The Adhesion of Photocured Polymers to Ceramic Substrates

by

Alison M. Taylor  B.Eng(Hons)

A thesis submitted to the University of Surrey for the degree of Doctor of Philosophy

Department of Materials Science and Engineering
University of Surrey, Guildford, Surrey, UK.

September 1994
Abstract

The adhesion and subsequent failure of a commercially available photocured resin applied to various ceramic substrates, used for electronics applications, has been investigated. The adhesive system was studied under both ambient and hostile, (water immersion at 50°C) conditions. The environmental stability of the system was investigated using two different mechanical tests, (simple butt-joints and a modified Boeing wedge test). In each case, the precise locus of failure was determined by a combination of surface analytical (XPS and ToF-SIMS) and microscopy techniques, (SEM).

On the basis of these results, adhesion and failure mechanisms are proposed for the system. The presence of defects within the adhesive was found to initiate failure under ambient, (dry) conditions. Prolonged immersion in water, (for at least 2 weeks), was found to result in near-interfacial failure with a thin, (of the order of nanometres), overlayer of polymer remaining on the surface of the adherend. Subtle differences between this polymer overlayer and the bulk resin were observed. A model is proposed in which one of the minor resin components aggregates at the inorganic surface, creating a localised region which is extremely hydrophillic in nature. This makes the system particularly vulnerable to attack by water.

In order to test this model, a reformulated batch of resin underwent the same environmental tests. The modified resin displayed a modest improvement in its ability to withstand hostile conditions, (prolonged immersion in water at 50°C) and the polymer residue remaining on the inorganic substrate was identical to that of the bulk polymer.

This project has provided a unique opportunity to study the adhesion of a specific class of adhesives to bulk ceramic oxides, rather than to oxides of metals. One of the major benefits of which, was therefore the absence of any effects due to corrosion of the substrate. The project was also unusual in that it effectively went "full-circle", with the resin undergoing reformulation on the basis of the results obtained from the standard resin. The reformulated product was found to have superior wet adhesion, but poor mechanical properties.
Acknowledgements

Special thanks go to Dr. J.F. Watts, (University based supervisor) and Dr. H. Duncan, (Industrial supervisor), for their help and guidance throughout this project. The financial support of both ICI Chemicals & Polymers Ltd. and the SERC, is gratefully acknowledged by the author for funding this CASE award.

Access to IRS equipment at the sponsors research facilities, (The Heath, Runcorn), was much appreciated, and in particular, the assistance of Dr. D. Barnes and D. Lowden for their assistance in carrying out this section of the work. The informative discussions held during progress meetings at the Heath, which were attended by both the sponsors and the manufacturers of the resins, (ZENECA Specialties Ltd.), were also of great technical value.

Many thanks go to Dr. C.H. McLean for his continued support throughout this project, and particularly for his assistance, together with Dr. M. Charlton, with the molecular modelling work carried out at the ZENECA Specialties Research Centre, Blackley.

Thanks also to Dr. G. Beamson at the RUSTI, SERC Daresbury Laboratory, for his invaluable assistance with the monochromated XPS analysis. Access to IGC equipment at CNRS, Paris was also much appreciated, and especially the expertise of Dr. M. Chehimi and Marie-Laure Abel in using this technique. The help of Dr. I.W. Fletcher at the ICI Wilton Materials Research Centre with the iXPS work is gratefully acknowledged.

Finally, the author would like to express sincere thanks to all the members of the Surface and Interface Reactions Group, (SIRG), both past and present, in the Department of Materials Science and Engineering, for their technical advice and encouragement throughout this project. A special note of thanks to Stephen J. Davis for taking the photographs of the apparatus included in this thesis.
## CONTENTS:

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>...i</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>...ii</td>
</tr>
<tr>
<td>Contents</td>
<td>...iii</td>
</tr>
<tr>
<td>List of Acronyms</td>
<td>...ix</td>
</tr>
<tr>
<td>Chapter 1 INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>Chapter 2 PRACTICAL ASPECTS OF ADHESION THEORY APPLIED TO POLYMER COATINGS ON CERAMIC SUBSTRATES</td>
<td></td>
</tr>
<tr>
<td>2.1 Industrial Background</td>
<td></td>
</tr>
<tr>
<td>2.1.1 Electronics Packaging Technology</td>
<td></td>
</tr>
<tr>
<td>2.1.2 Radiation Curable Adhesives</td>
<td></td>
</tr>
<tr>
<td>2.1.3 Visible Light Cured Resins</td>
<td></td>
</tr>
<tr>
<td>2.1.4 Encapsulation/Potting Techniques</td>
<td></td>
</tr>
<tr>
<td>2.2 Practical Aspects of Adhesion Theory</td>
<td></td>
</tr>
<tr>
<td>2.2.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>2.2.2 Mechanisms of Adhesion</td>
<td></td>
</tr>
<tr>
<td>2.3 Adsorption of Polymer Molecules on to Surfaces</td>
<td></td>
</tr>
<tr>
<td>2.4 Wetting and Spreading</td>
<td></td>
</tr>
<tr>
<td>2.4.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>2.4.2 Contact Angle</td>
<td></td>
</tr>
<tr>
<td>2.4.3 Critical Surface Tension for Wetting</td>
<td></td>
</tr>
<tr>
<td>2.4.4 Surface Free Energy</td>
<td></td>
</tr>
<tr>
<td>2.4.5 Work of Adhesion</td>
<td></td>
</tr>
<tr>
<td>2.5 Modes of Failure</td>
<td></td>
</tr>
<tr>
<td>2.6 Locus of Failure</td>
<td></td>
</tr>
<tr>
<td>Chapter 3 EXPERIMENTATIONAL TECHNIQUES</td>
<td></td>
</tr>
<tr>
<td>3.1 X-ray Photoelectron Spectroscopy (XPS)</td>
<td></td>
</tr>
<tr>
<td>3.1.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>3.1.2 Basic Principles and Theory</td>
<td></td>
</tr>
<tr>
<td>3.1.3 XPS Analysis of Insulating Samples</td>
<td></td>
</tr>
<tr>
<td>3.1.4 Depth of Analysis</td>
<td></td>
</tr>
<tr>
<td>3.1.5 Spectral Interpretation</td>
<td></td>
</tr>
<tr>
<td>3.1.5.1 Primary Structure</td>
<td></td>
</tr>
<tr>
<td>3.1.5.2 Secondary Structure</td>
<td></td>
</tr>
</tbody>
</table>
3.1.6 Binding Energy: The Influence of Initial and Final State Effects
3.1.7 Quantification and Sensitivity Factors
3.1.8 Experimental Requirements Specific to This Project
3.1.9 Instrumentation
  3.1.9.1 X-ray Sources
  3.1.9.2 Monochromated XPS
  3.1.9.3 Charge Compensation: Electron Flood Guns
  3.1.9.4 Analysers
  3.1.9.5 Resolution
  3.1.9.6 Experimental Operating Conditions
3.1.10 Imaging XPS (iXPS)
3.1.11 Angle-resolved XPS (ARXPS)

3.2 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)
  3.2.1 Introduction
  3.2.2 Instrumentation
  3.2.3 SIMS Imaging

3.3 Microscopy Techniques
  3.3.1 Scanning Electron Microscopy (SEM)
  3.3.2 Confocal Scanning Laser Microscopy (CSLM)

3.4 Fourier Transform Infrared Spectroscopy (FT-IR)
  3.4.1 Basic Principles
  3.4.2 Application to this Study

3.5 Inverse Gas Chromatography (IGC)
  3.5.1 Introduction
  3.5.2 Experimental Detail
  3.5.3 Calculation of Thermodynamic Properties

3.6 Molecular Modelling
  3.6.1 Introduction
  3.6.2 Experimental Detail

3.7 Mechanical Testing
  3.7.1 Introduction
  3.7.2 Experimental Detail

3.8 Summary

Chapter 4 CHARACTERISATION OF THE AS-RECEIVED MATERIALS AND THE ADHESIVE/ADHEREND SYSTEM
  4.1 Introduction
4.2 Characterisation of the Adherend
4.2.1 Introduction
4.2.2 XPS Analysis
4.2.2.1 Sample Preparation
4.2.2.2 Results of XPS Analysis
4.2.3 Results of Analysis by ToF-SIMS
4.2.4 SEM Results
4.2.5 CSLM Results

4.3 Investigation of the Resin (LCR000) Properties
4.3.1 Introduction
4.3.2 Resin Composition
4.3.3 XPS Analysis
4.3.3.1 Sample Preparation
4.3.3.2 Results of XPS Analysis
4.3.4 Inverse Gas Chromatography
4.3.4.1 Sample Preparation and Experimental Detail
4.3.4.2 Results From IGC Experiments

4.4 Joint Design and Manufacture
4.4.1 Introduction
4.4.2 Joint Design
4.4.3 Joint Manufacture

4.5 Analysis of Dry Failures
4.5.1 In-situ Fracture
4.5.2 SEM Results
4.5.3 Results of XPS Analysis
4.5.4 iXPS Results
4.5.5 ToF-SIMS Imaging
4.5.6 Scienta ESCA300 XPS Results

4.6 Model for Dry Failure

4.7 Summary

Chapter 5 THE EFFECT OF WATER ON THE INTERFACIAL CHARACTERISTICS OF THE ADHESIVE SYSTEM

5.1 Background Theory
5.1.1 Introduction
5.1.2 Ingress and Movement of Water in Adhesive Joints
5.1.3 Mechanisms of Environmental Attack

5.2 XPS Analysis
5.2.1 Experimental Procedure
5.2.2 XPS Results
Chapter 7 DURABILITY STUDIES
7.2.3 Durability Studies
7.2.3.1 Experimental Details
7.2.3.2 Results

Chapter 7.3 TOF-SIMS ANALYSIS
7.3.1 Introduction
7.3.2 Sample Preparation
7.3.3 Results
7.3.4 Discussion

Chapter 7.4 INVERSE GAS CHROMATOGRAPHY (IGC)
7.4.1 Introduction
7.4.2 Results

Chapter 7.5 MOLECULAR MODELLING
7.5.1 Introduction
7.5.2 Experimental Procedure
7.5.3 Results
7.5.4 Discussion

Chapter 7.6 MECHANICAL TESTING
7.6.1 Introduction
7.6.2 Experimental Detail
7.6.3 Results
7.6.4 Boeing Wedge Tests

Chapter 7.7 SEM RESULTS

Chapter 7.8 SUMMARY

Chapter 8 THE ADHESION AND FAILURE OF PHOTOCURED RESIN/CERAMIC SYSTEMS
8.1 Introduction
8.2 Difficulties Associated With Working With The LCR000/Alumina System
8.2.1 Substrate Heterogeneity
8.2.2 Photocured Resins
8.2.3 The Scienta ESCA300 Spectrometer
8.3 Failure Mechanisms
8.3.1 Dry Failure
8.3.2 Failure Under a Hostile Environment
8.3.3 Mechanisms of Water Attack
8.4 Polymer Adsorption: The Role in Joint Integrity
8.4.1 Introduction
8.4.2 Movement of Polymer Molecules
8.4.3 Selective Adsorption
8.4.4 Structure of the Adsorbed Layer
8.5 Comparison of LCR000 With ModLCR000
8.6 Summary

Chapter 9 CONCLUSIONS
9.1 Conclusions
9.2 Suggestions for Future Work

References

Publications
**LIST OF ACRONYMS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.c.</td>
<td>alternating current</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ARXPS</td>
<td>Angle Resolved X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>BE</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>CAA</td>
<td>Chromic Acid Anodised</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant Analyser Energy</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CMA</td>
<td>Cylindrical Mirror Analyser</td>
</tr>
<tr>
<td>CRR</td>
<td>Constant Retard Ratio</td>
</tr>
<tr>
<td>CSLM</td>
<td>Confocal Scanning Laser Microscope</td>
</tr>
<tr>
<td>DCB</td>
<td>Double Cantilever Beam</td>
</tr>
<tr>
<td>d.c.</td>
<td>direct current</td>
</tr>
<tr>
<td>DC</td>
<td>Differential Charging</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infra Red Spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HRXPS</td>
<td>High Resolution X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>HSA</td>
<td>Hemispherical Sector Analyser</td>
</tr>
<tr>
<td>ICI</td>
<td>Imperial Chemicals Industries</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>IEPS</td>
<td>Isoelectric Point on the Surface</td>
</tr>
<tr>
<td>IGC</td>
<td>Inverse Gas Chromatography</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic Mean Free Path</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>IRS</td>
<td>Infra Red Spectroscopy</td>
</tr>
<tr>
<td>iXPS</td>
<td>Imaging X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>LCR</td>
<td>Light Cured Resin</td>
</tr>
<tr>
<td>LDC</td>
<td>Lateral Differential Charging</td>
</tr>
<tr>
<td>MIR</td>
<td>Multiple Internal Reflection</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (methylmethacrylate)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly (tetrafluoroethylene)</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>RTP</td>
<td>Room Temperature and Pressure</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning Auger Microscopy</td>
</tr>
<tr>
<td>SATP</td>
<td>Standard Air Temperature and Pressure</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SMT</td>
<td>Surface Mount Technology</td>
</tr>
<tr>
<td>SNMS</td>
<td>Scattered Neutral Mass Spectrometry</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>SSIMS</td>
<td>Static Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>Tri (ethyleneglycol) dimethacrylate</td>
</tr>
<tr>
<td>TOA</td>
<td>Take off angle</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of Flight</td>
</tr>
<tr>
<td>TV</td>
<td>Television</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VDC</td>
<td>Vertical Differential Charging</td>
</tr>
<tr>
<td>WBL</td>
<td>Weak Boundary Layer</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

The increased use of ceramic substrates, notably alumina, within the electronics industry, has stimulated interest from adhesives manufacturers in formulating products suitable for applications such as screen printing and device encapsulation. Electronics manufacturers stipulate that all adhesives/encapsulants used in their components must be able to withstand hostile environments, (i.e. exposure to moisture and/or thermal shock). Visible light cured resins (e.g. Luxtrak™ resins from ZENECA Specialties Ltd.), provide an example of one class of products available for use in this area. These particular products are derived from aromatic methacrylate-type oligomers and are based on non-epoxy chemistry. The properties which make them of particular interest for such applications include their rapid cure times, (a matter of seconds at room temperature), cure initiated by a blue light source, (wavelength approximately 470 nm), plus the ability to cure through a variety of translucent materials including alumina (Rogers, 1988(a)).

The surface composition of many of the substrates used for electronics applications is heterogeneous. In the case of a commercial alumina such as Coors AD96, (which is a 96% debased alumina), this is believed to arise from the movement of silica and other species such as magnesia, added during the manufacturing process and results in the formation of a heterogeneous bonding surface. Silica forms the glassy phase during liquid phase sintering, while the presence of other additions, notably MgO, aids densification (Coble, 1962 and Sung et al., 1992). Resin formulators need to be aware of the existence of regions of such heterogeneity, particularly, as in this case, when the acid/base properties of these regions vary so widely. Alpha alumina can be described as an amphoteric oxide, magnesia is relatively basic in nature and silica tends to have more acidic properties (Lee, 1991). The task for the formulators
is therefore more complicated than formulating a resin which will adhere well to alumina. The work was of industrial interest to, in particular, the microelectronics industry. The project was therefore particularly demanding, as a study of the interactions between a fully formulated commercial adhesive system and a heterogeneous substrate was carried out. In general, seeking to understand the interface chemistry, involves either the use of a model substrate, or a fully characterised homopolymer, due to the complexities of working on "real systems". In addition to the regions of chemical heterogeneity, the roughness of the surface of as-received alumina introduced added complications. These factors made it necessary to incorporate some additional substrates in to the study, in order to create artificially on separate samples, each of the features present on the as-received substrate. This allowed the individual contributions of the various compounds present on the surface of the alumina to be evaluated.

The Surface Analysis Laboratory in the Department of Materials Science and Engineering at the University of Surrey, is equipped with a range of surface analytical facilities, (XPS, ToF-SIMS, AES, and the scanning probe microscopies, STM and AFM), which therefore made it the appropriate choice for this project. The technique used predominantly for this work was X-ray photoelectron spectroscopy, (XPS) and to a lesser extent, time of flight secondary ion mass spectroscopy, (ToF-SIMS). The highly insulating nature of the alumina substrate was to provide an additional challenge to the project. The Microstructural Studies Unit in the Department of Materials Science and Engineering is equipped to study both the morphology and topography of samples, by a combination of scanning electron microscopy, (SEM) and confocal scanning laser microscopy, (CSLM).

The aim of this work was to employ surface specific techniques, to investigate the manner in which a typical photocured resin interacts with an inorganic substrate, in this case a 96% pure debased alumina. To achieve this aim, it was necessary to first characterise both the adhesive and adherend, before moving on to study the adhesive system as a whole. The next stage of the work was to establish adhesion and failure mechanisms for the system, first, in standard conditions, (i.e. standard air temperature
and pressure, SATP) and then in the presence of a hostile environment, (water at 50°C). Information gained at this stage was to be fed back to resin formulators, to form the basis of guidelines for future formulations, in the design of new, more durable products.

Butt-joints were found to be the most suitable specimen geometry to study the adhesive system. The primary reason for this particular choice of geometry, was that specimens could be accommodated into the XPS system at Surrey, (a VG Scientific ESCALAB MkII) and fractured in-situ with the aid of a heavily modified VG Scientific T-peel stage. Preliminary studies (with emphasis placed on durability), were carried out using as-received alumina adherends. This caused obvious complications due to the chemically heterogeneous, rough nature of the substrate. In order to define the precise locus of failure within the joints, angle dependent XPS studies were carried out (angle resolved XPS). However, a pre-requisite of ARXPS is to design a system which is both flat and extremely smooth, hence a necessity to work with polished rather than as-received alumina. To study the separate effects of substrate heterogeneity on the durability of the system, other substrates were included in the work; these were quartz and single crystal silicon (plus it’s native oxide), which, like quartz had a mirrored finish. By polishing the alumina, it was possible to remove surface segregated silica to produce a flat alumina surface. Thus, the three types of specimen provided an opportunity to study the different chemical effects present on the as-received alumina surface with the increased depth resolution offered by ARXPS. Quantitative analyses obtained by ARXPS were later used to generate compositional depth profiles of the failure surfaces using a forward transform routine (#Angular).

Monochromated angle resolved XPS analyses were also carried out on the failure surfaces of adhesive joints previously immersed in water at 50°C for varying lengths of time, (0-5 weeks). These results complemented conventional ARXPS data, as the alumina samples in particular, proved to be susceptible to charging effects. The locus of failure occurred close to the inorganic surface. XPS results also revealed subtle differences between this thin polymer overlayer and the bulk material.

Photocured resins, typical of most adhesives, are multicomponent systems. A
combination of surface analytical, (XPS and ToF-SIMS) and molecular modelling techniques have been used to study the transport properties of the various components within the adhesive and their interactions with an alumina substrate. The results from this work indicated that in certain instances, various components can aggregate at the interface to produce a region which not only differs in its chemical properties, but also in its mechanical response to load and exposure to aggressive environments such as water. This phenomenon, which has not been widely recognised, indicates the crucial role of such additives in determining the locus of failure within a joint. It may be of practical importance to the formulation chemists in the design of new or improved adhesives with enhanced durability.
Chapter 2

Practical Aspects of Adhesion Theory Applied to Polymer Coatings on Ceramic Substrates

2.1 Industrial Background

2.1.1 Electronics Packaging Technology

Recent changes in electronics packaging technology have resulted in a sharp increase in the use of ceramic materials, in particular, alumina. Alumina substrates offer a range of properties which make them suitable for use in, for example, ceramic chip packages (Grovenor, 1989). Mechanical properties are important, as the chip requires both insulation and support during the metallisation procedure; alumina has both a high elastic modulus and good thermal shock resistance (Davidge, 1986). Its high resistivity ensures complete electrical isolation of the chip and good chemical stability reduces the possibility of reaction with either the metal tracks, or the aggressive chemicals used during the etching stage of processing. Alumina can also be produced completely free from open porosity, a low value of porosity helps reduce outgassing after packaging. In addition to fulfilling the technical requirements, alumina substrates can be mass produced fairly cheaply, an important factor, in the continual drive to reduce the cost of microelectronics components.

Device packaging and surface mount technology (SMT), provide examples of specific electronics applications. Alumina substrates are often used as supports for device packaging. The alumina acts as a base for the other components (wire connections, pins etc.) and the whole assembly is then hermetically sealed in a metal or polymer can. Figure 2.1 depicts a surface mounted component. The chip is bonded
to the ceramic substrate and contacts are made between the chip and the metallic conduction tracks on the ceramic surface. The metallic tracks may be connected to an array of pins, as in Figure 2.1(b), or to other external electrical contacts. The development of leadless chip packages has produced several benefits. The packing density of chips on substrates can be increased, of particular use to the designers of complex printed circuit boards (PCB's). Improved reliability of automated assembly lines has also been observed with the advent of SMT. These changes in packaging technology have in turn, created a demand for new types of adhesives and encapsulants which adhere well to alumina.

The electronics industry sets extremely high demands in terms of the expected performance of all the adhesives it employs. Any potential adhesive must satisfy rigorous standards for both durability and thermal shock before consideration. Some manufacturers make use of pressure cooker tests, which, exactly as the name suggests, involves the sample being exposed to the hostile conditions inside a pressure cooker, (Buchwalter, 1990). Adhesives manufacturers are also faced with the challenge of meeting several other criteria. For example, in order to keep production steps to a minimum, there is often a reluctance to add a substrate precleaning stage prior to

Figure 2.1 A surface mounted chip on (a) a leadless ceramic substrate, (b) a pin grid array, (after Grovenor, 1989).
bonding. Analysis of the alumina substrates from one microelectronics production line revealed the presence of some unexpected contaminants, for example, Brasso™, and various silicones (Duncan, 1991).

A further complication, is that aluminas typically used as substrates by the electronics industry are in the order of 94.5-96.5% pure. Additions such as silica and magnesia are added as sintering aids during the manufacturing process and result in the production of a heterogeneous bonding surface (Taylor et al., 1972 and Clarke, 1980). The fabrication of alumina sheets for microelectronics applications is generally by the "doctor blade process" (or tape casting), a continuous casting method. Ceramic powders are mixed with various additives (binders, plasticisers etc.) in a solvent such as toluene or ethanol to produce a liquid precursor known as "slip". The slip is contained in a reservoir and as a flexible support tape on a conveyor belt passes beneath it, a uniform layer of slip is retained by the tape. The thickness of the layer is dictated by the height of the doctor blade. Figure 2.2 is a schematic of the process.

![Diagram of the doctor blade process](image)

Figure 2.2 Schematic of the doctor blade process, (after Grovenor, 1989).

After passing through a drying region, the continuous sheet has enough "green strength" to be cut into sections and removed from the tape ready for sintering. Firing occurs at about 1550°C (approximately two thirds of the melting point). The additions
of MgO and SiO₂ form a liquid phase \((\text{MgO/Al}_2\text{O}_3/\text{SiO}_2)\), which allows sintering to take place at a reduced temperature. Liquid phase sintering routes produce well-densified alumina, but a microstructure in which the grain boundary regions are enriched in silica and magnesia. The rapid growth in this area of technology has created an opening in the market for new classes of adhesives and encapsulants.

2.1.2 Radiation Curable Adhesives

Considerable interest has been shown in one particular category of adhesives; "radiation curables". These materials are rapid setting adhesive systems where polymerisation reactions are induced by some form of electromagnetic radiation (McGinniss, 1984). Depending upon the system, cure may be initiated by ultraviolet radiation (UV), an electron beam or photons. Photocured resins, as with ultraviolet systems, contain a photoinitiator which, on activation by the correct wavelength of light, generates free radicals causing polymerisation reactions to occur.

Radiation curables offer several major advantages over other classes of adhesive. Cure occurs extremely rapidly (Rogers, 1988(b)), so these materials lend themselves to high production line speeds. Rapid cure times also reduce the chance of component mis-register occurring, a problem frequently encountered by manufacturers of, in particular, opto-electronic components (Murray and Jones, 1988). Other advantages, related to environmental concerns include their low energy requirements and the fact that there is no solvent emission into the atmosphere (Stueben, 1984).

Many adhesives, typically epoxy-based systems, rely upon a thermally activated cure, which precludes their use on heat-sensitive substrates. Both Pappas, (1984) and Decker (1987), have recorded the benefits radiation has over thermal energy to cross-link polymers. The potential for improved adhesion to the substrate due to grafting, also exists with certain radiation curables (Stueben, 1984).

2.1.3 Visible Light Cured Resins

Photocured resins also fall under the umbrella term of radiation curables. The
resins investigated during the course of this study are derived from aromatic methacrylate type oligomers and are based on non-epoxy chemistry. Resins are combined with a photoinitiator system which provides free radicals in the presence of light between the wavelengths of 400-500 nm (Luxtrak™ product data sheet), with optimum photon absorption occurring at 470 nm. The free radicals generated lead to polymerisation which produces an increase in the viscosity of the system. Eventually, the viscosity of the system becomes so high that unreacted polymer can no longer diffuse, thus preventing further reaction (Murray and Jones, 1988).

Visible light cured resins (LCRs), offer several additional advantages over their competitors. They create none of the Health and Safety problems associated with say, UV cured adhesives, (the wavelength necessary to cure UV resins lies between 340 and 400 nm). UV cured systems were at one time being considered for use as dental restoratives, but concerns were raised that repeated exposure to high intensity UV radiation could lead to physiological damage (Hutchinson, 1989). This provided the necessary driving force to develop materials that cured at longer, visible light wavelengths. The next section aims to provide the reader with a summary of the main features that distinguish LCRs from other classes of adhesive.

In general, LCR materials have low shrinkages on cure, typically 3-3.5 % by volume shrinkage. Polymerisation produces a reduction in the number of chain ends and therefore a corresponding decrease in the amount of free volume associated with the chain ends (Young, 1983). It is this reduction in free volume that causes shrinkage to occur on cure. The degree of volume shrinkage in LCRs is minimised by the use of oligomers in preference to monomers, (as they have fewer free chain ends to start with). Alternatively, an inorganic filler may be incorporated. High volume shrinkages are undesirable, as they can produce stresses in the adhesive which partially supply the force needed to remove the adhesive from the substrate. In certain instances, the shrinkage stresses produced on cure are sufficient to produce spontaneous debonding of the coating. (Kendall, 1975). It is worth noting that although visible light cured resins have in general, much lower shrinkages than UV cured materials, cure still occurs in a matter of seconds, giving little opportunity for stress relief.
Chapter 2. Polymer Coatings on Ceramic Substrates

For the same intensity, visible light is able to provide a greater depth of cure than UV radiation, (5-10 mm, depending upon the percentage of filler, versus 3 mm). Below about 10 mm however, the photon flux is too low to allow cure within an acceptable timescale. Luxtrak™ resins also have good solvent resistance, to alcohols, hydrocarbons and ketones, a pre-requisite in many production environments where large quantities of solvents are still used in cleaning processes. Another useful characteristic is the ability to cure the resins through a variety of translucent materials, including alumina.

Photoinitiator systems are obviously of great interest in the study of this particular group of adhesives. Details of the precise photoinitiator used in Luxtrak™ adhesives are unavailable, due to the commercial sensitivity of the product. This section will therefore be limited to a brief discussion of the various known candidate materials. Adhesive formulators need to make a careful selection of photoinitiator for their system. Properties such as surface or through-curing efficiency, discoloration due to yellowing, adhesion, and mechanical response are directly related to the amount (and choice) of photoinitiator incorporated in the formulation (Gatechair and Wostratzky, 1984). Many of the photoinitiators described in the literature have been developed for use in UV systems, (Crivello, 1984 and Hageman and Jansen, 1988), but can equally well be activated by the visible blue wavelength of light. Cure may be initiated by the generation of either free-radicals or cations. Examples of photoinitiators for free radical polymerisation include benzoin derivatives and benzil ketals, (Hageman, 1985). The photoinitiator (PI), absorbs radiation of a particular wavelength to form an electronically excited photoinitiator (PI*). In general, there are two mechanisms by which the PI* can proceed to form free radicals. In the first mechanism, the photoinitiator undergoes homolytic bond cleavage resulting in the formation of two free radical units, P* and I*. In the second instance, photoinitiators undergo hydrogen abstraction from a second molecule (RH), producing two different free radical species ("PIH and R*). Propagation stages result in the formation of polymer by the addition of successive monomer (or, in this case oligomer) units. Termination may occur via three different mechanisms: (i) by combination which
results in an increase in molecular weight, (ii) chain transfer, which causes a decrease in molecular weight and finally, (iii) reaction with oxygen, which causes a decrease in molecular weight coupled with the formation of peroxide or hydroperoxide by-products, (see Figure 2.3).

Free radical photoinitiators are most widely used to polymerise oligomers which have been substituted with multiple acrylate (or methacrylate) ester groups, mixed with low molecular weight mono-, di- or trifunctional acrylate monomers. One of the major drawbacks of acrylic systems, however, is their susceptibility to polymerisation inhibition by oxygen, (Wight, 1978). Competition between the polymerisable species and interdiffusing oxygen for free radicals, results in the presence of a layer of uncured polymer at the atmospheric interface.

![Figure 2.3 Photoinitiated Free Radical Polymerisation Steps, (after Gatechair, 1984).](image-url)
Work has been carried out to develop photoinitiators for free radical polymerisation which counter the effects of oxygen inhibition (Hageman and Jansen, 1988), though this may not always be appropriate. The potential effects of photoinitiator selection on resin properties were described earlier in this section. Resin formulators may therefore be tied to a particular choice of initiator, in order to produce specific mechanical or optical properties. Where a free selection cannot be made, oxygen inhibition effects may be minimised by adopting any of the following measures. It may be possible to design out free surfaces (i.e. remove the atmospheric interface altogether). Working under aerobic conditions or using a much stronger photon flux can also help alleviate the problem. Where none of these measures are appropriate, as a last resort, a solvent rinse will remove the inhibited layer. Luxtrak™ resins are known to display this oxygen inhibition effect (Murray and Jones, 1988).

The main advantage of systems polymerised by cations, is that they are not inhibited by the presence of oxygen. The most frequently used cationic photoinitiators include triarylsulphonium salts of very strong acids, such as hexafluorophosphoric acid, (Crivello, 1984). Most of these salts do not absorb UV particularly well (Pappas, 1986), so they are generally used in conjunction with a strongly absorbing photosensitiser. Cationic photoinitiators are used in the polymerisation of epoxy resins, with mono- or difunctional epoxy compounds added to control the viscosity of the system. With the exception of epoxyacrylates, epoxy systems are not curable with free radicals. Cationic photoinitiators work by generating acidic species (reactive electrophiles), which in turn, catalyse the cationic polymerisation reactions of the epoxy resin. Photons generated by cationic photoinitiators are more stable than free radicals, so a post cure period often occurs after removal from the UV source. Volume shrinkages in these systems are also generally lower. The main disadvantage is that reaction rates are substantially slower, though improvements in cure speeds have been observed by the addition of a suitable sensitiser (Crivello and Lee, 1981).

2.1.4 Encapsulation/Potting Techniques

Potting compounds are used extensively by the electronics industry. After
fabrication, it is standard practice to encapsulate the devices for protection during service. Once in use, a device will be exposed to a potentially hostile environment. It is essential that components are hermetically sealed, to ensure long term reliability. For example, the connection paths on silicon chips are extremely delicate, and exposure to a hostile environment would result in failure within a short timescale. Encapsulation also minimises the risk of mechanical damage to, in particular, the wire connections, during handling.

There are a series of requirements for materials used in potting applications, the primary one being that the material is a good insulator. Potting is usually carried out by allowing a highly fluid thermoplastic or thermosetting polymer to flow over the chip and substrate. On solidification, a solid block protects both the device and wire connections. The polymer flow properties are also important, as entrapment of bubbles of gas could later act as stress raisers, or localised corrosion sites. The thermal expansion coefficient of the polymer should ideally be matched as closely as possible to that of the substrate material. The addition of inorganic fillers such as silica, to the polymer, is one method of reducing the mismatch in properties. Fillers also help reduce the volume shrinkage on cure of the polymer. The dramatic effects of large shrinkages on cure can be seen in Figure 2.4, a schematic illustration of the types of damage which can occur (Grovenor, 1989). Good adhesion to the substrate is important, in addition to a low rate of moisture diffusion, (as the encapsulant is there to exclude the atmosphere). Chemical resistance to solvents frequently used by the microelectronics industry is also an advantage.

Encapsulation has traditionally been perceived as the "low-tech" side of the electronics industry. The above description of some of the demands placed on potting compounds is intended to illustrate the challenge faced to develop suitable encapsulants.
2.2 Practical Aspects of Adhesion Theory

2.2.1 Introduction

Adhesion is a multi-disciplined field, which involves engineers, pure and applied scientists all working within closely related areas. This sometimes creates a degree of ambiguity, particularly in the choice of terminology. For example, to a physical chemist, "adhesion" refers to the attraction between a solid surface and a second (usually a liquid) phase. The magnitude of this attraction is evaluated by taking contact angle measurements of various liquids on substrates, from which interfacial free energies, \( \gamma \), can be estimated. To a technologist however, "adhesion" is understood to refer to the resistance offered by a joint to separation using mechanical means. Adhesion in this sense is affected by numerous factors. In addition to both the bulk and interfacial properties, factors including joint geometry, failure mode, film thickness and testing rate all have a direct relation on measurements. "Adhesion" cannot therefore be described as a material property. In a recent review given by Mittal (at ECASIA '93), the term "practical adhesion" was suggested in relation to
coatings, where practical adhesion is defined as the force or work necessary to remove the coating from a substrate. This term has yet to be widely adopted, hence the need for some clearly defined international standards. Until such time, authors need to define their terms clearly.

2.2.2 Mechanisms of Adhesion

A comprehensive literature review of all the adhesion mechanisms that have previously been suggested, might leave the reader feeling at the very least, confused. Four main theories have been suggested, mechanical interlocking, diffusion theory, electronic theory and adsorption theory. Each has its proponents, who have supplied scientific evidence to substantiate their theories. A considerable number of experiments have also been contrived in order to obtain data which will disprove one or other of the theories. The result is that there is now a wealth of conflicting information in the literature. The scientific community of Russia has generally proclaimed its support for the electronic and diffusion theories, (both proposed by Russian scientists). However, the adhesion community as a whole favours the adsorption theory, (which includes both primary and secondary force interactions), and has been found to be more widely applicable (Brewis and Briggs, 1985).

This conflict may in part be due to an earlier conviction held by many workers, that they should search for a single mechanism of adhesion (Kinloch, 1987). Added to the confusion, was the often inappropriate selection of test methods. Fortunately, today, a rather more liberal approach is adopted and the search for the elusive mechanism responsible for all adhesion phenomenon observed, has been abandoned. Mittal has diplomatically chosen to describe adhesion as "the quality and quantity of intimacy". Therefore, anything which is able to improve either the quality or the quantity of interfacial contact, is liable to enhance the practical adhesion of a system.

Several detailed reviews are available in the literature, which evaluate the experimental evidence both for and against each of the main theories (Wake, 1982; Kinloch, 1982 and 1987). The following section will therefore be limited to a brief description of those mechanisms.
(a) **Mechanical Interlocking**

The mechanical interlocking theory suggests that for an adhesive joint to be formed, interlocking or "hooking" of the adhesive in pores or irregularities in the substrate is required. There are very few practical examples of true mechanical interlocking, that is, where geometry alone is relied upon to keep the joint together. Mechanical fasteners such as Velcro™ are sometimes included in this category. The most frequently cited example is that of the undercut cavity made by a dentist in order to fill a tooth with mercury amalgam. In the hostile environment of the mouth, dental restoratives need to be able to withstand repeated thermal cycling, mechanical abrasion as well as chemical attack. In order to achieve an acceptable service life, (7-10 years), the dentist prefers to include the added security of joint geometry to keep the restorative in place (Kendall, 1988). The tooth is undercut at an angle of about 7°, to produce an "ink-bottle" shaped cavity. Unfortunately, this tends to involve the removal of more tooth material than is strictly necessary, (i.e. some healthy material). The development of in particular, radiation cured dental restoratives (Ali *et al.*, 1990), where considerable effort has gone into promoting primary bonding to the dentine, has helped reduce this reliance upon geometry and hence the need for undercutting, (e.g. Luxtrak™ resins).

There are two main criticisms of this particular mechanism. The first is that, very smooth surfaces have also been observed to strongly resist separation by mechanical means. This observation was first made by Hooke and recorded in 1730 by Sir Isaac Newton, (1730). "The separation of two glass lenses, pressed together to form a contact circle, results in an audible klink". More recently, Tabor *et al.* reported good practical adhesion between sheets of perfectly smooth mica (Tabor and Winterton, 1969). Mechanical interlocking cannot therefore be a general requirement for adhesion. It may however, aid in the joining of porous materials such as paper, cloth or wood.

The second major criticism is that many of the surface pretreatments used on adherends such as grit blasting, whilst creating an overall surface roughening effect, do not in fact produce the classic "ink-bottle" geometry required for mechanical
interlocking to occur. The reported increases in joint strength are more likely to be as a result of (i) removal of surface contaminants, which could act as potential, weak boundary layers, WBLs, (Bikerman, 1967), (ii) an extension of the path length available for bonding, or, finally (iii) as a means of providing a route to dissipate energy within the adhesive (Gent and Kinloch, 1971; Evans and Packham, 1979).

(b) Diffusion Theory

The diffusion theory was developed primarily for applications involving polymers, to account for the driving forces involved in autohesion (the intrinsic adhesion of polymers to themselves) and heterohesion, their adhesion to each other. The theory was first proposed by Voyutskii in 1963 (Voyutskii, 1963), and suggests that joint strength occurs as a result of polymers diffusing across the interface, surface contact alone is insufficient. The evidence to support this idea comes from the observation of the functional dependence of strength for polymer-polymer joints, on contact time, temperature, polymer type, molecular weight and viscosity. These are all examples of parameters traditionally associated with diffusion controlled processes. Vasenin, in subsequent publications (1965(a), (b) and 1969), continued to develop the theory with the introduction of quantitative models based on Fick’s first law. Although, Fick’s Law is rather an inappropriate choice for modelling polymer interdiffusion, as it is only applicable to steady-state diffusion processes.

Diffusion theory has attracted several major criticisms, most serious of which is the fact that it cannot be applied universally. In certain classes of material, such as glass and metal oxides, the rate of diffusion would be so low at room temperature and pressure (RTP), that it cannot be considered a viable mechanism. In addition, the diffusion theory makes the assumption that the polymer chains of both adhesive and adherend are mobile (able to reptate), and mutually soluble. The value of the solubility parameter gives a strong indication of the likelihood of mutual solubility occurring. In general, the closer the solubility values, the easier it is to form a solution. Inherent in this assumption is the fact that the polymer needs to have an amorphous structure, (i.e. as crystalline or heavily cross-linked polymers would be both insoluble and restricted in mobility).
Chapter 2. Polymer Coatings on Ceramic Substrates

Vasenin's model has also been criticised for not taking account of any of the energy dissipative processes which result during mechanical testing. Perhaps more serious, is the criticism by Anand (1973), that the observed increases in joint strength following longer contact times, increased temperatures etc., (i.e. diffusion controlling parameters), may not be as a result of diffusion at all. Anand argues that the improvements could equally well be due to the kinetics of wetting. Raising the temperature lowers the viscosity of the polymer, which in turn aids more uniform spreading over the substrate. An improvement in the adhesive/adherend interfacial contact will thus enable the formation of more secondary (van der Waals), bonds across the interface, creating better performance.

The existence of several fundamental weaknesses therefore makes the diffusion theory of limited usefulness.

(c) Electronic Theory

Electronic theory, (alternatively known as electrostatic theory), proposes that joints are held together by electrostatic forces that arise between the adhesive and substrate. The theory was suggested by Deryagin, Krotova and co-workers, (Deryagin, 1955; Deryagin et al., 1957). They maintain, that when two materials, each with a specific electronic band structure, are brought together in direct contact, electron transfer will occur to balance this difference in charge. The joint essentially behaves as a capacitor, with its strength due to the formation of an electrical double layer at the interface. Experimental evidence for this view comes from the observation of electrical discharges, (sparks), when for example, pressure sensitive adhesive tapes are stripped from a substrate. This is where the major controversy arises; the electrical phenomena on which the theory is based, are only observed when the joint is broken, and critics are unwilling to accept them as a means of explaining joining. Deryagin et al. regard these electrical effects as the basis for good adhesion, while critics argue that they are more likely to be as a consequence of high recorded strengths. In other words, opponents of the theory believe that electrical discharge is a result rather than a cause of good adhesion. The chemical and rheological properties of the adhesive are also quite different before and after joining, (with the exception of pressure-
sensitive adhesives), so "like is not compared with like".

Again, as with the diffusion theory, the electronic theory is not universally applicable, for example, the theory would not predict joint formation between conductive materials. A further criticism is, that while humidity would be expected to help bleed off electrical charge during breaking, thus causing a decrease in strength, there is no evidence to support this. Similarly, the presence of ionising radiation during fracture has no observed effect on strength, (Sharpe, 1993).

Manufacturers do make use of these electrostatic attractions in photocopying technology, but they also need to melt the particles in contact with the paper, electrostatic forces alone are inadequate. There are in fact very few examples where electronic interactions have been demonstrated to make a significant contribution. As with the previous two mechanisms of adhesion, the electronic theory is therefore of limited application.

(d) Adsorption Theory

Adsorption theory is regarded by the adhesion community as the most significant of the four mechanisms described, primarily due to its widespread applicability. The theory involves the adsorption of organic molecules onto a substrate, which are then held by a combination of physical and chemical forces. The most common physical interactions are van der Waals forces, which maybe induced by permanent dipole-dipole interactions, (Keesom forces), dipole-induced dipole interactions, (Debye) and dispersion, (or London forces). Dispersion forces arise due to electron motions and are independent of dipole moments. Van der Waals forces, (by virtue of the magnitude of their bond energies), are described as secondary bonds. Some scientists prefer to define an upper limit of the strength of physical interactions, arbitrarily set at a value of about 84 kJ mol⁻¹.

Alternatively, adhesive molecules may react chemically with a substrate (chemisorption), to form primary bonds, which may be ionic, covalent or metallic in nature. A third class of bond also exists, (produced by donor-acceptor interactions), and their energies lie midway between the generally accepted values of primary and secondary bonds. Of these, acid-base interactions are most widely documented (Lee,
It is more appropriate to include hydrogen bonds in this category. Heats of formation for hydrogen bonds have been shown to depend on the acid strength of the hydrogen donor and the base strength of the hydrogen acceptor (Pimentel and McClennan, 1960). Unlike the dipole-induced van der Waals interactions, hydrogen bonds have definite bond angles and lengths.

Some of the most significant contributions to our understanding of acid-base interactions, have been made by Fowkes and co-workers. Acids are defined as electron acceptors (Lewis acids) or alternatively as proton donors (Brønsted acids), while bases are defined as electron donors (Lewis bases) or proton acceptors (Brønsted bases). In systems where adhesive and substrate have acid-base character, acid-base interactions are believed to contribute strongly to the intrinsic adhesion forces operating. Drago originally proposed that the exothermic enthalpy of acid-base interactions (in kcal mol\(^{-1}\)), for a variety of Lewis acids in a neutral solvent, could be determined by the following relation:

\[
-\Delta H_{AB} = C_A C_B + E_A E_B \quad \ldots \text{Eq. 2.1}
\]

where \(\Delta H_{AB}\) is the enthalpy of the acid-base interactions, and \(E\) and \(C\) are the two parameters used to characterise the Lewis acid or base, (the subscripts \(A\) and \(B\) referring to the acid and base), (Drago \textit{et al.}, 1971). The \(E\) and \(C\) parameters, as they are referred, relate to the affinity of a given species to undergo electrostatic, (\(E\)) and covalent, (\(C\)), interactions, (Chehimi \textit{et al.}, 1992).

Gutmann adopted a different approach to calculate the enthalpy of formation of a Lewis acid-base adduct, (Gutmann, 1978). He devised the terms donor and acceptor numbers, (\(DN\) and \(AN\)), where, \(DN\) is a measure of the basicity and \(AN\), the acidity of a Lewis acid/base. The donor and acceptor numbers are approximately related to \(\Delta H_{AB}\) via the following equation:

\[
-\Delta H_{AB} \approx \frac{DN \cdot AN}{100} \quad \ldots \text{Eq. 2.2}
\]

Bolger devised an alternative means of measuring acid-base properties, (Bolger, 1983). He defined what is known as a delta parameter, the magnitude of which gives
an indication of the level of interaction between the two phases. The delta parameter is defined as the numerical difference between the isoelectric point of the inorganic surface, (IEPS), and the acid ionisation constant of the polymer, (pKₐ):

\[ \Delta \text{pH} = \text{pH}_{\text{surf}} - \text{pK}_a \] ...Eq. 2.3

Bolger then went on to produce an empirical index of acid-base interactions for a series of organic compounds on acidic, basic and neutral surfaces. The data in the index were then grouped in three separate categories, (i) large, negative values of \( \Delta \), indicating little or no acid-base interaction, (ii) a small positive or negative value, suggesting some acid-base character, and finally, (iii) a large positive value of \( \Delta \), indicating strong acid-base character. N.B It is not always beneficial to have strong acid-base interactions at a surface, as in some instances chemical attack of the surface might be induced, (e.g. dodecyl sulphonic acid attacks magnesium oxide, Bolger, 1983).

In addition to acid-base interactions, other examples of primary bonding across an interface have been reported in recent years. In some instances, it has been possible to elucidate the formation of very specific bonds with a well defined bond length and angle. The best examples of this type of bonding include bonding of certain organic coatings on steel e.g. polybutadiene on steel (Watts, 1983), metallised plastics such as titanium on polyimide, (Ohuchi and Freilich, 1986) and finally in the use of adhesion promoters such as silane coupling agents.

Although the adsorption theory is perhaps the most promising, none of the theories described above is universally accepted. It is therefore worth regarding them merely as a starting point in our understanding of adhesion.

### 2.3 Adsorption of Polymer Molecules on to Surfaces

As adsorption is now widely recognised as a significant factor in adhesion, it is therefore important to consider the various aspects of polymer adsorption onto surfaces. One of the properties which makes polymers particularly suited in applications such as coatings and adhesives, is their ability to become readily adsorbed...
onto solid surfaces, (Roe, 1980). Molecules may either be physisorbed, or chemisorbed onto a surface. Physisorbed species are held by van der Waals forces, (i.e. by dispersive interactions) and are less strongly bound than chemisorbed molecules. Adsorption at an interface produces either an enhancement or a depletion of species in the region immediately adjacent to the interface. A series of interesting features has been observed to occur in polymer adsorption, as distinct from the adsorption of for example, simple gaseous molecules onto surfaces.

The adsorption of macromolecules tends to be high, even from dilute solutions. Macromolecules have large surface areas which result in correspondingly high surface activities, (Silberberg, 1980), thus facilitating adsorption. One of the most well documented features of polymer adsorption is the molecular weight dependence, (Cohen Stuart et al., 1980). In systems containing polymers of varying molecular weight, (but otherwise equivalent), molecules of high molecular weight are adsorbed in preference to the smaller ones. This result is a little surprising at first sight, especially when the smaller and hence more mobile species would be expected to reach the interface first. In fact, on arriving at the interface, larger molecules will often displace the smaller ones. This produces an increase in entropy, because it allows larger numbers of small molecules to return to the bulk, each of which has an entropy associated with it.

Clearly, it is relatively easy to study dilute polymer systems where the only variable is the molecular weight. However, most commercially available coatings and adhesives are multicomponent systems, containing molecules which may not be equivalent, either in terms of molecular architecture or their chemical properties. In some cases, (Jones, Kramer et al., 1992), model systems have been constructed, where polymer chains are labelled with deuterium and forward recoil spectrometry is used to study segregation effects. This is obviously an area which warrants more detailed investigation.

A second, though equally important feature of macromolecular adsorption, is that thermodynamic equilibrium is very often not achieved. Additional factors therefore need to be taken into account. For a non equilibrium system, factors such
as chemical potential gradients and transport coefficients are important. The transport coefficient of a given molecule in a system will be heavily dependent on its coefficient of friction within the melt. The size of a molecule and in particular, the degree of branching will affect the mobility, (i.e. short linear molecules have lower coefficients of friction). Selective adsorption of polymers from solution also occurs if there are differences in adsorption affinity, once a molecule is in close proximity to a surface. In a polymer blend, small differences in surface energies can lead to pronounced segregation effects. Resin formulators need to be aware of this influence, to avoid the deleterious effects which may be caused by segregation occurring within a coating or adhesive.

In a system where selective adsorption is believed to occur, several properties are of interest:

(i) the quantity of anchored chains, or degree of grafting to the surface, (i.e. surface coverage)
(ii) the geometry of the grafted layer, (some molecules tend to adsorb in a preferred orientation)
(iii) the sharpness of the interface between the selectively adsorbed layer and the bulk
(iv) the kinetics of the arrival of the chains at the interface

Previous studies relating to the geometry of grafted layers have revealed two different conformations, (see Figure 2.5). Linear flexible molecules are observed to produce surface-held "trains", free-hanging loops, with the ends of the molecule referred to as "tails". Other molecules may either be too short to produce loops and trains, or instead possess groups which are preferentially adsorbed onto the surface. In this case, a polymer "brush" results, (Sanchez, 1992).

In the case of homopolymers, this is likely to result in the reorientation of molecules adjacent to the interface, as reported by Chehimi and Watts, 1993. In the case of multicomponent systems however, the possibility exits for the various components to stratify, producing regions of varying composition.
In the above section, considerable attention has been paid to the way in which polymer molecules are adsorbed on to surfaces. In order for adsorption to occur, it is first necessary for the molecules to come into close contact with the surface. In the case of an adhesive, good wetting of the adherend surface facilitates the adsorption of the adhesive molecules. The following section therefore considers the theory of wetting and spreading.

Figure 2.5 Schematic to illustrate (a) the formation of loops and trains and (b) a polymer brush.
2.4 Wetting and Spreading

2.4.1 Introduction

In the previous section, adsorption was described as the most significant theory currently used to account for adhesion. Lee describes diffusion and wetting as the kinetic means of obtaining good adsorption of a polymer on a surface (Lee, 1991). Wetting allows the polymer molecules to come into intimate contact with the substrate, thus enabling the formation of polymer/substrate interactions.

2.4.2 Contact Angle

When a drop of adhesive (or any other liquid) makes contact with a solid surface, wetting and spreading occur until such time as an equilibrium (stable or metastable) contact angle is reached. Theta is the contact angle, $\gamma_{LV}$ is the liquid-vapour tension, $\gamma_{SL}$ the solid-liquid tension and $\gamma_{SV}$ the solid-vapour tension. A force per unit length of triple line acts along each interface. In the case of a sessile drop, (Figure 2.6), these forces must balance, as Young showed in the following expression:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

...Eq. 2.4

When $\theta$ is equal to zero (or near zero), maximum interfacial contact is obtained, thus providing the best opportunity for adhesive/substrate interactions to occur.

Although, as indicated by Huntsberger, (1967), near-zero values of contact angle are not necessarily a pre-requisite for good adhesion. In fact, it has been shown that the criterion where $\theta$ makes an angle of less than $90^\circ$ with the substrate, includes the majority of practical situations (Brewis and Briggs, 1985). However, one of the benefits of a low contact angle is, that uniform surface coverage is possible using the minimum amount of adhesive/coating.

The sessile drop depicted in Figure 2.6, is assumed to be resting on a smooth, non-deformable, impervious solid. In real systems, the presence of surface contamination, dust, grease etc. can inhibit wetting. Factors such as surface topography and porosity will also have a significant affect on the value of the contact
angle, (contact angle tending to increase with roughness). Not surprisingly, the use of idealised surface contact measurements is often criticised in relation to real systems. Another criticism, is that macroscopic equilibrium measurements should not be used as a means of establishing microscopic phenomena, (i.e. molecular interactions), because of factors such as contact angle hysteresis, observed only on the macroscopic scale.

**Figure 2.6** Cross-section of a sessile drop of liquid on a solid, showing the balance of forces at equilibrium.

### 2.4.3 Critical Surface Tension for Wetting

Zisman took the concept of contact angle measurement a stage further, by introducing a "critical surface tension for wetting" (Zisman, 1965). After taking contact angle measurements from a series of liquids on various solids, Zisman noted a linear relationship between the cosine of the contact angle, \( \cos \theta \) and the surface tension of the liquid \( \gamma_{LV} \). Extrapolation of this line to the point where \( \cos \theta = 1 \), yielded a corresponding value for surface tension, which Zisman termed the critical surface tension, \( \gamma_C \). The critical surface tension can be considered as the surface tension of the liquid that will spontaneously wet the solid. This term was regarded by Zisman as purely an empirical parameter "whose relative values act as one would expect of the
specific surface free energies of the solids". This perhaps explains the subsequent misuse of the term $\gamma_C$ as the surface energy of the solid.

2.4.4 Surface Free Energy

Zisman's work on critical surface tension, was one of the first attempts to characterise low energy polymeric surfaces. Polymeric materials, as with other organic compounds, fall under the heading of low energy surfaces (values typically between 20-50 mJ m$^{-2}$). High energy surfaces include metals, metal oxides and ceramics (values lie anywhere between several hundred and over a thousand mJ m$^{-2}$). Surface free energy is an important consideration to include in adhesion studies, as it is significantly more difficult to bond to low energy surfaces. A problem frequently encountered by the packaging industry, where the surface energy of materials often needs to be artificially increased by corona discharge or similar methods, to enable the polymer to be either bonded, or printed on.

It has been shown by Fowkes, that the surface free energy term, ($\gamma$) can be represented as the sum of seven different contributions. In general, only the first three contributions are quoted, as they tend to predominate, i.e:

$$\gamma = \gamma_D + \gamma_P + \gamma_M + ...$$

...Eq. 2.5

where, $\gamma_D$ is the dispersion component, $\gamma_P$, the polar component and $\gamma_M$, the metallic component. Other contributions arise from electrostatic, covalent and hydrogen bonds, in addition to minor contributions from dipole-dipole interactions, (Keesom forces) and dipole-induced dipole interactions, (Debye forces).

2.4.5 Work of Adhesion

The thermodynamic work of adhesion ($W_A$), utilises the concept of surface and interfacial free energies to predict whether or not adhesion is energetically feasible. In a similar way that the change in Gibbs free energy, ($\Delta G$), is used to evaluate whether or not a reaction is thermodynamically likely to occur, without considering the kinetics of the process, $W_A$ is used to express the likelihood of two materials becoming
Chapter 2. Polymer Coatings on Ceramic Substrates

separated, (spontaneously). Work of adhesion is defined as the work required to generate 1 m² of new surface, illustrated schematically in Figure 2.7. A negative $W_A$ value suggests that separation is energetically favourable, while a positive value indicates that separation is unlikely.

![Figure 2.7 Schematic illustrating the creation of two new surfaces.](image)

In order to calculate $W_A$ it is first necessary to have an estimate of the interfacial free energy, $\gamma_{AB}$. Provided the interfacial free energies of the two components are known, $W_A$ may be calculated from the following equation, referred to as the Dupré equation:

$$W_A = \gamma_A + \gamma_B - \gamma_{AB}$$

...Eq. 2.6

An attempt was then made to draw an analogy with the Berthelot relationship, a concept originally developed for looking at the attractive constants between both similar and dissimilar molecules. This approach proved unsuccessful, as it failed to
take account of the different types of interfacial interactions operating. The Berthelot relationship is stated below:

\[ \gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A\gamma_B} \]  ...Eq. 2.7

Fowkes noted that for most systems, the first two terms in equation 2.5, (i.e. the dispersion and polar forces) dominate. He was therefore able to adapt the Berthelot type equation, by incorporating a geometric mean term to account for the polar and dispersion interactions.

Thus, for two components A and B, the net energy of phase A is:

\[ E_A = \gamma_A - \sqrt{\gamma_A\gamma_B} - \sqrt{\gamma_A\gamma_B} \]  ...Eq. 2.8

and for phase B:

\[ E_B = \gamma_B - \sqrt{\gamma_A\gamma_B} - \sqrt{\gamma_A\gamma_B} \]  ...Eq. 2.9

This is illustrated schematically in Figure 2.8.

Figure 2.8 Schematic of the calculation of the net energy of two phases, A and B, (after Fowkes, 1964).
Chapter 2. Polymer Coatings on Ceramic Substrates

such that the interfacial free energy may be calculated as:

\[ \gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A\gamma_B} \]  

...Eq. 2.10

hence, by substitution in the Dupré equation, (Eq. 2.6), the work of adhesion is defined by:

\[ W_A = 2\sqrt{\gamma_A\gamma_B} + 2\sqrt{\gamma_A\gamma_B} \]  

...Eq. 2.11

Under dry conditions, \( W_A \) values are, almost without exception, positive in value. In practical systems, (again under dry conditions), it is extremely rare to see true interfacial separation, thus supporting the results of the thermodynamic calculations, (i.e. positive work of adhesion values).

Fowkes et al., (1988) went further, to define the work of adhesion as:

\[ W_{AB} = fN (\Delta H_{AB}) \]  

...Eq. 2.12

where \( N \) is the number of moles of acidic or basic functional groups per unit area and \( f \) is a term converting the enthalpy term to an energy one. In order to make this conversion, \( f \) is set equal to unity, an assumption strongly criticised in recent publications, (Vrbanac and Berg, 1991). "Setting it, \( f \), equal to unity, as has been done to this point, is tantamount to ignoring any entropy change associated with the formation of acid-base adducts at the solid-liquid interface, an assumption which has not yet been justified". Work by Vrbanac et al. has gone some way to correct this error and their results suggest that \( f \) may be substantially less than one.

The Dupré equation (Eq. 2.6), can be modified to consider the presence of a third, usually liquid phase, \( L \). In service, joints will almost without exception, come into contact with a third phase. Water is the most frequently encountered fluid, but other common liquids include organic solvents and aviation fuel. In this particular study, it is the presence of water which is of most concern. If joint separation occurs in the presence of this third phase rather than say, in air, equation 2.6 becomes:
Chapter 2. Polymer Coatings on Ceramic Substrates

\[ W_{AL} = \gamma_{AL} + \gamma_{BL} - \gamma_{AB} \] ...Eq. 2.13

The surface free energy, (\( \gamma \)) of a material is the sum of seven contributions, the most dominant of which are the polar and dispersive components, as indicated by equation 2.5. Substituting into equation 2.13 for \( \gamma_{AB} \), \( \gamma_{AL} \) and \( \gamma_{BL} \) gives:

\[ W_{AL} = 2[\gamma_{YL} - (\gamma_{AYL})^{1/2} - (\gamma_{YbYl})^{-1/2} - (\gamma_{YbYl})^{1/2}] \] ...Eq. 2.14

By using values for the polar and dispersive components of surface free energy, it is possible to calculate the thermodynamic stability of a system in the presence of a third phase, (L). Negative values of \( W_{AL} \) suggest that the system will be unstable in the presence of this phase. However, in practise, negative \( W_{AL} \) values do not always result in interfacial failures. This apparent discrepancy between the results of the thermodynamic calculations and practical situations, can be explained by the fact that the rate of diffusion of water in a polymer, (in the region close to the interface), is often much faster than the rate of polymer displacement from the substrate. Thermodynamic calculations give an indication of whether a process is likely to occur, without taking the kinetics of the process into account.

2.5 Modes of Failure

Adhesive failure will occur if one of the following conditions arises:

(i) poor contact between the "wetting phase" and the substrate

(ii) the presence of a weak boundary layer (WBL)*

* A WBL is defined as a region of low cohesive strength, (Brewis in Packham, 1992).

(iii) stress concentrations which could lead to disbonding or, exposure to hostile environmental conditions which leads to one of the above conditions. Exposure to hostile environments will be dealt with in detail in the section on durability studies.
Three different loading modes are generally defined, (see Figure 2.9):

(a) Inplane-opening or tensile mode, given the notation Mode I failure
(b) Inplane-shear or shearing mode, Mode II failure
(c) Antiplane-shear or tearing mode, Mode III failure.

It is not unusual for some form of mixed-mode failure to occur, sometimes due to the test methods employed. This makes characterisation of the mechanical properties of the adhesive system more complicated, though not impossible.

![Diagram showing failure modes: (a) tensile, (b) shear, (c) tear.](image)

**Figure 2.9** Failure modes, (a) tensile, (b) shear and (c) tear, (after Lawn and Wilshaw, 1975).

### 2.6 Locus of Failure

Determining the locus of failure forms an important part of adhesive failure analysis, and may even help to reveal how the failure occurred. There are three potential modes of failure: cohesive, (which may occur in either the adhesive or the adherend), interfacial, (sometimes referred to as adhesive) and mixed-mode. Cohesive failures generally occur within the layer of adhesive, though on occasion, in the actual substrate. An interfacial failure occurs at the adhesive/substrate interface. Mixed-mode is the term given to fracture surfaces which contain regions of differing loci of failure.
The first stage in failure analysis is generally a visual inspection. This may prove misleading, as an overlayer of polymer often remains on one of the fracture surfaces, but is invisible to the naked eye. The next stage is analysis by either optical or electron microscopy, but even with the magnification of a scanning electron microscope, it is not possible to observe an overlayer below about 100-200 nm thick. In order to establish the true locus of failure, surface specific techniques (with sampling depths of the order of a few nanometres) are required. Of these, X-ray photoelectron spectroscopy, (XPS), is most frequently applied. In practise, XPS analysis is carried out prior to investigation by SEM, in order to avoid sample contamination. The science of adhesion is a well established field, with detailed models proposed to account for experimental observations. In order to propose a failure mechanism for a system, and subsequently suggest improvements for the system, it is first essential to establish the precise locus of failure.
3.1 X-ray Photoelectron Spectroscopy (XPS)

3.1.1 Introduction

The key technique used during the course of this work was XPS, used initially in the characterisation of both the adhesive and adherend, and also extensively in the analysis of the failure surfaces of the adhesive joints. Since the commercial availability of X-ray photoelectron spectrometers 25 years ago, the technique has been widely adopted in many areas, particularly in the field of adhesion, (Brewis and Briggs, 1985). It's strength lies in the ability to provide elemental analysis from a depth of a few nanometres, with two additional advantages over other surface analytical techniques, (i) chemical state information is available and (ii) the data can be readily quantified. This assumes homogeneity within the sampling volume, which for the majority of cases is a reasonable assumption, as analyses are often required relative to other samples. In most cases, the data can be quantified to a high degree of accuracy. One of the main advantages of XPS over other methods of analysis, is the modest influence of matrix effects, which allows atomic sensitivity factors to be used.

XPS, together with other surface analysis techniques, have contributed to our understanding of adhesion phenomena in three main areas, (Watts, 1990). Firstly, in the analysis of surfaces prior to bonding, whose purpose maybe twofold, (i) to characterise the adherend surface and (ii) as a means of establishing the cleanliness of the surface, (Moyer and Wightman, 1989). The second area often involves some form of elaborate sample preparation, "probing the buried interface", (Castle and Watts, 1988), in order to investigate substrate/polymer interactions directly, within the interfacial region. Finally, as a means of determining the precise locus of failure in an
adhesive joint. In cases where a thin, (less than 10 nm), overlayer of adhesive remains on the failure surface, surface analysis provides the only viable means of establishing that a failure was cohesive rather than interfacial.

The development of commercially available spectrometers is a relatively recent event in the chronology of XPS. It was Hertz who first discovered the photoelectric effect in 1887, (Briggs and Seah, 1990). At the turn of the century, early experiments were also being carried out at Rutherford’s Manchester laboratory by Moseley, Rawlinson and Robinson. Research activity in this area was then seriously curtailed by the outbreak of the First World War. After the War ended, Robinson resumed work in this area, with de Broglie in France, also developing an interest in the field. Progress continued, until once again, wartime halted any further significant advancement of the technique.

The most rapid progress was made in the period following the Second World War. It was during this time, that the potential for the technique as a means of chemical analysis was realised. Steinhardt, a postgraduate student at Lehigh University, published a thesis entitled "An X-ray photoelectron spectrometer for chemical analysis". However, it was the work of Kai Siegbahn, (Nobel Prize laureate), together with his colleagues at Uppsala in Sweden, who helped the technique to gather impetus. The first XPS spectrum, as we would recognise it today, (obtained from a sample of cleaved sodium chloride), was produced in 1954, using an iron-free double-focusing spectrometer. The original acronym by which the technique was known, ESCA, (electron spectroscopy for chemical analysis), was also devised by Siegbahn. The Uppsala group went on to make significant advancements in electron spectroscopy between 1955-1970, until 1969-1970, the first commercial instruments became available, from UK and USA manufacturers.

3.1.2 Basic Principles and Theory

A brief introduction to XPS follows, with particular attention paid to aspects of the technique which are relevant to this project. For more detailed information, the reader is referred to the following comprehensive texts on the subject, (Briggs and

XPS, as the name implies, utilises X-rays as the primary excitation source. The X-rays cause photoionisation of the atoms in the specimen, which in turn results in a process known as photoemission. During photoemission an electron is ejected from the core level of an atom by an X-ray photon of energy, $h\nu$. Photoelectrons have a kinetic energy ($E_R$) which can be related to the X-ray energy ($h\nu$, where $h$ is Planck's constant and $\nu$ is the frequency of light), and the binding energy ($E_B$) by the Einstein relation:

$$E_K = h\nu - E_B \quad \ldots \text{Eq. 3.1}$$

It is important to note that $E_K$, although the experimental quantity measured by the spectrometer, is not a material property and depends on the energy of the X-ray source used. The binding energy of the electron ($E_B$) is however specific to an electron, in terms of both its parent element and atomic energy level (Watts, 1990), thus allowing qualitative elemental analysis of a sample. Experimentally, the parameters involved in XPS are related via a modified form of the Einstein equation as follows:

$$E_K = h\nu - E_B - E_R - \Phi \quad \ldots \text{Eq. 3.2}$$

where the additional parameters are, $E_R$, the recoil energy, (only about 0.1-0.01 eV) and therefore generally ignored, and $\Phi$ is the spectrometer work function. The work function accounts for the extra energy needed to remove an electron far enough away to prevent it from recombining with the atom. Provided that the sample is conducting, and has not been insulated from the spectrometer by some means, then the value of $\Phi$ is virtually constant for most spectrometers, at a value of about 4.5 eV. The value of 4.5 eV corresponds to the work function of the analyser material, (stainless steel). The concept of the spectrometer work function is returned to overleaf. Figure 3.1 is a schematic of the XPS process.
Chapter 3. Experimental Techniques

Figure 3.1 Schematic of the XPS process

Figure 3.2 Energy diagram in relation to the photoemission of an electron and its passage through a simple analyser, (after Watts, 1994(a)).
In practice, low-energy (soft), X-rays are used to irradiate the sample surface under ultra-high vacuum conditions. Photoelectrons which result from the photoemission process are analysed by the electron spectrometer. The data is displayed as a graph of intensity (or counts per second) versus electron energy and is termed an X-ray photoelectron spectrum. The spectrometer actually measures kinetic energy, but as this quantity is related to the binding energy, it is more usual for data to be displayed on a binding energy scale. The photoelectron binding energy is defined as the energy required to remove it to infinity with a kinetic energy of zero, (Feldman and Mayer, 1976). The binding energies are generally referenced to the Fermi energy, \( E_F \), though this is not strictly the zero point of the electron energy scale. The actual value of zero is the standard vacuum level, \( E_V \). The Fermi energy and the vacuum energy level are approximately related via the following equation,

\[
E_F - E_V = \Phi \tag{3.3}
\]

where \( \Phi \) is the work function of the material. For a conducting sample in electrical contact with the spectrometer, the Fermi levels of the specimen and the spectrometer are equal, (see Figure 3.2). The incoming photon, of energy \( h\nu \), causes the photoemission of an electron of kinetic energy, \( E_{\text{kin}} \), relative to \( E_V \), the vacuum level of the sample. The energy of the electron, measured by a spectrometer of work function, \( \Phi_{\text{spec}} \), is:

\[
E_{\text{kin}} = E_{\text{kin}}^{1} - (\Phi_{\text{spec}} - \Phi_{s}) \tag{3.4}
\]

where, \( \Phi_{s} \) is the work function of the sample. This may alternatively be written as:

\[
E_{\text{kin}} = E_{\text{kin}}^{1} + (\Phi_{s} - \Phi_{\text{spec}}) \tag{3.5}
\]

This indicates that for a photoelectron passing from the sample surface to the spectrometer, it will experience a potential equal to the difference between the spectrometer work function and the work function of the sample, (Feldman and Mayer, 1976). However, Figure 3.2, shows that the binding energy of a conducting
sample may be determined relative to the Fermi level, (which is aligned with the spectrometer), such that:

\[ h\nu = E_B^F(k) + E_{xin} + \Phi_{spec} \]  \hspace{1cm} \text{... Eq. 3.6}

where \( h\nu \) is the energy of the incoming photons, \( E_B^F \) is the binding energy referred to the Fermi level and \( k \) refers to the \( k \)th level from which the photoelectron is ejected. Equation 3.6 demonstrates that for a conducting sample, only the work function of the spectrometer needs to be taken into account.

3.1.3 XPS Analysis of Insulating Samples

In this study, it is particularly important to consider the effects of analysing non-conducting samples, as both the adhesive and adherend are insulators. In a conducting sample, there is an overlap of the valence and conduction bands, and the uppermost occupied state is known as the Fermi level. Insulating samples have a band gap which separates the valence band from the conduction band. The spectrometer also has a Fermi energy, of the same value as a conductor. In the case of an insulator, or where a conducting sample has been isolated from the spectrometer by some means, there will be a difference in Fermi levels, due to a lack of thermal coupling. This misalignment is sometimes referred to as a "floating Fermi edge". The lack of thermal coupling means that it is no longer valid to reference XPS energies to the zero Fermi edge of the spectrometer. Considerable effort has been directed towards evaluating true XPS binding energies by eliminating problems associated with charging, in order to measure chemical shifts accurately, but more progress in this area is still required. Figure 3.3 illustrates the differences in thermal coupling when an insulator is analysed as compared with a conducting sample.
Figure 3.3 Energy level diagrams for XPS analysis, (a) conducting sample and (b) insulating sample, (Briggs and Seah, 1990).
Sample charging is most frequently observed by a positive shift, $\delta E$, (on the binding energy scale) of an XPS spectrum, such that equation 3.2 may be re-written:

$$E_K = h\nu - E_B - E_R - \Phi - \delta E \quad \ldots \text{Eq. 3.7}$$

to take the electrostatic charging of the sample into account. Photoemission causes a depletion of electrons at the sample surface. For subsequent electrons to leave the sample, they must first overcome a slight positive charge on the surface. This results in an extra energy requirement, of magnitude $\delta E$, (in addition to the binding energy), for an electron to leave the sample, causing a corresponding reduction in the kinetic energy of the outgoing photoelectrons.

Differential charging, (DC), may also be observed during analysis by XPS. It occurs "as a result of the spatial variation of sample potentials in the XPS sampling volume", (Yu and Hantsche, 1993(a) and (b)). In addition to a positive shift on the binding energy scale, differential charging may also manifest itself in several other ways, by peak broadening, or even by distortion of the actual shape of the photoelectron peak. Peak broadening is a common observation, and on occasion a "doubling up" of peaks can be seen. The problem of lateral differential charging, LDC, is well documented in the literature, (Ebel and Ebel, 1972; Beamson et al., 1990), and arises if there is a non-uniform overlayer present (i.e. lateral inhomogeneity), or alternatively, if there is non-uniform charge neutralisation by the electron flood gun, over the area of X-radiation or electron collection. One of the most classic sample-types to display LDC, is one where there is an island-like distribution of one phase on top of another, (see schematic in Figure 3.4). Vertical differential charging, (VDC), was first proposed by Barr in 1989, (Barr, 1989). VDC was also used to account for a variation in the binding energy shift of the C1s peak, as the thickness of PMMA films was increased, (Beamson et al., in 1991). Appreciation of these charging effects is essential, as they can lead to shifts in peak position, peak broadening, or more seriously, alteration of the actual peak shape.
Several approaches have been adopted to counteract the effects of charging. The first is to assume that specific peaks, (e.g. Al2p in Al2O3) have a fixed value, regardless, such that other peaks can be referenced to them (Stranick et al., 1987). Other work has indicated that this is often an incorrect assumption, (Barr, 1989). The second technique is to make use of the adventitious hydrocarbon contamination layer on the surface of the sample. In this case, the C1s peak is set at 285 eV and all other peaks are then referenced to it, the relative merits of this approach have been discussed, (Swift, 1981). The major criticism lies in the fact that the shift caused by charging and the lack of thermal coupling, are independent effects. Artificially moving a peak by a distance equal to the C1s shift, may therefore be unable to fully compensate for a lack of sample/spectrometer coupling. An additional factor to be aware of, is that the position of the C1s peak can vary by as much as 0.4 eV (from 284.6 eV to 285 eV), depending upon the nature and thickness of the contamination. An element of caution is therefore necessary before shifting all the photopeaks so that the C1s peak lies exactly at 285 eV. It is also possible to use gold (and other noble metals), in order to calibrate spectra. A monolayer of, (usually) gold, is evaporated onto the sample, this is ideally deposited in-situ, to avoid contamination. A sufficiently
thin layer of gold will still allow a signal to be obtained from the substrate beneath it, and the position of the gold peak will provide a standard which the other peaks can be referenced to. The major concern with this particular technique is that the sample is in some way altered. A variation of this approach was developed at the University of Surrey during the mid-eighties, known as bias referencing, (Edgell et al., 1986(a) and (b)). Rather than coating the entire specimen with gold, a dot was placed on the sample. Flooding the surface with electrons allowed the Fermi level of the insulator to become aligned to that of the gold, permitting accurate measurement of peak positions. It should be noted however, that the binding energies measured were not independent of the work function of the reference metal, in this case gold.

The fourth approach, is to use an electron flood gun to neutralise excess surface charge. Unfortunately, this method is often unsuitable for specimens prone to differential charging, the problem of referencing XPS binding energies still needs addressing, (Lewis and Kelley, 1980).

Finally, it is possible to make use of parameters which are independent of sample charging, the most widely documented is the Auger parameter. This is an elegant method devised by Wagner, (Wagner, 1975), who made use of the fact that even when a sample charges, the relative shifts on both the Auger and photoelectron peaks will be the same within the XPS spectrum. The separation between these two lines was defined as the Auger parameter (\( \alpha \)) and is numerically calculated as the kinetic energy of the Auger transition, (\( E_K(jkl) \)) minus the kinetic energy of the photoelectron, (\( E_K(i) \))

\[
\alpha = E_K(jkl) - E_K(i) \quad \ldots\; \text{Eq. 3.8}
\]

In an attempt to account for some of the shortcomings of the original parameter, a modified parameter, \( \alpha^* \), has been proposed. The modified Auger parameter was devised to avoid the negative values of \( \alpha \), which sometimes result and is calculated as follows:

\[
\alpha^* = \alpha + hv \quad \ldots\; \text{Eq. 3.9}
\]
where, \( h\nu \) is the photon energy. By combining equations 3.8 and 3.9, \( \alpha^* \) may be expressed, simply as the sum of the kinetic energy of the Auger peak and the binding energy of the photopeak, (Eq. 3.10). \( E_{K(hkl)} \) is the kinetic energy of the Auger peak

\[ \alpha^* = E_{K(hkl)} + E_B \]...

and \( E_B \) is the binding energy of the photopeak.

Auger parameters are extremely useful for the study of insulating samples, as they are completely independent of electrostatic charging (Castle, 1992). It is however, important to have first validated that the spectrometer energy scale is linear over the required range. This is particularly important during monochromated XPS, where use of an electron flood gun can result in a non-linear energy scale, (Edgell et al., 1975).

3.1.4 Depth of Analysis

The surface sensitivity of XPS is one of the factors, (coupled with its chemical specificity), that has led to such widespread application. Figure 3.5 illustrates electron emission from a planar surface. It is the escape depth of the electrons forming the spectrum which determines the analysis depth, (though in fact the incoming X-rays penetrate much deeper into the sample). The concept of escape depth is explained by considering a plane of atoms at a depth \( x \), in a sample irradiated with X-rays, (Castle, 1983). The deeper within the sample \( x \) lies, the greater the probability that escaping electrons will be inelastically scattered (i.e. by colliding with neighbouring atoms), and hence have insufficient kinetic energy to escape from the sample. The probability of inelastic scattering increases exponentially with the distance away from the surface, (Henke, 1972), such that,

\[ N = N_0 \exp(-x/\lambda(E)) \]...

where, \( N \) is the flux of electrons reaching the surface, \( N_0 \) is the electron flux emitted perpendicularly to the surface from the surface layer itself and \( \lambda(E) \) is the inelastic mean free path, (IMFP) of an electron. The intensity, \( (I_o) \), is just another way of
expressing the total flux of electrons. Integrating the above equation for all the planes between zero and infinity, gives,

\[ I_o = N_0 \lambda(E) \]  \hspace{1cm} \text{... Eq. 3.12}

It can also be shown that the intensity from a depth of \( \lambda(E) \) is 65\% of \( I_o \) and an intensity of 95\% of \( I_o \) comes from a depth of \( 3\lambda(E) \), at normal emission. Several relationships have been suggested which relate \( \lambda \) to the electron energy and the material, (e.g. Seah and Dench, 1979). The fact that 95\% of the signal emanates from a depth of \( 3\lambda \), is a good indication of its surface specificity. The escape depth for an electron is in fact about 0.1\% of the attenuation for X-rays of comparable energy, but as it is the escape depth that determines the analysis depth, the technique is clearly very surface specific. Although, it is also important to remember that the depth of analytical information varies with electron energy and material.

Figure 3.5 Electron emission from a plane surface. The hatched area represents the probability of escape as a function of depth, (after Castle, 1983).
Chapter 3. Experimental Techniques

It is possible to combine equations 3.11 and 3.12, to produce the more familiar expression, known as the Beer-Lambert Law:

$$I_d = I_0 \exp \left( - \frac{d}{\lambda \sin \theta} \right)$$ ...

Eq. 3.13

where, $I_d$ is the intensity of the substrate signal with an overlayer present, $I_0$ is the intensity from a clean substrate, $d$ is the thickness of the overlayer, $\lambda$ the inelastic mean free path and $\theta$, the take-off angle.

As it is the escape depth of the electron that determines the analysis depth, it is sometimes possible to record spectra for regions which have different analysis depths, e.g. using AlK$\alpha$ radiation, the magnesium 1s (KE = 180 eV) and 2p (KE = 1430 eV) electrons have IMFP's of about 0.82 nm and 3.39 nm respectively, (calculated by Tanuma, Powell and Penn, 1991). This can be useful in cases where there is non-uniform depth distribution of various components.

3.1.5 Spectral Interpretation

This section can be sub-divided into two sections, information from (i) primary structure and (ii) secondary structure, which will be dealt with in turn.

3.1.5.1 Primary Structure

On careful examination of a photoelectron spectrum, three different types of peak may be observed, due to:

(i) photoemission from core levels
(ii) photoemission from valence levels, and
(iii) X-ray excited Auger emission.

A typical survey spectrum of carbon (graphite) has been included in Figure 3.6, to illustrate these features. In addition to the series of photoelectron and Auger peaks in the spectrum, a broad continuous background exists, which can also provide additional information during spectral interpretation. The background generally increases from high to low kinetic energy, (vice versa on a binding energy scale), with the background also increasing in a step-like manner after each peak. The major
contribution to this background is from the inelastic scattering of electrons in the solid. There is also a minor contribution from electrons excited by the Bremsstrahlung ("breaking radiation") continuum, this will be considered in more detail in the section on monochromated XPS. The actual shape of the background can also provide additional information, for example, if a phase is buried by a thin overlayer, the higher BE side of the photoelectron peak will have a positive slope, (Castle et al., 1990). This is due to the fact that the electrons from the buried phase are attenuated by the layer above, resulting in a decrease in kinetic energy, therefore more of them will appear on the low kinetic energy (and hence high binding energy) side of the peak. In some cases, the peak itself may be absent, but its presence indicated by the change in background slope.

![Figure 3.6 A typical survey spectrum obtained from carbon, (graphite).](image)

The basic parameter which governs the relative intensity of the photopeaks (i) is the photoelectron cross-section, $\sigma$, which varies both between orbitals and from element to element. This parameter is considered in more detail in the section on
Chapter 3. Experimental Techniques

quantification. Varying the primary excitation source also affects $\sigma$, although the difference between the two most frequently used sources, (i.e. AlK$\alpha$ and MgK$\alpha$), is relatively small. The transmission characteristics of the analyser also have an influence, which will be discussed in the section on instrumentation.

The peak width, $\Delta E$, of a photoelectron line, otherwise referred to as the full width at half the maximum height, (FWHM), is determined by the combination of three different factors:

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2} \quad \ldots \quad \text{Eq. 3.14}$$

where,

$\Delta E_n$ = the natural or inherent width of the core level, which is a direct reflection of the uncertainty in the lifetime of an ion following photoemission. Core hole lifetimes are controlled by the processes that follow, (i) X-ray fluorescence (emission of an X-ray photon), (ii) emission of an Auger electron and (iii) emission of an electron in the Coster-Kronig process, (a transition which can occur during Auger emission, where the final doubly charged ion has one hole in a shell of the same principle quantum number (n) as that of the original ion, (Briggs and Seah, 1990)).

$\Delta E_p$ = the line width of the photon source, which for the AlK$\alpha_{1,2}$ doublet is about 1.0 eV, and for MgK$\alpha$ is about 0.8 eV

$\Delta E_a$ = the analyser contribution, which is the same for all of the peaks in the constant analyser energy, (CAE) mode, preferred for XPS, but varies across the spectrum in the constant retard ratio, (CRR) mode.

The valence levels are those occupied by electrons of low binding energy, between about 0-20 eV and they are involved in de-localised or bonding orbitals. The photoelectron cross-section, $\sigma$, for valence levels is much lower than for the core levels, so it is necessary to acquire valence band spectra over much longer times. A useful related technique for the study of the electronic band structure, of in particular,
Chapter 3. Experimental Techniques

semiconductors, is ultra-violet photoelectron spectroscopy, (UPS). In some cases, the facility for UPS is included on a conventional XPS system. A differentially pumped gas discharge lamp which produces lines at HeI (21.2 eV) and HeII (0.8 eV), can be used as the primary excitation source, (Walls, 1989, Chapter 1). Auger peaks are also observed in a photoelectron spectrum, created when the core holes produced by photoelectron ejection are subsequently filled. Four different series of X-ray induced Auger peaks, (c), may be observed in conventional XPS, the KLL series (from sodium to magnesium), LMM (Cu, Zn, Ga, Ge, As and Se) and two different MNN series, (the first from molybdenum to neodymium) and the second series which can only be observed using a higher energy source, such as AgLa, (Briggs and Seah, 1990, Chapter 3). The NOO series can also be detected, for Au, Hg, Tl, Pb and Bi, (Handbook of Electron Spectroscopy, 1979). A useful feature of Auger electrons is that their kinetic energy values are independent of the type or energy of the primary excitation source, (i.e. it is characteristic of the material itself). This explains why when the X-ray source is changed from MgKα to AlKα radiation, all the photopeaks increase in kinetic energy by 233 eV, while the Auger peaks remain unchanged. (N.B. for spectra plotted directly on a binding energy scale, the converse is true).

One of the main advantages of XPS over other analytical techniques, is the ability to infer chemical state information. Non-equivalence of atoms may arise due to differences in any of the following factors: oxidation state, molecular environment or lattice site. Kai Siegbahn first used a charge potential model to interpret chemical shifts, however, this model neglected the relaxation effects which will be discussed fully in the section on "The Influence of Initial and Final State Effects". In general, the observed binding energy shift increases with increasing electronegativity of the attached groups, viz., for the N1s photoelectron peak, NH₂ occurs at 400 eV, NO₂ at 404 eV and NO₃ at 406 eV. The magnitude of the Auger shift is often greater than the photoelectron shift, due to a greater influence of relaxation effects. For the KLL series, good chemical state information can be obtained from the elements fluorine to silicon and then for the LMM series, from copper to germanium. There is also a dependence on whether electrons involved are core-hole (e.g. Si) electrons, or in the
band structure, (as in Ti, Fe or C). Electrons emitted from the band structure do not have discrete energies, they have a range of energies, so chemical state information is unavailable.

3.1.5.2 **Secondary Structure**

In addition to the three main types of peaks described in the previous section, a whole series of secondary features may also be present to provide the spectroscopist with additional information.

(i) **X-ray satellites and ghosts**

These features are not "true" secondary structures. X-ray satellites arise when achromatic radiation is used, and are observed as a series of low intensity peaks which occur at set distances below the main photoelectron peak, (Watts, 1990). Satellite peaks are produced when the minor components of the X-ray spectrum present in achromatic sources excite the characteristic photoelectron transitions, such as the Cls transition by the AlK\(_{\alpha_{3,4}}\), AlK\(_{\alpha_{5,6}}\) and AlK\(_{\beta}\) components.

Ghosts are due to the presence of impurity elements in the X-ray source, the most common being AlK\(_{\alpha_{1,2}}\) from a MgK\(_{\alpha}\) source. These impurities result in the production of secondary electrons inside the source which may go on to hit the thin aluminium window. Aluminium impurities lead to the production of weak ghosts 233 eV above the KE of those excited by the MgK\(_{\alpha_{1,2}}\). This feature may be used to diagnose the problem of "cross-talk" which sometimes arises in twin anode systems, such as the VG Scientific ESCALAB MkII which was used during these studies. Ghosts also give an indication of the condition of an anode. For example, OK\(_{\alpha}\) may be observed with an old anode, (\(h\nu = 523\) eV), or CuL\(_{\alpha}\) (\(h\nu = 923\) eV), if the anode has deteriorated to the extent that the copper beneath it has broken through.
Table 3.1 lists the high energy satellite lines which arise from Mg and Al targets, (data obtained by Krause and Ferreira in Carlson, 1976).

<table>
<thead>
<tr>
<th>X-ray line</th>
<th>Separation from $K\alpha_{1,2}$ (eV) and relative intensity ($K\alpha_{1,2} = 100$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>$K\alpha'$</td>
<td>4.5 (1.0)</td>
</tr>
<tr>
<td>$K\alpha_3$</td>
<td>8.4 (9.2)</td>
</tr>
<tr>
<td>$K\alpha_4$</td>
<td>10.0 (5.1)</td>
</tr>
<tr>
<td>$K\alpha_5$</td>
<td>17.3 (0.8)</td>
</tr>
<tr>
<td>$K\alpha_6$</td>
<td>20.5 (0.5)</td>
</tr>
<tr>
<td>$K\beta$</td>
<td>48.0 (2.0)</td>
</tr>
</tbody>
</table>

(ii) **Shake-up satellites**

Shake-up satellites arise following the excitation of a valence band electron from an occupied molecular orbital to a higher, unoccupied level coincident with the primary photoionisation event, (López *et al.*, 1986). The shake-up transition produces a discrete energy loss peak on the low KE, (high BE) side of the photoelectron peak.

The $\pi - \pi^*$ shake-up satellite was of interest to this particular study, as it is indicative of the presence of aromatic groups. The transition involves the $\pi$ bonds of a C=C double bond. In certain molecules, the absorption of a photon can be linked to the excitation of the electrons of specific atoms in the molecule, (Atkins, 1986). These groups of atoms are referred to as *chromophores*. In C=C double bonds, absorption of a photon results in the promotion of a $\pi$-electron into the $\pi^*$ antibonding orbital. In bonding orbitals, the probability of finding an electron between the two nuclei is enhanced, while for an antibonding orbital, the likelihood is reduced, (Jean *et al.*, 1993).

The satellite occurs at about 6.7 eV to the low KE (high BE) side of the carbon
Chapter 3. Experimental Techniques

1s photopeak, and is between 8-10% of the intensity of the main peak. Figure 3.7 is a molecular orbital diagram depicting the bonding to anti-bonding transition for the \( \pi \) molecular orbital.

![Molecular Orbital Diagram](image)

**Figure 3.7** Schematic of the bonding to anti-bonding transition characteristic of organic molecules.

(iii) **Shake-off satellites**

These are very similar to shake-up satellites, but the valence electrons may be completely ionised, (i.e. excited to an unbound continuum state). Shake-off satellites are very broad features.

(iv) **Plasmon losses**

Electrons with sufficient energy passing through a solid can excite one or other of the modes of collective oscillation in the sea of conduction electrons. These oscillations have frequencies characteristic of the material of the solid.

Finally, multiplet splitting, (otherwise known as exchange or electrostatic splitting) occurs in the 4s levels of rare earths, if the system has unpaired electrons. This is obviously not relevant to this particular study.
Chapter 3. Experimental Techniques

3.1.6 Binding Energy: The Influence of Initial and Final State Effects

The potential usefulness of XPS as a means of obtaining chemical state information, had already been recognised by the late sixties. This was illustrated by the widespread use of Siegbahn’s acronym, ESCA, (electron spectroscopy for chemical analysis), to refer to the technique. The photoelectron binding energy was known to be independent of the energy of the X-ray source, and as such could be described as an intrinsic material property. Shifts in the binding energy were therefore, solely attributed to differences in chemical state. This is however, an oversimplification of the photoemission process.

This model makes the assumption that Koopmans Theorem is valid. In Koopmans Theorem (1934), it is assumed that the electron orbitals remain effectively "frozen" during photoemission, and effects such as screening by other electrons, are simply ignored. Over successive years, there followed serious debate as to whether initial (as Koopmans Theorem implied), or final state effects determined the magnitude of the observed chemical shift. More recently, work in this area has shown that Koopmans Theorem is only an approximate method of calculating expected values of binding energy, experimentally recorded values of electron binding energies are lower than Koopmans Theorem predicts. The reason for this discrepancy is attributed to the relaxation energy term, which is a final state effect. Other final state effects in solids, such as core hole screening, polarisation of the neighbouring ions, the outward flow of electrons, (producing a slightly positive, attractive, force), all contribute to an effective reduction in the kinetic energy of the emitted photoelectron, and hence a positive shift on the binding energy scale, (Castle, 1992). Some of these processes are illustrated schematically in Figure 3.8.

It is now universally accepted that the relaxation energy (and other final state effects), have by far the greatest affect on the observed chemical shift in inorganic systems. A detailed review of the work carried out in this area, leading to this universal acceptance of the influence of final state effects, can be found in "Electronic Properties of Surfaces", (Weightman, 1984).
Chapter 3. Experimental Techniques

Rare earth metals display a negative chemical shift on the binding energy scale, for the Me\(^{x^+}\) cation relative to the metal, (Me). The Me\(^{x^+}\) cation has lost \(x\) electrons, so, considering only the initial state effects, for subsequent electrons to escape from the attractive forces of the nucleus, an additional energy requirement would be expected, (i.e. a positive shift on the binding energy scale). As several examples in The Handbook of Electron Spectroscopy, (1979) indicate, this is not found to be the case. For example, cerium appears at a binding energy of 883.5 eV, while cerium oxide appears at 881 eV. This is due entirely to final state effects.

There is however, more recent evidence to suggest that in the case of polymeric materials, the influence of final state effects may not be as significant as have been found for inorganic materials, (Beamson, 1994). The most likely reason for this is that the various polymer side groups result in a series of partial positive and negative charges (\(\delta^+\) and \(\delta^-\)), which influence results, (e.g. the slight positive charge on a \(+\text{NH}_3\),

Figure 3.8 Schematic of some of the final state effects which contribute to the chemical shift.
In the case of polymeric materials, composed predominantly of carbon, the shifts on the C1s peak allow the polymer to be characterised. The functional groups present in the polymer produce chemical shifts on the C1s peak, of varying magnitude, which can be measured accurately. For example, an oxygen atom bonded to a carbon atom will produce a shift of about 1.6 eV. More detailed information on the fine structure is available, provided the instrument itself has suitable resolution. Resolution of the fine structure of a number of polymers is shown in *High Resolution XPS of Organic Polymers*, (Beamson and Briggs, 1992)

### 3.1.7 Quantification and Sensitivity Factors

It is often desirable to have quantitative information pertaining to a sample surface in order to compare the effects of sample history on chemical composition. It is usual to obtain high resolution spectra of all the elements present in the survey spectrum, in order to carry out a more accurate quantification. The next stage is to subtract a suitable background (either linear or Shirley) prior to measurement of the peak areas. Peak areas are converted to atomic percentages by the use of experimentally determined sensitivity factors \( F \). The sensitivity factor includes a term for the cross-section of electron production, \( \sigma \), a term which itself covers instrumental parameters, including the transmission function of the spectrometer, \( K \) and the inelastic mean free path \( \lambda \). Provided the X-ray flux remains unaltered for the duration of the experiment, the atomic percentages may be calculated as follows:

\[
[A] \text{ atomic } \% = \left[ \frac{I_A}{F_A} \right] \div \left[ \Sigma \left( \frac{I}{F} \right) \right] \times 100 \ \% \quad \ldots \text{Eq. 3.15}
\]

where \( I_A \) is the intensity of A and \( I \) is the total intensity.

In addition to their usefulness in quantification, high resolution scans also provide chemical state information. Chemical shifts of peaks allow us to ascertain which chemical state an element is present in, for example, oxide or metallic.
3.1.8 Experimental Requirements Specific to this Project

This section is intended as a brief look at some of the specific analytical problems encountered during the course of this study. These factors imposed certain restrictions on the equipment used for analysis and eventually made it necessary to use additional instruments, other than those located at the University of Surrey. Firstly, the fact that both the substrate (Coors AD69 alumina) and the adhesive are insulating materials meant that it was always necessary to charge reference the spectra, (the various charge referencing techniques having previously been described). This in itself was a problem. Alumina substrates are produced by various methods of sintering and are comprised of discrete grains, such that they form a discontinuous phase. From an analytical point of view, the charging problems associated with a material similar to alumina are worse than for a continuous phase. It is possible for each individual grain to hold a slightly different charge and potential, making effective charge neutralisation increasingly difficult, (Le Gressus, 1993). Also, analysis of the substrate with a thin overlayer of polymer residue remaining on the surface can produce peculiar differential charging effects. If the material under analysis is a single crystal, added complications may arise due to a phenomenon known as forward scattering. Photoelectron diffraction occurs at the crystal planes of single crystals, resulting in additional fine structure being superimposed on the spectrum, this is of relevance to the analysis of single crystal substrates.

XPS cannot be described as a non-destructive technique. XPS analysis of polymeric materials introduces additional problems. Polymers tend to be more susceptible to XPS induced damage during analysis, often making it necessary to acquire spectra over much shorter analysis times. XPS induced damage may be due to a combination of any of the following factors, there is no universal mechanism, (i) heating effects, from the X-ray gun, (although the anode is water cooled, the filament still becomes hot); (ii) X-rays, certain materials are susceptible to X-ray damage, (iii) time dependent effects, other materials degrade over a period of time due to either X-ray induced damage, loss of electrons, or even exposure to UHV conditions, and finally, (iv) electron damage by electrons generated either at the Al window, or by the
electron flood gun. It is important in XPS analysis to establish a safe analysis time, so that the material under analysis at the end of the experiment is the same as at the beginning, (Beamson and Briggs, 1993).

In summary, this particular project placed certain demands on the technique, most notably:

(i) the demand for both high resolution and good sensitivity, to allow spectra to be recorded before the onset of specimen damage.
(ii) the need for means of effective charge neutralisation and energy referencing.

The following section will describe the instrumentation in more detail. It is not intended as a comprehensive review of instrumentation for XPS analysis, but is instead meant to draw attention to the areas of particular importance to this project, (i.e. those features which enabled analysis to be performed on what must be considered as difficult samples). For a more comprehensive review of instrumentation, the reader is referred to Rivière’s review in Chapter 2 of Briggs and Seah, (1990).

3.1.9 Instrumentation

3.1.9.1 X-ray sources

XPS requires the generation of soft X-rays of around 1 keV. The selection of the X-ray source is important, as it has a bearing on the resolution achievable by the spectrometer. To enable suitable resolution, the choice of source is therefore limited to those materials whose natural line width is below 1.0 eV. The Kα lines of aluminium and magnesium are most frequently used. Zirconium is used to a lesser extent, as its line width is about 1.8 eV, giving much poorer resolution. The system used for routine XPS analysis during this study, was a VG Scientific ESCALAB MkII spectrometer. This system is equipped with a twin anode X-ray gun, of the type shown schematically in Figure 3.9. Access to both AlKα and MgKα radiation proved extremely useful during this study as XPS analysis of the alumina substrate revealed the presence of silica. In AlKα radiation, a Bremsstrahlung induced Auger peak occurs
coincident with the silicon peak, making it appear that a greater concentration of silicon was present. Changing to MgKα radiation subsequently allowed the amount of silicon present to be determined.

![Diagram of a soft X-ray source with twin anode](image)

**Figure 3.9** Schematic of a soft X-ray source with twin anode, (after Barrie).

A filament, (held close to the potential of earth), is heated to produce electrons by thermionic emission, which are then used to bombard the anode material, (held at a high positive potential). Depending upon which side of the anode is under electron bombardment, either AlKα X-rays at an energy of 1486.6 eV with a natural line width of 1.0 eV for the AlKα₁,₂ doublet, or MgKα X-rays (energy 1253.6 eV, line width 0.8 eV) are produced. The anode itself is generally produced by depositing about 10 μm thickness of the material onto a copper block, which facilitates anode cooling during operation. It is necessary to use excitation energies about an order of magnitude higher than the energy of the source, so for AlKα and MgKα, whose energies lie between about 1250 and 1500 eV, an accelerating potential of up to 15 kV is required. The photon flux produced is proportional to the current, so it is necessary to use as
high an electron bombarding current as possible, (although the maximum power
dissipation is limited to about 1 kW for AlKα, and 0.5 kW for MgKα, before water
cooling becomes an insufficient means of dissipating heat).

The sample is shielded from the anode by a thin, (about 2 μm) window of a
material relatively transparent to X-rays. This helps prevent material from either the
filament or the anode from being deposited on the specimen. Aluminium is most
frequently used for the window and this produces a flux attenuation of 24 % for MgKα
radiation and slightly lower, about 15 % for AlKα radiation, (Rivière, 1992).
Electrons generated at the Al window also help to neutralise excess charge on the
sample surface.

3.1.9.2 Monochromated XPS

So far, only achromatic X-ray sources have been discussed. In the course of this
study, the use of a monochromated X-ray source was vital in order to achieve good
spectral resolution. The term X-ray monochromation refers to the procedure used to
reduce the natural X-ray line width, (in AlKα from 0.85 eV to 0.4 eV and AgLα from
2.6 to 1.2 eV). AlKα radiation has an energy of 1486.6 eV and AgLα, 2985 eV.
Although the main benefit of using a monochromated source is the observed decrease
in X-ray line width, monochromation offers the additional advantages of removing
unwanted satellite peaks and the *Bremsstrahlung background.
(*Electrons from the filament in the X-ray gun strike the anode material to produce
characteristic X-rays on a broad Bremsstrahlung background. This background is a
function of the energy of the electrons from the filament which strike the X-ray source.
Part of the Bremsstrahlung continuum passes through the window separating the X-ray
source from the sample, where on interaction with the sample, additional features are
produced).

X-ray monochromators utilise the principle of Bragg’s Law,
Chapter 3. Experimental Techniques

\[ n\lambda = 2d \sin \theta \]  

... Eq. 3.16

where \( n \) = diffraction order
\( \lambda \) = X-ray wavelength
\( d \) = crystal spacing
\( \theta \) = Bragg angle

For a quartz 1010 crystal, within geometrical adjustments,
\( n = 1 \) for AlK\( \alpha \), \( n = 2 \) for AgL\( \alpha \)
\( n = 3 \) for TiK\( \alpha \), \( n = 4 \) for CrK\( \beta \)

It should be noted that as the diffraction order, \( n \), is increased, the flux decreases dramatically.

X-rays are dispersed by diffraction at the interatomic planes of a quartz crystal, quartz is particularly suited to this application. In addition to having an appropriate crystal spacing (0.425 nm), quartz can be elastically deformed or ground to fit the Rowland (or focusing) sphere, and is also able to withstand the temperatures reached during bake-out of the spectrometer, (up to 100°C). Figure 3.10 illustrates the principle of monochromation. The X-ray anode is located at one point on the Rowland circle and when X-rays strike the quartz crystal, they are dispersed and then refocused at the point on the sphere where the sample is positioned. In this way, it is possible to select the K\( \alpha_1 \) component of the usually unresolved K\( \alpha_{1,2} \) doublet, (the K\( \alpha_1 \) component is selected as the K\( \alpha_2 \) component has a much lower intensity).

As with any technique, monochromation also has its limitations. The most noticeable drawback is the dramatic reduction in photon flux available, as compared with an achromatic source at the same power. In addition, quartz cannot be used to monochromate a magnesium X-ray source, as it does not fulfil the Bragg condition. The VG Scientific ESCALAB MkII is equipped with an X-ray monochromator, but unfortunately the associated dramatic reduction in photon flux, makes it necessary to use longer analysis times, increasing the likelihood of specimen damage.
Figure 3.10 Schematic of an X-ray monochromator. (Fisons Instruments S-Probe with micro-focus X-ray source).

Figure 3.11 illustrates the separation of the $K\alpha_{1,2}$ doublet.

Figure 3.11 Separation of the Al$K\alpha_{1,2}$ doublet.
The other obstacle associated with monochromated XPS is the severity of sample charging which arises, due to inadequate electron flux reaching the sample surface. With a twin anode system, the aluminium photoelectrons excited from the aluminium window, go some way towards charge neutralisation. Low energy electron flood guns are employed to neutralise this excess of charge, however, the operation of such charge compensation methods demands a very high level of operator skill.

3.1.9.3 Charge Compensation: Electron Flood Guns

The effects of sample charging during analysis with an achromatic X-ray source can generally be compensated for by any of the methods previously described. In cases where relatively small shifts in core electron binding energies are to be measured, or where the sample is particularly susceptible to charging, it may be necessary to use an electron flood gun of the type reported by Huchital and Mckeon, (1971), which consists of a tungsten filament. A flood gun is relatively ineffective with a twin anode, as the X-ray footprint is too large for efficient compensation by the available flux of electrons. Monochromation however, results in much more severe charging effects, which always require some means of charge neutralisation, for the analysis of non-conducting materials. Monochromation results in the removal of the Bremsstrahlung component, which, in an achromatic X-ray source is responsible for exciting the secondary electrons which help to neutralise surface charge. This accounts for the increased severity in charging observed. Inadequate charge compensation not only produces large shifts in peak position, but can also obscure the true shape of a peak by a combination of vertical and lateral charging effects, (Beamson and Briggs, 1992). This project involved the detection of relatively small differences, spectroscopically speaking, which therefore demanded the elimination of these charging effects. As previously mentioned, the difficulties associated with working with these particular samples, exposed the instrumental limitations of the VG Scientific ESCALAB MkII.

Part of the XPS analysis was therefore carried out on the Scienta ESCA300 spectrometer, formerly located at the ICI Wilton Materials Research Centre and subsequently moved to RUSTI (Research Unit for Surfaces, Transforms and
Chapter 3. Experimental Techniques

Interfaces), at the SERC Daresbury Laboratory. Optimisation of the charge compensation system for the ESCA300 was a lengthy process. The ESCA300 is currently fitted with two electron flood guns. A VSW EG2 thermionic emission electron flood gun, located underneath the electron lens, supplies a relatively high electron flux. A second, Leybold Hereaus (FG 10/35) flood gun is also used at low take-off angles. A charge coupled device, (CCD) camera relays the photoelectron signal to a TV monitor, to enable the operator to optimise conditions by varying sample position, angle and also the flood gun settings themselves. The operator seeks the conditions under which maximum peak height and minimum spectral width are observed, as this will provide the best spectral resolution.

3.1.9.4 Analysers

Two main types of analyser are produced for electron spectrometers, the cylindrical mirror analyser (CMA) and the hemispherical sector analyser (HSA). In the past, the CMA has been associated primarily with Auger electron spectroscopy, (AES) and the HSA with XPS, but recently there has been a trend for manufacturers of Auger instruments to fit HSA-type analysers. As both the ESCALAB MkII and ESCA300 spectrometers are equipped with HSA analysers, the discussion on analysers will be restricted to the operation of a HSA.

A HSA consists of two hemispheres of inner radius $R_1$ and outer radius $R_2$, positioned concentrically, (see Figure 3.12).

A potential, $\Delta V$, is then applied between the hemispheres, such that the outer hemisphere is negative with respect to $\Delta V$ and the inner surface is positive. An equipotential surface of radius $R_0$ exists between the two hemispheres. During analysis, the sample from which photoelectrons are emitted is held at earth potential, but the analyser is isolated from earth and is described as "floating on a variable potential pedestal", (Rivière, 1992). The analyser may then be operated in either fixed analyser transmission (FAT) mode, otherwise known as constant analyser energy (CAE) mode, or in fixed retard ratio (FRR), alternatively described as constant retard ratio (CRR) mode. In CRR mode, (used only during the imaging XPS section of this
The voltages applied to the hemispheres are increased with the energy of the spectrum, such that the ratio of the kinetic energy of the electrons to the pass energy remains constant. Whereas, in CAE mode, a constant voltage is applied to the hemispheres, which allows electrons of a specified energy to pass between them. Photoelectrons reach the focal point of the analyser assembly via a transfer lens, where they are retarded electrostatically, prior to entry into the HSA. Electrons with energies matching the analyser pass energy will enter the analyser and are subsequently detected by one or more channeltron detectors. Pass energies of 10, 20, 50 or 100 eV are most frequently used in XPS. In this study, pass energies of 20 eV for high resolution spectra and 50 eV for survey spectra were used.

The CAE mode offers better spectral resolution, but reduced sensitivity at the low binding energies, while CRR mode offers the reverse. CAE is the mode generally used for XPS analysis.
3.1.9.5 Resolution

The individual components contributing to the FWHM have been considered in section 3.1.5.1. This section has been included to discuss the contribution made by the instrument itself in more detail. Manufacturers continually strive to improve the resolution of their instruments. Not only have considerable improvements been made in spectral resolution, but more recently, there has been considerable effort directed towards improving the spatial resolution of the technique. This section will be limited to a discussion of the parameters affecting the spectral resolution of an instrument, as spatial resolution is considered in the section on imaging XPS (iXPS).

There are two separate definitions of resolution:

(i) **Absolute resolution** ($\Delta E_a$)

The spectral resolution, $\Delta E$, is a combination of several factors, as indicated in section 3.1.5.2. This is usually defined as being the full-width at half the maximum height, (FWHM), of a chosen peak. The absolute resolution of the analyser, $\Delta E_a$, is one of the factors which controls the FWHM, and it is due to analyser broadening. Analyser broadening accounts for the slight spread of energies which occurs when electrons of the same energy as the pass energy enter the analyser.

(ii) **Relative resolution** ($R = \Delta E_a / E_0$)

The relative resolution is the absolute resolution divided by the kinetic energy of the peak. This value is sometimes expressed as a percentage. Alternatively, the resolving power, ($q$) may be referred to, which is simply the reciprocal of $R$.

One of the strengths of XPS, is the ability to determine chemical state information, by measuring the chemical shifts on peaks and this demands good absolute resolution across the spectrum. To obtain the required resolution, that is, a resolution which approaches the natural line widths of the X-ray sources at their highest energies, (i.e. 0.8 eV at 1253.6 eV and 1.0 eV at 1486.6 eV for Mg and AlKα radiations respectively), it is necessary to retard the electrons. This pre-retardation
stage allows good spectral resolution to be obtained, while still maintaining a compact analyser design, (Watts, 1994(a)).

It can also be demonstrated that the relative resolution is related to the spectrometer slit width, (Rivièvre, 1992).

$$\frac{\Delta E_a}{E_o} = 0.62 \left( \frac{w}{R_0} \right) \quad \text{... Eq. 3.17}$$

where,

- $\Delta E_a$ = absolute resolution
- $E_o$ = kinetic energy of electron in analyser
- $w$ = slit width
- $R_0$ = mean radius of analyser

To achieve a specified resolution, appropriate values of the pass energy and slit width can be selected. For example, the mean radius, $R_0$ of the ESCALAB MkII analyser is 150 mm, and the slit width generally used is 15 x 6 mm, which gives absolute resolutions of 0.5 and 1.2 eV at pass energies of 20 eV and 50 eV respectively. The Scienta ESCA300 spectrometer has a very much larger analyser than conventional instruments, (300 mm), and a monochromated X-ray source, making it possible to achieve both high count rates and good energy resolution within an acceptable timescale, (Beamson and Briggs, 1992, Chapter 2).

3.1.9.6 Experimental Operating Conditions

VG. Scientific ESCALAB MkII Spectrometer

Analyses were obtained using a VG Scientific ESCALAB MKII spectrometer with a 150° hemispherical sector energy analyser. Figure 3.13 gives a front elevation of a typical VG Scientific XPS spectrometer of this type. The twin anode X-ray source was used to supply AlK$\alpha$ radiation (1486.6 eV) for analysis of the resin samples and both AlK$\alpha$ and MgK$\alpha$ radiation (1253.6 eV) for analysis of the alumina ceramic. Survey spectra were recorded at pass energies of 50 eV and subsequently, high
resolution spectra were recorded at pass energies of 20 eV. In the case of LCR000, high resolution scans of C1s and O1s regions and for alumina, C1s, O1s, Si2s, Si2p, Al2s, Al2p, Mg1s and Mg2p were recorded. (Note, for this instrument the default setting for plotting data is from low to high binding energy, though this can be overridden, so that the data is plotted in the same orientation as data from the ESCA300 spectrometer).

The variation of composition with depth was determined using several techniques. Angle resolved XPS was used to study the alumina substrate, (the electron take-off angles varying between 15 and 90°, relative to the sample surface). An attempt was also made to discover whether segregation of sintering aids (silica and magnesia), had occurred in the substrate material. High resolution scans were recorded in both AlKα and MgKα radiation.

Preliminary studies also involved the use of argon ion etching as a means of carrying out destructive depth profiling on the alumina substrate.
Chapter 3. Experimental Techniques

Key:
1. Fast entry specimen insertion lock (stainless steel).
2. UHV specimen preparation chamber (stainless steel).
3. UHV experimental/analysis vessel (mu-metal).
5. Rotary drive to specimen transfer mechanism.
6. Titanium sublimation pump vessel (stainless steel).
7. Viewport.
9. High precision (X, Y, Z translation and θ tilt) specimen manipulator.
10. Twin anode X-ray source (Al/Mg).
11. UV discharge source (UPS).
12. Monochromated X-ray source (Al/Ag).
14. Scanning ion source.
15. Electron energy analyzer vessel (mu-metal).
16. Detector (single or multichannel).
17. Specimen fracture stage.
18. Static, broad beam ion source.
19. High pressure gas reaction/catalysis cell.
20. "Wobble stick" specimen transfer fork.
21. 6-specimen mobile carousel.
22. 10-specimen auto-carousel.
23. Preparation vessel specimen transfer "railway".
24. Binocular microscope.
25. Alternative fast-entry lock position, or optional extension chamber port.
26. Port for monochromated electron source.
27. Port for specimen heating/cooling stage.

Figure 3.13 Schematic of the VG Scientific ESCALAB MkII.
Scienta ESCA300 Spectrometer

An example of one monochromated XPS spectrometer currently available, is the Scienta ESCA300, developed in Uppsala, Sweden. It has two special features which help to compensate for the loss of signal intensity generally associated with using a monochromated XPS source. The use of a rotating anode, to allow rapid heat dissipation, has enabled the power to be increased by an order of magnitude, \((ca\ 5\ kW\ at\ 4000\ rpm\ and\ 8\ kW\ at\ 10000\ rpm)\). Gelius \textit{et al.} have demonstrated that the maximum power dissipation is related to the square root of the speed of rotation, \((Gelius\ \textit{et al.},\ 1974)\). The anode consists of a 300 mm diameter disc constructed from a titanium alloy, and the electron gun can be directed on to either the aluminium or the chromium strips which encircle the disc to produce AlK\(\alpha\) (1486.6 eV) or CrK\(\beta\) (5946.7 eV) radiation after monochromation. X-rays produced are collected by the monochromator and focused on the sample.

The monochromator consists of seven toroidally bent crystals of \(\alpha\)-quartz, which enable the sharp focus of X-rays at the sample surface. An increase in the area of the quartz crystal results in a higher percentage of the X-radiation being available for diffraction. The Scienta ESCA300 utilises an arrangement of seven crystals, (which prove easier to manufacture with the correct tolerance than one very large crystal). Once in position, the exact location of the crystals can be adjusted by heaters.

Photoelectrons from the sample are collected by a multi-element lens and focused on a slit-aperture pair at the entrance plane of the hemispherical electron energy analyser, see Figure 3.14, (Beamson, 1992).
Figure 3.14 Schematic of a Scienta ESCA300.
3.1.10 Imaging XPS (iXPS)

Conventional XPS is an area integrating technique, which does not pose a problem for samples that are laterally homogeneous, however, often heterogeneous samples are supplied for analysis. Analyses are requested from chemically different regions of the same sample, hence the demand for spatially resolved information. Two approaches have been adopted to achieve this aim, (i) defined source and (ii) defined collection. The relative merits of these two approaches are discussed by Drummond et al., (1985). Micro-focus X-ray sources have been developed as one means of obtaining a defined source, though this approach tends to be costly. Other methods, such as the use of collimators to define the source, although cheaper, produce a significant reduction in the signal intensity. Modern instrument manufacturers have concentrated on the development of defined collection systems. Several instruments are now commercially available.

The instrument used in this study was a VG Scientific ESCASCOPE, at the ICI Wilton Materials Research Centre, Middlesborough. The ESCASCOPE has a similar lens/analyser configuration to the ESCALAB MkII, (see Figure 3.15) the main difference being the addition of two quasi Fourier Transform lenses. The system is described in detail by Coxon et al., (1990). The electrons arriving at the first FT lens from different parts of the specimen, (i.e. with x, y co-ordinates) are converted to angular information. The object plane of the analyser coincides with the diffraction plane of the first FT lens, ensuring that electrons leaving the surface at different points, (x, y), enter the analyser at different angles, (θ). This angular information is retained during passage through the analyser. The analyser forms an image of the diffraction plane from the first FT lens, at its own image plane, and also introduces energy dispersion of the information. The angular data is then re-converted at the second FT lens, to provide a spatially resolved energy selected image of the sample surface at a position sensitive detector.
Figure 3.15 Schematic of a VG Scientific ESCASCOPE.
3.1.11 Angle-resolved XPS (ARXPS)

XPS is described as a surface analytical technique, but in spite of this fact it is possible to use it as a means of obtaining compositional information as a function of depth (Watts, 1990). Compositional depth profiling may be achieved in several ways. The analysis depth in XPS is controlled by the parameters of the Beer-Lambert equation, (Eq. 3.13):

\[ I_d = I_\infty \exp \left( -\frac{d}{\lambda \sin \theta} \right) \]

where,
- \( I_d \) = the intensity from a depth, \( d \)
- \( I_\infty \) = the intensity from an infinitely thick clean substrate
- \( d \) = depth
- \( \lambda \) = inelastic mean free path of the photoelectron analysed
- \( \theta \) = electron take-off angle relative to the sample surface

Figure 3.16 Variation of analysis depth with electron take-off angle, (after Watts, 1990).
Chapter 3. Experimental Techniques

Non-destructive methods of depth analysis involve manipulation of some of the terms of this equation. It is possible to alter the electron take-off angle $\theta$, Figure 3.15 illustrates how varying this particular parameter allows information to be collected from different depths. Angle resolved XPS (ARXPS) data can be used to generate compositional depth profiles from a sample. A pre-requisite for the technique is that the surface is flat, ideally a mirror finish, if not atomically smooth. In the case of the as-received Coors AD96 alumina substrate, this was clearly not the case, with the maximum height of grains varying by up to 4 $\mu$m, (making it necessary to use polished alumina during part of the study). The effects of surface roughness on XPS intensities cannot be ignored, especially when investigating the possibility of for example, surface segregation occurring. Fadley, (1974), reported that two of the main factors to be wary of in the analysis of uneven surfaces are (i) areas of the surface are effectively shaded from X-ray incidence and/or electron escape and (ii) the angles of X-ray incidence and electron escape will differ from those expected for a perfectly flat surface. In calculating overlayer thicknesses on uneven surfaces, Cross and Dewing (1979), calculated that it was possible to overestimate the overlayer thickness of a spherical particle by a maximum of a factor of two. It is unlikely however, that the problem will be as severe for the alumina, whose grains are elongated rather than spherical.

Spectra obtained from varying TOA’s, although useful as a means of illustrating preferred orientation, do not correspond with unique "slices" within the sample. A series of algorithms have therefore been developed which can convert the quantitative analyses obtained at varying angles into a compositional depth profile. The relative merits of the algorithms are discussed in several review articles, (Fulghum, 1993 and Watts, 1994(b)). In a recent paper, (Cumpson, 1993), it was concluded that, in terms of their accuracy, there is little to distinguish one method from another. The maximum entropy routine, however, (due to Smith and Livsey, 1992), by arriving at a unique solution, is likely to provide more consistent results. In all cases, it is imperative to have as much prior information about the specimens, to avoid misinterpretation of the data.
Chapter 3. Experimental Techniques

Reconstruction of Depth Profiles from ARXPS Data: # Angular

The completed experimental angular profiles (i.e. TOA versus atomic %) were used in conjunction with the #ANGULAR computer programme, which has been fully described elsewhere in the literature, (Paynter, 1981; Watts et al 1986) to postulate a compositional depth profile. In essence, #ANGULAR is a forward transform routine which calculates the expected angular depth profile from a hypothetical compositional depth profile (i.e. depth in nm versus atomic %). Comparison of this calculated angular profile with the experimental data enables the operator to assess whether the hypothetical depth profile is a realistic option. The criterion used is to obtain a mean difference of <10% between the two angular profile data sets, (although in practice, it is more convenient to define a weighted mean parameter, as it is almost impossible to obtain a value of <10%, for all data sets). In practice the absence of a unique solution to the experimental angular profile means that some prior knowledge concerning the sample is required. In the current work it is sufficient to know that the polymer is present as a uniform overlayer on the inorganic substrate.

Validation of Lateral Homogeneity

All ARXPS routines implicitly assume lateral homogeneity unless some coverage factors are included in the calculation, (Watts, 1994(b)). Steps were taken, using a Beer-Lambert model, to ensure validity of this assumption for these specimens. As a test of such uniformity, graphs of $\ln I_{\text{substrate}}$ versus $1/\sin \theta$ were constructed for the substrate materials investigated, a straight line indicating the uniformity of the organic overlayer. The test of uniformity is developed from the Beer-Lambert equation, (Eq. 3.13). After taking logs of both sides, a graph of $\ln I_o$ versus $1/\sin \theta$ may be plotted where $-d/\lambda$ is the gradient and $\ln I_o$ is the intercept with the y axis. The thickness of the overlayer can also be estimated ($d = - \text{slope} \times \lambda$).

Alternatively, it is possible to obtain information from different depths in the sample, either by using different core levels of the same element (e.g. magnesium 1s and 2p peaks), or by changing X-ray source and hence using different X-ray energies, for example, changing from MgK$\alpha$ to AgK$\alpha$ radiation. Many X-ray photoelectron spectrometers also have the facility to carry out destructive depth profiling by
sputtering with inert gas ions. Unfortunately, non-destructive methods are limited to analysis of 5-10 nm of the material and to profile deeper into a sample, material must be removed by ion bombardment. Ion etching is generally restricted to inorganic/metallic specimens. Both the ESCALAB MkII and the ESCA300 spectrometers used during the course of this study are fitted with argon ion guns, (VG Scientific Type AG21). Finally, it may be possible to use some means of mechanical sectioning (Castle and Watts, 1991), to expose a region close to the interface.

The following sections of this chapter describe the other techniques used during the course of this study, either to support XPS data, or to answer specific questions, which could not be resolved by XPS.

3.2 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

3.2.1 Introduction

SIMS is the mass spectrometry of ionized particles which are emitted when a surface, usually a solid (although it may be a liquid), is bombarded by energetic primary particles.

The SIMS process was first documented by Sir J.J. Thompson, who in 1910 observed the emission of positive secondary ions when primary ions bombarded a metal surface in a discharge tube, (Vickerman, 1989). It is believed that the first modern SIMS instrument was not constructed until as late as 1949 by Vieboeck in Vienna. At this time, the technique was known as ion probe, with analysis resulting in the progressive removal of the surface layers. In the late 1960's, Benninghoven showed that by using the right experimental conditions, (a primary ion flux below $10^{12}$ ions cm$^{-2}$), it was possible to complete the analysis before the onset of damage occurred, that is, before the probability of a primary ion striking a previously analysed area became significant. The ability to extend surface monolayer lifetimes to hours or even days provides us with a surface sensitive mass spectrometry usually referred to as static SIMS or SSIMS. Static, because analysis is completed before the sample
surface changes.

The energy from the primary particles, (ions), is transferred to the atoms in the sample by a collision cascade, often referred to as a billiard-ball-type process. On occasion, collisions return to the surface and result in the emission of atoms and atom clusters (a process known as sputtering). A portion of these species become ionised and these secondary ions are detected and analysed by a mass spectrometer. Figure 3.17 illustrates this process schematically. Secondary ions may be either positively or negatively charged. Although most samples tend to produce either a very strong positive or a strong negative ion yield, it is usual to record both positive and negative ion spectra. Secondary ions are detected by a mass spectrometer and identified on the basis of their charge to mass ratios. The sputtering process itself is still not fully understood, but for a comprehensive review of the various theories, the reader is referred to Volume II of Briggs and Seah, (1992).

![Figure 3.17 Schematic of the SIMS process](image)

The secondary ions can be further subdivided into atomic ions, (indicating which elements are present on the surface), but potentially more useful are the cluster ions, which relate to the chemical groups on the surface. The mass spectrum obtained from
Chapter 3. Experimental Techniques

the cluster ions, or fragmentation pattern, as it is often referred to as, enables compounds comprised of the same elements to be differentiated from each other. Under the correct conditions, it is also possible to detect molecular ions using SIMS. The most successful method to date, of obtaining high mass peaks, appears to be to prepare very dilute solutions of the polymer and spin cast them on to silver substrates, (Reed and Vickerman, 1993). The use of metal, in particular, silver substrates results in a process known as cationisation. Cationisation "involves the formation of precursors of the finally emitted secondary ion on the surface, prior to any ion bombardment", (Leggett and Vickerman, 1994). The precursors may then be sputtered as (M + H)⁺ or (M - H)⁻ ions. Benninghoven et al., (1980), have demonstrated that cationisation is an effective means of determining the average molecular weight distributions of polymers. SIMS has also been used successfully to obtain molecular weight distributions of polymers, the results of which tend to agree well with data obtained using alternative methods such as gel permeation chromatography, (Reed and Vickerman, 1993).

3.2.2 Instrumentation

Instrumentation has developed dramatically over the past thirty years, such that the instruments available today, are capable of detecting masses over the range of 0 - 10000 Daltons, with sensitivities of parts per billion. Instruments are broadly categorised into three areas, quadrupole, magnetic sector and time-of-flight instruments. Quadrupole spectrometers are probably the most widely available, due to their low cost and ease of operation. Quadrupole mass analysers operate by applying a.c. and d.c. potentials to a series of four rods, hence the term quadrupole. The ions are separated by mass as they pass through the analyser. Ions of high kinetic energy cannot be separated, thus warranting the use of an electrostatic filter placed between the specimen and the analyser to remove them. Quadrupole mass analysers are effective up to masses of about 1000 Daltons, and are restricted by their mass resolution. Above masses of about 1000 Daltons, the transmission falls dramatically, making quadrupole analysers unsuitable for the detection of high mass fragments.
Magnetic sector analysers have even lower mass ranges, (up to 250 Daltons), making them of limited usefulness for polymer analysis. The characteristic mass peaks resulting from the fragmentation of organic macromolecules are of the order of several hundred Daltons and the molecular ions may have masses an order of magnitude higher again. This makes analysis by time-of-flight SIMS the preferred choice for polymeric materials.

The University of Surrey houses two VG Scientific Time-of-Flight SIMS (ToF SIMS) instruments, the main difference being in the design of their analysers; Poschenrieder versus reflectron-type. The analysers use different methods of energy compensation. The Poschenrieder-type has an electrostatic section in the flight tube, which allows low energy ions to take a shorter flight path. The reflectron-type analyser compensates for the distribution in ion energies with the aid of an electrostatic mirror. Both rely on liquid metal (gallium) ion guns for the primary ion source. The principle of time-of-flight analysis relies on the fact that ions of different masses will take varying lengths of time to reach a detector. A pulsed primary beam is used, with a sufficiently large pulse width to allow even the heaviest ions to reach the detector before the next pulse strikes the sample. ToF-SIMS allows much greater sensitivity, important for analysis of samples which degrade under prolonged ion bombardment, such as polymers. A higher mass range, theoretically unlimited, is available and there is also superior mass resolution, with the ability to separate peaks of the same nominal mass, (e.g. the CHO+ and C2H5+ peaks from a sample of PMMA, at masses of 29.0027 and 29.0390 amu respectively, can be differentiated).

Regardless of the type of instrument used, one of the most limiting features of SIMS is the ability to quantify the data. Quantification is made difficult by the fact that ion yields are heavily dependent on the ease of ionisation of a particular species and are therefore not a direct reflection of the amount of that species present in the sample. In addition to the variation of secondary ion yield between elements, the secondary ion yield also varies for the same element depending upon the matrix it is in. This is described as the matrix effect and it produces added difficulties for quantification.
During SIMS analysis, only about 10% of the material sputtered from the surface are ionised species, the remainder, (90%), being comprised of neutral species. To address this fact, a variation of the SIMS technique has been developed, sputtered neutral mass spectrometry, (SNMS). SNMS is very similar to the SIMS technique. Low energy ions are used to bombard the sample surface and a mass spectrometer analyses the secondary particles. Unlike SIMS however, the true secondary ions are discarded and it is the secondary neutrals which form the basis of the analysis. The neutrals are deliberately post-ionised and detected with the aid of the mass spectrometer, (Walls, 1989). Post-ionisation is carried out using either a low pressure plasma, an electron beam or a laser. The major advantage of SNMS over SIMS, is that the data may be readily quantified, as the ionisation cross-section is independent of the matrix effects described previously.

The following section does not include a definitive account of the operation of a ToF SIMS spectrometer, it is intended simply to draw attention to certain features specific to the VG Scientific Type 23 instrument used during this study. A liquid metal ion gun (gallium source), produces a beam of 30 kV primary ions, with the addition of a Wien filter to select a single isotope of gallium. Secondary ions are detected by a series of channel plates within a single stage reflectron time-of-flight analyser. Charge neutralisation of insulating samples was achieved with the aid of a pulsed electron gun, (Briggs et al., 1990). Specific analysis details are recorded with each of the results sections, as the precise conditions were altered depending on sample type.

3.2.3 SIMS Imaging

As with XPS, spatially resolved information from a sample surface is often required. Systems equipped with liquid metal ion guns can readily be used in the imaging mode. Unlike X-ray sources, ion beams can be focused easily using standard ion optics to produce a sub-micron beam, which may be rastered over the sample to produce an image of selected mass. This allows a map of the distribution of a given species to be generated. It must however be remembered that the sample topography
will have a significant influence on such images. The primary ion beam for the (MIG30) on the VG Scientific Type 23 instrument has a 200 nm spot size, which when pulsed has a spot size of about 1 μm.

3.3 Microscopy Techniques

3.3.1 Scanning Electron Microscopy (SEM)

The principle application of SEM is in the study of the surface topography of bulk specimens. It is a technique particularly suited to the study of the failure surface morphologies of adhesive joints.

A scanning electron microscope is operated by scanning a fine beam of electrons across a specimen. The electrons are produced by an electron gun, usually of a tungsten or LaB$_6$ filament, of the thermionic emission variety, which produces electrons and accelerates them to energies of between 2 keV and 40 keV. On striking the specimen, this results in the emission of low energy secondary electrons (or other forms of radiation), which are detected. The spot of a cathode ray tube is scanned across the screen concurrently, the brightness of which is modulated by the signal from the detector to produce an image of the sample surface. SEM is a standard tool used in materials analysis and a more detailed description of the technique can be found in "Electron Microscopy and Analysis", (Goodhew and Humphreys, 1988).

3.3.2 Confocal Scanning Laser Microscopy (CSLM)

CSLM is a relatively recent technique in the field of materials analysis, although the biologists have significantly more experience in the use of this technique. One of the major advantages being that specimens do not have to be mounted in a vacuum chamber. Figure 3.18 is a schematic of the main components of the Zeiss CSLM housed at the University of Surrey. During operation in the reflection mode, the laser beam is expanded to illuminate the objective lens, which focuses a diffraction-limited spot onto the object plane. The object is scanned across the spot in a pattern in the
x-y plane similar to a video raster. Light reflected from the specimen passes back through the objective lens, is reflected from the half-silvered mirror and falls onto the photodetector, whose output, after amplification, modulates the brightness of a video display (scanned simultaneously with the object) to form an image. If the object is then moved out of the focal plane, with the aid of a stage connected to various stepper motors, reflected light is no longer brought to a focal point at the detector, creating a significant drop in the detected signal intensity. Out of focus information is thus suppressed rather than blurred as it would be in a conventional microscope. Hence, it is possible to carry out non destructive optical sectioning on samples to study subsurface damage and features. The sample is moved up a fraction at a time (in steps of a few hundred nanometres), with images taken of the regions previously not in the focal plane of the laser. Finally, the series of images obtained in this way can be reconstructed to give three-dimensional information.

Figure 3.18 Schematic of a CSLM
3.4 Fourier Transform Infrared Spectroscopy (FT-IR)

3.4.1 Basic principles

FT-IR spectroscopy is one of the few techniques able to provide information about the chemical bonding in a material. As with the complementary technique of Raman spectroscopy, FT-IR makes use of the vibrational motion of chemical bonds in order to detect them. The technique also has a number of advantages over other analysis methods. FT-IR spectroscopy is non-destructive and does not require expensive vacuum hardware, factors which have contributed to its widespread application. The effectiveness of the technique is however, determined by the sensitivity of the various chemical bonds to detection. For example, regardless of their concentration in a material, carbon to sulphur bonds cannot be detected, while other bonds, such as silicon to oxygen, can be detected at very low concentrations, (J. Neal Cox, 1992). Detailed tables of IR data are available which list the positions of all of the bond stretches detectable using FT-IR, (e.g. "Introduction to Organic Spectroscopy", Lambert et al., 1987).

The basic principle of FTIR is to measure the change in intensity of an infrared beam as a function of either wavelength or frequency, after it has passed through the sample. A spectrophotometer disperses light from an infrared source, (the optical path for which is usually purged with nitrogen at atmospheric pressure). The intensity of the infrared beam is detected after interacting with the sample at each frequency. An infrared spectrum is produced by plotting the ratio of the initial intensity of the IR source, \( I_0 \) to the intensity of the IR beam after interaction with the sample (I), against the frequency of light (f). The data may be plotted in any of the following formats:

(i) transmittance, where the value for I is the intensity of the transmitted beam, \( I_t \), so, 
\[
T_f = \left( \frac{I_t}{I_0} \right)_f
\]

(ii) reflectance, where the value for I is the intensity of the reflected beam, \( I_r \), so, 
\[
R_f = \left( \frac{I_r}{I_0} \right)_f
\]

(iii) absorbance, where the absorbance is related to the Beer-Lambert Law,
so,  \[ A_f = -\log T_f \]

During the course of this study, data were recorded in either transmittance or reflectance modes. The IR source can interact with a sample in a variety of ways, to suit the particular sample under test.

(i) In the single pass transmission mode, the beam is allowed to make a single pass through the sample before the transmitted beam reaches the detector.

(ii) Reflection mode tends to be used in cases where the substrate material is opaque. This mode allows the angle of incidence to be set at the grazing angle, to improve the surface sensitivity of the technique.

(iii) In attenuated total reflection (ATR) mode, the infrared beam is directed into a crystal which then acts as a waveguide. The sample is placed next to the crystal and at the points where the IR beam strikes the outer surface of the waveguide, (i.e. the surface which the sample is in direct contact with), the beam is able to interact with the sample.

(iv) Emission IR spectra are sometimes recorded from materials such as coal, by utilising the fact that on heating materials, a characteristic IR spectrum, is produced, which can be recorded.

(v) Finally, IR microscopes are available for analysis of small areas (20 µm spot size). IR microscopes can be used in either transmittance or reflectance modes.

3.4.2 Application to this study

During this study, IR spectroscopy was used to answer specific questions, where information was unavailable using the principal technique, (i.e. XPS). In the study of adhesive systems, the question of whether or not the adhesive has fully cross-linked often arises, as regions of low crosslink density are cited as possible reasons for reduced joint performance, or even premature failure, (Kerr, 1970). IR spectroscopy is particularly suited to measuring this parameter. The degree of unsaturation, (i.e. number of double bonds), can be used as an indication of the crosslink density, as they are the sites involved in the formation of crosslinks. The degree of cure can be
correlated to the ratio of the absorbance readings at 1636 cm\(^{-1}\) and 1605 cm\(^{-1}\), the lower the ratio, the greater the degree of cure. Signals were measured and compared with those obtained for a fully-cured sample of the same polymer, to look for either enhanced or reduced crosslink density.

IR spectroscopy is also particularly useful for the study of water uptake in materials. The magnitude of the water bands (which occur at 1640 and 3400 cm\(^{-1}\)), can be measured as a function of time at a given temperature. In recent papers, (Nguyen et al., 1991), a variation of the FT-IR technique, (FT-IR in multiple internal reflection, MIR, mode) has been used to make in-situ measurements of water at the coating/substrate interfaces. Unfortunately, the nature of the topography of the as-received alumina substrate used during these studies, precluded the use of such methods. FT-IR was used simply to monitor the rate of water uptake at 50°C (273 K), over a period of several weeks.

### 3.5 Inverse Gas Chromatography (IGC)

#### 3.5.1 Introduction

The use of IGC as an analytical technique was first reported by Kislev in 1967 in "Advances in Chromatography". IGC first developed as a branch of gas chromatography, (GC), (Schreiber and Lloyd, 1989), but is now recognised as a useful technique in its own right. IGC offers several advantages over other techniques, which have doubtless contributed to its widespread application. The cost of capital equipment is relatively low compared to other analytical techniques, analysis times are short and it is also possible to acquire data over a range of temperatures. In addition, the technique is extremely versatile and is suited to a wide variety of materials ranging from polymers to foodstuffs. An assortment of different parameters can be determined by IGC, including glass, (and other) transition temperatures for polymers, solubility parameters and polymer/solvent Flory parameters and thermodynamic work of adhesion values. Of interest to this study however, was the determination of the surface
thermodynamic properties of polymers and in particular their acidity/basicity. The role of acid-base interactions in adhesion has been discussed in the section on mechanisms of adhesion in Chapter 3. IGC has been demonstrated as an effective means of determining enthalpies and free enthalpies of adsorption, from which acid-base constants can be calculated, (Chehimi and Watts, 1993).

3.5.2 Experimental detail

The term "inverse" GC arose because the material of interest forms the stationary phase in the column. Chromatographic columns are prepared by packing them with the material under test, ideally leaving no gaps in the column. This is generally achieved, (for powders or granules), by the "tap and fill" method, also a standard means of filling moulds in ceramics processing. The actual columns are usually made from either stainless steel or poly(tetraflouroethylene), PTFE, (otherwise referred to as Teflon™), though the precise length and diameter of the column must be determined for each individual material. Properties such as specific surface area and surface energy vary for each material and this in turn will affect the choice of column dimensions. See Figure 3.19 for a photograph and schematic of the apparatus.

After the column has stabilised at the appropriate temperature, a volatile probe of known properties is injected into the column at infinite dilution. At infinite dilutions, probe/stationary phase interactions are favoured. The probe is then swept out through the column by an inert carrier gas such as helium or nitrogen. A flame ionisation detector is located at the opposite end of the column to the point of probe injection. The parameter measured in IGC experiments is the net retention volume, \( V_N \), for each probe. The net retention volume is calculated from the following equation:

\[
V_N = j F t_N \quad \ldots \text{Eq. 3.18}
\]

where, 
- \( j \) = a pressure gradient correction factor
- \( F \) = the corrected flow rate
- \( t_N \) = the net retention time
Figure 3.19 Photograph and schematic of IGC apparatus.
Chapter 3. Experimental Techniques

The net retention time is the basic parameter from which all of the thermodynamic properties of the materials are derived.

3.5.3 Calculation of Thermodynamic Properties

Detailed calculations of the thermodynamic properties for this system are included in the results chapter, so this section is intended only as a brief introduction to the calculation of thermodynamic properties. At infinite dilutions, $\Delta G_a$, the free energy of adsorption is related to the net retention volume by the following equation:

$$-\Delta G_a = RT \ln V_N + C$$ ... Eq. 3.19

where, $R$ is the gas constant, $T$ is the temperature of the column and $C$ is a constant which takes into account the weight and specific surface area of the sample, plus the standard states of the probes in the mobile and in the adsorbed phases, (Meyer, 1980).

In this particular study, IGC was used to determine (i) London dispersive interactions, (ii) acid-base interactions and (iii) the acid and base constants for the system. The dispersive component of the surface energy, ($\gamma^d$), is used to describe the potential for a solid material to undergo London dispersive interactions. Dorris and Gray, (1980), devised a standard method of determining $\gamma^d$, by using a series of alkanes (n-alkanes). If $\Delta G_a$, or values of $RT \ln V_N$ are plotted versus the number of carbon atoms, ($n_C$). The gradient gives a value of $\Delta G^{CH2}$, the free energy of adsorption of a methylene group, from which $\gamma^d$ can be derived using the following formula, suggested by Dorris and Gray, (1980), based on the earlier pioneering work of Fowkes, (1964):

$$\gamma^d = \left(\frac{\Delta G^{CH2}}{N a_{CH2}}\right)^2 / 4 \gamma_{CH2}$$ ... Eq. 3.20

where, $N$ is the Avogadro number, $a_{CH2}$ the cross-sectional area of an adsorbed $CH_2^-$ group, (which is approximately 6 Å$^2$) and $\gamma_{CH2}$ is the surface energy of a solid containing only methylene groups, (e.g. polyethylene).

Several approaches have been proposed to separate the dispersive and acid
Chapter 3. Experimental Techniques

base contributions to $\Delta G_a$. This study has made use of the Sawyer and Brookman approach, (1968), in which $\Delta G_a$ values are related to the boiling points of the probe molecules. The n-alkane series produces a linear plot which can then be used as a reference for London dispersive interactions. The interaction of polar probes is expected to produce a deviation from this linear correlation. Dispersive and acid-base interactions are assumed to be additive, so the subtraction of $\Delta G^{AB}$ from $\Delta G_a$ is straightforward, corresponding to the vertical distance between the n-alkane reference line and the molecular probe of interest:

$$-\Delta G^{AB} = -(\Delta G_a - \Delta G_a^d) = RT \ln(V_N / V_{N,ref}) \quad \text{... Eq. 3.21}$$

where $V_N$ and $V_{N,ref}$ are the net retention volumes of the polar probe and a hypothetical reference n-alkane with the same boiling point, respectively. This is illustrated schematically in Figure 3.20.

Finally, several approaches have also been suggested to determine the acid-base constants $K_D$ and $K_A$, where D and A are abbreviations for donor and acceptor, respectively:

$$-\Delta G^{AB} = K_D \ AN^* + K_A \ DN \quad \text{... Eq. 3.22}$$

which may alternatively be written as,

$$-\Delta G^{AB} / AN^* = K_A(DN / AN^*) + K_D \quad \text{... Eq. 3.23}$$

A plot of $-\Delta G^{AB} / AN^*$ versus $(DN / AN^*)$, usually produces a linear correlation, with gradient of $K_D$ and an intercept of $K_A$. The main criticism of this approach is that it combines $\Delta G$ and Gutmann's numbers derived from $\Delta H$ terms and cannot therefore be fundamentally correct. It has proved however, to be effective in monitoring changes in the surface compositions of related materials, which made it an appropriate choice for this particular study.
3.6 Molecular Modelling

3.6.1 Introduction

With the recent improvements in computing power, there has followed a rapid growth in the area of molecular modelling, a technique which is heavily dependent on computer processing speeds. The technique enables molecular structures to be generated and any conformational changes monitored when the molecule is interacted with say, a model surface. A series of interaction energies can be measured for molecules on surfaces to calculate the energetically most favourable interaction with the surface. Previous studies carried out by Sennett et al., (1990), Zukas et al., (1992) and Wentworth et al., (1993), have monitored the interaction of various adhesive

Figure 3.20 Schematic to illustrate the concept of $-\Delta G_{AB}^*$, from IGC data.
precursor molecules with alumina surfaces in order to try and predict the performance of adhesively bonded joints. Part of the work also included introducing water molecules into the model, to study the effects of their presence on the adhesive molecules in the system.

3.6.2 Experimental Detail

The molecular modelling work carried out during this project has not attempted to produce models anywhere near as complicated as those used by Wentworth's group. Molecular modelling was carried out to provide supporting evidence for some of the data obtained using other techniques, rather than playing a major role in the study.

Molecular modelling of the system was carried out at ZENECA Group plc. Specialties Research Centre, Blackeley, UK. The experimental details are included in the results section.

3.7 Mechanical Testing

3.7.1 Introduction

During this study, emphasis was not placed on obtaining practical adhesion values for the system. The main reason for this, was the fact that the adhesive used in these studies (LCR000), had previously failed the leak test specified by a potential user. The test involved submerging the devices, in this case potentiometers, which had been encapsulated in LCR000, in a bath of fluorescent dye at 85°C (358 K) for one minute. The device failed if a stream of bubbles was observed, as this indicated the presence of a leak. Devices were also tested for resistance to thermal shock by cycling them for thirty minutes at -55°C (218 K), five minutes at room temperature, thirty minutes at 120°C (393 K) and a further five minutes at room temperature. After each cycle was completed, the devices were also leak tested. A device needed to survive five cycles to pass the test. The actual value of practical adhesion for the system was to a great extent therefore, purely academic. Work was instead directed at understanding
how the system failed, in order to improve its performance.

3.7.2 Experimental Details

To compare the performance of the photocured resins with other adhesives, a suitable mechanical test was first designed. The choice of mechanical tests available was limited by the nature of the properties of both the substrate and adhesive. The alumina adherends have a high stiffness and are also extremely brittle. In cases where the adhesive is fairly pliable, this does not cause too many difficulties, as tests can be devised where the adhesive coating is peeled away from the substrate. In this case, however, the adhesive cured to produce a highly cross-linked network, which was also relatively brittle.

Two different joint geometries have been used in this project. Butt-joints were used initially, as this particular specimen geometry lent itself to application in in-situ fracture experiments. This will be dealt with in more detail in the section on joint design in the following chapter. Butt-joints were also used as the simplest means of monitoring the decrease in mechanical properties on exposure to a hostile environment, (water at 50°C). In order to assess the performance of the resins, separate tests were conducted. The double cantilever beam, (DCB) test had already been demonstrated as a suitable method to study these particular materials. DCB tests allow a value of the fracture energy to be calculated, via any one of five alternative formulae, summarised by Priour, (1992). An adaption of the DCB test is the Boeing wedge test, used to monitor the decrease in fracture energy as a function of exposure time to particular environmental conditions, and as its name suggests, is frequently used by the aerospace industry. The test involves driving a wedge into the joint, which proves disastrous with alumina adherends, the substrate shatters as the wedge is driven into the joint. A modification of the Boeing wedge test was therefore chosen. Rather than driving a wedge into the joint to initiate the crack, an opposing screw thread was used to open up a crack. The various geometries are illustrated in Figure 3.21.
Figure 3.21 Schematic of the joint geometries
3.8 **Summary**

The various analytical and mechanical testing techniques used during this study have been outlined in this chapter. The project involved the use of a wide variety of techniques, as it was important to be able to relate the results of surface analysis, (the main area of the work), and any changes in the surface morphology to the mechanical performance of the system.

The following section contains results from characterisation of the resin and substrate, in addition to a detailed study of the performance of the adhesive system under ambient conditions.
Chapter 4

Characterisation of the As-Received Materials and the Adhesive/Adherend System

4.1 Introduction

The results discussed in the following chapter can broadly be categorised in four main areas, characterisation of: (i) the adherend, (ii) the adhesive, (iii) the adhesive system as a whole and finally, (iv) the response of the system to load. The investigation has drawn on a combination of surface analytical, microscopy and mechanical testing techniques. The chronological order in which experiments were conducted was (i) to (iv). It was necessary to gain as much information about the adhesive and substrate as possible, before considering the interactions between them.

4.2 Characterisation of the Adherend

4.2.1 Introduction

An initial study was carried out of the as-received alumina substrate in order to characterise the adherend surface prior to bonding. This was particularly important, as the surface chemistry of many of the substrates used for electronics applications was known to be heterogeneous. Studies on the densification of ceramics, (Taylor et al., 1974 and Clarke, 1980) have shown that the diffusion of sintering aids such as silica and magnesia during the manufacturing process, results in the production of a heterogeneous bonding surface. The adhesive manufacturer’s problem is therefore not simply a case of formulating a resin which will adhere well to alumina.
4.2.2 XPS Analysis

4.2.2.1 Sample Preparation

Coors AD96 alumina was supplied by the Laser Cutting Company in the form of discs, 10 mm in diameter and 1mm thick. With the exception of a water rinse following the laser cutting process, the discs received no additional cleaning. This was in order to reproduce the adhesive bonding process used during production, as accurately as possible. Most manufacturers are reluctant to include additional steps in the production process, (including precleaning), as they constantly strive to minimise manufacturing costs. The alumina discs were mounted on sample stubs with double-sided adhesive tape just prior to analysis by XPS.

4.2.2.2 Results of XPS Analysis

The survey spectrum obtained from the as-received surface of a Coors AD96 alumina disc (Figure 4.1), revealed a relatively small carbon 1s peak, which indicated a low level of carbon contamination. The oxygen 1s line is the most dominant, and the remaining species detected included, aluminium, silicon, calcium, magnesium and sodium. Unfortunately for this particular study, when AlKα radiation is used for the analysis of aluminium compounds, an Auger peak (the AlKL₂,₃ L₂,₃ peak at a kinetic energy of 1386 eV), appears coincident with the silicon 2p peak at a binding energy of 100 eV. This meant that if quantification of the spectrum were to be attempted, then, the overlap of the two peaks would make it appear as if that there was a greater concentration of silicon present. An alternative would have been to use the Si2s peak at 149 eV. A second aluminium Auger peak (the AlKL₁ L₂,₃ peak) is however present at 1341 eV, (KE). Although the AlKL₁ L₂,₃ peak is not coincident with the Si2s peak, the low concentration of silicon as compared with that of aluminium made it difficult to distinguish the Si2p peak from the background of the Auger peak. For this reason, it was decided to run routine spectra in AlKα radiation and spectra we wished to quantify in MgKα radiation. Analysis using magnesium radiation is also slightly more surface specific than using aluminium radiation. This is illustrated by the fact that C1s electrons have a constant BE of 285 eV, which equates to a kinetic energy of 969 eV.
in MgKα radiation and a higher value of 1202 eV in AlKα radiation. These kinetic energies yield analysis depths of approximately 6 and 7 nm respectively, (Watts, 1990). With MgKα radiation, the Mg1s peak is not accessible, so the Mg2p peak has to be used for quantification. Figure 4.1(b) was obtained from an as-received Coors AD96 alumina sample using MgKα radiation. Both spectra were recorded with analyser pass energies of 50 eV, a step size of 1.0 eV and a dwell time of 200 ms per channel. Table 4.1 indicates the surface composition of the as-received alumina surface.

Table 4.1 The surface composition of as-received alumina using MgKα radiation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>Surface Concentration /Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>C1s</td>
<td>38.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O1s</td>
<td>33.2</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al2p</td>
<td>17.1</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si2p</td>
<td>3.0</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na1s</td>
<td>3.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca2p</td>
<td>1.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg2s</td>
<td>2.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N1s</td>
<td>0.9</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl2p</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Figure 4.1 Survey spectra obtained from as-received Coors AD96 alumina using (a) AlKα and (b) MgKα radiation.
Chapter 4. Characterisation of the As-Received Materials

Sputter-depth profiling experiments (using an argon ion gun), were used to obtain compositional information from different depths in the sample. Interpretation of results was difficult, because one of the most likely places for segregation to occur is at the grain boundaries. As the use of an argon ion gun involves sputtering over the entire surface, it is possible for localised variations in composition to remain undetected.

An attempt was also made to use angular resolved XPS to look for surface segregation of species such as silicon. Unfortunately, the topography of this particular substrate was not ideally suited to this application, as indicated by the CSLM results, (page 102). An ideal surface for angular resolved work would be one which is atomically smooth, but the peak to trough height of the grains in Coors AD96 can vary by up to 4μm. Angle dependent studies were carried out later in the project on highly polished surfaces.

In other cases where topographic effects were found to obscure data, e.g. characterisation of powders using XPS, (Davis, 1992), a more acceptable solution was found to be analysis using different core levels of the same element. High resolution scans of the magnesium 1s and 2p regions were recorded for an alumina sample. High counts were recorded from the Mg1s region, (27,000 counts), the count rate for the 2p region was much lower, (less than 1000 counts). It must be remembered, however, that the photoelectron cross-section for the 1s region is larger than the 2p. Part of this difference can therefore be accounted for by a variation in the photoelectron cross-sections. The ratio of these parameters for a homogeneous sample is typically about 20, (Cappleman et al., 1985), and the ratio recorded from the alumina sample in this case is higher, (about 27), supporting the idea that the surface composition of alumina does contain a higher magnesium concentration than the bulk. Similarly, analysis of polished versus as-received alumina indicated that polishing removed the silica and other surface contaminants, such as magnesia. AES has in the past been used successfully to carry out depth profiles, of for example, oxide and sulphide inclusions in metals, (Baker, 1990). AES is often a useful technique to study surface enhancement or depletion. However, the severity of the charging effects observed
during AES analysis of bulk ceramic oxides, especially alumina, made it necessary to
seek an alternative method of depth profiling. Polycrystalline insulating samples such
as the Coors AD96 alumina have in the past proved much more difficult to analyse
than single crystals of, for example, sapphire. The reasons for this are discussed in the
section on the analysis of insulating samples (pages 39-41).

Further composition depth profile work was carried out using ToF-SIMS with
the added accuracy of a high degree of spatial resolution, enabling the depth profile
of an individual grain to be obtained.

4.2.3 Results of Analysis by ToF-SIMS

Static SIMS spectra were recorded using a VG Scientific Type 23 ToF-SIMS
system, with a single stage reflectron-type analyser and a 30 kV gallium source.
Spectra were recorded with the ion gun operating in the synchronous mode at a
frequency of 10 kHz and a pulse width of 25 ns. Figure 4.2 shows the positive ion
SIMS spectrum recorded from the surface of an as-received alumina disc. In addition
to the presence of additives from the sintering process such as silica, SIMS analysis also
detected strong sodium and potassium signals, at 23 and 39 Daltons respectively.
Although, both sodium and potassium have very strong ion yields, neither species is
added deliberately during the production of alumina. The potassium and sodium are
therefore assumed to be as a result of contamination from the production process, or
from subsequent sample handling. In this case, the former is favoured, as sample
handling, (once the material had been received), was carried out using tweezers and
gloves.
4.2.4 SEM Results

Scanning electron photomicrographs were obtained from an as-received Coors AD96 alumina disc using a Cambridge Instruments Stereoscan 250 in secondary electron mode. A rough surface was revealed, comprised of grains ranging from about 5 to 25 μm across their widest point, referred to as the maximum feret, (see Figure 4.3). Samples were sputter coated with gold prior to analysis.
4.2.5 CSLM Results

The surface of an as-received Coors AD96 alumina disc was investigated with the aid of a Zeiss LSM 30 confocal scanning laser microscope, at the University of Surrey, (with the assistance of K. Powell). The Zeiss system was equipped with an internal HeNe 633 nm laser and an external Ar laser. The image obtained from the surface of the alumina has been displayed in two different formats. Figure 4.4(a), (a plan view), was produced by taking a series of optical sections and combining the information from each of them in a single image, rather like a contour map, with different colours corresponding to specific heights on the sample. The intensity of each pixel is proportional to the location of the brightest pixel in the montage of optical sections, (Powell et al., 1992). In Figure 4.4(b), the same information has been displayed in 3-D, making the extent of the surface relief immediately apparent. The computer software package linked to the CSLM also allowed surface roughness values to be calculated, a parameter which would previously have been obtained by carrying
out separate experiments using a Talysurf. The roughness value, ($R_a$, the arithmetic average surface roughness) for as-received alumina was calculated as 0.89.

**Figure 4.4** CSLM image of the surface of as-received alumina (a) plan view and (b) 3-D reconstruction from (a).
Chapter 4. Characterisation of the As-Received Materials

4.3 Investigation of the Resin (LCR000) Properties

4.3.1 Introduction

In some circumstances, it is necessary to analyse the uncured resin, as it is in the uncured state that the resin is brought into direct contact with the adherend surface. This is not always possible using certain techniques, (e.g. inverse gas chromatography, (IGC)). With other techniques, for example, XPS, it was possible to analyse samples of both the cured and uncured resin. Analysis of the fully-cured resin is also important, as results of failure analysis will relate to the cured rather than the uncured resin.

4.3.2 Resin Composition

The LCR000 resin used during the course of this study was a fully formulated, commercially available system. The resin is produced by ZENECA Specialties under the tradename of Luxtrak™. As the precise formulation details are commercially sensitive, some of the details of the formulation are unavailable. The information necessary for understanding the behaviour of LCR000 as an adhesive, has however been provided by the manufacturer.

LCR000 is comprised of approximately:

91 % - base resin (based on highly aromatic methacrylate-type oligomers and produced in-house, i.e. not a product which can be obtained from a commercial supplier).

9 % - TEGDMA (tri ethylene glycol dimethacrylate, added as a reactive diluent to reduce the viscosity of the system).

< 1% - light cure initiator (identification sensitive).

< 1% - co-initiator (identification sensitive).

ppm - stabiliser (identification sensitive).

The structure of TEGDMA is illustrated in Figure 4.5.
Chapter 4. Characterisation of the As-Received Materials

Figure 4.5 Structure of a molecule of TEGDMA.

4.3.3 XPS Analysis

4.3.3.1 Sample Preparation

Samples of LCR000 were prepared for XPS analysis by casting the resin from syringes onto standard ESCALAB stubs used for sample mounting. Strips of Melinex™ film were placed over the resin prior to cure, to prevent the tackiness which arises when the resin cures in contact with oxygen, due to an oxygen inhibition effect, (Decker, 1979). The resins were then cured with visible light using a Luxor™ high intensity lamp, for a minimum of 2 minutes. The Melinex™ also acted as a protective film once the resin had cured and was removed just prior to loading the samples into the spectrometer.

4.3.3.2 Results of XPS Analysis

A survey spectrum obtained from fully-cured LCR000 (AlKα radiation) revealed two major peaks, one for carbon and the other for oxygen (Figure 4.6(a)). The carbon to oxygen ratio for the resin was consistently found to be about 4. The position of the carbon peak at 287 eV, indicated sample charging of about 2 eV. A high resolution scan of the carbon region produced a fairly broad peak which initially proved quite difficult to resolve into its component parts (Figure 4.6(b)). After obtaining further similar results, an attempt was made to peak fit the carbon region. Confidence in the
peak fit was gained later, after the sample was analysed on a spectrometer (a Scienta ESCA300), with superior spectral resolution (see section on high resolution XPS results), with completion of the analysis prior to the onset of sample degradation. It would appear that the polymer is comprised mainly of C-C and C-O groups with about 8% of C=O groups and a small $\pi \rightarrow \pi^*$ shake-up satellite, caused by the bonding-antibonding transition in aromatic organics, discussed in detail in the section on secondary structure, (see pages 51-52). Table 4.2 indicates the relative proportions of the various groups within the resin. Also included in Table 4.2 are the relative proportions of each of the functional groups of an LCR000 sample which was scraped with a scalpel blade prior to analysis, (to ensure that the Melinex™ film had no effect on results). Results are plotted with binding energy decreasing from left to right, (i.e. on an increasing kinetic energy scale).

<table>
<thead>
<tr>
<th>Bond</th>
<th>LCR000</th>
<th>LCR000 (scraped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C / C-H</td>
<td>69</td>
<td>70</td>
</tr>
<tr>
<td>C-O</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>C=O</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

N.B. Melinex™, is an ICI Ltd. tradename for polyethylene terephthalate, (PET).

Implicit in the use of Melinex™ film, was the assumption that when the film was peeled away, failure occurred in a true interfacial manner. To confirm this, the side of the Melinex™ film that had previously been in contact with the LCR000, was analysed. The high resolution C1s spectrum obtained, closely matched the reference spectrum for polyethylene terephthalate, (PET), in "High Resolution XPS of Organic Polymers", (Beamson and Briggs, 1993).
Figure 4.6 (a) survey and (b) high resolution C1s spectra obtained from fully-cured LCR000 resin.
In addition, the surface of a sample of LCR000 was scraped with a scalpel and analysed. The Cls spectrum obtained from the scraped sample was indistinguishable from the spectrum acquired from a surface protected by Melinex™. These results indicated that the chosen method of sample preparation was perfectly acceptable, and transfer of the resin to the film or vice versa, did not occur.

High resolution spectra of the carbon 1s region for the as-received polymer had proved difficult to peak fit. The process was aided by analysing a sample of the resin on the Scienta ESCA 300, a spectrometer capable of achieving a high degree of spectral resolution. Figure 4.7 compares the carbon 1s scan from the ESCALAB MkII with the data from the Scienta ESCA300. Even with the added instrumental capabilities of the ESCA300, analysis of the polymer was by no means straight forward. The initial Cls spectrum recorded was not as well resolved as might have been expected for a similar polymer, (e.g. PMMA). It took several minutes for the electron flood gun to eliminate sample charging sufficiently, in order to reveal the now characteristic functional groups associated with LCR000. Data from the Scienta ESCA 300 helped considerably in the identification of the constituent groups in the polymer, but also validated the previous peak fitting work.

In addition to the work on fully-cured LCR000, spectra were also acquired using the Scienta ESCA300, from dilute solutions of the resin in toluene. These results are discussed in Chapter 7.

In summary, XPS has been used in the preliminary part of the study to obtain as much information as possible about the surface composition of the adhesive and adherend. This information will provide a useful standard with which to compare materials made up into adhesive joints and to study the effects of exposure to hostile environments.
Figure 4.7 Comparison of the C1s spectra obtained from a fully-cured sample of LCR000 using (a) Scienta ESCA300 and (b) VG ESCALAB MkII.
4.3.4 Inverse Gas Chromatography

4.3.4.1 Sample Preparation and Experimental Detail

The potential importance of acid-base interactions in the adhesion of polymers to ceramic substrates has previously been emphasised. The Luxtrak™ range of photocuring polymers and in particular, LCR000, which was used for the major part of this study, are supplied as highly viscous, (greater than 60 kg m⁻¹s⁻¹, or 600 poise) resins. In order to carry out IGC experiments, the LCR000 resin had to be cured and then ground to a fine powder. The resin was cured between two sheets of Melinex™, then broken into small pieces. The coffee grinding attachment to a Moulinex blender proved the most effective means of grinding up the polymer, without introducing contaminants. Next, the powder was sieved to between 100-200 μm. A PTFE column, with an outer diameter of 6 mm and a length of 1 m, was packed with 9 g of the powder using the traditional tap and fill method.

A gas chromatograph (Girdel 330) fitted with a flame ionisation detector was employed for IGC experiments. Methane (supplied by Alltech) was used as the non-interacting marker (to measure the zero net retention time), and the carrier gas was a high purity grade of nitrogen (supplied by Air Liquide). A regulator was used to maintain a gas flow rate of 18.5 ml min⁻¹, measured by a soap-bubble flowmeter. A digital thermometer inserted through the oven wall was used to record the temperature at which the column was held. The injector and detector temperatures were approximately 110°C. The column itself was conditioned at 110°C under a stream of nitrogen for 16 hours prior to chromatographic measurements. The probe vapours were injected manually via a Hamilton gas-tight syringe. A Delsi 21 digital recorder was used to record data, with net retention times determined graphically using the tangents method, (Conder and Young, 1979). Figure 4.8 is a typical trace, obtained after injection of a probe into the chromatographic column. To measure the retention time, a tangent was drawn either side of each peak and the two points of intersection with the x-axis were measured. These two values were added and divided by two, to give a value of retention time. This method of net retention time measurement helps to remove any of the effects of asymmetry of the peak. A series of apolar n-alkanes
Figure 4.8 A typical trace obtained after injection of a probe into the chromatographic column, with measurement of retention times illustrated.
were used as probe molecules, followed by an acidic, a basic and an amphoteric species. The resin was known to be comprised of aromatic methacrylate-type oligomers, so it was felt that PMMA would act as a suitable material with which to compare the data. A similar column containing 10 g of PMMA beads was also prepared. The difference in surface areas of the PMMA beads and the ground LCR000 was accounted for in the calculation of the free energy of adsorption by the constant, C, (see page 88). With the exception of the flow rate (5.5 cm$^3$ min$^{-1}$), all other experimental parameters remained unaltered.

4.3.4.2 Results From IGC Experiments

Table 4.3 lists the thermodynamic properties of the various probes, where DN and AN stand for Gutmann's donor and acceptor numbers. The AN values have been corrected in order to take the van der Waals interactions into consideration, to give AN* values, (Riddle and Fowkes, 1990). The values for both DN and AN* are in kJ mol$^{-1}$.

The resin was studied at a temperature of 25°C (298 K). Figure 4.9 illustrates the data obtained from the adsorption of a series of n-alkanes onto LCR000 at room temperature, (25°C). Table 4.4 contains the values of $\Delta G^{CH2}$ and $\Delta G^{AB}_a$ for the n-alkane series and the polar probes respectively, adsorbed onto LCR000 at 25°C. Figure 4.10 shows the variation of $RT \ln (V_N)$ versus $T_b$ for LCR000 at 25°C. The values for the polar probes lie well above the reference line defined by the n-alkanes, indicating that the resin behaves amphotERICALLY.

Table 4.5 displays the data pertaining to the material properties, with values for $\gamma^d$ and the acid-base constants $K_D$ and $K_A$ included. Data for PMMA beads is also included for comparative purposes. The $\gamma^d$ value for LCR000 is comparable to that obtained for PMMA. The determination of the acid-base constants is shown in Figure 4.11. The photocured resin is less basic than PMMA at ambient temperature, as illustrated by the $K_D$ values, but has a very similar value for $K_A$. The experiments were repeated in triplicate for each resin type and although small, the differences in acid-base constants were greater than the degree of scatter found within the data.
Chapter 4. Characterisation of the As-Received Materials

Table 4.3 Probes used to characterise LCR000 and PMMA

<table>
<thead>
<tr>
<th>Probes</th>
<th>$T_b$ (°C)</th>
<th>DN</th>
<th>AN*</th>
<th>DN/AN*</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane ($C_7$)</td>
<td>98.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Prolabo</td>
</tr>
<tr>
<td>Octane ($C_8$)</td>
<td>125.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fluka</td>
</tr>
<tr>
<td>Nonane ($C_9$)</td>
<td>150.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fluka</td>
</tr>
<tr>
<td>Decane ($C_{10}$)</td>
<td>174.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fluka</td>
</tr>
<tr>
<td>Chloroform (TCM)</td>
<td>61.2</td>
<td>0</td>
<td>22.6</td>
<td>0</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Ethylacetate (EtAc)</td>
<td>77.1</td>
<td>77.1</td>
<td>6.3</td>
<td>11.4</td>
<td>Prolabo</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>66.0</td>
<td>83.7</td>
<td>2.1</td>
<td>39.9</td>
<td>Prolabo</td>
</tr>
</tbody>
</table>

Table 4.4 Measurements of the adsorption behaviour of the probes.

<table>
<thead>
<tr>
<th>Materials</th>
<th>T(°C)</th>
<th>$-\Delta G^\text{CH}_2$</th>
<th>$-\Delta G^\text{AB}_{(\text{CHCl}_3)}$</th>
<th>$-\Delta G^\text{AB}_{(\text{EtAc})}$</th>
<th>$-\Delta G^\text{AB}_{(\text{THF})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCR000</td>
<td>25.0</td>
<td>2.8</td>
<td>5.5</td>
<td>4.6</td>
<td>4.2</td>
</tr>
<tr>
<td>PMMA</td>
<td>25.0</td>
<td>2.7</td>
<td>6.3</td>
<td>4.7</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 4.5 Material properties of LCR000 and PMMA

<table>
<thead>
<tr>
<th>Material</th>
<th>T(°C)</th>
<th>$\gamma_s^d$ (mJ/m²)</th>
<th>$K_D \times 100$</th>
<th>$K_A \times 100$</th>
<th>$K_D / K_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCR000</td>
<td>25.0</td>
<td>42.0</td>
<td>23.7</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>PMMA</td>
<td>25.0</td>
<td>38.8</td>
<td>25.5</td>
<td>4.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Chapter 4. Characterisation of the As-Received Materials

Figure 4.9 Adsorption of n-alkanes on LCR000 at 25°C.

Figure 4.10 $RT \ln (V_N)$ versus $T_b$ for LCR000 at 25°C.
IGC results have indicated that the LCR000 resin behaves amphoterically. The adherend surface is also known to be amphoterically, but the presence of silica and magnesia at the surface also means that there are acidic and basic sites present, (respectively). Having completed characterisation of the resin and substrate, the next stage was therefore to study the performance of the adhesive system under ambient conditions.

4.4 Joint Design and Manufacture

4.4.1 Introduction

In order to provide some form of comparative assessment between adhesive systems, numerous mechanical testing techniques have been devised. Owing to the
great diversity of adhesives and adherends under test, many tests are specific to a particular industry. In general, the most widely used tests are not the most rigorous method of assessing bond strengths, but are the quickest and cheapest to carry out. Lap shear tests are often used for rigid substrates and peel tests where one or both of the substrates is flexible. More accurate tests are available, such as the double cantilever beam (DCB) test, however, these tests are often more costly and laborious to execute.

4.4.2 Joint Design

An additional problem was posed during this study, the requirement to carry out in-situ fracture tests in the XPS preparation chamber and this restricted the choice of mechanical tests somewhat. The joint design chosen was a simple butt-joint geometry. Such a test clearly has major limitations in the assessment of bond strength.

The first problem with this type of test is accurate monitoring of the glue line thickness of the joint. Butt-joint strength has been reported to be dependent on the thickness of the glue, strength decreasing with increasing glue line thickness. This is contrary to stress analyses carried out on a variety of joints. Modelling the stresses in several joint geometries, suggests that joint strength will increase with a corresponding increase in glue line thickness, (Crocombe, 1994). Experimental results however, indicate that the reverse is true. This phenomenon was reported in 1948 by Meissner and Merrill. Kendall produced an equation in 1971 to account for this phenomenon, which agreed well with experimental data.

\[ F = 2\pi a^2 \left( \frac{2K\gamma}{t} \right)^{0.5} \]

Where
- \( F \) = Adhesive force, (strength of butt-joint)
- \( a \) = Radius
- \( K \) = Bulk elastic modulus
- \( \gamma \) = Adhesive energy
- \( t \) = Glue line thickness
The above equation (Eq. 4.1), indicates that the breaking force required is not limited by the strength of the adhesive, strength does not appear in the equation. This may also account for the peculiarity that a butt-joint may in fact be stronger than the adhesive which holds it together.

The adhesives used during the course of this study cure to form a highly crosslinked three-dimensional network. A high degree of crosslinking prevents close alignment of the polymer chains that would form crystallites. The material is therefore classed as an amorphous, or a glassy polymer rather than a crystalline one. In terms of their mechanical behaviour, amorphous polymers, (below their glass transition temperature), fall into the category of semi-brittle materials, (Lawn and Wilshaw, 1975). The strength of amorphous materials such as glasses is known to be determined by the size of defects such as cracks within the material, (Griffith, 1920). This might, in a qualitative way, help to explain the anomaly between experimental data and stress analysis of the influence of glue line thickness on joint performance. The larger the volume of adhesive used, the greater the probability exists, of a defect such as a cavity being present, at which failure can initiate at a reduced load. Modelling does not account for the possibility that such defects exist, therefore predicting higher rather than lower joint strengths.

On first inspection, it might appear that the stress in a butt-joint would be uniform across the layer. This only applies in a situation where the adherends and adhesive either do not deform, or deform by an equal amount, (i.e. if the ratio of the Poisson’s ratio $v$, to the Young’s Modulus $E$ were the same for both materials). It is far more usual for the ratio to be higher in the adhesive. As a consequence of this, stress concentrations arise on application of the load (Kinloch, 1982).

In addition to carrying out mechanical testing in ambient conditions, there is normally considerable interest in an adhesive’s performance in a hostile environment, (i.e. elevated temperature and or humidity). It is important that during environmental testing, the test should mimic, as far as is practicably possible, the conditions that the component will experience in service. Care should be taken not to exaggerate the test conditions too much (Brewis and Briggs, 1985).
In this case, the test was to be used primarily to create new fracture surfaces without exposure to the atmosphere, so the author feels that this was a reasonable choice. It later proved necessary to carry out more rigorous mechanical tests.

4.4.3 Joint Manufacture

In spite of the limitations previously described, the joint geometry chosen was a simple butt-joint (otherwise known as a poker-chip joint). The main reason for this choice was to enable an existing T-peel stage to be adapted to accommodate samples which could be fractured in-situ in the XPS preparation chamber.

A series of ESCALAB stubs were manufactured with a thinner platform than usual, on which to glue the alumina discs, to allow as much travel as possible for the jaws of the fracture stage inside the instrument. The opening of the jaws was restricted by the diameter of the opening in the flange on which the fracture stage was mounted, (35 mm). Figure 4.12 depicts a standard butt-joint. They are comprised of two ESCALAB stubs which were abraded and 10 mm diameter Coors AD96 alumina discs bonded to them with high shear strength Araldite adhesive. The two halves of the joint were secured in the rig pictured in Figure 4.13. The gauge was set to zero and the top half of the joint removed in order to apply the resin. This was applied directly from a syringe (in accordance with manufacturers directions). On re-securing the joint half, the new reading on the dial was noted, as this gave a value for the glue line thickness of the joint. The entire rig was then placed under a bifurcated lamp and the joint cured. Thus the production of well-aligned joints of known bond line thickness, (ranging from 150 to 200 μm), was ensured.
Figure 4.12 Schematic of a butt-joint.

Figure 4.13 Rig for joint production.
Chapter 4. Characterisation of the As-Received Materials

4.5 Analysis of Dry Failures

4.5.1 In-situ Fracture

To enable in-situ fracture of butt-joints to be carried out, a standard VG Scientific T-peel stage, designed to test laminate type materials, was re-designed to accommodate the butt-joint specimens described overleaf. The existing jaws were amputated and a new set of jaws manufactured which could accommodate poker-chip joints. Figure 4.14(a) depicts both sets of jaws alongside the fracture stage. The alterations were carried out in such a way that the two sets of jaws are now interchangeable, both T-peel specimens and butt-joints can be tested with the same piece of apparatus. In order to peel, for example, a polymeric coating from an aluminium can, considerable plastic deformation needs to be overcome. The T-peel jaws were therefore used in conjunction with a spring-type assembly inside the apparatus. This spring-type assembly was removed for fracture work. The modified in-situ fracture stage (see Figure 4.14(b)) was located on the flange identified in Figure 3.13. It was then possible to load butt-joints (singly), in the vertical position into the sample preparation chamber. With the aid of a modified wobble stick, the joint was rotated through an angle of 90 degrees so that it slotted into the jaws of the fracture stage. The jaws of the fracture stage were controlled via a handle outside the spectrometer chamber. Following fracture, both halves of the joint were recovered and loaded into the analysis chamber for further study. The wobble stick had to be modified in order to provide 360° sample rotation. The conventional grip was removed from the end of the wobble stick and replaced with a clothes peg-type assembly. The end of the wobble stick was fabricated from a beryllium copper alloy, as this provided the optimum mechanical properties for repeated grasp and release of samples. It was then possible to force the wobble stick to rotate, (ratchet round), by making it come into direct contact with the jaws of the fracture stage, (see Figure 4.15). The jaws of the fracture stage have a scissor-type action, such that there would have been a slightly higher tensile strain on the bottom edge of the butt-joint than the top. This would have increased the likelihood of failure occurring closer to the bottom edge. However,
Figure 4.14 In-situ fracture stage (a) both sets of jaws, (b) close-up of the jaws used to fracture joints.
Figure 4.15 Photograph of a butt-joint in the modified wobble stick, (a) before fracture and (b) following fracture.
when the fracture surfaces of joints fractured in-situ were compared with those fractured in the J.J Lloyd tensile tensometer, there were no obvious differences between them.

Once the chemical analysis was complete, samples were removed from the spectrometer ready for investigation using a scanning electron microscope.

4.5.2 SEM Results

Scanning electron microscopy studies carried out on the fracture surface of an untreated joint fractured in simple tension provided interesting information. The closest description of the observed fracture surface morphology which could be found in the literature is actually used to describe the fracture surface of a glass or an amorphous polymer which has undergone brittle failure. Figure 4.16 is the fracture surface of a glass rod broken in tension (Lawn and Wilshaw, 1975).

Failure is described as having occurred conchoidally, (Lawn and Wilshaw, 1975). Figure 4.17 is a schematic depicting the main features of a conchoidal fracture surface. Failure is believed to initiate at a defect within the mirror zone; at this stage, crack propagation is rapid giving rise to the smooth mirror zone region. At some stage during the fracture the crack starts to divide along its front (Andrews, 1968), to produce a "hackle zone" consisting of "tear lines." In some systems an intermediate region termed the "mist zone" has also been observed. Figure 4.18 is a schematic of the conchoidal fracture surface observed in this particular system, scanning electron photomicrographs obtained from various areas of the surface have also been included. Failure has occurred near interfacially within the region of the mirror zone. The advancing crack has then moved away from the interface, such that the remaining fracture surface was visibly cohesive in nature. SEM studies of the detail inside the mirror zone have revealed what appears to be a defect, visible on both halves of the fracture surface. It is believed that the defect is a form of bubble/cavity, which present in the resin, then acted as failure initiation sites, as indicated in Figure 4.18.
Figure 4.16 Conchoidal fracture of a glass rod.

Figure 4.17 Schematic of the main features of a conchoidal fracture.
Figure 4.18 Schematic of a conchoidal fracture surface, scanning electron photomicrographs depicting the detailed fracture surface morphology of each region.
4.5.3 Results of XPS Analysis

Figure 4.19 is a survey spectrum from a butt-joint fractured in-situ. There is a strong C1s signal from the polymer, but an aluminium signal from the ceramic surface can also be identified. Conventional XPS cannot distinguish between information recorded from chemically different regions of the same sample. The X-ray "footprint" from the ESCALAB MkII, covers an area about 1cm², and the electron optics of the analyser, (the slits and transfer lens), define a rectangular analysis area of 2 mm by 5 mm. Any features smaller than the dimensions defined by the slits, are therefore indistinguishable from the rest of the analysis area using this technique. Examination of the in-situ fractured samples by eye, revealed two distinct regions on the sample, as described in detail above, (SEM results). The next step was therefore to analyse similar samples using imaging XPS, (iXPS).

![Figure 4.19 Survey spectrum obtained from an alumina joint fractured in-situ.](image-url)
4.5.4 iXPS Results

The opportunity arose to study the aforementioned samples by iXPS using a VG Scientific ESCASCOPE at the ICI Wilton Materials Research Centre. The failure surfaces were analysed using AlKα radiation, (1486.6 eV), with the analyser operated at a constant retard ratio (CRR) of 4. The edge of the two visibly different regions was mapped overnight using iXPS. The Al2p signal was selected as characteristic of the adherend surface, and the C1s signal as diagnostic of the polymer. There was obviously some atmospheric hydrocarbon contamination present on the exposed alumina, but the possibility also existed for a thin layer of polymer to remain within this region. It was therefore first necessary to distinguish in what form the carbon was present. A high resolution C1s spectrum was acquired from within this region. The peak was symmetrical, of the type generally observed for adventitious hydrocarbon contamination, (i.e. none of the functional groups characteristic of the polymer were visible). The threshold for imaging the carbon was set below the level recorded in the spectrum from this region. The image in Figure 4.20 was obtained by superimposing the Al2p and C1s maps. The image suggests that the region to the left of the map is devoid of polymer, (i.e. that failure within this region has occurred interfacially). The area to the right of the image appears to be entirely comprised of polymer, (i.e. a region of cohesive failure).

4.5.5 ToF-SIMS Imaging

ToF-SIMS imaging was carried out on the same VG Scientific Type 23 system used to acquire ToF-SIMS spectra. The edge between the visibly different regions of a conchoidal fracture surface was imaged, (a similar sample to the one used for iXPS). Three different mass "windows" were selected, corresponding to the secondary ions for magnesium, aluminium and calcium and 128 x 128 pixel images were recorded. A primary ion induced electron image of the same region was also recorded, shown in the first quadrant, (a), of Figure 4.21. Enhanced magnesium and calcium signals were observed in quadrants (b) and (d), indicating possible localised variations in the surface chemistry. Quadrant (c) is the aluminium image.
Chapter 4. Characterisation of the As-Received Materials

Figure 4.20 Mirror zone edge, obtained by iXPS.

Figure 4.21 ToF-SIMS image of the mirror zone edge of a conchoidal fracture.
The sensitivity of the ToF-SIMS technique allowed the study of such localised variations in the surface chemistry.

4.5.6 Scienta ESCA300 XPS Results

High resolution Cls spectra recorded from the region, which the results from iXPS had previously indicated as being devoid of polymer, are presented in Figure 4.22. The characteristic functional groups of the resin are clearly visible, indicating that at least some polymer residue remains. It is unclear whether the polymer is present as a thin continuous layer, or as a patchy, island-like structure.

![Figure 4.22](image.png)

Figure 4.22 High resolution Cls spectrum recorded from the mirror zone using the Scienta ESCA300 spectrometer.
4.6 **Model for Dry Failure**

The detailed scanning electron photomicrographs obtained from the fracture surfaces of both sides of the joint, coupled with XPS data, have provided valuable information, which enable a precise failure mechanism to be proposed. Listed below, is a sequence of events which the author believes constitute the failure mechanism for this particular system, together with a schematic of the failure process.

**Failure Mechanism**

1. A crack is initiated at a defect, a cavity or bubble
2. Propagation of the crack close to the interface
3. Instability of the crack, movement away from the interface
4. Remaining area of the failure is visibly cohesive

![Diagram of failure mechanism](image)

**Figure 4.23** Schematic illustration of the proposed failure mechanism.
During the first stage, a crack initiated at a defect such as a cavity, which was present in the resin as the joint was fabricated. The resin used in these studies (LCR000), has a high viscosity, (600 poise) and it is difficult to avoid entrapment of gas bubbles, even though the syringes are designed specifically to help minimise the problem. The crack then runs very close to the interface for a distance of about 2-4 mm. Eventually, the crack becomes unstable and moves further from the interface, so that the remaining fracture surface is visibly cohesive, within the layer of adhesive. With the exception of peel tests, regardless of the adhesive, in dry joints it is unusual for a crack to run interfacially, (or even very close to the interface), for any significant distance. The presence of a defect, (or crack starter deliberately placed at the interface), can concentrate stresses to cause initiation of an interfacial-type failure, but the crack does not have to travel a great distance before becoming unstable.

This result is not so surprising when the surface topography of a real adherend is considered. The surfaces have a somewhat irregular, three-dimensional profile. On probability grounds alone, failure cannot be expected to follow this "predetermined, highly irregular, three-dimensional path in response to an external load", (Sharpe, 1993). In addition to this purely logical argument, the application of a simple load (e.g. tension), will be transformed into far more complex modes of loading, due to the irregularity of that interface. In other adhesive systems, interpenetration of the materials occurs, so there is no clearly defined interface, instead a more diffuse interphase region exists. These factors help explain why interfacial cracks rapidly become unstable.

4.7 Summary

The initial aim of this work, (i.e. characterisation of both the resin and substrate), has been completed. Considerable knowledge relating to both the surface chemistry and topography of the adherend surface has been gained. In addition, the main functional groups present in the resin have been identified using XPS and the acid-base properties of the resin have also been investigated by IGC.
Chapter 4. Characterisation of the As-Received Materials

This next section of the work, aimed at studying how the two materials interact, (without the added complication of an aggressive environment being present), has also been completed. Finally, the systems response to load was investigated. Results from this area of the work subsequently enabled an adhesion failure mechanism to be proposed, for the system under ambient conditions. This provides a standard with which to compare data obtained in more hostile conditions.
Chapter 5

The Effect of Water on the Interfacial Characteristics of the Adhesive System

5.1 Background Theory

5.1.1 Introduction

Water is one of the most aggressive environments an adhesive joint is likely to come into contact with. The development of adhesives with long term durability is probably still one of the greatest challenges faced by adhesive formulators. Electronics manufacturers in particular, like aerospace manufacturers, set high standards for durability, which all potential adhesives and encapsulants must meet prior to use in microelectronics devices and components. Several possible mechanisms have been suggested to explain the particularly detrimental effect that water has on joints. Again, as the adhesion theories proposed in Chapter 2 indicate, several of these mechanisms could be occurring concurrently, although it is likely, that at any one time, only one of the mechanisms will predominate.

The damaging effects of humid air on various adhesive systems were reported in 1964 by Falconer et al. Since then, numerous research groups have attempted to elucidate the precise mechanisms by which attack occurs, that they might be able to design systems capable of withstanding wet or humid conditions, (Kerr, MacDonald and Orman, 1967). Several comprehensive reviews of the experimental data obtained in durability studies have been published, (Kinloch, 1987; Minford, 1983). This section is therefore intended only as a brief synopsis of the proposed mechanisms.

The interfacial region of a joint has been identified as the area most vulnerable to attack by moisture. One suggestion for this openness to attack, is that this is often a region of lower polymer crosslink density, (Kerr, 1970). A frequent observation in
Chapter 5. The Effect of Water on Interfacial Characteristics

durability studies, is a move from visibly cohesive failure in dry conditions, to near interfacial failure in the presence of water, (Gettings, Baker and Kinloch, 1977). "Near" interfacial, because true interfacial failure is rare, and there is usually a layer of polymer of the order of nanometres remaining on the fracture surface, (Watts, 1990). There are four main reasons suggested for this instability in the presence of water: (i) a loss of interfacial bonding due to the thermodynamic displacement of the adhesive phase by water, (ii) corrosion of the substrate, which gives rise to cathodic disbondment, (iii) hydration of the oxide layer to which the adhesive is bonded, (iv) gross diffusion of water into the polymer to cause swelling and perhaps plasticisation.

Thermodynamic work of adhesion calculations are often used to consider the stability of an adhesive system in the presence of a third phase, generally water, (though equally, aviation fuel or any other solvent likely to come into contact with the adhesive, may be chosen). In dry conditions, most adhesive systems have a positive work of adhesion value, indicating stability. The introduction of a third phase can lead to a negative $W_A$ value being obtained. Although such calculations give no indication of the kinetics of disbondment, they do suggest whether there is a strong likelihood of failure occurring or not, (i.e. whether the reaction is thermodynamically possible).

Actual corrosion of the substrate, (i.e. where anodic dissolution occurs), has been reported for a number of different systems, (Venables, 1984). A more frequent event however, tends to be the loss of adhesion associated with the formation of cathodic sites, (i.e. cathodic disbondment). It has now become widely accepted, that in many cases, corrosion of the adherend occurs as a post, rather than as previously thought, a precursor to the failure event.

The degree of stability of the oxide layer plays an important role in durability studies. Much of the literature on durability is devoted to investigation of the oxides on metallic substrates, rather than bulk ceramic oxides, (Venables, 1984). In the case of aluminium, this is of particular importance in aerospace applications. There is some early evidence to suggest that hydration may lead to mechanical weakening of the oxide film, (Noland, 1975), though again, this may in fact be a post failure event. It is also less likely to occur in the case of bulk, ceramic-type oxides.
Also of interest, is the role played by other ions present in the oxide layer. A correlation between poor durability and high magnesium content in the oxide was observed in one study on aluminium-magnesium alloys, (Kinloch and Smart, 1981). In a later study by Poole and Watts (1985), however, no such correlation was apparent. Failures involving MgO are often caused by the brittle nature of the magnesium oxide layer. The difference in these results can be accounted for by the fact that in the Poole and Watts study, the substrate was grit blasted prior to the chromic acid anodising treatment, to remove the friable magnesium oxide layer present on the surface. Any further magnesium oxide produced during the CAA treatment, was therefore likely to have been strongly bound up in the oxide film. In the earlier study, (Kinloch and Smart, 1981), the alloy surface was not grit blasted prior to the CAA treatment. Hence, a friable layer of magnesium oxide resulted in poor durability of the joints. General applicability of this finding has yet to be proved, but it is a factor which requires consideration, as the alumina used during the course of this study does have magnesia added as a sintering aid. There is also a wealth of evidence in the literature to suggest that the magnesia preferentially segregates to the free surfaces during sintering, (Jorgensen, 1964; Sung et al., 1992). A degree of caution is necessary though; as yet, there is no evidence to suggest that the MgO in a bulk ceramic is especially friable in nature.

The final mechanism, that of polymer swelling, clearly warrants some attention. In the same way that unreasonably high shrinkages on cure can reduce the force necessary for debonding, (discussed in Chapter 2), it is not unreasonable to suggest that stresses arising from polymer swelling will produce a similar effect. A more detailed discussion of the movement of water in adhesive joints is included below.

It can therefore be concluded that failure in the presence of a third phase (i.e. water), is extremely complex and may be due to a combination of interrelated factors.

5.1.2 Ingress and Movement of Water in Adhesive Joints

Several mechanisms have been suggested to explain how the ingress of water occurs in adhesive joints. The four main routes via which water is likely to enter a
joint have been summarised in a review of "The Kinetics and Mechanisms of Environmental Attack", (Comyn, 1983). Water may enter a joint by: (i) diffusion through the adhesive, (ii) "wicking", in which the water is transported along the interface, (iii) by capillary action, through defects in the coating itself, (e.g. cracks, crazes, or reinforcements like nylon net) and finally, (iv) if the substrate itself is permeable, then this will allow water to reach the interface.

Adhesive systems vary considerably in both the rate and extent of water uptake. Variations in temperature and relative humidity (RH) also have significant effects on the durability of a system. Globally, both temperature and RH values vary considerably, (e.g. rainy, tropical climates such as South America, versus humid continental climates of the type found in southern Europe), and this needs to be taken into account, if an adhesive is intended for worldwide application.

In the past, considerable effort has been directed at monitoring the rate of water uptake for various adhesive systems, in different environments, (Brewis, Comyn et al., 1980). If water diffuses into a joint, then it is possible to model the process using Fick's laws of diffusion and to obtain values for the diffusion coefficient of water in the adhesive. The relevant equations are detailed in "The Mathematics of Diffusion", (Crank, 1975). The calculation of diffusion coefficients for a variety of joint geometries is indicated. Fickian diffusion is characterised by linear uptake of water and is typical of polymers above the glass transition temperature, $T_g$. Not all polymers display Fickian behaviour, (Fujita, 1961), glassy polymers tend to show non-Fickian water uptake, with non-linear water uptake curves. The water uptake versus time plots for certain polymers are observed to "plateau off" after a certain length of time, corresponding to the adhesive reaching equilibrium uptake. Not all adhesives however, reach equilibrium, even after prolonged periods of time. Other systems show a second uptake stage after the plateau region, (Althof, 1979) and the second stage will not necessarily have the same rate of water uptake as the initial stage. Following durability experiments, it is useful to carry out elemental analysis of the water. In some instances, leaching of components in the formulation can make it appear as if no water uptake is occurring, (i.e. if the amount of material leached out exceeds the
quantity of water taken up by the adhesive). This may be ascertained by the careful use of gravimetric methods.

5.1.3 Mechanisms of Environmental Attack

So far, the possible routes via which water ingress occurs have been discussed. The next stage is to consider the effects of the presence of water on the integrity of the joint. The ability for an adhesive system to withstand prolonged exposure to a wet environment, without significant deterioration in mechanical properties, is sometimes referred to as "wet adhesion". The diffusion of water molecules into an adhesive interrupts the hydrogen bonding between the polymer chains, (Kinloch, 1987), which can lead to plasticisation of the polymer, (Brewis, Comyn et al, 1980). During the manufacture of flexible polymer products such as food-wraps, small molecules are deliberately introduced. The large free volume associated with these molecules, generally referred to as plasticisers, prevents close alignment of the longer polymer chains, resulting in a much more pliable end-product, (Young, 1981). Diffusion of water molecules may produce a similar effect, unintentionally. Fortunately, not all of the effects of water uptake are irreversible. A frequent observation in durability studies is that if a joint is dried out again, then a significant proportion of the strength is recoverable, (Watts et al., 1990). Polymer swelling can introduce additional stresses in to the joint, but again this effect is often recoverable.

More serious, are the irreversible effects which result in permanent damage to the joint. Hydrolysis of either the adhesive or adherend may occur owing to the hydrophillic nature of the adhesive and/or the substrate. Cracking and crazing of the adhesive may also result. Under certain conditions however, joints can be subjected to hostile environments for prolonged periods, without suffering any adverse effects, (Comyn et al., 1980). This result, coupled with similar observations by other workers in the field, have led Kinloch et al., (1980) to propose that "there must be a critical water concentration in the adhesive layer, below which environmental weakening does not occur". The region where this critical water concentration is exceeded can then be treated as a crack of length $a$ within the joint. When a fracture mechanics approach
was then applied to the model, Kinloch et al. calculated that the critical water concentration below which no deterioration in joint strength was observed lay at 1.35 %, (see Figure 5.1). Although this idea is not universally accepted, it has been applied successfully to a number of systems.

![Figure 5.1 Schematic of water acting as a crack of length a.](image)

The concept of the thermodynamic work of adhesion for a system has been outlined in Chapter 2. Work of adhesion calculations are often carried out to investigate whether the joining of two materials is energetically favourable. Surface free energy values (in mJ m\(^{-2}\)) have been determined for many of the most widespread adhesives and substrates used. The values of the materials relevant to this particular study are included in Table 5.1.
Chapter 5. The Effect of Water on Interfacial Characteristics

Table 5.1 Surface free energies of adherend, adhesive and water.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma^D$/ mJ m$^{-2}$</th>
<th>$\gamma^P$/ mJ m$^{-2}$</th>
<th>$\gamma$/ mJ m$^{-2}$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>100</td>
<td>538</td>
<td>638</td>
<td>Schonhorn, 1967</td>
</tr>
<tr>
<td>PMMA*</td>
<td>35.9</td>
<td>4.3</td>
<td>40.2</td>
<td>Owens, 1969</td>
</tr>
<tr>
<td>Water</td>
<td>22.0</td>
<td>50.2</td>
<td>72.2</td>
<td>Fowkes, 1967</td>
</tr>
</tbody>
</table>

* Surface free energy values for PMMA have been selected, because results from the IGC studies in Chapter 3 indicated that the dispersive component of the surface free energy of LCR000 lay very close to the value for PMMA.

The work of adhesion for LCR000 on alumina may be calculated as follows, using the values in Table 5.1:

\[
W_A = \gamma_{\text{LCR}} + \gamma_{\text{Al}_2\text{O}_3} - \gamma_{\text{LCR}/\text{Al}_2\text{O}_3}
\]

\[
W_A = 2 \left[ (\gamma_{\text{LCR}}^D \cdot \gamma_{\text{Al}_2\text{O}_3}^D)^{1/2} + (\gamma_{\text{LCR}}^P \cdot \gamma_{\text{Al}_2\text{O}_3}^P)^{1/2} \right]
\]

\[
W_A = 216 \text{ mJ m}^{-2}
\]

Thermodynamic work of adhesion calculations can be taken a step further to include the presence of a third phase, as indicated in Chapter 2. For the photocured resin/alumina substrate system in the presence of water:

\[
W_{\text{AL}} = \gamma_{\text{LCR}/\text{H}_2\text{O}} + \gamma_{\text{Al}_2\text{O}_3/\text{H}_2\text{O}} - \gamma_{\text{LCR}/\text{Al}_2\text{O}_3}
\]

\[
W_{\text{AL}} = 2 \left[ (\gamma_{\text{LCR}}^D \cdot \gamma_{\text{H}_2\text{O}}^D)^{1/2} - (\gamma_{\text{LCR}}^D \cdot \gamma_{\text{H}_2\text{O}}^P)^{1/2} - (\gamma_{\text{Al}_2\text{O}_3}^D \cdot \gamma_{\text{H}_2\text{O}}^D)^{1/2} - (\gamma_{\text{Al}_2\text{O}_3}^P \cdot \gamma_{\text{H}_2\text{O}}^P)^{1/2} \right] + (\gamma_{\text{LCR}}^P \cdot \gamma_{\text{Al}_2\text{O}_3}^D)^{1/2} - (\gamma_{\text{LCR}}^P \cdot \gamma_{\text{Al}_2\text{O}_3}^P)^{1/2}
\]

\[
W_{\text{AL}} = -102 \text{ mJ m}^{-2}
\]
Chapter 5. The Effect of Water on Interfacial Characteristics

The negative value of $W_{AL}$ suggests that the joint will be unstable in the presence of water, but the calculation gives no indication of the kinetics of the process, (i.e. how long it will take before the joint becomes unstable). This is determined by the rate of aggregation of water molecules at the interface and the speed at which interfacial or, near-interfacial bonds are broken. Work of adhesion calculations of this type indicate thermodynamically what is likely to occur if the system is left undisturbed. In the case of this particular project and most other adhesion studies, this is not the case. In general, an external load is applied to joints after immersion in water for varying lengths of time. The results from such studies will therefore give no indication of what might have occurred spontaneously, (i.e. without the application of an external load). This may account for the fact that the work of adhesion calculations often predict interfacial separation, while experimental evidence suggests that true interfacial failure is extremely rare. In addition to this, the work of adhesion calculations do not take the kinetics of the process into account. It is therefore possible, that the rate of water movement into the polymer, close to the interface, occurs faster than displacement of the coating itself.

5.2 XPS Analysis

5.2.1 Experimental Procedure

A series of butt-joints was also prepared for the durability studies, (i.e. photocured resin sandwiched between two alumina discs). The difficulty in finding an adhesive capable of bonding the ceramic discs to the stubs for the duration of the water immersion, made it necessary to attach them just prior to fracture within the spectrometer. Joints were immersed in Milli-Q water, (de-ionised, then filtered to remove both organic and inorganic contaminants), at 50 °C, for varying lengths of time, (between 0-5 weeks), and fractured in the ESCALAB MkII sample preparation chamber. In order to study the effect, (if any), of the surface segregated silica on the durability of the system, additional substrates were also included in the study. These
Chapter 5. The Effect of Water on Interfacial Characteristics

were single crystal silicon wafers with a layer of native oxide and quartz discs. Two additional series of butt-joints were also fabricated using the extra substrate materials. Analysis was carried out using MgKα radiation, with pass energies of 50 eV for survey spectra and 20 eV for high resolution spectra.

5.2.2 XPS Results

ESCALAB MkII Data

XPS results from the side of an as-received alumina joint which had no visible polymer remaining on it (see Figure 5.2(a)), revealed a symmetrical C1s peak, of the type indicative of adventitious hydrocarbon contamination. None of the functional groups associated with the polymer could be resolved. This result was surprising because, as mentioned earlier, true interfacial failures are a very rare occurrence. The shape of the peak was broad, yet fairly symmetrical, as might be expected from hydrocarbon contamination. None of the characteristic oxygen containing functional groups from the polymer were apparent on the ceramic side of the failure, tending to support the idea of failure occurring interfacially, or within a pre-existent adventitious layer of hydrocarbon contamination. Due to the susceptibility of the alumina to differential charging, it was at this stage unclear whether the carbon detected on the ceramic side of the failure was hydrocarbon contamination, or whether vertical differential charging, (VDC), was in fact obscuring the true shape of the C1s peak, (Yu and Hantsche, 1993). It is unclear precisely why alumina should display such peculiar charging phenomena, although it does have a very high resistivity value, (greater than $10^{12} \, \Omega \, m^{-1}$). It has also been suggested that insulators comprised of discrete grains like alumina are liable to charge both non-uniformly and more severely than a continuous insulating phase, such as quartz, (Le Gressus, 1993). Non-uniform charging will obviously be more difficult to eliminate than uniform charging.
Chapter 5. The Effect of Water on Interfacial Characteristics

Figure 5.2 Comparison of the C1s spectra obtained from a polished alumina joint using (a) ESCALAB MkII and (b) Scienta ESCA300 spectrometers.
Chapter 5. The Effect of Water on Interfacial Characteristics

The survey spectra in Figure 5.3(a) and (b) were recorded from either side of an alumina joint immersed in water at 50°C for two weeks and fractured in-situ. Figure 5.3(c) and (d) depicts the spectra obtained from the fracture surfaces of a silicon joint previously immersed in water at 50°C and fractured. A strong nitrogen signal was apparent which was somewhat surprising, as the polymer contains only a fraction of a percent of nitrogen containing groups. The signal is therefore too strong to be solely attributed to the polymer itself. This feature is returned to in the section on water analysis.

Scienta ESCA300 Data

The two fracture surfaces of an alumina sample were also analysed using the Scienta ESCA300 spectrometer, (conditions; 1.1 mm slit width, hv source 2-8 kW, 200 mA at 14 kV). With the flood gun settings optimised, it became clear from the shape of the C1s peak, that immersion in water brought about cohesive failure in the polished alumina joints, not interfacial failure as the data from the ESCALAB suggested. A comparison of the C1s spectra obtained from the two failure surfaces using ESCALAB and ESCA300 spectrometers is shown overleaf (Figure 5.2). It should be pointed out that optimisation of the electron flood gun settings was not a trivial exercise. The problems associated with analysing polycrystalline insulating samples having previously been emphasised. A VSW EG2 flood gun was used, with settings of 7 eV, 2.3 mA and a focus potential of about 17 V.

Another observation from the Scienta ESCA300 spectrum was the absence of any aromatic character (as deduced from the $\pi \rightarrow \pi^*$ satellite) in the polymer overlayer on the ceramic side of the failure. This will be discussed in the next chapter, as it was an effect also observed when other ceramic substrates were investigated.
Figure 5.3 Survey spectra obtained from (a) the alumina side (b) the polymer side of an alumina joint, (c) the silicon side and (d) the polymer side of a silicon joint.
Chapter 5. The Effect of Water on Interfacial Characteristics

5.3 Water Analysis

XPS results obtained from the failure surfaces of joints involved in durability studies, revealed the presence of unexpectedly high nitrogen levels. Unexpectedly high, because LCR000 resin has only a fraction of a percent of nitrogen containing groups in the formulation, and the as-received alumina less than one percent. Similar results have been observed in other long term durability experiments, but there, the high nitrogen levels were attributed to nitrogen in the air which was dissolved in the water, as the water was not de-aerated, (Watts, 1990). High resolution N1s spectra were recorded using the Scienta ESCA300 spectrometer, in order to investigate this observation, see Figure 5.4.

The water source used in durability studies is obviously important, as the presence of any water impurities directly affects the XPS results recorded from samples following prolonged water immersion. Tap water should not be used, as it contains a variety of organic and inorganic contaminants. In addition, chloride ions are added as part of the water purification process, which therefore precludes its use in the study of many materials, especially those which corrode. De-ionised water should be monitored, as contamination from the ion exchange beads sometimes occurs. Ideally, a constant supply of distilled water should be available, as distillation produces the most pure source of water. Distilled water was unavailable during this study, so Milli-Q water was used instead. The water is de-ionised and passed through a series of different filters to remove the various organic and inorganic contaminants. Water purity is checked with the aid of a conductivity meter fitted to the filtration system and when the conductivity rises above a specified level, the filters are changed.

One of the suspected problems with Milli-Q water was that any bacteria already present in the water could increase in numbers, particularly in long term durability experiments. Milli-Q water which was left in a sealed container for several weeks, smelt stagnant when opened. To find an explanation for this, samples of fresh Milli-Q water and water which had contained the adhesive joints were sent to the Analytical and Physical Sciences Group at ICI Chemicals & Polymers Ltd., The Heath, Runcorn, for elemental analysis. The results of analysis are presented in Table 5.2.
Figure 5.4 High resolution N1s spectrum obtained from an alumina joint involved in durability studies.

Table 5.2 Results of water analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH$_3$ mg cm$^{-3}$</th>
<th>NO$_2$ mg cm$^{-3}$</th>
<th>NO$_3$ mg cm$^{-3}$</th>
<th>Total Organic Carbon mg cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milli-Q</td>
<td>&lt; 0.02</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Water used for durability tests</td>
<td>0.56</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Chapter 5. The Effect of Water on Interfacial Characteristics

There were two significant differences between the fresh water and the water used for durability tests. Firstly, the specimen soaked water contained significantly higher quantities of NH₃, which, as previously indicated, could not have come from the polymer itself. There was also a much higher total organic content in the specimen soaked water. It is possible that leaching of the polymer could account for part of this increase, but it could equally well be related to the increase in NH₃ levels. In order to avoid the added complication of microbial contamination, it is suggested that for future studies, any Milli-Q water intended for long term durability work should first be exposed to intense UV light, to destroy any bacteria already present in the water.

5.4 Mechanical Testing

5.4.1 Butt-joints

In addition to the series of butt-joints fabricated for in-situ fracture, a second series of butt-joints was also fabricated for mechanical testing. The LCR000 resin was sandwiched between as-received Coors AD96 alumina discs and the samples immersed in water at 50°C for varying lengths of time, (0-2 weeks). On removal from water, sample stubs (generally used for mounting samples for XPS analysis) were attached to either side of the ceramic/photocured polymer sandwich, using standard Araldite™. Samples were then located in specially designed grips (see Figure 5.5) and the load to failure recorded using a J.J. Lloyd tensile tensometer, (1 kN load cell, crosshead speed of 1mm minute⁻¹). The grips consisted of replicas of the butt-joints, to locate the joints in position in the tensometer. The failure stress of the joints could not be recorded, as, the adherends were themselves secured to the stubs using a separate adhesive, (Araldite™) which also deformed during mechanical testing. Figure 5.6(a) is a typical load extension curve for a butt-joint. Figure 5.6(b) is a graph of load to failure versus immersion time in water for the series of alumina joints.
Figure 5.5 Specially designed grips to locate butt-joints in a J.J. Lloyd tensile tensometer.
Chapter 5. The Effect of Water on Interfacial Characteristics

Figure 5.6 (a) Typical load extension curve for an alumina butt-joint and (b) load to failure versus immersion time in water for a series of alumina butt-joints.

(b) = average of data sets
5.4.2 Boeing Wedge Tests

Although it was important to carry out mechanical tests using simple butt-joints in order to obtain a direct correlation with the in-situ fracture experiments, this was not an ideal specimen geometry to work with. To measure the mechanical properties of the system quantitatively, separate tests were necessary. At the beginning of this study, a separate project was being undertaken by an MSc student, in the Department of Mechanical Engineering at Imperial College, to look specifically at the most appropriate mechanical test methods for this system. Finding a suitable test for this system had proved difficult, due to the brittle nature of the adherend, compounded by fact that the adhesive had very little compliance. This study has now been completed, (Priour, 1992), and the most suitable tests appeared to be based on double cantilever beam (DCB) type geometries.

DCB tests allow a value of the fracture energy to be calculated. An adaption of the DCB test is the Boeing wedge test, used to monitor the decrease in fracture energy as a function of exposure time to particular environmental conditions. It is a test frequently used by, the aerospace industry, as it is a relatively simple test to carry out, hence large numbers of specimens can be analysed. The test involves driving a wedge, in a controlled manner, into the joint and monitoring the crack growth as a function of time under specified conditions of temperature and relative humidity, (RH). This method is completely unsuitable for alumina adherends, as the brittle substrate fails catastrophically as the wedge is driven into the joint. A modification of the Boeing wedge test was therefore chosen. Rather than driving a wedge into the joint to initiate the crack, an opposing screw thread was used to open up a crack, (see Figure 5.7).

Wedge test specimens were produced from alumina adherends, 1 mm thick, width 20 mm and 100 mm long. The LCR000 resin was spread over the adherend surface with a spatula and the adherends were clamped together securely with the aid of bulldog clips until the joints had been fully cured. Samples were placed in a sealed polyethylene container in an oven at 50°C. A relative humidity of 95 % was achieved by making up a saturated solution of potassium sulphate in the sealed containers.
Samples rested on glass racks to prevent them coming into direct contact with the solution. Approximately every 24 hours, the specimens were removed from the oven and the crack lengths monitored with a travelling microscope.

Figure 5.7 Photograph of a Boeing wedge test sample, with an opposing screw thread to replace the wedge.

Figure 5.8 indicates the crack growth for each of the three specimens with time. The crack growth data are readily converted to fracture energies, by treating the specimen as a DCB-type geometry, (Watts and Dempster, 1992). Figure 5.9 is a graph of fracture energy versus exposure time for the alumina samples.
Figure 5.8 Durability data: crack growth as a function of time.

Figure 5.9 Fracture energy as a function of time for alumina wedge test samples.
The fracture energy \( G \), at each stage was determined using the following equation:

\[
G = \frac{E d^2 h^3}{16} \times \frac{3 (a + 0.6 h)^2 + h^2}{[(a + 0.6 h^3) + a h^2 ]^2}
\]

... Eq. 5.1

where,

\( E \) = Young's modulus of the adherend, (193 GPa)
\( d \) = displacement of the adherends at the load line
\( h \) = the adherend thickness, (1 mm)
\( a \) = the crack length measured from the load line

5.5 Monochromated XPS

5.5.1 Introduction

Results from environmental studies carried out on LCR000/as-received alumina butt-joints, indicated that, due to the nature of the electrostatic charging of the alumina samples, it was not possible to identify the true locus of failure using conventional XPS. The Cls spectra recorded from the ceramic sides of the failures, were broad and featureless, with no evidence of the functional groups characteristic of the resin. Using monochromated XPS, with an electron flood gun to neutralise surface charge, charging problems were minimised and it became apparent that there was in fact some polymer residue remaining on the failure surfaces.

As a consequence of these findings, the possibility of upgrading the existing monochromator on the VG Scientific ESCALAB MkII was investigated. The upgrade consisted of having a Surface Science Instruments, (SSI), microfocus style X-ray source fitted in to the standard VG Scientific 0.5 m monochromator. The microfocus source produces a spot size of about 800 \( \mu \)m and has been specified to achieve 100,000 counts, with a resolution of 0.65 eV on silver. It is also possible to carry out analysis of smaller areas, (400 and 150 \( \mu \)m), with a reduction in the intensity of the signal.
5.5.2 Experimental Detail

The failure surfaces of a LCR000/as-received alumina Boeing wedge test specimen were investigated using monochromated XPS. Samples approximately 1 cm by 2 cm were cut from the adherends using a diamond scribe. The samples were then mounted on standard stubs with double-sided adhesive tape. A survey spectrum was recorded at a pass energy of 100 eV, (0.2 eV step size and 400 ms dwell time per channel). High resolution Cls and O1s spectra were also recorded at pass energies of 50 eV. The electron flood gun was set at 0.25 mA and 10 eV.

5.5.3 Results

Figure 5.10 contains the survey spectrum recorded from the alumina side of the failure.

Figure 5.10 Monochromated XPS spectrum recorded from the alumina side of a LCR000/alumina Boeing wedge test sample, Cls region inset.
There are several differences between the spectrum depicted in Figure 5.10 and spectra previously recorded from butt-joints, notably:

(i) the removal of unwanted satellite peaks
(ii) the presence of a strong potassium signal and sulphur peaks
(iii) a low carbon signal, with a symmetrical peak, (characteristic of hydrocarbon contamination)
(iv) the absence of a nitrogen signal

5.5.4 Discussion

The presence of potassium and sulphur peaks in the spectrum are likely to be as a consequence of the sample history. In order to achieve a RH of 95%, Boeing wedge test specimens were suspended over a saturated solution of potassium sulphate. Both the potassium and sulphur signals are therefore likely to be a result of contamination from environmental testing. The absence of a nitrogen signal is interesting, as it was observed in all previous spectra recorded from samples which had been immersed in water. This sample had previously been suspended on a glass rack in a sealed polyethylene container, at 95% humidity, rather than totally immersed in water.

The symmetry and low intensity of the C1s peak suggest that failure occurred interfacially, within a layer of pre-existent hydrocarbon contamination. This was not unexpected, as the very geometry of the test tends to focus the crack towards the interface.

5.6 SEM Results

Scanning electron photomicrographs have also been obtained from both halves of butt-joints exposed to water at 50°C for between 0-14 days prior to fracture. Three different modes of failure were observed, which depended upon the period of immersion in water. Figure 5.11 illustrates the three fracture surface morphologies
schematically. Dry failures were recognised by the characteristic conchoidal fracture surface morphology, described in detail in Chapter 4. Joints immersed in water for less than two weeks, displayed a mixed mode of failure, with patches of polymer remaining on both sides of the joint.

![Diagram of Mirror Zone, Alumina, Polymer with Tear Lines](image)

**Figure 5.11** Effect of water immersion on the morphology of the failure surface, (a) conchoidal, (b) mixed and (c) near-interfacial.

The photomicrographs in Figure 5.12 depict the morphology of the surfaces of a joint which failed after two weeks immersed in water. The detailed morphology of type (b) failures resembled that of type (c) samples, (i.e. the impression of the alumina grains was also clearly visible in the polymer side of the failure). Failure occurred close to the interface. In spite of this fact, the joint still had sufficient residual joint strength for it to require the application of an external force to break it, the joint did not simply fall apart on removal from water. The polymer now appears almost as a mirror image of the alumina substrate. Plasticisation of the polymer itself was not suspected. A sample of LCR000 cleaved from an alumina substrate with the aid of a crack initiator, (a strip of Melinex™ film placed at the interface between the resin
and substrate), revealed a similar fracture surface morphology to that of the joint exposed to water, indicating that the impression of the alumina grains in the polymer side of the failure was not as a result of plasticisation.

![Figure 5.12 Photomicrographs showing the morphology of the failure surfaces on prolonged exposure to water.](image)

### 5.7 IR Spectroscopy

#### 5.7.1 Background

IR spectroscopy was employed to answer two specific questions, which could not be resolved using XPS.

(i) During the course of this study, butt-joints were fabricated with the photocured polymer sandwiched between two translucent alumina adherends. The possibility therefore existed for the crosslink density of the polymer in the joint to be lower than the value obtained from a sample of polymer cured between two pieces of Melinex™ film. Alumina is translucent rather than optically transparent and its surface is also quite rough, which could have resulted in a reduction in the light intensity necessary to produce full cure.

(ii) The importance of understanding how the uptake and subsequent movement
Chapter 5. The Effect of Water on Interfacial Characteristics

of water occurs in a joint, has previously been discussed. IR spectroscopy was used to monitor water uptake in a sample of LCR000 sandwiched between two microscope slides, in order to ascertain the timescale over which water ingress occurred.

All of the IR spectroscopy work was carried out in collaboration with ICI Chemicals & Polymers Ltd., at The Heath, Runcorn, as there was not ready access to IRS equipment at the University of Surrey.

5.5.2 Experimental Details

The butt-joints which underwent tests to measure their crosslink density were prepared in the usual manner and immersed in water at 50°C for two weeks. They were kept in water until reaching the ICI Chemicals & Polymers Laboratories at Runcorn. The fracture stage was also taken, so that the joints could be fractured in air just prior to analysis using a Nicolet 20SX fitted with an optical microscope.

Samples for monitoring water uptake were prepared by curing the LCR000 between two microscope slides and immersing the sample in water at 55°C. The sample was removed at intervals and water uptake measured by a Technicon Infra-Alyzer 500.

5.5.3 Results

Absorbance spectra were recorded from the polymer sides of failures and a linear background was subtracted across the region of interest, (1650 - 1550 cm⁻¹). The degree of cure can be correlated to the ratio of the absorbance readings at 1636 cm⁻¹ and 1605 cm⁻¹. The lower the ratio, the greater the degree of cure. Table 5.3 lists the absorbance ratios obtained from the various samples.

Table 5.3 Absorbance ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio of 1636 / 1605</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully-cured LCR000 sample</td>
<td>0.5</td>
</tr>
<tr>
<td>Polymer side of an alumina joint</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Figure 5.13 IR absorbance spectra obtained from (a) LCR000 and (b) the polymer side of a failed butt-joint.
Chapter 5. The Effect of Water on Interfacial Characteristics

The values in Table 5.3 indicate that the resin sandwiched between the butt-joints is fully-cured. The crosslink density in some instances may be even higher than the sample of LCR000 cured between Melinex™ film.

Figure 5.13 shows a typical absorbance spectrum obtained from (a) LCR000 and (b) the polymer side of a failed butt-joint. The measurement of the relevant peak heights is indicated in the diagram.

Figure 5.14 is a graph of water uptake, (determined from the peak height of the water peak, at 3400 cm⁻¹), versus immersion time in water at 55°C. There is a definite change, (an increase), in the rate of water uptake occurring at 13-14 days, (see page 135). This is interesting, as near-interfacial failure was only observed after a similar timescale.

Figure 5.14 Water uptake, (from peak height) versus immersion time in water at 55°C.
Chapter 5. The Effect of Water on Interfacial Characteristics

5.8 Discussion

Characterisation of samples used during environmental testing revealed some interesting results. There were visible differences, i.e. the change in failure mode from conchoidal under dry conditions, to mixed mode and eventually near-interfacial failure, (following prolonged water immersion). The change from mixed to near interfacial failure following 2 weeks water immersion was significant, as IR results indicated a much faster rate of water uptake after an initial 14 days. XPS spectra recorded from the failure surfaces of butt-joints, (after 2 weeks in water), indicated the presence of functional groups which were attributed to the polymer. Due to the nature of the electrostatic charging of the alumina samples, this result was only apparent using monochromated XPS. There was also a subtle difference between the overlayer of polymer remaining on the ceramic side of the failure and the opposite half of the joint, where polymer was visible to the naked eye. The spectrum recorded from the polymer side of the joint was indistinguishable from the spectrum of the bulk resin, however, on the opposite side of the failure, there was an absence of any aromatic character, (indicated by the lack of the $\pi \rightarrow \pi^*$ shake-up satellite). This result was surprising, as the molecules which make up approximately 90% of the formulation are highly aromatic.

Another interesting feature of the XPS results from samples used in environmental tests, was the presence of a strong nitrogen signal. This was unexpected, as neither the adhesive or substrate contain nitrogen in such quantities. Tests to determine the source of the nitrogen suggested that it may have been as a result of microbial contamination.

In order to assess the mechanical performance of the LCR000/alumina system, an existing mechanical test (the Boeing wedge test), was modified to take in to account the brittle nature of the adherend. This test proved very useful, as it was relatively easy to fabricate samples and it also allowed several samples to be tested concurrently. Monochromated XPS results of the failure surfaces of wedge test specimens indicated that failure occurred within a layer of pre-existent hydrocarbon contamination. The difference in loci of failure between butt-joints and wedge tests can be explained by the

161
fact that the geometry of the wedge test tends to focus the crack towards the interface.

5.9 Summary

From this section of the study, it can be concluded that immersion in water alters the mode of failure for this system, summarised in Figure 5.11. Dry joints fail with a characteristic conchoidal fracture surface morphology, with failure initiated at some form of defect. Joints immersed in water for short lengths of time (up to 2 weeks) displayed a mixed mode of failure, with patches of adhesive observed on both fracture surfaces. Finally, water immersion for greater than 14 days moved the locus of failure very close to the interface. This timescale is significant as IRS results indicate that water uptake occurs much faster after this initial 14 day period.

Work of adhesion calculations suggested failure would occur interfacially, (i.e. large negative $W_A$ values). XPS analysis of the failure surfaces revealed that although failure occurred close to the interface, it could not be classed as a true interfacial failure, due to the presence of a thin overlayer of polymer remaining on the surface of the adherend. This apparent contradiction between the thermodynamic calculations and the experimental data, is explained by the fact that $W_A$ calculations fail to take the kinetics of the various processes in to account. It is therefore possible, that the rate at which water movement in the polymer region close to the interface occurred, simply exceeded the rate of displacement of the coating.

Unfortunately, the surface roughness of the adherend made it impossible for us to make an accurate calculation, (using an XPS, Beer-Lambert approach), of the thickness of the polymer overlayer remaining on the inorganic substrate. It was also unclear whether the overlayer was continuous, or patchy.

A failure model for the wet system has not been included at this stage, as it was first necessary to obtain more detailed information about the chemistry of the interphase region. This involved incorporating additional, highly polished substrates in to the study, to provide specimens suitable for angle resolved XPS (ARXPS), in order to obtain more detailed information about the region close to the interface.
6.1 Introduction

Part of the aim of this work was to feed back any information gained about the interphase chemistry to the manufacturers, who would in turn use that knowledge to help formulate new or more durable products. Obtaining information from the interphase region was severely hampered by the complicated nature of the adherend, in terms of both its surface roughness and chemical heterogeneity.

Durability studies had previously indicated that failure was occurring close to the interface. A signal from the substrate was detected by XPS, indicating that failure occurred either cohesively, with less than 5 nm of polymer remaining on the failure surface, or that a discontinuous (patchy) overlayer remained. Clearly, more detail was required about this overlayer of polymer. Angle-resolved XPS studies had proved particularly useful in the past at obtaining information from interfacial regions, (Watts, et al., 1986). However, a pre-requisite of ARXPS is a smooth, flat surface to work on, making the as-received alumina completely unsuitable. It was therefore necessary to include some additional substrate materials in the study. Alumina discs were polished to a 1 micron finish, which in addition to producing a smooth surface, also removed surface segregated silica, (calcia, magnesia and other impurities). Quartz and single crystal silicon with its layer of native oxide, (of thickness about 3 nm), were also included. Thus, the three types of specimen provided an opportunity to study the different chemical effects present on the as-received alumina surface, with the increased depth resolution offered by ARXPS. Durability experiments on simple butt-joints were repeated with these materials, and results used to help correlate data from the as-received alumina.
6.2 Additional Substrate Materials

Quartz was obtained in the form of discs, 10 mm in diameter and 1.5 mm thick. Single crystal (100), silicon wafers were sectioned into squares approximately 10 mm by 10 mm using a diamond scribe. The Coors AD96 alumina was the standard material described in Chapter 4. The as-received quartz and silicon samples had a mirror finish to them and required no further surface preparation for angular resolved XPS. However, the variation in topography of the alumina samples made polishing essential. The alumina discs were polished to a 1 μm finish and cleaned ultrasonically in isopropanol before being heated overnight in an oven at 120°C to remove any remaining polishing residue.

6.3 Angle-resolved XPS

6.3.1 Experimental Detail

Joints were fractured in the UHV preparation chamber of the ESCALAB MkII, using the modified VG Scientific T-peel stage. Similar samples were also analysed with the Scienta ESCA300, but were fractured in air just prior to analysis rather than in-situ.

XPS spectra were obtained using AlKα and MgKα radiation at a power of 340 W, the analyser was operated in the CAE mode with pass energies of 50 eV for survey spectra and 20 eV for high resolution spectra. Analyses of both halves of the joint were carried out at a series of take-off angles, (TOAs), (15, 25, 35, 45, 60, 75 and 90°), relative to the sample surface. The transfer lens iris assembly was set at a reduced value to provide an analyser/transfer lens acceptance angle of 6°, (plus or minus 3°), which allows adequate counting statistics within a reasonable time scale. A survey spectrum was recorded initially at 45° TOA and repeated after analysis at the seven angles was complete, to check for sample degradation. High resolution spectra for the Cls, O1s and either Si2p or Al2p regions (depending on the substrates), were recorded at each angle. In order to minimise the effects of thermal damage from the heat
generated by the X-ray gun in spectra acquired using the VG Scientific ESCALAB MkII, the gun was partially withdrawn, to give a gun to sample distance of approximately 2.5 cm. No sample degradation was observed during this procedure, a typical analysis time was around 60-70 minutes, for a complete set of ARXPS data. Degradation was assessed by monitoring the carbon to oxygen ratio at a TOA of 45°, at both the start and after the final analysis had been recorded. The C1s spectra were peak fitted using the procedure outlined in Chapter 3.

![Degradation Expt.](image)

**Figure 6.1** Montage of C1s peaks obtained during the extended degradation study.

Analyses of the fracture surfaces of polished alumina joints and related quartz and silicon samples, following two weeks aqueous exposure, were also carried out using the ESCA300 X-ray photoelectron spectrometer. The Scienta ESCA300 allowed a good signal to noise ratio to be obtained in the short time available before sample degradation took place. It had been noted during previous studies, that alumina
samples appeared to be particularly susceptible to charging during analysis. By utilising the ESCA300’s monochromated X-ray source (to provide superior spectral resolution), coupled with an electron flood gun for charge neutralisation, additional valuable information was obtained. An extended degradation study was also carried out on a quartz sample from a fractured test specimen, with ten spectra being acquired over a period of about 5 hours in order to determine the timescale over which degradation of the sample occurred for these particular analysis conditions (i.e. monochromated source, slit width of 0.5 mm, 200 mA and 14 kV), see Figure 6.1. As with the ESCALAB data, all spectra were recorded within a time window where no degradation was observed.

6.3.2 ARXPS Results

ARXPS spectra are presented from the Scienta ESCA300, as the counting statistics from this data are much better. Figure 6.2 shows the ARXPS C1s spectra obtained from the silicon side of a failed specimen that had undergone aqueous exposure for three weeks. The enhancement of the methoxy component at high take-off angles is readily apparent, indicating that these species tend to be adjacent to the inorganic surface. A consistent feature of these (and data sets from other substrates) was the lack of an aromatic component of the C1s peak, although this feature was still clearly visible on the polymer side of the failure, as shown in Figure 6.3. Analysis of the polished alumina at varying take-off angles using the Scienta ESCA300 also indicated that oxygen groups (in particular the methoxy groups), were oriented towards the ceramic interface, though the effect did not appear to be as pronounced as with quartz and silicon samples. Data obtained from quartz and silicon samples on the ESCA300 were consistent with the ESCALAB data, but again, spectra from alumina samples recorded on the ESCALAB did not reveal the characteristic functional groups of the resin. This result tends to suggest that the alumina samples are more prone to vertical differential charging, VDC, (Yu and Hantsche, 1993), than others, possibly due to differences in their electrical properties. This once again highlights the difficulties associated with working with polycrystalline insulating materials.
Figure 6.2 Montage of Cls peaks obtained from the fracture surface of a silicon joint at varying take-off angles, Scienta ESCA300 spectrometer.

Figure 6.3 Carbon 1s spectra obtained from the surfaces of an alumina joint, (a) alumina side and (b) polymer side.
6.4 Compositional Depth Profiling

6.4.1 Theory

The montage of Cls peaks depicted in Figure 6.2, although useful as a means of illustrating preferred orientation, does not correspond to a series of unique slices within the sample. A series of algorithms have therefore been developed which can convert the quantitative analyses obtained at varying angles into a compositional depth profile.

The depth profiles obtained from ARXPS data were reconstructed using the #ANGULAR routine, outlined in Chapter 3.

6.4.2 Results From Test to Validate Lateral Homogeneity

The use of packages such as #ANGULAR implicitly assumes lateral homogeneity of the substrate. As a test of such uniformity, graphs of \( \ln I_{\text{substrate}} \) versus \( 1/\sin \theta \) were constructed for the three substrate groups, a straight line indicating the uniformity of the organic overlayer, as indicated in Chapter 3. The test of uniformity is developed from the equation:

\[
I_d = I_o \exp \left( - \frac{d}{\lambda \sin \theta} \right) \quad \text{... Eq. 6.1}
\]

where, \( I_d \) is the intensity of the substrate signal with an overlayer present, \( I_o \) is the intensity from a clean substrate, \( d \) is the thickness of the overlayer, \( \lambda \) the inelastic mean free path and \( \theta \), the take-off angle. Taking logs of both sides gives:

\[
\ln I_d = \ln I_o - \frac{d}{\lambda \sin \theta} \quad \text{... Eq. 6.2}
\]

if a graph of \( \ln I_d \) versus \( 1/\sin \theta \) is then plotted, \(-d/\lambda\) is the gradient and \( \ln I_o \) is the intercept with the y axis. Such a plot is shown in Figure 6.4 for the alumina substrate and the good match achieved (least squares regression fit, R of 0.999) indicates the uniformity of the overlayer. Values of \( R = 0.994 \) and 0.965 were obtained for the quartz and silicon substrates respectively. The thickness of the overlayer can also be
estimated \( d = -\text{slope} \times \lambda \) and a value of 1-2 nm was obtained for all substrates. The fact that the silicon data does not fit as well as the other two substrates is assumed to be a result of the forward scattering of the Si2p photoelectrons from the single crystal substrate. Although buried below some 3 nm of SiO₂ and the polymer overlayer, it is clear that this is sufficient to distort the ARXPS profile. The alternative possibility, that of local variations in the overlayer thickness, were examined by SPM, (scanning probe microscopies). AFM of the silicon surface indicated a slight undulation of the surface profile with a periodicity of around 100 nm which appeared to replicate that of the polished substrate.

6.4.3 Results

Figure 6.5 depicts the depth profiles obtained from the various substrates.
Chapter 6. Interphase Chemistry of the Resin/Ceramic System

Figure 6.5 Compositional depth profiles generated from (a) silicon, (b) quartz and (c) polished alumina.
A consistent observation was the aggregation of the polar carbon species adjacent to
the inorganic substrate for the acidic materials. It should be noted that because of the
difficulties described above concerning the Cls spectrum from the alumina substrate
acquired on the ESCALAB system, this profile is merely expressed in terms of
elemental concentration. For the other substrates, the Cls spectra have been peak
fitted, to indicate the distribution of the various carbon species within the interphase
region.

6.5 Model for Environmental Failure

Angle-resolved XPS has proved an effective means of discovering more detail
about the nature of the polymer overlayer remaining on the failure surface. The
thickness of the overlayer lies in the region of 1-2 nm, and orientation of the functional
groups within the overlayer is apparent. This has enabled an adhesion failure
mechanism to be proposed for the system under hostile environmental conditions.

Detailed analysis of the experimental data obtained from in particular, the
ARXPS and durability studies, have revealed some interesting aspects. There are two
main observations which arise from the depth profiles constructed from the angle
resolved XPS data. Firstly, there is preferred orientation of the oxygenated functional
groups within the overlayer of polymer remaining on the ceramic fracture surfaces.
In the case of silicon (the most acidic of the substrates investigated), it is the methoxy
(C-O) component which is most strongly orientated to the interface. This is in contrast
to work carried out on PMMA films on glass, where the C=O component was found
most strongly orientated towards the glass, (Chehimi and Watts, 1993). Although it
should be noted that the angle-resolved data does not correspond to a series of unique
depths within the sample. This point is returned to in the general discussion. The
Luxtrak™ resin used during these studies was a multicomponent system, the major
constituent of which, is based on aromatic methacrylate type oligomers. It is assumed
that the differences in orientation observed in this system, are the result of steric
hindrance effects. Alternatively, the C=O groups may in some way be involved in the
cross-linking mechanism of the polymer. When dealing with a commercially available system, of complex formulation, it is more difficult to comment on the acid/base nature of the polymer itself. The fact that certain groups (i.e. C-O and C=O) are attracted towards very acidic substrates tends to suggest basic character. Results obtained from polished alumina (amphoteric in nature), also suggest partial orientation of oxygen (methoxy), groups towards the interface; (a fact which, on the alumina substrates, may have been overlooked without access to a Scienta ESCA300). This apparent anomaly may be explained by the fact that many polymers display mixed character and it depends very much on the material with which they are interacting, whether or not they behave in an acidic or a basic manner (e.g. PMMA which is regarded as a basic polymer, and interacts strongly via the oxygen of the carbonyl group with acidic probes such as trichloromethane, will exhibit acidic character when probed with a classical base such as pyridine, (Chehimi et al., 1992)). Analysis of the polymer used in this work by IGC, indicated that this was in fact the case; the polymer displayed mixed character, with a bias towards basic properties.

The next significant observation from the data is the fact that, regardless of the substrate used, the aromatic component of the polymer (the $\pi \rightarrow \pi^*$ shake-up satellite) is absent in the polymer overlayer, but present on the polymer side of the failure. Such an observation has been reported in the past, though not fully explained, by Pignataro et al. (1983 and 1985), for a chemically similar, Novolac resin. (Luxtrak™ resins are comprised of about 90% of a highly aromatic base resin, 9% TEGDMA and various minor additives, while Novolac resins have the structure, $(\text{C}_6\text{H}_3(\text{OH})\text{CH}_2)_n$). There are several possible explanations for this observation: (i) stereochemical effects at the interface prevented the intimate association of the aromatic component of the resin and the inorganic substrate, (ii) the lack of any specific interactions between these two moieties ensured that interactions between the substrate and the methoxy and carbonyl groups of the TEGDMA molecules dominated the interphase region, and (iii) interpolymer interactions resulting from surface free energy considerations left the interphase region depleted in aromatic character.

The resin used in the course of this study is a multicomponent system, the major
constituent of which is hydrophobic in nature. This is the component containing largely aromatic groups and forms a very rigid structure. One of the minor components, TEGDMA, is shorter and unbranched. The conformation of this molecule is such, (due in part to an absence of any aromatic groups), that it is able to rotate freely. This molecule is also hydrophillic in nature due to the presence of oxygenated functional groups. The model proposed, is that the hydrophillic components of the resin migrate towards the inorganic interface in preference to the less mobile, hydrophobic molecules which make up the base resin. This would account for the strongly bound nanometre or so overlayer of polymer present on the failure surface, and also the absence of any aromatic character within the overlayer remaining on the failure surface.

The segregation of TEGDMA molecules towards the interface, followed by their preferential adsorption onto the substrate could produce serious consequences. TEGDMA molecules are very hydrophillic, so the presence of water at the interface would be likely to produce instability within the region adjacent to the interface.

Combining the information provided above, it is possible to postulate a failure mechanism for the polymer/inorganic surface previously immersed in water at elevated temperature. In the intact state it is envisaged that the carbonyl and the methoxy groups of the TEGDMA interact with the substrate. Donor-acceptor (or acid-base) interactions are thought to play an important role in this process, (Buchwalter et al., 1987) and this means the interaction is more intense for the more acidic substrates. The methoxy group is at the plane of the interface in greater concentration than the carbonyl-like species and aromatic species are by-and-large absent from this region. The co-operative interaction results in a nanoscale interphase region of the type reported for PMMA on acidic substrates, (Chehimi and Watts, 1993). See Figure 6.6.

On exposure to water, lateral diffusion from the joint edge brings about failure at the edge of the interphase zone, due to the transition in both chemical and mechanical properties. The interfacial polymer surface is spectroscopically indistinguishable from the standard XPS spectrum of the bulk polymer. Interfacial failure is precluded as a result of the discrete interfacial interactions described above.
Chapter 6. Interphase Chemistry of the Resin/Ceramic System

Although chemically similar, there is a clear distinction between the interphase composition of the polymer applied to an alumina system and to the quartz and silicon systems. This is ascribed to the extent of acid-base interactions achieved between the polymer and the three substrates, and such possibilities should be considered when the as-received alumina substrate is employed. A complete understanding of interphase chemistry provides a potential route to the design of a system with enhanced durability. The next stage of the work was to develop a correlation between interphase chemistry, durability and mechanical properties for the systems described here.

Figure 6.6 Schematic of the polymer/ceramic substrate nanoscale interphase region.
6.6 Mechanisms of Adhesion

One of the difficulties associated with discovering which particular adhesion mechanisms operate for a given system, is that adhesion studies almost always involve destruction of the joint in order to obtain information about the interfacial (or, interphasial) region. The concern is therefore, that the very information which was contained within that region may be destroyed when the joint fails. An additional complication is that in almost all cases, several adhesion mechanisms are likely to be operating.

Hence, it is often much easier to propose a failure mechanism than an adhesion mechanism for a given system. In the case of the LCR000/as-received alumina system, results have indicated that several factors play a role in adhesion. Firstly, specimens made from polished alumina discs were observed to have less residual strength than their as-received counterparts, following prolonged immersion in water. Joints comprised of polished alumina had a tendency to fall apart on removal from water. It can therefore be concluded that the rough surface of the alumina in some way, facilitates adhesion. The nature of the surface roughness is also likely to have been important. The resin was able to wet the surface fully, there were no pores which were too narrow for the adhesive to penetrate. The surface simply provided a higher surface area available for bonding.

The results from angle resolved studies indicate that the oxygen containing groups present in the resin orientate themselves towards the substrate, thus providing the opportunity for polymer/substrate interactions to occur. The orientation of the TEGDMA molecules towards the silica substrate was the most pronounced in all the substrates investigated. The possibility that the silica plays a role in adhesion cannot therefore be ruled out.

6.7 Summary

During this section of the work, additional substrates were included to study the influence of the individual features present on as-received alumina, (i.e. polished
alumina to remove the influence of topography and quartz and silicon wafers, to study the effects of surface segregated silica).

XPS results indicated that failure following prolonged immersion in water occurred near-interfacially, with 1-2 nm of polymer remaining on the inorganic substrate. The locus of failure remained unaltered, regardless of the substrate investigated, suggesting that any influence of localised variations in the surface chemistry was being overshadowed.

ARXPS studies indicated that the overlayer of polymer was continuous, rather than island-like in structure. Angle resolved work also indicated that there was orientation of some of the functional groups of the resin towards the inorganic interface. These orientation effects were most pronounced with silicon wafer samples, (the most acidic of the substrates investigated).

For all samples investigated, there was an absence of any aromatic character within the overlayer of polymer remaining on the adherend surface. This led to the proposal of a model for environmental failure. The basis of the model was, that one of the other components in the resin was aggregating at the inorganic interface, effectively resulting in the production of an in-situ WBL. Of the components which make up LCR000, TEGDMA was considered as the most likely component to be responsible for the production of the in-situ weak boundary layer, (partly due to its hydrophillic nature). The next stage of the work was therefore to test the likelihood of this hypothesis.
7.1 Introduction

Prolonged, (greater than 14 days), immersion in water at 50°C has been shown to result in cohesive failure, with 1-2 nm of polymer remaining on one of the ceramic substrates. An absence in the high resolution C1s spectrum of the $\pi \rightarrow \pi^*$ shake up satellite, the component attributable to the highly aromatic molecules of the base resin, suggested that one of the other resin components was aggregating at the organic/inorganic interface to produce an in-situ weak boundary layer (WBL). TEGDMA, the reactive diluent in the formulation, was the most likely candidate. This compound contains no aromatic groups, which is significant, as the polymer residue detected on the failure surfaces also contained no signature characteristic of aromatic groups, (i.e. the $\pi \rightarrow \pi^*$ shake-up satellite). TEGDMA molecules are unbranched and contain no aromatic groups, both factors likely to increase their mobility.

The next stage was to convince the Luxtrak™ business Group at ZENECA Specialties of the scientific worth of manufacturing a prototype batch of the resin, with the reactive diluent removed from the formulation. The prototype resin is referred to as ModLCR000. This introduced practical difficulties, as the viscosity of the resin increased dramatically without the presence of the diluent (generally added as about 9% of the formulation). This made it necessary to heat the resin to a temperature of about 50°C prior to fabrication of the joints, in order to reduce the viscosity. This temperature was selected after consultation with the manufacturers, as being sufficiently high to allow the resin to flow, without causing it to gel. During manufacture, the resin is heated to above 50°C to allow the photoinitiator and other minor components to dissolve.

The interactions of some of the organic molecules present in the original
formulation, with a model α-alumina surface, were investigated using molecular modelling to indicate the most favourable interactions with the substrate. Durability studies were also carried out on a reformulated photocured resin, to investigate the effect of the removal of the TEGDMA, the compound suspected of being the principal component within the WBL.

Both XPS and ToF-SIMS have been employed to characterise the reformulated product. A sample of TEGDMA was also obtained in order to acquire XPS and ToF-SIMS spectra from that specific component, without the contribution from other additions to the formulation. Finally, the mechanical performance of ModLCR000 is assessed in relation to the standard formulation.

7.2 XPS Studies

7.2.1 Modified LCR000 Resin

A batch of ModLCR000 was heated to 50°C in an oven, then cast onto stubs of the type used to mount specimens for XPS analysis. The samples were cured for two minutes with a visible light source, through a piece of Melinex™ film. The film was removed just prior to XPS analysis. Spectra were recorded using (a) a VG Scientific ESCALAB MkII and (b) a Scienta ESCA300 spectrometer. A survey spectrum was acquired on the ESCALAB MkII using AlKα radiation, at a pass energy of 50 eV; a high resolution C1s spectrum was also obtained (pass energy 20 eV). Figure 7.1 depicts a survey spectrum obtained from the fully-cured ModLCR000 using the Scienta ESCA300 spectrometer, (as the spectra recorded using the ESCA300 had superior resolution), with the high resolution C1s spectrum inserted. The spectrum appears similar to that obtained from a sample of LCR000, (compare with Figure 4.6). Table 7.2 compares the relative proportions of the functional groups for each of the two resins, (note that both samples were scraped with a scalpel just prior to analysis).
Chapter 7. The Study of a Reformulated Resin

Table 7.2 Comparison of LCR000 and ModLCR000

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Intensity</th>
<th>C:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-C / C-H</td>
<td>C-O</td>
</tr>
<tr>
<td>LCR000</td>
<td>70</td>
<td>21</td>
</tr>
<tr>
<td>ModLCR000</td>
<td>70</td>
<td>20</td>
</tr>
</tbody>
</table>

The main differences between the two spectra are firstly, a slight enhancement in the intensity of the π-π* shake-up satellite in the high resolution C1s spectra obtained from the modified resin. It should be noted however, that the errors associated with the measurement of the intensity of the shake-up satellite are likely to be high, (up to 100 %). As expected, the removal of the TEGDMA component produced a slightly higher C:O ratio in the modified resin, 4.3 versus 3.8.

Figure 7.1 Survey spectrum obtained from fully-cured ModLCR000 with the high resolution C1s region inserted.
7.2.2 Spin-casting Experiments

7.2.2.1 Introduction

The failure mechanism proposed for the LCR000 resin/ceramic system in the presence of water suggests that the TEGDMA component is selectively adsorbed onto the surface of the adherend, effectively producing an in-situ WBL, hydrophillic in nature, along which failure can occur. In order to test this hypothesis, it was necessary to acquire spectra from (i) LCR000, (ii) TEGDMA and (iii) ModLCR000 on the various adherends, to provide a means of comparison with spectra obtained from the failure surfaces of actual joints.

N.B the failure mechanism was assumed to be the same for each of the three substrates investigated in the durability studies, (i.e. silicon wafer, quartz and alumina).

7.2.2.2 Experimental Details

Dilute solutions of LCR000 resin, ModLCR000 and the TEGDMA were made up in toluene, (at concentrations of between 3.3 - 4.3 mg cm\(^{-3}\) toluene). Silicon wafers were cut in to squares, (about 1 cm by 1 cm) with a diamond scribe and cleaned ultrasonically in isopropanol. Alumina discs were supplied by the Laser Cutting Company, (as described in Chapter 4). A drop of the solution was placed at the centre of each sample, (which had previously been secured to sample stubs using conductive adhesive) and the excess solvent was removed by spinning the samples, held in the chuck of a variable speed drill, with the drill located inside a fume cupboard, at about 3600 rpm. This produced a film of fairly uniform thickness for analysis. Preliminary experiments were carried out using the VG Scientific ESCALAB MkII located at the University of Surrey, but were later duplicated on the Scienta ESCA300 at the RUSTI, SERC Daresbury laboratory. The results presented here were obtained using the ESCA300, due to both the improved counting statistics and spectral resolution achievable with this instrument.

7.2.2.3 Results

Figure 7.2 shows the survey spectra obtained from (a) LCR000 in toluene, (b) ModLCR000 in toluene and (c) TEGDMA in toluene spun cast onto as-received Coors AD96 alumina substrates.
Figure 7.2 Survey spectra obtained from (a) LCR000 in toluene, (b) ModLCR000 in toluene and (c) TEGDMA in toluene, spun cast on to alumina.
Figure 7.3  Survey spectra obtained from (a) LCR000 in toluene, (b) ModLCR000 in toluene and (c) TEGDMA in toluene, spun cast on to silicon.
Inset are the high resolution C1s spectra indicating the various functional groups of the resin present on the surface. Figure 7.3 depicts the equivalent spectra for solutions (a) to (c) which have been spun cast on to silicon wafer substrates.

7.2.3 Durability Studies

7.2.3.1 Experimental Details

Durability studies were also carried out on ModLCR000, in order to compare its performance with standard LCR000. As with the first set of durability experiments, (Chapter 4) two sets of butt-joints were fabricated, one using alumina adherends and the other, squares cut from silicon wafers. Joints were produced following the method described previously. XPS analyses were carried out on both sides of the failure following in-situ fracture, using the ESCALAB MkII. Additional samples were also analysed using the Scienta ESCA300.

7.2.3.2 Results

Figure 7.4 depicts the spectra obtained from the failure surfaces of a silicon joint after immersion in water at 50°C for two weeks. In contrast to the spectra obtained from an LCR000 joint, the $\pi \to \pi^*$ satellite was clearly visible in the C1s spectra obtained from both sides of the failure, not just the side where polymer was visible to the naked eye.

Analysis of an equivalent as-received alumina joint also revealed the presence of polymer on the ceramic side of the failure, (see Figure 7.4(c) and (d)). However, the $\pi \to \pi^*$ shake-up satellite is less clearly visible, due to the presence of the two potassium 2p$_{1/2}$ and 2p$_{3/2}$ peaks at binding energies of 296 and 293 eV respectively. The original survey spectrum recorded from the surface of an as-received Coors AD96 alumina disc, from a batch supplied to ICI Chemicals & Polymers Ltd. in 1991, by the Laser Cutting Company, did not reveal the presence of any potassium, (see page 98). In spectra recorded from subsequent batches of alumina discs, (supplied in 1992 and 1993) however, a potassium signal was detected. During fabrication of alumina, the exact composition of the sintering aids added is known to vary, thus explaining the slight change in composition, (i.e. the presence of potassium in later batches).
Chapter 7. The Study of a Reformulated Resin

Figure 7.4 Survey spectra obtained from ceramic/ModLCR000 joints, (C1s spectra inserted), (a) polymer side of a silicon joint, (b) silicon side, (c) polymer side of an alumina joint and (d) alumina side.

184
7.3 ToF-SIMS Analysis

7.3.1 Introduction
In addition to the XPS studies, ToF-SIMS was employed as a means of characterising the polymer overlayer remaining on the ceramic side of the failure. Both positive and negative ion spectra were obtained from the various resin components in addition to the fracture surfaces of joints following immersion in water, and the peaks were assigned to various fragments of the polymer.

7.3.2 Sample Preparation
Samples for ToF-SIMS analysis were prepared as follows:

(i) Dilute solutions of LCR000 resin, ModLCR000 and TEGDMA were made up in toluene, (between 3.3 - 4.3 mg ml\(^{-1}\) toluene).

(ii) Silicon wafers were cut in to squares, (about 1cm by 1cm) with a diamond scribe and cleaned ultrasonically in isopropanol.

(iii) A drop of the solution was placed on a clean square of silicon and the excess solvent drained off onto filter paper. This produced a film which varied slightly in thickness across the sample. Moving the sample position then allowed the optimum thickness for analysis to be located. The silicon substrates were then placed in spring loaded sample stubs.

(iv) Both positive and negative ion spectra were recorded over a mass range of 0-400, m/z, using a VG Scientific Type 23 (Fisons Instruments, East Grinstead, UK) system. This system is equipped with a single stage reflectron time-of-flight analyser and a MIG300PB pulsed liquid metal ion gun (gallium source). Static SIMS conditions were employed using a pulsed (20 kHz and 20 ns) 30 keV \(^{69}\text{Ga}^+\) primary ion beam, (i.e. less than 10\(^{12}\) ions cm\(^{-2}\) analysis\(^{-1}\)).

(v) Positive and negative ion spectra were also recorded from the failure surfaces of ceramic/photocured resin joints, previously immersed in water at 50\(^\circ\)C for a least 14 days and fractured just prior to analysis.
7.3.3 Results

Figure 7.5 shows the positive ion mass spectra recorded from (a) TEGDMA dissolved in toluene and cast onto a silicon wafer, (b) the silicon fracture surface from a silicon/standard LCR000 joint, fractured after 14 days immersion in water and (c) ModLCR000 resin, dissolved in toluene and cast onto a silicon wafer. The spectra have been plotted between 5-160 m/z, with inserts made of the regions of particular interest, together with the appropriate scaling factors. The spectrum from the ModLCR000 resin, (c), has also been plotted between 160-370 m/z to indicate the higher mass peaks which appear to be diagnostic of the standard, (base) resin. Repeated analysis of type (a) and (b) samples failed to produce the characteristic higher mass peaks observed in (c). Spectra from samples (a) and (b) have therefore been plotted over a lower mass range. Negative ion spectra have not been included, as they provided no additional useful information.

7.3.4 Discussion

The positive ion ToF-SIMS spectra depicted in Figure 7.5, support the idea originally presented, that the TEGDMA molecules aggregate at the inorganic surface to produce a "nanoscale interphase region" along which failure can occur. The spectrum obtained from the silicon fracture surface is similar, though not identical to the spectrum obtained from the TEGDMA. Table 7.2 lists the major peaks of interest, together with their peak assignments.

There is a strong signal from the silicon substrate in all of the samples analysed, with peaks at 28 and 29 Daltons. In each of the spectra (a)-(c), the usual hydrocarbon features are observed, the C\textsubscript{3} cluster (39, 41 and 43 D) is clearly visible, (Briggs, 1992). Certain peaks, (e.g. 69 and 73 D) were observed in all three of the spectra, making them of limited use for distinguishing between samples. A characteristic peak at 149 D, (the C\textsubscript{6}H\textsubscript{13}O\textsubscript{4}\textsuperscript{+} ion) was also observed in both spectra (a) and (b), but not in (c), which suggests it is a peak characteristic of the TEGDMA. The peak at 183 D is also believed to originate from the TEGDMA, the C\textsubscript{7}H\textsubscript{11}O\textsubscript{3}\textsuperscript{+} ion resulting from the cleavage of a symmetrical TEGDMA molecule. An absence of certain peaks may also
prove significant. High mass peaks at 165, 281 and 365 Daltons were observed in spectrum (c). The peak at 281 m/z is believed to originate from the repeat unit of the base resin molecule (C_{18}H_{17}O_3\textsuperscript{+}) and the peak at 165 from the (C_{3}H_{9}O_3\textsuperscript{+}) ion. The absence of the peaks at 165, 281 and 365 Daltons, in the spectrum obtained from the fractured silicon joint, again provides evidence that the polymer overlayer remaining on the failure surface is predominantly comprised of TEGDMA, with some hydrocarbon contamination. It was unlikely that a perfect match with the spectra would be obtained for the spectra from the silicon fracture surfaces and the standards, as the sample histories were so different, (i.e. samples (a) and (c) were produced by casting solutions of the polymers onto clean pieces of silicon wafer, while the silicon joints were immersed in water for 14 days, then fractured in air prior to ToF-SIMS analysis). The results discussed above were, however, reproducible.
Table 7.2 Major peaks and their assignments.

<table>
<thead>
<tr>
<th>Peak m/z</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 and 29</td>
<td>Si⁺ / SiH⁺</td>
</tr>
<tr>
<td>39, 41 and 43 (C₃ cluster)</td>
<td>C₅H₃⁺ / C₃H₅⁺ / C₂H₇⁺</td>
</tr>
<tr>
<td>69</td>
<td>C₄H₅O⁺ / C₃H₉⁺</td>
</tr>
<tr>
<td>73</td>
<td>C₃H₅O₂⁺ / C₄H₉O⁺</td>
</tr>
<tr>
<td>147</td>
<td>C₇H₁₅O₃⁺</td>
</tr>
<tr>
<td>149</td>
<td>C₆H₁₃O₄⁺</td>
</tr>
<tr>
<td>152</td>
<td>C₁₂H₈⁺</td>
</tr>
<tr>
<td>165</td>
<td>C₅H₉O₃⁺</td>
</tr>
<tr>
<td>183</td>
<td>C₇H₁₁O₃⁺</td>
</tr>
<tr>
<td>281</td>
<td>C₁₈H₁₇O₃⁺</td>
</tr>
<tr>
<td>365</td>
<td>C₂₂H₂₁O₅⁺</td>
</tr>
</tbody>
</table>
Chapter 7. The Study of a Reformulated Resin

Figure 7.5 Positive ion ToF-SIMS spectra obtained from (a) TEGDMA, (b) the ceramic side of a silicon wafer/LCR000 joint and (c) ModLCR000 resin.
Chapter 7. The Study of a Reformulated Resin

7.4 Inverse Gas Chromatography (IGC)

7.4.1 Introduction

IGC studies carried out on LCR000, (as detailed in Chapter 4), were repeated using the modified resin. The detailed experimental procedures are listed in Chapter 4. For ease of comparison of the data, results from the standard LCR000 have again been included at this stage.

7.4.2 Results

Figure 7.6 contains data obtained from the adsorption of the series of n-alkanes on the polymers at room temperature, (25°C). The n-alkane series produced a linear plot which then acted as a reference line for London dispersion interactions. For polar probes interacting specifically with the stationary phase, \( \Delta G_a \) values show a positive deviation from this line. If the assumption is made that dispersive and acid-base interactions are additive, the subtraction of \( \Delta G_a^{AB} \) from \( \Delta G_a \) corresponds to the vertical distance between the n-alkane reference line, as indicated on page 90. Values for all the polar probes lay significantly above the n-alkane reference line, indicating the amphoteric nature of both resins. A significant change in the position of the tetrahydrofuran, (THF) datum point for the LCR000 and ModLCR000 plots indicated that the ModLCR000 is somewhat more acidic than LCR000 at 25°C.

Table 7.3 contains \( \Delta G_{CH2} \) and \( \Delta G^{AB} \) values for the series of n-alkanes and the polar probes adsorbed on LCR000 and ModLCR000 at 25°C. The values for the acid-base component of the free energy of adsorption for chloroform and ethylacetate for the two polymers were similar. The value for tetrahydrofuran, however, was significantly higher for the modified resin at room temperature, than for LCR000. These results are consistent with a decrease in surface basicity on modification of the LCR000 resin by removal of the TEGDMA component.
Table 7.3 Measurements of the adsorption behaviour of the probes.

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>$\Delta G_a^{\text{CH}_2}$</th>
<th>$\Delta G_a^{\text{AB}}$</th>
<th>$\Delta G_a^{\text{AB}}$</th>
<th>$\Delta G_a^{\text{AB}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CHCl$_3$</td>
<td>EtAc</td>
<td>THF</td>
<td></td>
</tr>
<tr>
<td>LCR000</td>
<td>25.0</td>
<td>2.79</td>
<td>5.5</td>
<td>4.6</td>
<td>4.2</td>
</tr>
<tr>
<td>ModLCR000</td>
<td>25.0</td>
<td>2.71</td>
<td>5.1</td>
<td>4.9</td>
<td>5.8</td>
</tr>
<tr>
<td>PMMA</td>
<td>25.0</td>
<td>2.68</td>
<td>6.3</td>
<td>4.7</td>
<td>4.4</td>
</tr>
</tbody>
</table>

$\Delta G_a$ values are in kJ mol$^{-1}$.

Figure 7.6 Adsorption of n-alkanes on LCR000 and ModLCR000 at 25°C.
Figure 7.6 illustrates the amphoteric nature of both resins. Values of $RT\ln V_N$ were plotted versus $T_b$, (the boiling point of each probe) and the values for both the acidic and the basic probes lay above the n-alkane reference line, (i.e. both acid and basic sites must be present).

From these results it was possible to determine the materials thermodynamic properties. Values for the two resins are listed in Table 7.4, together with the data for PMMA, (the dispersive component of surface free energy, $\gamma^d$ and the acid-base constants $K_A$ and $K_D$). The values were determined from the data presented in Figure 7.7. Based on Fowkes' method, (1964) to evaluate the dispersive contribution to the work of adhesion between two materials, Dorris and Gray, (1980), suggested a method of determining $\gamma^d$ using $\Delta G^{CH_2}$, (see page 88). The $\gamma^d$ values measured for the two polymers were consistent with methacrylate based polymers and comparable to that of PMMA. At room temperature, PMMA is the most basic, followed by LCR000 and finally, the modified resin, ModLCR000. The modified resin was the most acidic of the polymers investigated, PMMA, the least acidic.

Following the approach of Saint-Flour and Papirer, (1983), the acid-base constants $K_A$ and $K_D$ were determined. Plotting $-\Delta G^A/AN*$ versus $(DN/AN*)$ produced a linear correlation with a slope $(K_A)$ and an intercept, $(K_D)$. The overall acid-base ratio $K_D/K_A$ decreased with $K_D$, supporting the idea that ModLCR000 is the least basic resin. Reformulation of the resin therefore appears to have produced subtle effects on the surface properties of the polymer, characterised by a decrease in basicity, which IGC has been able to detect and quantify.

Table 7.4 Material properties of LCR000, ModLCR000 and PMMA

<table>
<thead>
<tr>
<th>Material</th>
<th>$T$ (°C)</th>
<th>$\gamma^d$ / mJm$^{-2}$</th>
<th>$K_D \times 100$</th>
<th>$K_A \times 100$</th>
<th>$K_D/K_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCR000</td>
<td>25.0</td>
<td>42.0</td>
<td>23.7</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>ModLCR000</td>
<td>25.0</td>
<td>39.8</td>
<td>15.1</td>
<td>6.5</td>
<td>2.3</td>
</tr>
<tr>
<td>PMMA</td>
<td>25.0</td>
<td>38.8</td>
<td>25.5</td>
<td>4.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Figure 7.7 $RT \ln V_N$ versus $T_b$ for (a) LCR000 at 25°C and (b) ModLCR000 at 25°C.
Figure 7.8 Evaluation of $K_D$ and $K_A$ for the two resins at 25°C.
7.5 Molecular Modelling

7.5.1 Introduction

The failure mechanism proposed for this system is based on the assumption that one of the minor components of the resin moves preferentially towards the inorganic surface, where it becomes selectively adsorbed. On the basis of the XPS and ToF-SIMS results in the previous chapter, the interaction of, both the TEGDMA and the base resin molecules with an α-alumina surface, were investigated using molecular modelling techniques. This work was carried out in collaboration with the sponsors, using their facilities located at the ZENECA Specialties Research Centre, Blackley, UK.

7.5.2 Experimental Procedure

The structure for α-alumina was obtained from the Inorganic Crystal Structure Database at Daresbury, (ICSD), structure number 4685. A commercial materials modelling package, (Cerius), was used to build up first the unit cell and then a larger array of the solid, (43Å by 37Å). The crystal was cut along the (102) direction. In alumina, the widest interplanar spacings, occur between the (102) planes and there is a correlation between the energetically most favourable faces, (that would tend to result when polishing) and the magnitude of lattice parameter, d, (Donnay and Harker, 1937). The major interaction energy between the alumina and the organic components of the resin is likely to be electrostatic due to the polarity of the inorganic surface. Assigning purely ionic charges of +3 and -2 to the Al and O respectively, would fail to account for the degree of covalency in the system, hence the charge equilibrium method within Cerius was used, with typical values of +1.95 and -1.3 assigned arbitrarily, (still maintaining the 2:3 ratio).

The conformation of the organic molecules was optimised using a second modelling package, (Sybyl, 1989). Electrostatic charges were obtained from a single point calculation using the AMI semi-empirical method in MOPAC, (MOPAC, 1993). Interactions of the organic molecules with the substrate were investigated using the
dock option within Sybyl, which allowed the interaction energies to be minimised. It should also be noted that during all minimisations, the alumina surface was held rigid (i.e. not allowed to relax). Individual TEGDMA molecules were allowed to approach the substrate in a variety of orientations in order to obtain the most favourable one for interaction with the surface. The model was subsequently expanded to study several molecules interacting with the surface.

7.5.3 Results

Figure 7.9 illustrates how a TEGDMA molecule might "dock" with the alumina substrate, using the C=O oxygen atom within a terminal methacrylate group as the principal site to bind with an aluminium ion of the substrate, to enable the maximum number of molecules to interact with the substrate and hence optimise the total interaction energy. The TEGDMA molecule can be seen approaching a section of an α-alumina substrate at an angle of about 40° to the substrate, with the result that the opposite end of the TEGDMA molecule lies between 8 and 9Å above the surface. The TEGDMA molecule has also been studied at angles of between 30 to 40° to the substrate, with energy values appearing to be relatively angle-independent at these values.

7.5.4 Discussion

As shown in Chapter 6 by XPS joints comprised of the standard resin failed with a thin polymer overlayer remaining on the ceramic substrate of thickness 1-2nm. The results of the molecular modelling correlated well with this data. In order to achieve the maximum possible interaction with the substrate, it is necessary to maximise the interaction energy/unit area, a parameter known as the interaction density. The greatest interaction energy was recorded for the TEGDMA molecule oriented parallel to the substrate, (see Table 7.4). However, this does not give the largest value for interaction energy/unit area, due to the large surface coverage of the molecule. It is possible to produce an increase in the interaction energy per molecule if the carbonyl oxygens in both of the methacrylate end groups are angled towards the
substrate, (as the carbonyl oxygens are about 1.3 times more negative than the ether oxygens). This is achieved by internal rotations within the molecule, with the molecule oriented parallel to the surface. Alternatively, the total interaction energy may be increased by angling one of the methacrylate end groups of each TEGDMA molecule towards the surface. The cross-sectional area of the end of a TEGDMA molecule is only 38.2 Å², which would then allow large numbers of molecules to interact with the surface, giving a higher total interaction energy. In this orientation, the end of the TEGDMA molecule has been calculated to lie between 8-9 Å above the alumina surface, (see Figure 7.9). The thickness of the overlayer remaining on the fracture surface is a similar order of magnitude, (i.e. nm). This suggests that the polymer layer observed may be a molecular layer of TEGDMA remaining on the fracture surface.

An increase in interaction energy is also observed when raising the number of TEGDMA molecules from 1 to 10. This suggests that if one TEGDMA molecule interacts with the alumina, interaction of additional TEGDMA molecules at neighbouring sites is favoured, (i.e. cooperative effects may be present). This cooperative effect will also occur in the bulk of the resin, not only in the region immediately adjacent to the interface.

ARXPS studies indicated that the C-O bonds were oriented towards the substrate, rather than the C=O groups, (indicated by a higher C-O peak at low TOA's). This can be explained by considering the single molecule of TEGDMA adsorbed on to the surface of alumina, (Figure 7.9). Molecular modelling results suggested that the C=O bond was the most likely to interact with the substrate. However, this also meant that there were another four neighbouring C-O bonds, not necessarily interacting with, but in close proximity to the interface. This may therefore account for the enhanced C-O signal at low angles of XPS analysis.
### Table 7.4 Interaction energies of TEGDMA with α-alumina

<table>
<thead>
<tr>
<th>Number of molecules</th>
<th>$\Delta E_{\text{TOT}}$ / kJ</th>
<th>$\Delta E$ per molecule /kJ</th>
<th>Footprint area of molecule /kJ</th>
<th>Interaction density /kJÅ$^2$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-151</td>
<td>-151</td>
<td>87.7</td>
<td>-1.72</td>
<td>Molecule parallel to surface</td>
</tr>
<tr>
<td>1</td>
<td>-217</td>
<td>-217</td>
<td>87.7</td>
<td>-2.47</td>
<td>C=O groups towards surface</td>
</tr>
<tr>
<td>1</td>
<td>-117</td>
<td>-117</td>
<td>38.2</td>
<td>-3.06</td>
<td>Molecule at 40° to surface</td>
</tr>
<tr>
<td>10</td>
<td>-1531</td>
<td>-153</td>
<td>381.8</td>
<td>-4.01</td>
<td>As above</td>
</tr>
</tbody>
</table>

*$\Delta E_{\text{TOT}}$ = the total interaction energy (irrespective of the number of molecules interacting).*  

$\Delta E$ per molecule = the interaction energy per molecule.  

Footprint area of molecule = effective area of each molecule interacting with the surface.  

Interaction density = the interaction energy per molecule divided by the footprint area of the molecule.
red = oxygen, pink = aluminium, white = carbon and cyan = hydrogen

Figure 7.9 TEGDMA molecule "docking" with an α-alumina substrate, (a) molecular modelling image and (b) schematic.
Chapter 7. The Study of a Reformulated Resin

7.6 Mechanical Testing

7.6.1 Introduction

The aim of this section of the work was to assess the performance of the reformulated resin in the presence of water at 50°C. As with the LCR000 resin, studies using a butt-joint geometry were carried out in order to be able to relate the deterioration in joint performance to the XPS data recorded from in-situ fracture studies.

7.6.2 Experimental Detail

Two additional series of butt-joints were also fabricated for mechanical testing, from (a) LCR000 resin and (b) ModLCR000. The resins were sandwiched between (i) as received Coors AD96 alumina discs, (10 mm in diameter and 1 mm thick) and (ii) squares of single crystal silicon with 3 nm thickness of native silicon dioxide, (1 cm by 1 cm).

The joints were immersed in water at 50°C for periods of between 0 and 14 days. On removal from water, ESCALAB stubs were attached to either side of the ceramic/photocured polymer "sandwich", using standard Araldite™. Samples were then located in specially designed grips (see Figure 5.5) and the load to failure recorded using a J.J. Lloyd tensile tensometer, (1 kN load cell, crosshead speed of 1 mm minute⁻¹).

7.6.3 Results

Figure 7.10 shows the variation of load to failure with immersion time in water. The results from the standard LCR000 resin have been included for comparative purposes. The ModLCR000 joints all show superior durability compared with those fabricated from LCR000 resin. The improvement in load to failure is around 20% for the samples investigated.
7.6.4 Boeing Wedge Tests

As described in Chapter 4, the Boeing wedge test specimens provided a convenient means of assessing durability. Samples were also produced from ModLCR000 and placed in an atmosphere of 95% humidity at 50°C. Crack lengths were measured at intervals of approximately 24 hours. Figure 7.11(a) shows the crack growth as a function of time, Figure 7.11(b), the fracture energy. Figure 7.12(a) depicts the average crack growth data for ModLCR000 as compared with LCR000, 7.12(b) the corresponding fracture energy data. The data in Figure 7.12 indicates that the original formulation (LCR000) performed better during these tests. This is contrary to the data obtained from butt-joints. A possible explanation for this variation in ranking, is the fact that removal of the TEGDMA results in the production of a resin with more brittle properties, (i.e. a lower modulus of rupture).
Figure 7.11 Durability data for ModLCR000, (a) crack growth and (b) fracture energy as a function of time.
Figure 7.12 Comparison of (a) crack growth data and (b) fracture energy data for LCR000 and ModLCR000.
The TEGDMA molecules have a degree of flexibility, but the highly aromatic molecules of the base resin are extremely rigid. Removal of the TEGDMA therefore results in the production of a resin which adheres better to alumina, but has inferior mechanical properties. In addition to this, removal of the TEGDMA results in a significant increase in the viscosity of the resin. This made it extremely difficult to ensure the adherend surface was coated evenly by the adhesive. These results could therefore be due to the difficulties associated with manufacturing much larger samples, (100 mm by 20 mm, as opposed to discs, 10 mm in diameter for the butt-joints).

7.7 SEM Results

The failure surfaces of butt-joint samples fabricated using ModLCR000/alumina which had previously been immersed in water at 50°C for two weeks, were gold-coated prior to investigation by SEM. There was a distinct difference between results from standard LCR000 joints and ModLCR000 joints. On the ceramic side of failures of LCR000 joints no polymer debris was visible. However, as Figure 7.13 indicates, angular fragments of the polymer were clearly visible on the failure surfaces of ModLCR000 joints.

Figure 7.13 SEM photomicrograph obtained from the failure surface of a ModLCR000/alumina joint.
Polymer debris was also reported on the failure surfaces of GFRP samples by Cazeneuve et al., (1989), though the precise cause of these angular fragments is unclear.

7.8 Summary

XPS spectra recorded from a fully-cured sample of ModLCR000, revealed only minor differences between the spectra obtained from standard LCR000. As expected, there was a slight increase in the C:O ratio of the modified resin, and the intensity of the $\pi \rightarrow \pi^*$ shake-up satellite increased. This was predictable, as the only component present in the formulation, not containing aromatic groups, had been removed.

Results obtained from XPS analysis of the individual components of the resin, (spun cast from solutions of toluene on to the various substrates), were very similar and therefore, could not be used to verify the WBL theory. Hence, the need for ToF-SIMS analysis. ToF-SIMS spectra recorded from the failure surfaces of silicon joints used for the environmental studies, contained none of the higher mass peaks attributed to the molecules of the base resin. Peaks identified as characteristic of the TEGDMA, were however identified on the failure surfaces. These data provided evidence for the WBL theory.

Molecular modelling studies indicated that interaction of TEGDMA molecules with an $\alpha$-alumina surface produces polymer/substrate interactions which are energetically favourable.

The results from this section support the idea that TEGDMA molecules present in the unmodified resin are responsible for in-situ WBL formation, the hydrophillic nature of which, leaves the joints particularly vulnerable to attack by water. Subsequent removal of the TEGDMA component resulted in a slight change in the acid/base properties of the resin, (from IGC results). Mechanical tests carried out on the reformulated resin, (ModLCR000), indicated that, although the adhesion of this trial resin to as-received alumina was superior in the presence of a hostile environment, (i.e. water at 50°C), the mechanical properties of the resin were
compromised by the reformulation.

The model proposed for failure of the LCR000/alumina system in the presence of a hostile environment has been substantiated using data from this section of the work. The reasons why aggregation of TEGDMA molecules at the inorganic interface should have occurred, will be considered in detail in the following chapter.
Chapter 8

The Adhesion and Failure of Photocured Resin/Ceramic Systems

8.1 Introduction

The results presented in the previous four chapters have enabled a detailed understanding of the failure mechanisms related to this particular adhesive system to be gained. The precise mechanisms for which are outlined later. Some of the findings of this work have wider implications in the field of adhesion, while other aspects relate specifically to this project. A discussion on the relevance of these findings has also been included in this chapter, with emphasis placed on areas where the information may find future application.

During the course of this study, although there was unlimited access to XPS, AES/SAM, ToF-SIMS and the scanning probe microscopies, STM and AFM, it became necessary to make use of very specialised surface analysis equipment in order to overcome some of the challenges associated with working on this system. The reasons for this have also been considered.

8.2 Difficulties Associated with the LCR000/Alumina System

8.2.1 Substrate Heterogeneity

One of the major problems associated with the study of the LCR000/as-received alumina system, was the heterogeneous nature of the substrate. Coors AD96 alumina is produced via a liquid phase sintering route, with silica forming the flux. The process is outlined in more detail in Chapter 2. The fact that during manufacture, migration of sintering aids results in the formation of a heterogeneous surface, is well documented, (Taylor, 1972 and Clarke, 1980). These earlier studies were undertaken
to try to establish the precise role that each of the various additives plays in the sintering process, with the ultimate aim to tailor mixtures of ceramic powders in order to achieve maximum possible densification. A depth profile obtained from the surface of as-received alumina using ToF-SIMS confirmed the surface heterogeneity reported in these earlier studies.

Conventional XPS analysis is an area integrating technique, so, ideally a laterally homogeneous sample is required. The heterogeneous nature of the alumina substrate used during these studies was further compounded by its surface roughness, (Chapter 4), making it completely unsuitable for ARXPS work, hence the need to incorporate model substrates into the study, (Chapter 6). Another problem encountered during XPS analysis of the adherend, was the severity and nature of the charging effects previously reported.

A combination of the factors outlined above, effectively pushed conventional XPS instrumentation, (i.e. the ESCALAB MkII), to which we had unlimited access, to the limit. Extremely useful information was obtained during preliminary studies using the ESCALAB Mk II. However, to examine minor, but nonetheless very characteristic features in the spectra, within an acceptable timescale, (i.e. before sample degradation became a problem), access to the most sophisticated instrumentation available proved essential, (see section 8.2.3).

8.2.2 Photocured Resins

In addition to the problems encountered with the adherend, the adhesives used during this study were fully-formulated and hence, multicomponent systems. Many adhesion projects are restricted to the study of homopolymers, or model systems, where the individual components have previously been well characterised. The Luxtrak™ series of resins is extremely complicated. Some of the individual components, (e.g. TEGDMA), can be obtained separately, but the base resin itself, which forms about 90 % of the formulation, is produced in-house and was therefore very difficult to characterise. The study of a fully formulated adhesive system provided a unique opportunity to investigate the adhesion and failure mechanisms operating in
a real, rather than a model, system.

8.2.3 The Scienta ESCA300 Spectrometer

The Scienta ESCA300 is currently the only spectrometer of its kind based in the U.K. A detailed account of the features which set the ESCA300 apart from other X-ray photoelectron spectrometers is included in Chapter 3. Access to the instrument was limited, (a total of nine days over three years), but with prior knowledge gained by extensive use of the ESCALAB MkII, this was sufficient to discover additional valuable information, which might otherwise have been overlooked.

The individual details of experiments carried out on the ESCA300 are included in the results chapters. The major benefits of the ESCA300 to this particular project, are summarised as follows: the spectrometer (a) minimised problems associated with differential charging, to reveal the true shape of peaks, (b) the enhanced sensitivity of the instrument allowed spectra to be obtained before the onset of sample damage occurred and finally, (c) the superior spectral resolution allowed much greater confidence in ascribing functional groups to the various components of the C1s peaks. These benefits should also be true of any monochromated source with the flood gun settings optimised, but the high transmission of the ESCA300 ensured that sample damage did not become an issue.

The undoubted advantage of using the monochromated XPS approach has led to a resurgence in the use of the method. Results from this project provided the necessary evidence to justify having the existing monochromated source on the VG Scientific ESCALAB MkII at the University of Surrey upgraded. This upgrade subsequently allowed spectra from the failure surfaces of DCB joints to be obtained at the University of Surrey, rather than relying solely on instrument time at the SERC Daresbury Laboratory, (pages 153-155).

8.3 Failure Mechanisms

8.3.1 Dry Failure

For both the reformulated and standard resins, butt-joints failed with the
characteristic conchoidal fracture surface described in detail in Chapter 4. Failure is believed to have initiated at a defect, such as a cavity in the polymer. The crack then travelled close to the interface for a distance of a few mm before becoming unstable and moving back into the bulk of the polymer, such that the remaining area of the fracture was visibly cohesive, within the layer of adhesive. At first sight there appeared to be some discrepancy between imaging XPS results obtained from of the conchoidal fracture surface and spectra acquired from the mirror zone using the Scienta ESCA300, however, this is thought to be merely an example of the problem of thresholding in iXPS. (Prior to the acquisition of an image by iXPS, it is necessary to set a minimum intensity, or threshold, below which no signal is recorded). The use of scatter diagrams has in the past proved extremely useful in the interpretation of Scanning Auger Microscopy, (SAM) images, (Castle et al., 1994). Current datasystems such as the Fisons Eclipse, make use of a form of this method for processing data obtained by iXPS. The image of the mirror zone edge, (page 128), suggested that failure within the region occurred interfacially, (i.e. there was no evidence of the characteristic signature of the polymer in this area). However, spectra acquired from this area at a later date, using the Scienta ESCA300 spectrometer did reveal the presence of groups characteristic of LCR000. Two possible explanations have been proposed to account for this anomaly. First, the VG Scientific ESCASCOPE, like the ESCALAB MkII is equipped with a twin-anode X-ray source. The area irradiated by X-rays is too large for an electron flood gun to work effectively. In addition, achromatic sources do not generally produce such significant charging effects as with a monochromated source, and the electrons generated at the aluminium window are usually sufficient to neutralise surface charge. The alumina substrate used during this particular study was particularly susceptible to charging, so it was possible that the differential charging effects described previously, (page 42), caused peak broadening, thus obscuring the true shape of the Cls peak. Alternatively, some samples may have failed interfacially within the mirror zone and others near-interfacially, depending upon the geometry and exact location of the defect at which failure was initiated. This is illustrated schematically in Figure 8.1.
Results from dry failures suggested that failures were initiated at defects lying close to the resin/ceramic interface. The explanation suggested for this observation is that there is a mismatch in the mechanical properties such as Poisson’s ratio in the interfacial region, thus increasing the likelihood that failure will initiate at a defect within this area, rather than at a defect in the bulk of the adhesive.

![Figure 8.1](image)

**Figure 8.1** Schematic of failure initiation at a cavity within the mirror zone, (a) interfacial failure and (b) near-interfacial failure.

### 8.3.2 Failure Under a Hostile Environment

It was possible to draw on the information obtained using the various experimental techniques in order to propose a detailed failure mechanism for the LCR000/alumina system in the presence of a hostile environment, (i.e. water at 50°C). Initial studies on LCR000/as-received alumina joints suggested that prolonged, (greater than 14 days) immersion in water at 50°C produced interfacial failures, (ESCALAB
MkII data. IRS results, (page 160) revealed a much faster rate of water uptake after an initial 14 day interval. This initial 14 day period appears to have been critical, either to allow water enough time to permeate to the centre of the joint, or to allow aggregation of water molecules to a certain critical concentration, (Kinloch, 1980). Examination of samples immersed in water for less than 14 days displayed a mixed mode of failure, with patches of polymer remaining on both sides of the failure. Diffusion of water from the edge of the joint inwards might have been expected to produce an annular type of failure, with an outer region of near-interfacial failure and an inner region of cohesive failure. Though, any asymmetry during loading could account for the more patchy failure surfaces actually observed.

In contrast to ESCALAB data from samples immersed in water for two weeks, information available using the ESCA300, subsequently revealed that although failure was occurring close to the interface, some polymer residue did remain on the fracture surface. This led to the failures being described as near-interfacial. There was a subtle difference observed between this overlayer and the bulk LCR000. The $\pi - \pi^*$ shake-up satellite, indicative of aromatic groups, was absent in the C1s spectra recorded from all samples of this type. As mentioned in the section describing the difficulties associated with working on this particular system, the rough, heterogeneous nature of the as-received alumina prevented us from studying the nature of this overlayer in more detail.

Additional information about the nature of this overlayer was obtained from samples fabricated using model substrates, (i.e. quartz, polished alumina and silicon wafers). Results from butt-joints made out of these materials immersed in water for in excess of two weeks, revealed that failure also occurred with a thin overlayer of polymer remaining on one of the joint surfaces. Again, there was no evidence of any aromaticity within this layer. ARXPS studies were carried out using both spectrometers, as these samples had a suitable surface finish. The overlayers appeared uniform, (consistent with AFM work, Bromley-Barratt, 1993) and the thickness of the polymer was calculated as lying between 1-2 nm. Orientation of some of the oxygen functional groups within this overlayer was also observed. This effect was most
pronounced with the more acidic substrates, (i.e. silicon). It is not unreasonable to expect a similar result with as-received alumina, however, it is not possible to substantiate this theory using ARXPS.

The discovery that the polymer residue remaining on the failure surfaces contained no aromatic groups was interesting, as the base resin, which forms about 90% of the total formulation, contains large numbers of such groups. This prompted the investigation of one of the minor components present in LCR000. The reactive diluent, (TEGDMA), added as about 9% by volume of the formulation, contains no aromatic groups and therefore warranted further consideration. The other components of the resin are added as fractions of a percent and therefore our attention was concentrated on TEGDMA. Again, the information available to us was as a result of post failure analysis, so it was necessary to make certain inferences about the precise events leading up to failure. Results from post failure analysis revealed the presence of a layer of polymer which contained no aromatic groups on one of the joint surfaces. The theory proposed was therefore, that the TEGDMA molecules aggregated at the interface, where they were selectively adsorbed in preference to the molecules of the base resin. This produced a strongly bound layer of TEGDMA, 1-2 nm in thickness. In the presence of water, the strongly bound layer would have prevented water molecules from reaching the interface itself, such that failure occurred at the transition between two different polymer phases. It should be noted, that the formation of a weak boundary layer of this type is atypical, because it is not a region of low cohesive strength. An adsorbed layer of polymer molecules at the interface would tend to reduce the free volume available, (i.e. as they are effectively pinned by polymer/substrate interactions), making it more likely for water molecules to aggregate between the polymer chains of the bulk, where there is more free volume.

From these results, it was not possible to ascertain whether the TEGDMA molecules displaced the molecules of the base resin from the interfacial region, or whether they were simply adsorbed in preference. In some polymer systems, the molecules of one of the components (above a certain concentration, known as the critical micelle concentration), aggregate to form micelles. The micelles tend to form
either spherical or rod-like structures. It was unclear whether the TEGDMA molecules combined initially in the bulk to form micelles which then aggregated at the interface, or whether individual molecules were adsorbed. The latter is favoured, as the TEGDMA molecules are symmetrical. Molecules that have a hydrophillic head and a hydrophobic tail are able to form micelles, but the TEGDMA molecule has a hydrophillic group at both ends. In addition, the large free volume necessary for the formation of micelles would also require the displacement of the heavily branched base resin molecules. It is therefore more likely that individual molecules reached the interface, rather than micellar aggregates of TEGDMA.

If the TEGDMA molecules are distributed evenly throughout the resin, cross-linking to other molecules occurs. However, if as this model proposes, the TEGDMA molecules aggregate at the interface, then the likelihood is, that not all of them will be involved in cross-linking, (i.e. as they will be packed closer together than in the bulk, hindering the approach of the branched molecules of the base resin). The water molecules would then be able to attack the free end of the TEGDMA molecule. In the dry case, the presence of a strongly bound layer of TEGDMA would not pose a problem, but in the presence of water, the unbound end of the TEGDMA molecule could interact with the water molecules, (as TEGDMA is a very hydrophillic molecule).

To test this failure model, ToF-SIMS was employed. Results from this technique again supported the idea that the TEGDMA formed an in-situ WBL at the interface, illustrated schematically in Figure 8.2. Conventionally, a WBL is classed as a region of low cohesive strength, (Brewis in Packham, 1992), but as Figure 8.3 indicates, in this instance failure has occurred at the interface between the strongly bound layer of TEGDMA and the bulk, not within the layer of TEGDMA itself.

In order for this type of failure to be observed, samples had to have been immersed in water for at least 14 days. IR spectroscopy studies on the uptake of water by a sample of LCR000 between two microscope slides indicated that there was a sharp increase in the rate of water uptake after about 14 days, (page 160). The next stage is therefore to consider the mechanism of water attack in more detail.
Chapter 8. The Adhesion and Failure of Photocured Resin/Ceramic Systems

Figure 8.2 Schematic of the formation of a WBL.

Figure 8.3 Locus of failure following prolonged immersion in water.
8.3.3 Mechanisms of Water Attack

Several different pathways along which diffusion of water could occur in organic coatings have been proposed, (Funke, 1988). Of the various pathways suggested, activated diffusion, which depends on the segmental mobility of the binder molecules, is the least likely. The LCR000 series of resins is known to form a highly crosslinked three dimensional network, which would not facilitate diffusion of polymer molecules. Non-activated diffusion occurs in defects in the polymer, such as cracks or pores. Post failure analysis of the LCR000/alumina joints by SEM, revealed the presence of what are believed to be cavities, present in the LCR000 resin. The cavities acted as sites for failure initiation to occur under dry conditions, and the same defects could also accelerate diffusion of water in wet conditions. The possibility of interfacial diffusion was also considered by Funke.

Buchwalter et al. have carried out detailed studies of organic coatings on ceramic substrates, in particular, on polyimide systems, (Buchwalter, 1990). When the thermodynamics of polymer/ceramic systems is considered, it is apparent that in cases where only secondary forces act across the interface, the presence of a third phase such as water, will result in displacement of the polymer coating, (Buchwalter, 1990). This was illustrated on page 139, in the work of adhesion calculations for the LCR000 system. To avoid the situation where spontaneous disbonding can occur, two approaches have been adopted. The first approach is to design a system which promotes primary bonding at the interface, (Kinloch et al., 1975). Alternatively, various measures may be taken to prevent the water from ever reaching the interfacial region. These measures have been summarised by Funke, (1987).

Firstly, in general if a high crosslink density can be achieved, the polymer will have good barrier properties. Although, this can sometimes lead to a compromise between the barrier and the mechanical properties. If the coating is brittle, there is also an increased likelihood of defects occurring, which provide a direct pathway to the interface. Crystalline polymers have very low permeability to water, however, they are seldom used in coatings applications. Another approach is to increase the path length along which the water must diffuse to reach the interface. Some systems contain fillers
with a plate like geometry, which in addition to altering the mechanical properties of the coating, also help to fulfil this role.

Finally, Funke introduces the concept of "co-operative bonding". Co-operative bonding involves the use of polymers with rigid backbones, with the sites which interact with the substrate present as pendant side groups. This is illustrated schematically in Figure 8.4. The theory proposed by Funke, (Funke, 1988), is that co-operative bonding operates by preventing water molecules from disrupting interfacial bonds. To displace a coating which utilises co-operative bonding, the water molecules would need to rupture all of the neighbouring bonds at the interface simultaneously. As this is an extremely unlikely event, the coating should have much better durability.

For co-operative bonding to occur, the polymer molecules must first be capable of aligning themselves parallel to the substrate surface, with the pendant side groups oriented towards the adherend surface, (rather like a comb). Although the theory for co-operative bonding appears reasonable, branched polymers generally become entangled in the melt, which would make it difficult for them to align

![Figure 8.4 Schematic illustrating Funke's concept of co-operative bonding.](image-url)
themselves neatly like a series of combs at the interface. The second flaw with the co-operative bonding argument, is that it is insufficient to have a strongly bound layer adjacent to the interface, without strong links between that layer and the rest of the coating. The production of a strongly bound layer incompatible with the bulk of the coating would simply move the locus of failure to the interface between those two regions, as observed with the LCR000 system.

Sufficient experimental evidence to support the theory of the in-situ formation of a layer of TEGDMA at the interface has been obtained, the next step is to consider why the TEGDMA molecules should behave in this manner.

8.4 Polymer Adsorption: The Role in Joint Integrity

8.4.1 Introduction
In order to have in-situ formation of a layer of TEGDMA molecules, there must have been an overall driving force operating which favoured this particular process. In some cases, this may result from a difference in the adsorption affinity of the individual components within the resin, (Roe, 1980). It has been demonstrated that the TEGDMA molecules do not segregate towards all surfaces, (i.e. the surface of LCR000 cured against Melinex™ film, revealed the characteristic Cls spectrum of the resin, the \( \pi - \pi^* \) satellite clearly evident). It is appropriate to consider the process of WBL formation in two separate stages: (a) movement of molecules towards the interface and (b) selective adsorption of one or, rejection of another component, (i.e. maintaining the layer at the interface).

8.4.2 Movement of Polymer Molecules
Polymer molecules are able to reptate, where various sections of the polymer chains rotate to take up different conformations. A detailed account of the theory of reptation, developed by de Gennes was published in *J.Chem.Phys.*, (1971).
Additionally, the chains themselves can move by Brownian motion, (Lee, 1992). The highly aromatic molecules which make up the majority of the LCR000 resin, are very rigid, due to the presence of aromatic groups along the chain, making it more difficult for the molecules to reptate freely. In addition to this, the molecules are also heavily branched, increasing the likelihood of entanglement occurring during Brownian motion. The TEGDMA molecules on the other hand, are shorter, (20 Å, approx.), linear and less stiff than the molecules of the base resin, (i.e. as they contain no aromatic groups in the backbone of the molecule). The molecules which comprise the base resin are at least 100 Å in length, (and of course, include side branches). These features allow TEGDMA molecules to move more freely within the polymer resin and are therefore likely to increase the overall distance they can travel before molecular entanglement occurs.

Increased mobility within the resin is obviously a factor which could allow the TEGDMA molecules to reach the interfacial region, the next stage is to consider what prevents them from then moving back into the bulk again. It is also unclear whether steric effects help effectively reject the base resin molecules from this region, or not.

8.4.3 Selective Adsorption

The importance of understanding the kinetics of polymer adsorption has been recognised for some time. A session at the International Conference on Adhesion and Adsorption of Polymers in Honolulu, 1979, was devoted to this very topic, (Lee, 1980). Lipatov reported there that "the problem of the structure of surface and boundary layers of polymers on solid surfaces is one of the most important in the theories of adsorption and adhesion of polymers", (Lipatov, 1980).

First, it would therefore be useful to consider what happens when a liquid is placed on a solid surface. Gregg reported the effect of a solid surface in increasing the density of a liquid, (Gregg, 1961). This effect is illustrated schematically in Figure 8.5.
This effect is explained by the fact that when a liquid is placed in contact with a solid surface, the molecules on one side of the liquid are replaced by those of the solid, (Figure 8.5(b)). This produces an effective increase in the density of liquid molecules at the interface, the liquid is then described as having been adsorbed on to the solid surface. Studies of the region immediately adjacent to the surface have indicated that the density of polymer molecules within this region is controlled by the following factors, (i) the cohesive energy of the polymer, (ii) the surface free energy of the solid and (iii) the flexibility of the polymer chain, (Lipatov, 1975).

First let us consider the situation where a homopolymer adsorbs on a surface, as this is one of the simplest possible scenarios. Previous studies on a variety of substrates, have indicated that it is possible to observe reorganisation of the polymer molecules close to the interface, (Chehimi and Watts, 1993). ARXPS has proved a useful technique to study the nature of the polymer close to the interface. Chehimi and Watts reported orientation of the PMMA molecules at the interface with a silica
substrate, (1993). In this particular example, the reorientation of molecules could be attributed not only to the acid/base interactions operating, but also longer range reorganisation of the functional groups. It is interesting to note that these reorientation effects may be observed over much larger distances than those over which chemical bonds operate, (Lee, 1991(a)). Table 8.1 lists typical interaction distances for various chemical bonds.

Table 8.1 Interaction distances for chemical bonds.

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Interaction distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>0.15 - 2.4</td>
</tr>
<tr>
<td>Ionic</td>
<td>0.15 - 2.4</td>
</tr>
<tr>
<td>Metallic</td>
<td>0.26 - 3.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.26 - 3.0</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>&lt; 3</td>
</tr>
</tbody>
</table>

Previous studies have also been carried out on mixtures of chemically similar polymers, where only the polymer chain length was varied. The results of this work revealed a molecular weight dependence on adsorption, (Encyclopedia of Polymer Science, Supplement Volume, 1989). The longer chains are preferentially adsorbed and will displace even small molecules which have previously been adsorbed, see Figure 8.6. The reason suggested for this, was that adsorption of long molecules enables a large number of smaller molecules to be returned to the bulk, thus producing an increase in the entropy of the overall system. A similar effect was observed during fractional precipitation of polymers, (Roe, 1980).

Adsorption studies in the past have often been carried out using very dilute solutions of polymers, (Silberberg, 1962). Silberberg remarked that for adhesives and coatings applications, it may be more appropriate to study the behaviour (e.g.
conformation), of individual polymer molecules rather than try to draw comparisons with data obtained from studies involving adsorption from dilute solutions, (Silberberg, 1980). The viscosity of the LCR000 system is very high, (greater than 600 poise), so it was particularly important to include information about the behaviour of polymer molecules in the melt, not just in dilute solution. Thus, the relevance of polymer adsorption research to adhesion science is clear, but a strong link between the two disciplines has yet to be established.

Figure 8.6 Schematic illustrating the molecular weight dependence of adsorption.
Chapter 8. The Adhesion and Failure of Photocured Resin/Ceramic Systems

The situation that exists with LCR000 will now be considered. In this system, the two main components in the resin are not chemically similar. They also vary in their structures, for example, branched versus unbranched, rigid versus flexible. Other studies involving systems comprised of dissimilar polymers have revealed some interesting results. Silberberg's work on the adsorption of polymers from the melt, (1980), revealed that for multicomponent systems in the presence of a high energy surface, (such as ceramics), preferential adsorption of one of the components was observed. A correlation between selective adsorption and the surface tension of the adsorbate was reported. Roe also recorded observing selective adsorption, which appeared to be independent of the solution concentration, (1980). Lipatov's work describes selective adsorption occurring during cure, resulting in the displacement of the other polymer species from the interfacial region, (Lipatov, 1980)

Of particular relevance to this system, are the results from a much earlier study of competitive adsorption. Gregg carried out work on the adsorption of a mixture of methyl acetate and benzene, onto the surface of alumina, (in Kipling, 1965). The methyl acetate was selectively adsorbed on to the alumina surface. This result is explained by the fact that the polar centre of the ester group in the methyl acetate molecule can bind with the polar groups present on the inorganic surface. This observation is particularly important, as the methyl acetate/benzene mixture provides a suitable model system with which to compare LCR000, (i.e. as the TEGDMA molecules also contain similar groups and the base resin is highly aromatic). This is illustrated schematically in Figure 8.7(a) and (b).

Chu and Murphy also report interaction of the carbonyl groups of a polyimide coating with the surface hydroxyl groups of an alumina surface to produce a hemiketal group, illustrated in Figure 8.7(c), (Chu and Murphy, 1992). Results from molecular modelling also suggested that the C=O link is the most likely section of the TEGDMA molecule to interact with the alumina substrate, (although in this case, the alumina surface generated by the model terminated with O²⁻ rather than OH⁻ groups). As the C=O link can interact strongly with both O²⁻ and OH⁻ groups this should not have affected results. Alumina substrates also have hydroxyl groups present on the surface,
(Chu and Murphy, 1992). Work by Olefjord et al. has indicated that the relative shifts on the O1s peak for OH\textsuperscript{-} and O\textsuperscript{2-} groups are very similar, to within about 0.2 eV, (Olefjord, 1994). This makes it difficult to determine the relative proportion of hydroxyl groups present on the surface by XPS. In addition to this, Al(OH)\textsubscript{3} is believed to degrade under exposure to X-rays, (Olefjord, 1994).

ARXPS studies indicated that it was in fact the C-O bonds that were oriented towards the substrate, rather than the C=O groups, (indicated by an increase in the intensity of the C-O peak at high TOA's). This can be explained by considering a single molecule of TEGDMA adsorbed on to the surface of alumina, (page 200). The angle at which the molecule docks most favourably with the substrate, about 40°, means that there will be four C-O bonds to every C=O bond, not necessarily interacting with, but in close proximity to the interface, making it appear as if the C-O bonds are in some way interacting with the substrate. In reality, the C=O sites on the TEGDMA molecules interact with the alumina and it is the angle at which the molecules approach the substrate which results in the increased concentration of C-O groups at high TOA's of analysis. This preferred orientation effect is therefore consistent with the work of Chehimi and Watts on PMMA on glass systems.
Figure 8.7 Interaction of a molecule of, (a) methyl acetate, (b) TEGDMA and (c) polyimide, with alumina.
8.4.4 Structure of the Adsorbed Layer

The structure of the adsorbed interfacial and boundary layers is liable to have an important influence on the properties of the adhesive system. Lipatov indicated from his studies, that the packing density of molecules within this region is higher than that of the bulk, (Lipatov, 1980). In the case of LCR000, the TEGDMA molecules adsorbed at the surface were too short (20 Å) to have enabled the formation of loops and trains, described earlier. In cases where surface coverage is low, molecules can lie parallel to the surface, but molecular modelling has indicated that the TEGDMA molecules are more likely to lie at an angle of about 40° to the alumina surface, (Chapter 7).

The TEGDMA molecule depicted in Figure 8.7(b) has a free end, capable of rotating to a certain degree. This is therefore likely to determine how closely the next TEGDMA molecule can be positioned to the first.

Selective adsorption of TEGDMA molecules from the resin must cause a depletion of TEGDMA in the region adjacent to the interface. Without access to information regarding the surface coverage of the alumina by TEGDMA, it is difficult to calculate accurately how far this region extends into the bulk resin. The sharpness of the transition in properties between an adsorbed layer and the bulk will influence the locus of failure, a gradual transition in properties being most desirable in the majority of cases.

Using the XPS data, it was possible to produce an estimate of the magnitude of the region of the bulk depleted of TEGDMA. This was carried out by comparing the intensity of the $\pi \rightarrow \pi^*$ shake-up satellite in the high resolution C1s spectra obtained from the fracture surfaces, with that obtained from a sample of LCR000. There was obviously a degree of inaccuracy in this particular method, as the shake-up satellite has only a fraction, (less than 10 %) of the intensity of the main C-C/C-H peak. It was therefore decided to measure differences in peak height rather than peak area. Table 8.2 compares the heights of the $\pi \rightarrow \pi^*$ shake-up satellites (relative to the height of the main peak), measured from the C1s spectra obtained from both failure surfaces.
Chapter 8. The Adhesion and Failure of Photocured Resin/Ceramic Systems

The fact that there is very little difference in intensity of the $\pi - \pi^*$ shake-up satellite between the two samples, suggests that the failure has occurred at the interface between the adsorbed layer of TEGDMA and the bulk. The XPS data indicates a rather abrupt interface between the TEGDMA and the bulk, which points to a monolayer or thereabouts of the reactive diluent having been adsorbed on to the surface of the alumina. This produced a corresponding minor depletion of TEGDMA in the bulk, undetectable using XPS, this is illustrated schematically in Figure 8.8. It is likely that the depleted region, (only 1-2 nm in thickness), is rapidly replenished with TEGDMA molecules from the bulk region, (between 150-200 $\mu$m thickness), so that there is no real transition in composition to be detected by XPS.

Table 8.2 Height of the $\pi - \pi^*$ shake-up satellite, relative to the C-C/C-H component.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative intensity of shake-up satellite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully-cured LCR000</td>
<td>1.5</td>
</tr>
<tr>
<td>Polymer side of a wet failure</td>
<td>2.2</td>
</tr>
<tr>
<td>Ceramic side of a wet failure</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Chapter 8. The Adhesion and Failure of Photocured Resin/Ceramic Systems

8.5 Comparison of LCR000 with ModLCR000

In simple tension, (i.e. butt-joints), the modified resin appeared to perform better than the standard resin. However, results from Boeing wedge test samples indicated that the reverse was true. This apparent anomaly is likely to be as a result of (i) the increased brittleness of the reformulated resin and (ii) the difficulties associated with obtaining a uniform glue-line with the modified resin due to its high viscosity.

With the removal of the TEGDMA molecules, bonding of ModLCR000 to the alumina is likely to occur through C=O sites present in the aromatic molecules of the base resin.
8.6 Summary

This chapter has drawn together data from all the various experimental techniques, in order to postulate adhesion failure mechanisms for the system under both ambient and hostile conditions. It has also provided detailed information about the adhesion and polymer organisation near the interface. The presence of water appeared to be particularly detrimental to this system, due to the formation of a layer of TEGDMA at the interface, extremely hydrophillic in nature. The formation of this layer having been facilitated by (i) the mobility of the TEGDMA molecules within the resin and (ii) the presence of carbonyl oxygen groups, (C=O), in the molecule which were able to bind to specific sites on the substrate once the molecules reached the interfacial region.

One of the most notable features of this project is that it has effectively gone "full circle". The system was characterised under both wet and dry conditions and on the basis of results a possible reformulation was suggested. Results from the new system, (ModLCR000), produced modest improvements in the properties of the adhesive. In order to reach this stage, it was necessary to identify the weakest link in the system, which in the case of LCR000 was the strongly bound layer of TEGDMA. This was an important observation, as it indicated that even with good bonding at the interface, joint performance may still be poor, if as in this case, the weakest link is simply moved slightly away from the interface. Once this link was identified, it was possible to modify the system correspondingly. Effects at the interface were of critical importance as they influenced the composition of the near interfacial region, which in turn caused slight changes in the composition of the polymer.

Some of the findings of this work are related specifically to the study of insulating materials. Notably, that in order to identify the locus of an adhesive failure accurately, (where both insulating adherends and adhesives are involved), great care must be taken to eliminate the charging effects which may otherwise obscure results.

Adhesives and coatings manufacturers might usefully carry out preliminary adsorption experiments using mixtures of the individual components from a suggested new formulation. If selective adsorption of one of the components were to be
observed, particularly if the component was hydrophilic in nature, it could be replaced before full scale production began, with minimum time and resources wasted. Adsorption studies could also be usefully applied in situations where a component is desired at an interface, such as an adhesion promoter. If a system could be produced where the adhesion promoter were preferentially adsorbed by the substrate, the quantity added to the formulation could be reduced.
Chapter 9

Conclusions

9.1 Conclusions

Several conclusions have been drawn from this work. Firstly, initial characterisation of the adherend revealed a rough, heterogeneous surface with which to bond. Investigation of the acid/base properties of the resin, (by IGC), indicated amphoteric properties, with a slight bias towards a more basic character. Subsequent studies of the LCR000/alumina system under ambient conditions, allowed an adhesion failure mechanism to be proposed, which centred on the presence of defects within the material initiating failure.

From the environmental studies, it was clear that the length of immersion in water at 50°C altered the failure mode, from conchoidal in dry conditions, to near interfacial, following prolonged immersion. A clear transition in the rate of water uptake was observed, (by IRS), following an initial 14 day exposure. It was also observed that following immersion in water for greater than two weeks, highly polished substrates had less residual strength than rough (i.e. as-received) substrates, the silicon joints had a tendency to simply fall apart. This is likely to be as a result of the increased path length available for bonding.

The use of a monochromated X-ray source, coupled with a low energy electron flood gun to neutralise surface charge, proved essential to determine the locus of failure within alumina joints accurately. This was due to the nature of the charging effects observed during analysis of alumina samples.

Prolonged water immersion results in near-interfacial failure, with about 1-2 nm of polymer remaining on the inorganic substrate. This polymer overlayer contained no aromatic groups, and was shown to consist mainly of a strongly adsorbed layer of the TEGDMA component. The locus of failure remained unaltered for all three substrates.
investigated, (i.e. polished alumina, silicon and quartz). This ruled out the possibility that the presence of silica and, or other impurity ions in the alumina were in some way contributing to its poor durability. Any effects due to localised differences in chemistry appear to have been overshadowed by the properties of the nanoscale region of polymer adjacent to the inorganic substrate, whose chemical properties are very different to those of the bulk polymer. This aggregation of the minor resin components towards the inorganic substrate can therefore lead to a transition in mechanical properties.

Although the locus of failure remained unaltered regardless of the substrate investigated, the orientation of functional groups within the polymer overlayer was more pronounced with increased substrate acidity. XPS and ToF-SIMS played an important role in the examination of the fracture surfaces. The complementary nature of the two techniques must also be emphasised. The ability of XPS to determine the overlayer thickness and identify aromatic components quite simply via the $\pi - \pi^*$ transition is well known, however when this is combined with the molecular specificity of ToF-SIMS a fully quantitative scheme can be produced, which has been supported with molecular modelling.

Of importance to adhesion scientists is, not so much the recognition of a segregated zone, as this has been reported in XPS studies several times going back many years, (Watts and Castle, 1984), but the recognition that it may reduce the environmental durability of a joint. The logical remedy is to reformulate the resin with the component removed. Reformulation resulted in a slight increase in the acidity of the material. There were also slight differences in XPS spectra recorded, (an increase in the C:O ratio and the intensity of the shake-up satellite). This is however, clearly an oversimplification, as the physical properties of the uncured resin may be compromised by removal of the diluent, (for example, the viscosity would increase). Removal of the TEGDMA component from the formulation produced a modest improvement in joint performance, but also introduced additional problems, particularly during the fabrication of joints, due to the increased viscosity of the resin. In order to assess the environmental stability of the resin/ceramic system, it was necessary to modify an
Chapter 9. Conclusions

existing test method, (the Boeing wedge test).

The key message this work should convey to formulation chemists is that, when choosing the components which make up a new formulation, consideration needs to be given as to how the individual components in a formulation might interact with each other, (i.e. the presence or absence of non-covalent intermolecular interactions), as well as with the adherend. It is possible that components purposely added for adhesion promotion could not only bind strongly to the adherend as desired, but additionally set up a region of weakness. Adhesion to the substrate would therefore be improved, but if the locus of failure is simply moved to the interface between the strongly bound layer and the bulk of the polymer, then joint performance will not have been improved.

Studies of this type provide a new and exciting route to the definition of adhesion failures and, perhaps, a more thorough understanding of the mass transport phenomena that occur prior to the curing of commercial resins used for adhesives, coatings or encapsulant applications. The importance of understanding the manner in which polymer molecules are adsorbed on to surfaces from the melt has clearly been emphasised here, suggesting a possible direction for future work. There is clearly a need to carry out more detailed investigations of the way in which medium sized molecules are adsorbed from the polymer melt on to surfaces.

9.2 Suggestions for Future Work

The importance of the link between classical physical chemistry experiments, (of, in particular the adsorption of macromolecules on surfaces) and adhesion has been illustrated. The potential therefore exists to include adsorption related experiments early on in the formulation process, in order to predict whether the individual components of a resin are likely to compete for sites on a specified adherend surface, or not. With access to powerful molecular modelling packages, these effects could also be studied systematically, rather than by making up a whole series of resins and
Chapter 9. Conclusions

assessing their performance by trial and error.

Considerable scope now exists for a more predictive approach to resin formulation. It would be interesting to use a combination of molecular modelling, with adsorption type experiments to investigate the extent to which the information could be used in the design of adhesives and coatings with good durability. Clearly, there would still be a need to study the mechanical properties of the coating, (viz. the brittle nature of ModLCR000), but, considerable time could be saved by first ensuring that the resin did not contain components which behave like TEGDMA in the presence of water. It may therefore be possible to avoid certain components altogether, rather than discovering in post failure analysis that they were in fact the cause of premature failure, or impaired performance.

It would also be interesting to carry out further, detailed studies of the interphase region, in order to discover more about the interphase chemistry of the reformulated resin/alumina system. This area of work would also involve the collection of additional durability data. Finally, the importance of determining the precise mechanisms by which diffusion of water occurs in these materials should not be forgotten, as it is necessary to study the kinetics, as well as the thermodynamics of a system.
References


References


References


Cerius, (materials modelling, diffraction simulation), v3.2, Molecular Simulations Inc., Cambridge, U.K.


Cumpson, P., "Composition-Depth Profiles by Angle-Resolved XPS: A Comparison of Methods", presented at ECASIA'93, 5th Conference on Applications of Surface and Interface Analysis, 4 - 8 October, 1993, Catania, Sicily, Italy.


References


References


References


Le Gressus, C. and Blaise, G., "Insulator Surface Analysis", presented at ECASIA'93, 5th Conference on Applications of Surface and Interface Analysis, 4 - 8 October, 1993, Catania, Sicily, Italy.


MOPAC '93, QCPE Program 455, University of Indiana, Bloomington, USA.


Newton, I., Opticks, (1730), reprinted by Dover 194, 376, 397, (1952).


References

Fransisco, 1960).


Rogers, S.C., reprinted from *Adhesives Age*, April, (1988(a)).

Rogers, S.C., Proc. SPIE/SIRA Meeting, 229-233, April, (1988(b)).


References


Sybyl (modelling package), SYBYL v6.03, Tripos Associates, centennial House, Bracknell, RG12 1NN.


References


Vasenin, R.M., *Adhesives Age*, 8(5), 21, (1965(a)).

Vasenin, R.M., *Adhesives Age*, 8(6), 30, (1965(b)).


Watts, J.F., *Vacuum*, 45(6/7), 653-671, (1994(c)).


Wentworth, S.E., Bergquist, P.R., Sennett, S.E., Mead, J.L. and Zukas, W.X., "Recent Investigations of Surface Effects on Adhesive Cure Chemistry", presented at Adhesion '93, the 5th International Conference, 6 - 8 September, 1993, The University of York, U.K.


