surface Analysis Laboratory

X-ray photoelectron spectroscopy performed using the Thermo Scientific K-Alpha system

- Monochromated X-ray source
- Fully automated acquisition

MAGCIS (monatomic and gas cluster ion source) used to produce craters

- Ar Cluster size up to 2000 atoms
- Ion energy = 2 - 8 keV

Monatomic Ar ion beam

[Image of MAGCIS device]

[Image of Thermo Scientific K-Alpha system]

www.surrey.ac.uk
Depth Profiling

Analysis on a K-Alpha using large cluster ions to etch \((\text{Ar}_{1000})\)

Depth calculation using estimate from Irganox reference.
ToF-SIMS Identification of Oxygenation

untreated

C$_3$H$_5$O

C$_4$H$_9$

treated

File: 1STTP1C.dat  PP 100

Mass / u

Intensity

$10^2$

$10^3$

$10^4$

$10^5$

$10^6$
ToF-SIMS of Oxidation Process

Untreated

8 passes

6 passes

3 passes

2 passes

1 pass

www.surrey.ac.uk
<table>
<thead>
<tr>
<th>Additive</th>
<th>Chemical structure</th>
<th>Characteristic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Bis-steramide</td>
<td><img src="https://via.placeholder.com/150" alt="Chemical structure" /></td>
<td>282, 310</td>
</tr>
<tr>
<td>Irganox™ 1010</td>
<td><img src="https://via.placeholder.com/150" alt="Chemical structure" /></td>
<td>57, 203, 219, 259</td>
</tr>
</tbody>
</table>
Ablation of Additives

**Ethylene Bis-steramide**

- **treated**
  - $C_{18}H_{36}NO$
  - $C_{20}H_{40}NO$

- **untreated**

**Irganox™ 1010**

- **treated**
  - $C_{15}H_{23}O$

- **untreated**
  - $C_{17}H_{25}O$
Conclusions

- Chemical analysis of interfaces responsible for adhesion requires careful sample preparation.
- In model systems explicit bond formation can be identified.
- In commercial systems the inter-diffusion and segregation of the individual components in a formulation may be equally (or even more) important.
- The use of this films allows bonding, configuration and bond density to be established.
- For extruded products residual processing aids or additives as well as low functionality may compromise adhesion. Pretreatments must remove the former and enhance the latter.