

**Society for Adhesion and Adhesives**

**Instrumental Techniques for  
Adhesion and Adhesives**

**One-day Symposium 6<sup>th</sup> December, 2001**

**Society of Chemical Industry, Belgrave Square,  
London**

## Programme

- 10.00 Registration and coffee**
- 10.30 Instrumental study of the degradation of aerospace waterborne primers**  
C Alderman, S R Church, C C Figgures and S J Harris  
, BAE SYSTEMS Advanced Technology Centre.
- 11.00 Mapping surface properties by atomic force microscopy**  
David Grandy IPTME, Loughborough University.
- 11.30 X-ray photoelectron spectroscopy**  
John Watts, Surrey University.
- 12.00 The rheology of structural adhesives**  
Gaynor Kavanagh, QinetiQ, Fort Halstead.
- 12.30 Lunch**
- 14.15 Quartz crystal microbalance: application to protein and cell adhesion**  
Alan Brain, Smith & Nephew Group Research Centre, York "
- 14.45 Acoustic microscopy and Adhesion**  
J M Sykes and G A D Briggs, Oxford University.
- 15.15 Secondary ion mass spectrometry**  
Marie-Laure Abel, Surrey University.
- 15.45 Contact angle measurements - still a useful surface analytical technique?**  
Steve Shaw, QinetiQ, Farnborough.
- 16.15 Tea**

This one-day symposium is one of an on going series organised by the Society for Adhesion and Adhesives.

Society for Adhesion and Adhesives Committee

D G Dixon (Chairman)  
R A Chivers (Vice-Chairman)  
M R Bowditch (Secretary)

S G Abbott  
R D Adams  
K W Allen  
J A Bishopp  
W Broughton  
J Comyn  
E J C Kellar  
A J Kinloch  
J D Palmer  
S J Shaw  
D A Tod

The next symposium due is "Adhesion and Adhesives – Greener Techniques" to be held at the SCI on Thursday 24<sup>th</sup> April 2001.

Details from

D A Tod  
QinetiQ  
CET/X50  
Fort Halstead  
Sevenoaks  
Kent  
TN14 7BP

01959 514492 phone  
01959 516014 fax  
[datod@qinetiq.com](mailto:datod@qinetiq.com) e-mail

D.TOD	QINETIQ
R.CHIVERS	SMITH & NEPHEW
J.BISHOPP	HEXCEL
D.DIXON	BAE SYSTEMS
J.COMYN	LOUGHBOROUGH UNIV.
K.ALLEN	OXFORD BROOKES
K.ARMSTRONG	CONSULTANT
D.GRANDY	LOUGHBOROUGH UNIV.
J.WATTS	SURREY UNIV.
G.KAVANAGH	QINETIQ
A.BRAIN	SMITH & NEPHEW
M.L.ABLE	SURREY UNIV.
S.SHAW	QINETIQ
J.SYKES	OXFORD UNIV.
S.HARRIS	BAE SYSTEMS
D.BENNETT	AWE
M.SPENCE	AWE
A.GRAHAMS	SME
G.CRITCHLOW	LOUGHBOROUGH UNIV.
R.DAHM	LOUGHBOROUGH UNIV.
I.MATHIESON	LOUGHBOROUGH UNIV.
T.CARTWRIGHT	LOUGHBOROUGH UNIV.
K.YENDALL	LOUGHBOROUGH UNIV.
A.COX	BOSTIK FINDLEY
M.KONIECZKO	ADVANCE TAPES INT.LTD.
A.TARRANT	IMPERIAL COLLEGE
C.KORENBERG	IMPERIAL COLLEGE
A.CUNLIFFE	QINETIQ
S.TORRY	QINETIQ
R.COOK	QINETIQ
M.FITTON	OXFORD BROOKES
N.HOOPER	OXFORD BROOKES
A.TAYLOR	IMPERIAL COLLEGE
J.PALMER	SEALOCRETE
L.GROVER	UNIVERSITY OF BIRMINGHAM
A.BELL	BAE SYSTEMS
RA.FREEMAN	QINETIQ
JSG.LING	CORUS

# Mapping surface properties by atomic force microscopy

David Grandy

IPTME, Loughborough University

## Abstract

The talk will consist of an introduction to the basic principles of atomic or scanning force microscopy. Particular emphasis will be given to the production of images of surfaces of materials generated by localised variations in mechanical properties. An outline of the subjects that will be covered is given below.

### 1. An introduction to basic AFM operation

- The piezo-electric scanner
- The optical force-feedback mechanism
- Magnification and resolution
- Probe design and selection

### 2. What properties can be mapped

- Physical topography
- Mechanical properties
- Others – thermal, chemical, electrical, magnetic and optical properties

### 3. Different operating modes

#### Contact modes

- Lateral force mode
- Force modulation mode

#### Force-distance curves (point spectroscopy)

- Local modulus, local adhesion measurements

#### Non-contact and intermittent contact modes (IC-AFM)

- Phase and amplitude detection (phase and amplitude imaging)
- Pulsed force mode (adhesion and stiffness imaging)

#### **4. Selected examples and results**

- **Contact mode imaging of a latex film**
- **Force modulation imaging of a fibre reinforced plastic**
- **Lateral force imaging of a rubber-rubber blend**
- **Phase detection and pulsed force mode imaging of phase separated polymer blends and copolymers**
- **Adhesion studies – contact angles, wetting and de-wetting**

# **X-Ray Photoelectron Spectroscopy**

**J F Watts**

**The Surface Analysis Laboratory  
School of Engineering  
UNIVERSITY OF SURREY  
Guildford Surrey GU2 7XH**

In the 30 years since it was first commercialized XPS has shown itself to be an extremely versatile technique in many areas of scientific endeavour. From the mid 1970s it has been increasingly applied to studies of adhesion. At the end of that decade there were only three surface analysis groups worldwide who had any profile in adhesion studies (including the University of Surrey Group!), and now all adhesion meetings report a significant amount of work which describes loci of failure, interphase chemistry and the like all being tracked by XPS and its partner in crime ToF-SIMS (which will be described later in the meeting).

In this talk the basic principles of XPS will be described and the various modes of operation, (high resolution, angle resolved XPS and imaging) outlined. XPS is able to provide a quantitative surface analysis of all vacuum compatible materials, and by studying the fine structure in the spectra chemical and "in-depth" information is also readily accessible. Quantitative depth profiling of polymers to a depth of around 5 nm can be achieved by the use of an appropriate reconstruction algorithm.

In addition adhesion failure is often associated with the aggressive action of molecular (water) or ionic (e.g  $\text{Na}^+$  or  $\text{Cl}^-$ ) species and XPS provides a useful manner in which to monitor damage brought about by these processes. In the case of electrochemical degradation of adhesively bonded metals the electrochemical activity can be deduced directly from the XPS data.

These aspects of XPS will be illustrated by examples taken from recent work at Guildford. In particular the following examples will be considered:

- Locus of failure of widgets in beer cans
- 
- Interface segregation in radcure systems as a cause of premature failure
- 
- Failure of adhesively bonded HDGS
- 
- Surface segregation of minor components in coil coatings

# The Rheology of Structural Adhesives

Gaynor M Kavanagh

QinetiQ

Fort Halstead

## What is Rheology?

- Science that studies the deformation and flow of materials in terms of material's elasticity and viscosity.
- Measuring the intrinsic mechanical properties, which can be related to a material's processing characteristics and performance.
- ELASTICITY is the ability of a material to store deformational energy and is the capacity of a material to regain its original shape after being deformed.
- VISCOSITY is a measure of the material's resistance to flow and reflects the material's rate of dissipation of deformation energy through flow.

## Application of Rheology to your needs

- Assess the starting material? Aid in the mixing?
- Determine the shelf-life once a drum has been opened?
- Look at batch-to-batch variations? The effect of fillers?
- Would changing to a new adhesive on the market reduce your costs and still give the same or better performance?
- Are your cure parameters optimised? Could you improve the cure by changing the cure temperature or the cure time profile?
- Has the adhesive you use been discontinued? If so what should you use instead?

## Theory of rubber elasticity

- When you measure  $G$ , measure the number of elastically active paths in the gel, not every point is elastic!
- You can have cyclic networks - defects where a molecule reacts with itself and forms a loop this loop has no effect, therefore elastically inactive.
- No of chains is expressed through the number-average molecular weight of the elementary chain  $M_c$  (segments between Xlinks). Density of the rubber and Avogadro's number.

## **DMA methods**

- Frequency/Temperature sweep
  - frequency sweeps performed at isothermal temperatures
  - enlarges the experimental window enabling Time Temperature Superposition application and hence ability to predictive material life
- Dynamic temperature (step) sweep
  - Conducted at a constant frequency
  - Temperature incremented
- Multi-wave temperature ramp
  - Several discrete frequencies simultaneously
  - Accumulates more mechanical information,  $T = 1/f$
  - Without increasing the experimental time (significantly) or the number of samples required

## **Conclusions**

Rheological changes occurring during the curing reaction can be measured as the resin transforms from a low melting solid to a low viscosity liquid, then through the gel point without disrupting the gel structure and finally to a highly crosslinked, stiff solid. In fact the entire curing process can be simulated by the rheometer to provide guidelines for production.

The polymer's morphology and structure to end-use performance. For example, measurements of the material's glass transition temperature and damping behaviour can be used to predict use temperatures, impact properties and stiffness.

## **Quartz Crystal Microbalance: Application to protein and cell adhesion**

The surface properties of implanted medical devices largely define the biological response.

We have a large range of techniques that allow us to characterise surfaces. Atomic Force Microscopy is a powerful tool that allows us to characterise the surface topography. Using phase imaging we can image viscoelastic differences and with micro thermal analysis we can identify separated phases. Recently, using Pulsed Force, it has become possible to image using mechanical properties.

An implanted device is first exposed to water and ions these are followed by proteins and finally cells. Until recently there were no direct methods of recording these interactions.

The Quartz Crystal Microbalance (QCM) has been used for many years to monitor coating thickness in vacuum coating systems. Recently there has been a resurgence of interest since the ability to use the technique in liquid environments has been developed. The driving force for this development has been protein-binding work. The QCM sensor is thin disc of quartz sandwiched between two electrodes. The resonant frequency of this device is altered by attached mass according to the Sauerbrey Equation:

$$\Delta f = -k \cdot \Delta m$$

By exciting the crystal for a short period and measuring the frequency and dissipation during the ringing it is possible to detect both mass change and a viscoelastic response. The QCM-D is sensitive to changes of less than 2 ng in liquid.

Two cells are available for the QCM-D, one is a flow cell used for protein binding and the other a window cell. The window cell allows observation of the sensor surface using an optical microscope during an experiment.

The quartz sensor has a gold surface; this may be coated with experimental materials of more relevance to system being studied. We have coated sensors with a range of 'biomaterials' including SiO<sub>2</sub>, TiO<sub>2</sub> and polymers.

Applications for the method include protein and cell adhesion, sensor development and the study of biodegradable polymers.

# Acoustic microscopy and Adhesion

J M Sykes and G A D Briggs

Department of Materials, Oxford University

## Abstract

This paper demonstrates how scanning acoustic microscopy can be used to examine a polymer-metal interface, detect local loss of adhesion during exposure to water and recovery on drying, and make quantitative measurements of micro-blisters formed during extended exposure.

The system studied is an unpigmented epoxy-polyamide lacquer applied to either 18:8 stainless steel or mild steel test panels. The substrates were vapour degreased using 1,1,1 trichloroethane and the lacquer applied by spin coating (thickness typically 20  $\mu\text{m}$ ). Coatings were cured for at least 14 d at ambient temperature.

Coatings were exposed to distilled water at 30° C for various periods, either in a water bath, or during observation on the microscope, then dried in a desiccator containing silica gel.

For adhesion testing either a 90° peel test was used, or lap-shear specimens were fabricated rapidly by bonding a coated strip to an uncoated strip using cyanoacrylate adhesive, then fractured in an Instron tensile test machine.

Some mild steel specimens were scribed with a scalpel to form a 10mm long defect, then exposed to 0.05 M NaCl to initiate corrosion of the exposed steel and cathodic disbonding alongside the defect.

Samples were examined, exposed to distilled water as coupling medium, in the OXSAM scanning acoustic microscope operating in reflection mode at 300 MHz.

## Scanning Acoustic Microscopy

In the scanning acoustic microscope (SAM) a transducer is used to produce short ultrasonic pulses, which a spherical sapphire lens, coupled to the sample by a droplet of water, brings to a focus, either on the surface of the sample, or within the sample (to produce subsurface imaging). Reflections returning from the surface (or microstructural features in the sample) are detected by the same transducer. The strength of the signal detected depends upon the elastic properties of the material.

In the OXSAM the sample is scanned mechanically beneath the lens, so that an image is built up in which contrast arises from variations in elastic properties within the specimen microstructure.

The microscope finds particular application in the examination of interfaces, where the strength of reflection depends on the difference in acoustic impedance (acoustic velocity x density) between the two materials. With multiple interfaces interference fringes can be generated from which further information may be gained.

Time-of-flight acoustic microscopy (TOFSAM) tracks the focussed beam along a line and by using very short pulses is able to detect a sequence of

echoes returning to the transducer. In effect the SAM operates like an echosounder and generates a cross-sectional view of the sample.

## **Adhesion Testing**

### **Lap-shear**

Dry testing results in cohesive failure of the adhesive, but after 0.5h exposure to water, cohesive failure occurs and the strength falls dramatically for both steels. Adhesion continues to fall over time, but some residual strength remains even after 1000h.

Samples placed in a desiccator after 24h exposure to water show a substantial recovery of adhesion after about 10h, but not to initial levels

### **Peel tests**

Peel testing shows similar behaviour to lap-shear, though (perhaps surprisingly) the fall in adhesion is apparently *greater* and recovery less complete.

## **Acoustic Microscopy**

When samples are examined dry with the focus at the steel-lacquer interface, the only contrast arises from surface defects on the steel. After about 0.5h exposure to water, many light patches start to be visible in the image. We interpret these as local loss of adhesion. If the polymer is well bonded to the substrate acoustic energy is transmitted into the metal, but local loss of adhesion generates a stronger (brighter) reflected signal. The size and number of these patches increases over time, but they do not continue to grow until they merge.

If samples are taken from the water and placed in dry air, then subsequent images show that the bright patches disappear quite quickly, but can be seen to return at the same sites during re-exposure to water in the SAM.

After longer exposure time the patches develop into micro-blisters and fringes start to appear in the images. These are developed from interference between rays from the polymer-water and water-metal interfaces within the blister. The number of fringes increases with time. By measuring the fringes it is possible to construct profiles of the blister. Surprisingly the height is found to be small in comparison to the diameter. Observations of blister sections have been confirmed using TOFSAM.

If these samples with large blisters are dried, some blisters disappear entirely, but many do not. The blisters that remain are bright without fringes, but surrounded by a narrow black line. This arises because the blister no longer contains any water and the reflection comes from a polymer-air interface where a phase reversal takes place. No acoustic signal reaches the metal. This interpretation is confirmed by TOFSAM images that only show the upper and lower surfaces of the coating in the disbanded area. A startling observation during one examination, was the abrupt appearance of one such blister at a site where a blister had once been, which had disappeared after drying. It appears that swelling of the polymer induces disbonding of a weakened interfacial bond.

## **Cathodic Disbonding**

When corrosion takes place at a coating defect, the anodic attack on the metal is partly supported by cathodic reduction of oxygen beneath the coating. With sodium ions in the test medium the hydroxyl ions generated from oxygen reduction can form a strongly alkaline solution that disbonds the coating. Using acoustic microscopy it is possible to measure the progress of this cathodic disbonding; for this coating an irregular light band grows on both sides of the scribe for about 0.75 h. After this period disbonding stops and parallel fringes start to appear, indicating that the edge of the coating is lifting.

As time goes on disbonded patches start to appear ahead of the stationary disbonding front, which then develop into blisters (with fringes). The extent of the blister zone increases with time and individual blisters grow at first in diameter, then in height. Comparison with thicker coatings (30  $\mu\text{m}$ ) suggests that the blisters' diameters increase at similar rates for both, but height grows more slowly with thicker coatings, controlled presumably by rates of water transport.

## **Further work**

The SAM is of most value with opaque coatings, where adhesion loss and blistering are difficult to detect. Further studies with the OXSAM on pigmented automotive coatings have shown that blistering can readily be detected. Studies are now in hand using a commercial SAM operating at 20-150 MHz that has greater penetrating power (at the lower frequencies) with resolution approaching that of the OXSAM at the highest. Routine imaging of much larger areas is now possible (at low magnification) to map salient features of corrosion damage beneath coatings. We are linking this to Kelvin probe measurements, so that damage can be linked to the local electrochemical activity that causes it.

## **Acknowledges**

We are pleased to acknowledge Jonathan Crossen, who carried out most of these observations while studying for his D.Phil. at Oxford. We also thank Courtaulds Coatings (International Paint) and the EPSRC for financial support.

## **References**

1. G.A.D. Briggs, *Acoustic Microscopy*, Clarendon Press, Oxford, 1992.
2. J.D. Crossen, J.M. Sykes, D. Knauss, G.A.D. Briggs and J.P. Lomas, *Advances in Corrosion Protection by Organic Coatings*, eds M. Kendig and J.D. Scantlebury, Electrochemical Society, Pennington N.J., 1995, p274.
3. J.D. Crossen, J.M. Sykes, G.A.D. Briggs and J.P. Lomas, *Organic Coatings for Corrosion Control*, ed. G.P. Bierwagen, ACS Symposia Series no. 689, American Chemical Society, Washington DC, 1998, p 106.
4. J.D. Crossen, J.M. Sykes, T. Zhai and G.A.D. Briggs, *Faraday Discussion* 107, Royal Society of Chemistry, London 1997, p417.

# **Time of Flight Secondary Ion mass Spectrometry**

**Marie-Laure Abel**

**The Surface Analysis Laboratory  
School of Engineering  
UNIVERSITY OF SURREY  
Guildford Surrey GU2 7XH**

Time of flight secondary ion mass spectrometry is a technique complementary to XPS. It is able to probe the very surface near region in the order of 1 to 2 nm for cluster ions and approximately 5 nm for elemental ions. This technique offers many advantages. In particular, it is more sensitive than XPS and allows for unambiguous identification of specific chemical species present at the surface. It is also able to identify specific covalent bonding occurring between various components present in an adhesive formulation and the substrate on which it is applied.

In the field of adhesion, ToF-SIMS may be used in various ways. To simply check the surface chemistry when, for example, a specific surface treatment has been used such as plasma treatment. The creation of particular functionalities can be identified. It is also possible to identify the locus of failure, segregating species at the extreme surface or contamination. Another way to use ToF-SIMS consists into designing the experiment to be able to probe an interface of interest such as primer to substrate interface. This particular methodology has long been used in Surrey with XPS, but is now being developed for ToF-SIMS too.

In a brief introduction, the basic principles of ToF-SIMS will be described, together with advantages and disadvantages for the particular topic of adhesion.

Various examples will be given during the lecture to illustrate the above and will include:

- Interface segregation in radcure systems as a cause of premature failure
- Surface segregation of minor components in coil coatings
- Probing the interface between aluminium and organosilane primer
- Identifying specific interaction between a primer and model adhesive and/or real adhesive