The Adhesion of An Optical Adhesive to Glass Substrates for Optoelectronics Applications

By

Nadarajah Sambasivan

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

November 2001

The Surface Analysis Laboratory
School of Engineering
University of Surrey
Guildford
Surrey, GU2 7XH, UK
ABSTRACT

Surface characterisation and failure mechanisms of adhesively bonded glass butt joints were studied. Materials of relevance to the adhesive bonding of fibre optic components were employed: a fine annealed Grade A glass (Schott™ BK-7), and a fast curing epoxy based optical adhesive. The joint behaviour and their durability under adverse environmental conditions were investigated, and the subsequent, failed joint fracture surfaces were examined using XPS, ToF-SIMS and SEM. Surface analysis techniques have been employed to characterise components of the adhesive systems and to interrogate the surface of failed joints with a view to establishing the locus of failure.

Joints were immersed in pure water for period of 0 - 270 days at 35°C. Substantial reduction in the bond strength within a few days of water immersion was observed. Also for the joints left in for a prolonged exposure periods (> 100 days) the strength values reached a minimum value. The surface analysis of the joints has indicated a cochoidal brittle fracture through the adhesive in dry conditions, and an interfacial failure for wet joint fractures. Calculations of the polymer thickness on the interfacial surfaces indicated a decrease in overlayer thickness. This reduction reached a constant value for joints left in water for more than 100 days. During this investigation surfaces segregation of minor components of the adhesive such as amine and diluent was also identified by ToF-SIMS and XPS. In order to study this phenomenon further, reformulation of the adhesive has been carried out.

Six adhesives were formulated, of which three resins were based on the change in diluent content of the system, three were based on the change in amine concentrations. This work has clearly identified amine segregation only at the interfacially failed joints. It is expected that when the joints cures very fast, even if the formulation contains very high proportion of amine, the segregation is minimal. Also, some evidence of diluent migration at the interfaces was observed during the reformulation studies.
The Adhesion of An Optical Adhesive to Glass Substrates for Optoelectronics Applications

ACKNOWLEDGMENTS

I would like to give my heart felt thanks to Professor John Watts, for his continuous support and the ever-lasting enthusiasm he has shown to obtain a very good outcome from this research. I would never forget the out of hour discussions and encouragements he has given, especially when things were not going as planned. Also, my sincere gratitude belongs to all the members of Surface and Interface Reactions Group, especially Professor Jim Castle, Mr Andy Brown and Mr Steve Greaves for their expert and timely advices on the development of this work.

For their generosity in the funding and flexibility in allowing me to utilise instruments, I wish to thank Alcatel Submarine Networks. Also I am grateful to Dr Phil Norman, Mr Simon Kendrick, Mr Mike Kitching and everybody at the materials group for their support and encouragement.

Last not least, I take this opportunity to thank my wife for putting up with me for the past few months while I was occupied with thesis writing for almost every weekend. Also, I pay my sincere gratitude to my parents, sister and brother-in law for their affectionate support during times of difficulties.
CONTENTS

ABSTRACT i
ACKNOWLEDGMENTS ii
TABLE OF CONTENTS iii

CHAPTER ONE – INTRODUCTION 1

CHAPTER TWO - APPLICATIONS OF OPTICAL RESINS AND SURFACE ANALYSIS 5

2.1 Industrial Background 5
   2.1.1 Epoxies for Optoelectronic Industry 5
       2.1.1.1 Use of Epoxies in Fibre Connections 6
       2.1.1.2 Epoxide Applications in Optical Devices 8
       2.1.1.3 Mercaptan Based Epoxy Resins for Optical Components 10

2.2 Practical Aspects of Adhesion Theory 11
   2.2.1 Mechanisms of Adhesion 11
       2.2.1.1 Mechanical Interlocking 12
       2.2.1.2 Diffusion Theory 14
       2.2.1.3 Electronic Theory 15
       2.2.1.4 Adsorption Theory 16

2.3 Adsorption of molecules on to the Surfaces 21

2.4 Wetting and Spreading 23
   2.4.1 Contact Angle 23
   2.4.2 Critical Surface Tension 25
   2.4.3 Surface Free Energy 25
   2.4.4 Work of Adhesion 26

2.5 Weak Boundary Layers 29

2.6 Locus of Failure 29
# CHAPTER THREE – CHOICE OF EXPERIMENTAL METHODS AND TEST MATERIALS

## 3.1 Introduction to Experimental Techniques

## 3.2 X-Ray Photoelectron Spectroscopy

- 3.2.1 Introduction
- 3.2.2 Basic Principles
- 3.2.3 Depth of Analysis
- 3.2.4 Spectral Interpretation
  - 3.2.4.1 Auger Electrons and Auger Parameter
  - 3.2.4.2 Valence Band
  - 3.2.4.3 Shake-up Satellites
  - 3.2.4.4 Chemical State Information
- 3.2.5 Quantification
- 3.2.6 Instrumentation
  - 3.2.6.1 X-Ray Source
  - 3.2.6.2 Analysers
  - 3.2.6.3 Angle Resolved XPS

## 3.3 Time of Flight Secondary Ion Mass Spectroscopy (ToF – SIMS)

- 3.3.1 Introduction
- 3.3.2 The SIMS Process
- 3.3.3 Instrumentation
  - 3.3.3.1 Primary Beam
  - 3.3.3.2 The Ion Sources
  - 3.3.3.3 Mass Analysers
  - 3.3.3.4 SIMS Imaging
- 3.3.4 Analysis of Polymers
  - 3.3.4.1 Sample Charging
  - 3.3.4.2 Static Limit for Sample Damage
- 3.3.5 Spectral Interpretation
- 3.3.6 Summary
CHAPTER THREE – SURFACE AND BULK CHARACTERISATION OF TEST MATERIALS

4.1 Introduction to Test Materials

4.1.1 Chemistry of Epoxy Resins – Tra-Con F125

4.1.1.1 Diglycidyl ether of bisphenol A (DGEBA)

4.1.1.2 Reactive Diluent - p-tert-Butyl-phenylglycidyl ether

4.1.1.3 Primary Curing Agent – Liquid Polysulphide

4.1.1.4 Co-curing Catalytic Agent – 1-(2-Aminoethyl) piperazine

4.1.2 Substrate Material – BK 7 Borosilicate Glass

4.1.2.1 Production of Glass Substrates

4.2 Material Characterisation

4.2.1 Introduction

4.2.2 Characterisation of F125 Adhesives and its Components

4.2.2.1 Analysis of Adhesive Components

4.2.2.1.1 XPS Results

4.2.2.1.2 SIMS Analysis of the Adhesive Components

4.2.2.1.2.1 SIMS of Epoxy Resin

4.2.2.1.2.2 SIMS of the Diluent

4.2.2.1.2.3 Analysis of Polysulphide by SIMS

4.2.2.1.2.4 SIMS of the Amine

4.2.2.2 Analysis of Cured F125 Adhesive System

4.2.2.2.1 SIMS of the Cured Adhesive System

4.2.2.2.2 XPS of F125 Adhesive

4.2.2.2.3 Bulk Analysis by DSC and DMA

4.2.2.2 Analysis of F125 Adhesive
4.2.2.2.1 SIMS of F125 Resin System  
4.2.2.2.2 XPS of the Adhesive  
4.2.2.2.3 Bulk Analysis by DSC and DMA  

4.2.3 Characterisation of Adherend  
4.2.3.1 Introduction  
4.2.3.2 XPS Analysis  
4.2.3.2.1 Sample Preparation  
4.2.3.2.2 Results of XPS Analysis  
4.2.3.3 Results of Analysis by SIMS  
4.2.3.4 SEM Results  

4.3 Summary  

CHAPTER FIVE – ANALYSIS OF INTERFACIAL SURFACES OF DRY  
FRACTURE  

5.1 Joint Geometry and Manufacture  
5.2 Analysis of Dry Fracture  
5.2.1 SEM Results  
5.2.2 Dry Fracture Analysis by XPS  
5.2.3 Results by ToF-SIMS Analysis  
5.2.4 Failure Mode for Dry Fracture  

5.3 Summary  

CHAPTER SIX – EFFECT OF WATER ON THE DURABILITY OF  
THE ADHESIVE JOINTS  

6.1 Background Literature  
6.2 Effect of Water in the Joint  
6.3 Mechanical Tests  
6.4 Visual Assessments by Optical Microscopy  
6.5 Analysis of Fracture Surfaces  
6.5.1 XPS Fracture Surface of 10 Days Water Soak  
6.5.2 XPS of 120 Days Water Soaked Fracture Surfaces
8.4.2 DMA of the Adhesives 180
8.4.3 XPS of the Adhesives 182
8.4.3.1 Results of XPS Analysis 182
8.4.4 ToF-SIMS of Diluent Free Resin 184

8.5 Summary 185

CHAPTER NINE – DURABILITY OF THE REFORMULATED ADHESIVE RESINS 186

9.1 Introduction 186
9.2 Fracture Strength of Joints Made from Reformulated Resins 187
9.3 Analysis of Dry Fracture of Diluent Variant Formulations 188
  9.3.1 SEM of Dry Fracture Surfaces of Diluent Variant Adhesives 188
  9.3.2 XPS of Dry Fracture Surfaces of Diluent Variant Adhesives 191
  9.3.3 SIMS of Dry Fracture Surfaces of Diluent Variant Adhesives 193
9.4 Analysis of Wet Fracture of Diluent Variant Formulations 196
  9.4.1 SEM of Wet Fracture Surfaces of Diluent Variant Adhesives 196
  9.4.2 XPS of Wet Fracture Surfaces of Diluent Variant Adhesives 199
  9.4.3 SIMS of Wet Fracture Surfaces of Diluent Variant Adhesives 202
  9.4.4 Comparison of SIMS Results 205
9.5 Analysis of Dry Fracture of Amine Variant Formulations 207
  9.5.1 SEM of Dry Fracture Surfaces of Amine Variant Adhesives 207
  9.5.2 XPS of Dry Fracture Surfaces of Amine Variant Adhesives 210
  9.5.3 SIMS of Dry Fracture Surfaces of Amine Variant Adhesives 212
9.6 Analysis of Wet Fracture of Amine Variant Formulations 214
  9.6.1 SEM of Wet Fracture Surfaces of Amine Variant Adhesives 214
  9.6.2 XPS of Wet Fracture Surfaces of Amine Variant Adhesives 216
  9.6.3 SIMS of Wet Fracture Surfaces of Amine Variant Adhesives 218
  9.6.4 Comparison of SIMS Results 221
9.7 Summary 223
CHAPTER TEN - THE FAILURE MECHANISMS OF THE COMMERCIAL AND REFORMULATED ADHESIVES 225

10.1 Introduction 225
10.2 Study of Commercial F125 Resin 225
10.3 The Study of Reformulated Adhesives 230

CHAPTER ELEVEN - CONCLUSIONS 237

11.1 Introduction 237
11.2 The Commercial Tra-Con F125 Adhesive 237
11.3 The Reformulated Resin Systems 238
11.4 Future Work 240

REFERENCES 242
CHAPTER ONE

INTRODUCTION

Formulations based on epoxy chemistry relevant to fibre optics, optoelectronics, optics, and lasers are used in a wide variety of bonding, coating, and encapsulating applications. They are valued for their excellent optical qualities, adhesive strength, durability and compatibility with wide range of substrates, and can be used in solvent-free formulations. Epoxies can be formulated to fill gaps effectively, and they are easily applied and cured, making them an appropriate material for high-throughput production environments. As the operating environments faced by epoxies are so varied, the attributes of specific epoxy formulations must also vary in many respects to produce optimal performance and reliability. As a result, many distinct epoxy formulations now exist that allow users to fine-tune the precise material for their specific needs.

Electronics manufactures 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). Fast curing epoxy resins, provide an example of one class of products available for use in this area and many of the products of this type are based on the di-glycidyl ether of bisphenol A (DGEBA) type epoxy chemistry. However the cure mechanism of the resin is different (based primarily on mercaptan) from many standard epoxide based adhesives, allowing them to cure with room temperature at rapid cure times. They also have the ability to cure through a variety of joints made with optically sensitive glass types of differing optical transmissibility and mechanical strength, such as borosilicate glasses.
Chapter One: 
Introduction

The surface composition of many of the substrates used for electronic applications is heterogeneous. A commercial borosilicate glass, with a composition of ~75% SiO₂ and ~15% B₂O₃, is generally regarded in the industry as having a higher homogeneity of the surface than that of many other optical glass surfaces such as fused silica. However it is believed that the movement of silica, soda and other species such as magnesia can result in a formation of a heterogeneous bonding surface. 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. B₂O₃ can be described as an amphoteric oxide, Na₂O and BaO are strongly basic in nature, but the silica tends to have acidic properties, and this can result in a complex adhesion situation and subsequent failure mechanism of the joint. The task for the formulators is therefore more complicated than formulating a resin, which will adhere well to silica. The work described in this thesis is of industrial relevance, in particular in the field of optical components joining technology. The project was therefore particularly demanding, as a study of the interactions between a fully formulated commercial adhesive system and a heterogeneous substrate is carried out. In general, seeking to understand the interface chemistry involves the use of the standard epoxide resin and fully formulated model epoxy resins. This allowed the individual contributions of the various components present in the model adhesives to be evaluated.

The Surface Analysis Laboratory in the School of Engineering at the University Of Surrey, is equipped with a range of surface analytical facilities, (XPS, ToF-SIMS, AES, and the scanning probe microscopes, STM and AFM), which therefore made it appropriate choice for this project. The techniques used predominantly for this work was X-ray photoelectron spectroscopy, (XPS) and time of flight secondary ion mass spectrometry, (ToF-SIMS). The MicroStructural Studies Unit is equipped with a range of scanning electron microscopes (SEM), to study both morphology and topography of the samples. Finally the bulk and cure characteristics of commercial and reformulated resins were carried out at Alcatel Submarine Networks, UK, using dynamic thermal and mechanical analyser (DMA) and differential scanning calorimetry (DSC).
The aim of this work was to employ surface specific techniques, to investigate the manner in which an optical epoxy F125 resin - Tra-Con Inc. USA, interacts with a glass substrate, in this case a borosilicate BK-7 glass - Schott, Germany. To achieve this aim, it was necessary to first characterise both adhesive and the adherend, before moving on to study the adhesive system as a whole.

The next stage of the work as described in Chapters 4, 5, 6, and 7 was to establish adhesion and failure mechanisms for the system, first, in standard conditions, (i.e. standard atmospheric temperature and pressure, SATP) and then in the presence of a hostile environment, (water at 35°C). Information gained at this stage was to be used in conjunction with the formulated model epoxy resins to achieve a complete understanding of the adhesive.

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 MkIII) and fractured in-situ with the aid of a heavily modified VG Scientific T-peel stage. It was also intended as a convenient geometry, to compare the results obtained from similar experiment previously carried out at Surrey. Finally the geometry also provides a direct resemblance of many optical components using BK-7 as substrate material.

In order to define the precise locus failure within the joints, angle dependant XPS studies were carried out (angle resolved XPS). Quantitative analyses obtained by ARXPS were later used to generate compositional depth profiles of the failure surfaces using a concentration-depth profile routine (ARTick stratification depth profile analysis). Monochromated XPS (a Thermo VG Scientific Sigma Probe) was also employed in the later stages of the programme, for the joints previously immersed in water at 35°C for varying lengths of time, (0-300 days). ToF-SIMS studies were enabled to identify the specific chemical nature of the interface, and the contribution of the individual components of the resin.
In the final part of the study (Chapters 8 and 9) model resins were formulated using the constitutive components of the commercial optical resins namely, an epoxy resin, a reactive diluent, a polysulphide curing agent and an catalytic co-curing amine. Each of the formulation components were individually characterised and the resulting six variant reformulated resins were analysed using XPS and SIMS and to a lesser extent by thermal analysis. The reformulated resins were then employed into the glass adhesive joints and their fracture behaviour in water further examined by means of surface analysis techniques.

The ambient temperature fast cure resins are essentially multi component systems. A combination of surface analytical techniques (XPS and ToF-SIMS) and reformulation of the polymers have been used to study the failure mechanism and transport properties of the various components within the adhesive and their interaction with a borosilicate substrate.
2.1 INDUSTRIAL BACKGROUND

The growth in the use of optical signals for communications and data transmission has led to demands for improved devices, and in turn improved materials for the processing of optical signals. With over a thousand different optical components being manufactured by the use of various joining techniques, choosing the right element for this project is daunting. However it is intended to use a most commonly utilised substrate material and a commercial adhesive resin for the failure analysis of the joints. Some of the glass based optical components and the use of epoxy resin as adhesives are briefed in this section.

2.1.1 Epoxies for Optoelectronic Industry

Optoelectronic devices are those which convert light into electrical energy or vice versa. In some cases the same device may perform both functions. In the past few years, a host of new devices have been developed for commercial applications - LED’s, photodiodes, laser diodes, and many more [1].

Epoxy resins are widely used in the manufacture of electronics due to their adhesive strength, heat durability, and good electrical properties. Applications to optical communications devices require precise bonding with sub-micron positioning accuracy because these devices have a small positioning tolerance. Because optical
epoxy adhesives are capable of adhesion and fixing in a few minutes at room temperature, it is easy to align optical components while assembling them. In contrast, heat-curable adhesives currently in use take 3-6 hours to cure at elevated temperatures of 60 - 100°C. There are, however, only a few conventional optical epoxies, and they cannot be used because they shrink more than 3% during curing and have a high heat expansion co-efficient of more than $6 \times 10^{-5}/°C$ [3]. Coupling with these requirements, high transparent optical adhesives, whose refractive index can be controlled to match the materials to be bonded, are also needed for making optical communication devices to obtain joints with low transmission losses and low return losses [2].

2.1.1.1 Use of Epoxies in Fibre Connections

Perhaps the simplest technique for permanently joining fibres together is to use a fusion splice. Here the fibre ends are held in a close proximity and heated up to the material softening point (about 2000°C for silica) [3]. The fibres are then pushed together and the two ends fuse to form a continuous length of fibre. Any slight initial misalignment of the fibre ends tends to be corrected as surface tension forces pull the fibres back into alignment.

The finished joint will be mechanically weak since the protective-coating layer, normally made of acrylic has to be removed before the process starts. To provide protection to the fused joint area, a small metal tube will be slid over the join and sealed to the fibre using epoxy resin (Figure 2.1). Both multimode and single mode fibres can be joined by this means and transmission losses can be less than 0.1 dB [4]. With a high precision centre alignment, deterioration of connector performance may occur due to environmental factors such as temperature, frequent cycle connection, moisture etc. Therefore, selection of adhesive is critical in these 'submicron-order' centring techniques [5].
Applications of Optical Resins and Surface Analysis

Figure 2.1 Encapsulation of an Optical fibre to the connector using a Tra-Con precision Epoxide adhesive (courtesy of EPO-TEK™)

As far as making permanent joins, which rely on butting fibres together and bonding with an epoxy resin is concerned, there are three main steps. First the two end faces of the fibres are made as flat and as perpendicular to the fibre axis as possible. Secondly the fibres are held in some sort of jig which allows them to be closely aligned (Figure 2.2). The final step is to fix the fibres permanently in place, with the aid of an epoxy resin.

Figure 2.2 Illustration of the use of V-groove for the alignment of fibre ends prior to jointing [5]
Chapter Two:  
Applications of Optical Resins and Surface Analysis

The refractive indexes of the hardened adhesive also determine the critical performance of an optical component. It is possible to keep light reflection from the adhesive section to within theoretical limits because the refractive index can easily be matched to those of optical glasses such as quartz \((n_{D}^{25}=1.46)\) and BK-7 borosilicate glass \((n_{D}^{25}=1.52)\). Therefore, the application of optical adhesives to the assembly of optical components and to optical fibre splicing makes possible the design of high-performance optical components.

2.1.1.2 Epoxide Applications in Optical Devices

The epoxide precision adhesives are now successfully applied to many optoelectronic components. The fabrication of a laser-diode module (LDM) and an optical modulator are shown in this section as examples. Figure 2.3 shows the cross-section of the laser package. A 0.6-mm diameter microball lens was fixed near the laser using a precision adhesive. The lens bonding processes are as follows. A 0.6 mm diameter TaF₃ micro-ball lens is carried by a vacuum pick-up tool to the position where the adhesive has been deposited prior to the lens pick up. The tool then contacts the lens with the adhesive. The pick-up tool can move in X, Y, Z directions with 0.1 μm step resolution. For this LDM, lateral tolerance measurement shows that a lens displacement of 1μm reduces the coupling power by more than 1dB. Therefore the lens bonding accuracy must be within 1μm. The lens movement during cure was reduced to about 1μm for a shrinkage of 2% and an adhesive thickness of about 50μm. This bonding accuracy is achieved by a 1-μm pre-offset to cancel the movement during the curing, although other adhesives cannot be used due to their high shrinkage. The temperature characteristic studies on LDM [6], strongly indicate that the displacement of the ball lens caused by the expansion of the conventional epoxy adhesive is too large. In contrast, the module with a precision adhesive shows good auto power control operation in the temperature range 10-60°C as the resin expands less.
There are some soldering techniques also available to fix micro lenses or single mode fibres. However the accuracy achieved in the of positioning the optical elements is so poor that epoxy adhesives are preferred instead for the LD modules.

Ease of use and reliability in the field repairs or modifications to fibre optic cable, is maximised by a colour change that occurs with some epoxies that are heat cured. This colour change indicates to a technician that the material is sufficiently cured for handling. When bonding single-fibre and fibre optic bundles into ferrules, the epoxy adhesive is applied to the sheath of the fibre bundle by the method of compressed air dispensing or dipping, and the sheath is then pushed into the sleeve.

**Figure 2.3** Cross-section of the laser collimator package with a micro-ball lens fixed by a UV-curable epoxy adhesive, and the SEM image of the micro-ball lens in the package [6].

**Figure 2.4** Schematic of optical fibre termination [7]
An optical fibre end sample which had been applied to LD (laser diode) modules is shown in Figure 2.4, where the adhesive is used to bond fibre end to BK-7 glass, coated with anti-reflection film. In optical fibre termination, in order to prevent reflection from the termination, BK-7 optical glass with anti-reflection film is attached to the end of the optical fibre by means of an optical adhesive.

A huge range of opto-electronic and optical devices can be joined together by using the more sophisticated epoxies. There are many uses of optically transparent epoxies such as bonds, coatings, and encapsulants include lasers, polarising lenses, optical films, lenses, prisms, beam splitters, filters, laser windows, LED’s, photodiodes, optical filters, replicated optics, and encoders.

Optically clear adhesives were first designed to add superior transparency to the other advantages of epoxy resins, such as toughness, durability, and low outgassing. To satisfy the need for highly reliable connections for single-fibre and bundled fibre optic applications, additional formulations can be developed that surpass industrial specifications and give maximised thermal and moisture resistance, polishability, and adhesive strength.

To meet the broadest range of requirements for both optics and fibre optics, additional epoxies have been formulated to exhibit special attributes such as UV transmission, biocompatibility, a low index of refraction, and curing by UV or visible light. New compounds are continually being formulated to meet the emerging needs of each of the industries that rely on optical grade epoxies.

2.1.1.3 Mercaptan Based Epoxy Resins for Optical components

Liquid polysulphides polymers are normally associated with the manufacture of high performance sealants for the construction, marine, double glazing, automotive and aircraft industries. The lower molecular weight, low viscosity liquid polymer is nevertheless used as an elastomeric modifier and as a curing agent for epoxy resins in
the production of optoelectronic adhesives and encapsulants. The epoxy-mercaptopan
coreaction is catalysed by the presence of organic bases particularly liquid amines.
This also encourages a rapid cure reaction at ambient temperature, as required by the
industry. The detailed formulation chemistry of the polysulphide/amine based resin,
used in this work is further explained in Chapter 4.

2.2 PRACTICAL ASPECTS OF ADHESION THEORY

Adhesion is a multi-disciplinary field, which involves engineers, pure and
applied scientists all working within closely related area. 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 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
this section, the content of the literature survey comprises a brief review of the
conditions necessary for bonding to occur, the functions and actions of an adhesive,
and the various factors, which contribute to the strength of a joint.

2.2.1 Mechanisms of Adhesion

A comprehensive literature review of all the adhesion mechanisms that have
previously been suggested, might have 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 been contrived in order to obtain data which will disprove one or
Chapter Two: Applications of Optical Resins and Surface Analysis

the other theories. The result is that there is now a wealth of conflicting information in the literature. The scientific community in Russia has generally proclaimed its support for the electronic and diffusion theories [8]. However, the adhesion community as a whole favours the adsorption theory, (which include both primary and secondary force interactions), and has been found to be more widely applicable [9].

2.2.1.1 Mechanical Interlocking

The surface roughness can influence adhesion, and the result of increased adhesion is often termed mechanical adhesion. The mechanical interlocking suggests that for an adhesive joint to be formed, interlocking or “hooking” of the adhesives 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 joints together. Mechanical fasteners such as Velcro™ are sometimes included in this category, but should be regarded as a fastening rather than adhesion. The most frequently cited example, is that of the undercut cavity made by the dentist in order to fill a tooth with amalgam.

Roughness can influence adhesion in several ways. First, effects which increase the level of adhesion are:

(i) Interlocking of adhesive with surface undercuts and holes,
(ii) Frictional resistance to separation of adhesive from a fibrous surface (e.g. from embedded fibres),
(iii) Most importantly, the increase in the true interfacial area (removal of surface contaminants, which could act as potential, weak boundary layers, WBLs),
(iv) Increase in the volume of the zone in which stress is concentrated (i.e. energy is dissipated).

For a given joint, all of these effects could be regarded as contributing to the 'mechanical' component of adhesion. From the above influences, contact between an adhesive is generally expected to increase the bond strength compared with smooth surfaces. However, a rough surface may show lower bond strength than a smooth
surface if the adhesive is unable to penetrate into the surface irregularities, so that a reduced true contact area is achieved. Thus, a highly viscous adhesive may only be able to achieve partial interfacial contact before it sets, or a pressure sensitive adhesive may never be able to achieve contact with a rough surface.

The general rule would therefore appear to be that roughening a surface would improve the bond obtained with a lower viscosity adhesive, but might well have the opposite effect for a highly viscous adhesive. Thus, a neoprene contact adhesive might well bond roughened leather shoe soles better than smooth ones, but a pressure sensitive adhesive would generally bond better to a smooth surface than to a rough one [10].

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 [11]. Tabor et al. reported good practical adhesion between sheets of perfectly smooth mica [12]. Some solids, though on a molecular scale, are soft enough to deform plastically under pressure to increase contact; metals such as aluminium and indium can be cold welded by this method if surfaces are scrupulously freed from oxides and other weak surface layers [10]. 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. Much work has been reported on the phenomenon of mechanical interlocking, although in most instances this has been due to roughening of surface topography, causing improved adhesion as a result of increased surface area and therefore allowing more chemical interaction between respective interfaces.
2.2.1.2 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. If the two materials are both polymers, the polymer chains can diffuse across the interface and entangle with each other, an effect, which can strongly increase the level of adhesion. The theory was first proposed by Voyutskii in 1962 [13], 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. Vesenin [14], has further developed this theory with a series of experiments on different molecular weight poly-isobutylene, and found out that the dependence of adhesion on molecular weight with time of contact. He then derived a complex equation, which suggests that the force is directly proportional to the rate of separation, and to the quarter power of the time for which the surfaces have been in contact. The use of Fick’s law in his calculations, is generally regarded as an inappropriate choice of modelling polymer interdiffusion as it is only applicable to steady-state diffusion process [15].

Diffusion theory has attracted several major criticisms, most serious of which is that it cannot be applied universally. In certain classes of material, such as glass and metal oxides, the rate of diffusion would be slow at ambient temperature and pressure, that it cannot be considered a viable mechanism. In addition, as relative molar mass (RMM) increases the need for similarity increases and, at very high RMMs, there are very few examples of miscible polymer pairs [16]. For this reason the importance of diffusion lies mainly in the coalescence of the same polymer across an interface, the result of which is called autohesion. There is considerable dispute about the extent of diffusion, which occurs between dissimilar polymers.
Chapter Two: Applications of Optical Resins and Surface Analysis

One body of opinion claims that even dissimilar polymers can mutually diffuse sufficiently to raise adhesion, even if it means only the interlooping of a few polymer chains at the extreme interface. However, general opinion is that diffusion is unimportant as a mechanism of adhesion, except for a few specialised cases where mobility is high. The other condition derived from this theory is that the molecules of the two miscible materials must be mobile enough to diffuse. This means that polymers which are crosslinked can never diffuse, polymers which are crystalline can only diffuse above their melting temperature ($T_m$), and polymers which are glassy can diffuse only above their glass transition temperature ($T_g$).

Vasenin’s model has also been criticised for not taking account of any of the energy dissipative process which result during mechanical testing. Perhaps more serious, is the criticism by Anand (1973) [17], that the observed increase in joint strength following longer contact times, 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. Yet, heat sealing of plastic bags is regarded as a successful practical example of polymeric diffusion.

2.2.1.3 Electronic Theory

The electrostatic theory was first proposed by Deryaguin [18], and can play an important role in fine particle adhesion. In his experiments, he discovered the existence of discharge phenomenon of which the most well known is the appearance of sparks jumping across the gap when a flexible adhesive tape is rapidly removed from a substrate. The principle of the treatment is, when an adhesive is intimate contact with the substrate, regard the surface of the adhesive as one plate of a condenser and the adherend as the other plate. To separate these plates work must be done against any electric charge separation occurring between them. Deryaguin et al.
[19] had considered the energy of the condenser to be equal to the work of adhesion, and then assumed that no other factor, such as van der Waals’ forces have to be overcome in carrying out the separation. 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 means of explaining joining.

Deryaguin 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.

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 critic 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 [20].

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 significant contribution. As with the previous two mechanisms of adhesion, the electronic theory is therefore of limited application.

2.2.1.4 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. With sufficient intimate molecular contact materials may adhere as a result of the intermolecular forces, which are established between atoms and molecules in the adhesive and the substrate.
Chapter Two: Applications of Optical Resins and Surface Analysis

The most common physical interactions are van der Waals forces, which may be induced by permanent dipole-dipole interactions, (Keesom forces), dipole-induced dipole interactions, (Debye) and dispersion, (or London) forces. The relative magnitudes of the various bond types are given table 2.1.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Ionic bonds</td>
<td>600-1100</td>
</tr>
<tr>
<td>Covalent bonds</td>
<td>60-700</td>
</tr>
<tr>
<td>Metallic bonds</td>
<td>110-350</td>
</tr>
<tr>
<td><strong>Donor-Acceptor Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Bronsted acid-base</td>
<td>Up to 1000</td>
</tr>
<tr>
<td>Lewis acid-base</td>
<td>Up to 80</td>
</tr>
<tr>
<td>Hydrogen bonds (including F)</td>
<td>Up to 40</td>
</tr>
<tr>
<td>Hydrogen bonds (excluding F)</td>
<td>10-25</td>
</tr>
<tr>
<td><strong>Van der Waals Secondary Bonds</strong></td>
<td></td>
</tr>
<tr>
<td>Permanent dipole-dipole</td>
<td>4-20</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td>Less than 2</td>
</tr>
<tr>
<td>Dispersion (London) forces</td>
<td>0.08-40</td>
</tr>
</tbody>
</table>

**Table 2.2** Bond types and typical bond energies [21]

Evidence shows [22] that intrinsic adhesion arising from secondary bond interaction alone, may result in adequate and high joint strength. It has in the last decade, however, become evident that the specific bonds take place at an adhesive/adherend interface, and depending upon the chemistry of the interface, primary bonds may form across the interface. Chemical interaction, which can best be described as primary covalent bonds, have typically 30 - 40 times higher bond energies and are formed due to adhesive molecules chemically reacting with the
substrate thus forming chemical bonds across the interface (chemisorption). The most well known way of introducing chemisorption is by means of coupling agent. These are reagents capable of reacting and forming covalent bonds with materials on both sides of an interface, and are mainly used in the bonding of organic polymers to metals or glass. They may be used either as a surface pretreatment or may be added to an adhesive.

All materials exhibit dispersion force interactions and these are frequently the forces responsible for both cohesive strength of the respective material and adhesion between dissimilar materials. Huntsberger et al. [23], showed that with dispersion forces alone at a separation of one nanometer the attractive force would result in a joint strength in tension of approximately 100 MPa. This value is considerably higher than the practical adhesion for most of the adhesive joints. This can be due to air filled voids, defects, etc, acting as stress raisers when the joint is loaded. However Huntsberger’s work reveals that high joint strength, in theory, may result from intrinsic adhesion that arises solely from dispersion forces acting across the interface.

A final category of the adsorption theory to be postulated are donor-acceptor bonds, with acid-base interactions the most widely applicable example. Although the magnitude of bond energies of the Lewis acid-base interactions are lower in comparison, as recommended by Fowkes et al. [24] these forces should also be classified primary forces on the basis that they have specific bond lengths and bond energies.

Many polymers have functionalised sites that are electron acceptors (Lewis acids) or alternatively are proton donors (Brønsted acids), or electron donor (Lewis bases) or alternatively are proton acceptors (Brønsted bases) that provide enhanced specific intermolecular interactions, with adhering substrates, known as acid-base interactions. In systems where adhesive and substrate have acid-base character, acid-base interactions are believed to contribute strongly to the intrinsic adhesion forces operating.
Chapter Two:  
Applications of Optical Resins and Surface Analysis

With reference to the strength of adhesion between a basic polymer and an acidic substrate, Figure 2.5 explains that upon evaporation of solvent less basic than the polymer, the polymer’s basic groups are hydrogen-bonded to acidic sites of the substrate and good strength is expected [25]. However when the polymer is cast from a solvent more basic than the polymer, the solvent molecules are more readily adsorbed to surface hydroxy groups.

![Diagram](image.png)

**Figure 2.5** Competition between basic polymer (PMMA) and (a) slightly basic solvent (CCl₄) or (b) more basic solvent, for access to the acidic SiOH sites on silica (P denotes basic groups of polymer, S denotes solvent molecules) [25].

Drago [26] proposed that the exothermic enthalpy of acid-base interaction (in kcal mol⁻¹), for a variety of Lewis acids in a neutral solvent, could be determined by a relationship. The exothermic enthalpy of the acid-base interactions (-ΔHₘₙ) is the most common way of defining these forces. Fowkes [27] applied the concept of Drago’s constants C and E, related to the tendency of the acid or base to form covalent or ionic bonds respectively, to evaluate ΔHₘₙ.
Chapter Two: 
Applications of Optical Resins and Surface Analysis

\[-\Delta H_{ab} = C_a C_b + E_a E_b \]  \hspace{1cm} 2.1

Values for C and E were obtained from the enthalpy of mixing or spectral shifts in the FTIR C=O band stretch and are tabulated by Drago et al. [26], using iodine as a reference acid with \(C = E = 1\). The E and C parameters, as they are referred to, relate to the tendency of a given species to undergo electrostatic, (E) and covalent, (C), interactions. The main shortcoming of this four-parameter approach is that configurational entropy is not taken into account. Drago originally carried out his work with small gas phase organic molecules. Polymer molecules are large and therefore may well change in conformational entropy in order for the rearrangement of the viscous polymer.

Gutmann [28] adopted a different approach to calculate the enthalpy of formation of a Lewis acid-base adduct. 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 relationship:

\[-\Delta H_{ab} \approx \frac{\text{DN}.\text{AN}}{100} \]  \hspace{1cm} 2.2

Bolger and Michaels [29] suggested that the important of non-dispersion interactions could be expressed in terms of acid-base theory. They defined a delta parameter as the numerical difference between the isoelectric point of an inorganic surface (IEPS) and the acid ionisation constant of the polymer (pK_A):

\[\Delta_A = \text{IEPS} - pK_{A(A)} \]  \hspace{1cm} 2.3

\[\Delta_B = pK_{A(B)} - \text{IEPS} \]  \hspace{1cm} 2.4

Where,
\(\Delta_A = \text{surface interaction with an organic acid}\)
\(\Delta_B = \text{surface interaction with an organic base}\)
Chapter Two:
Applications of Optical Resins and Surface Analysis

For a large negative delta parameter, acid-base interactions are considered negligible and interfacial forces are essentially Van der Waals. For a small negative or positive delta parameter, acid-base forces are said to be equivalent to the dispersion forces component, and a large positive parameter indicates a strong acid-base interaction, indicating that the reaction may go to completion, resulting in the loss of one of the components. Bolger’s approach, whilst useful in the specific case of adhesion between polymers and oxide surfaces, is limited to Bronstead acid-base interactions and any more general treatment should be based on electron donor-acceptor (Lewis acid/base) interactions.

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 the understanding of adhesion.

2.3 ADSORPTION OF MOLECULES ON TO SURFACES

As adsorption is now widely recognised as a significant factor in adhesion, it is important to consider the various aspects of polymer adsorption onto surfaces. One of the properties which makes polymers particularly suited in applications such as coating and adhesives, is their ability to become readily adsorbed onto solid surfaces [30]. 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 [31], thus facilitating adsorption. One of the most well documented features of polymer adsorption is the molecular weight dependence [32]. 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, model systems have been constructed, where polymer chains are labelled
with deuterium and forward recoil spectrometry is used to study segregation effects
[33]. 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.

Chehimi and Watts [34] more recently reported a reorientation of molecules
adjacent to the interface in homopolymers. In the case of multicomponent systems
however, the possibility exists for the various components to stratify, producing
regions of varying composition.
In any case for the 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 next section therefore considers the theories related to wetting and spreading.

2.4 WETTING AND SPREADING

2.4.1 Contact Angle

Lee [25] described diffusion and wetting as the kinetic means of obtaining good adsorption of a polymer on a surface. Wetting allows the polymer molecules to come into intimate contact with the substrate, thus enabling the formation of polymer/substrate interactions. If the liquid adhesive has a lower energy than the solid surface material, it will tend to wet the surface and penetrate fully into surface irregularities. Conversely, an adhesive of higher energy than the surface material will tend to de-wet and will form only a limited contact area. A measure of the wetting tendency is given by the contact angle $\theta$, which should be less than $90^\circ$ for wetting and is $0^\circ$ for spontaneous spreading (see figure 2.2). 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, these forces must balance, as Young showed in the following expression:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta$$  \hspace{1cm} 2.5

23
When $\theta$ is equal to zero (or near zero), maximum interfacial contact is obtained, thus providing the best opportunity for the adhesive/substrate interactions to occur. Although, as indicated by Huntsberger, (1967) [23], 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° with the substrate, includes the majority of practical situations [36]. However one of the benefits of a lower contact angle is, that uniform surface coverage is possible using the minimum amount of adhesive/coating.

![Figure 2.6](image)

**Figure 2.6** Cross-section of a sessile drop of liquid on a solid, showing the balance of forces at equilibrium: (a) $\theta < 90^\circ$ (b) $\theta > 90^\circ$

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.

It is clear from these considerations that the degree of contact eventually achieved depends on the difference in cohesive (or surface) energy between the adhesive and substrate. The rate at which this contact is achieved is determined by the viscosity of the adhesive and it is generally desirable for this to be as low as possible.

2.4.2 Critical Surface Tension

Zisman (1964) [36] showed that, if a surface is wetted with a series of homologous liquids (e.g. n-paraffins), \( \cos \theta \) appears to be linear function of \( \gamma_L \). If the straight line is extrapolated to the point where \( \cos \theta = 1 \) (i.e. \( \theta = 0 \)), the corresponding value of \( \gamma_L \) is called the critical surface tension, \( \gamma_c \). It is the tension of the liquid, which will just spread spontaneously on the surface. This term was regarded by Zisman as an empirical parameter “whose relative values act as one would expect of the specific surface energies of the solids”. This perhaps explains the subsequent misuse of the term \( \gamma_c \) as the surface energy of the solid.

2.4.3 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.

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:

$$\gamma = \gamma^D + \gamma^P + \gamma^M$$  \hspace{2cm} (2.6)

where, $\gamma^D$ is the dispersion component, $\gamma^P$, the polar component and, the $\gamma^M$, 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).

### 2.4.4 Work of Adhesion

Surface free energies are used to describe the thermodynamic stability of a joint; to predict the likelihood of two materials becoming spontaneously separated, by calculating the work of adhesion ($W_A$). The work of adhesion may be defined as the free energy change required to separate two phases, A and B, cleanly along the interface. A negative $W_A$ value suggests that separation is energetically favourable, while a positive value indicates that separation is unlikely.

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.
Chapter Two:
Applications of Optical Resins and Surface Analysis

\[
W_A = \gamma_A + \gamma_B - \gamma_{AB} \quad 2.7
\]

Early attempts to evaluate the \( \gamma_{AB} \) made use of an analogy with the Berthelot relationship, a concept originally developed for looking at the attractive constants between both similar and dissimilar gas phase molecules. This approach proved unsuccessful, as it failed to take account of the different types of interfacial interactions operating. The Berthelot relationship as analysed by Fowkes is stated below:

\[
\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A \gamma_B} \quad 2.8
\]

Fowkes noted that for most systems, the first two terms in equation 2.6 (i.e. the dispersion and polar forces) dominate. He was therefore able to adopt 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:

\[
E_A = \gamma_A \sqrt{\gamma_A \gamma_B^D} - \sqrt{\gamma_A \gamma_B^P} \quad 2.9
\]

And for phase B:

\[
E_B = \gamma_B \sqrt{\gamma_A \gamma_B^D} - \sqrt{\gamma_A \gamma_B^P} \quad 2.10
\]

Therefore the interfacial free energy can be calculated as:

\[
\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A \gamma_B^D} - 2\sqrt{\gamma_A \gamma_B^P} \quad 2.11
\]

Having determined the expression for the interfacial free energy, \( \gamma_{AB} \), the work of adhesion may now be calculated by substituting \( \gamma_{AB} \) into the Dupré equation.
Chapter Two:  
Applications of Optical Resins and Surface Analysis

\[ W_A = 2\sqrt{\gamma_A^D \gamma_B^D} - 2\sqrt{\gamma_A^P \gamma_B^P} \]  \hspace{1cm} 2.12

Under dry conditions, \( W_A \) values are, almost without exception, positive in value. In practical systems, again in 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). The Dupré equation, 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 one of the most frequently encountered fluids, but other common liquids include organic solvents and oils and fuel. In this particular study the presence of water is of most concern. If joint separation occurs in the presence of this third phase, the equation 2.13 can be modifies as follows:

\[ W_{AL} = \gamma_{AL} + \gamma_{BL} - \gamma_{AB} \]  \hspace{1cm} 2.13

Using the concepts introduced so far (i.e. taking into account dispersion and polar contributions) an expression for \( W_{AL} \) for an adhesive system in the presence a third phase may be written as :

\[ W_{AL} = 2[y_L - (\gamma_A^D y_L^D)^{1/2} - (\gamma_A^P y_L^P)^{1/2} - (\gamma_B^D y_L^D)^{1/2} - (\gamma_B^P y_L^P)^{1/2} + (\gamma_A^D \gamma_B^D)^{1/2} + (\gamma_A^P \gamma_B^P)^{1/2}] \]  \hspace{1cm} 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 third 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. Although $W_A$ is important in determining the final joint strength obtained, it is usually extremely small in magnitude compared with the overall separation work. Energy expended in deforming bulk components of the joint normally much greater than that required to generate new surfaces. Thus, for example, the maximum value of $78 \text{ mJ m}^{-2}$ for work of adhesion of polyethylene, calculated from the above equation, compares with practical values for joint strengths typically of $10^4$ times greater than this.

2.5 WEAK BOUNDARY LAYERS

It is expected that the substrate boundary region should not be weaker than other parts of a bonded joint (i.e. it should not be liquid or semi liquid, or brittle). It is well known that boundary layers of oils or greases adsorbed from the environment frequently have to be removed by solvent degreasing before bonds are made. Also, it is difficult to bond to high-energy surfaces in highly humid conditions because of adsorbed water. The reasons for these are obvious and also obvious is that it is not necessary to remove strong, well-bounded boundary layers which may well improve adhesion, especially if they are porous. However the subject of weak boundary layers is of great interest, as segregation of specific components to the interface is, analysed in this current study. This topic will be further elaborated upon in later sections.

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 50 nm thick. In order to establish the true locus of failure, surface specific techniques (with sampling depth of the order of a few nanometres) are required. Of these, X-ray photoelectron spectroscopy, (XPS), and secondary ion mass spectrometry, (SIMS) are most frequently applied. In practice, XPS analysis is carried out prior to investigation by SEM, in order to avoid sample contamination. In addition the need for coating the sample with gold in non-conducting samples for SEM analysis, will destroy all the analytical information that could be gained from XPS and SIMS.

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.
CHAPTER THREE

CHOICE OF EXPERIMENTAL METHODS

3.1 INTRODUCTION TO EXPERIMENTAL TECHNIQUES

The following chapter describes the techniques and materials used in the experimental work presented in this thesis. The key surface analytical techniques used during the course of this work were X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). They are 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. These two techniques complement each other, with both offering surface specific analytical informations. Since the commercial availability of X-ray photoelectron spectrometers 30 years ago, the technique has been widely adopted in many areas, particularly in the field of adhesion [37]. However, despite being successfully employed in a number of adhesion studies with quantitative surface chemical analysis [38, 39, 40], it inherently lacks the specificity to provide the molecular information that is essential for the full understanding of the adhesive and the interfacial chemistry. In contrast ToF-SIMS demonstrates the potential to fulfil this requirement with high spatial resolution by the use of a focused ion beam and a high degree of molecular sensitivity. The technique is eminently suited to study such effects as segregation of minor components of an adhesive to the surface and the orientation of polymer molecules against the substrate [41].
Experimental work has been carried out in the other areas, with the use of scanning electron microscopy (SEM), and with mechanical tests on the bulk properties of the polymers and adhesive joints. However, it is XPS and ToF-SIMS surface analysis techniques that will be used extensively throughout this study, and therefore specific emphasis will be made on these two techniques in this section.

### 3.2 X-RAY PHOTOELECTRON SPECTROSCOPY

#### 3.2.1 Introduction

The strength of XPS lies in the ability to provide elemental and chemical 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, has contributed to our understanding of adhesion phenomena in three main areas, (Watts, 1990) [42]. 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) [43]. The second area often involves some form of elaborate sample preparation, “probing the buried interface”, (Castle and Watts, 1988) [44], 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.
In this section consideration is given to the basic principles of X-ray induced photoemission, the various levels of information that may be extracted from an XPS spectrum and the manner in which such data should be interpreted. For a more detailed and discussion of the process and techniques there are a number of advanced texts available in the literature [45, 46, 47].

3.2.2 Basic Principles

XPS, as the name implies, utilises X-rays (usually AlKα or MgKα) 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, hv. Photoelectrons have a kinetic energy (E_k), which can be related to the X-ray energy (hv), and the binding energy (E_B) by the following relation:

\[ E_B = hv - E_k - W \]  \hspace{1cm} 3.1

Where W = is the work function of the spectrometer
h = Planck’s constant
v = frequency of X-ray

The process of photoemission is shown in Figure 3.1, where an electron from K shell is ejected from the atom. This electron is termed the 1s electron. All electrons with a binding energy less than the photon energy will be displayed in the XPS spectrum.
Chapter Three:  
Choice of Experimental Methods

Figure 3.1  Schematic of the XPS process, showing photoionization of an atom by the ejection a 1s electron.

3.2.3 Depth of Analysis

Figure 3.2 illustrates electron emission from a planar surface. It is the escape depth of the electrons forming the spectrum which determines the analysis depth, although 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 [48]. 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 sufficient kinetic energy to escape from the sample. The depth is dependent upon inelastic mean free path ($\lambda$), which varies as $E^{0.5}$ in the energy range of interest in XPS. The inelastic mean free path is a material parameter for the electron energy and the material type under consideration.
Figure 3.2  Electron emission as a function of depth, the horizontal dashed line represents a distance from the surface inelastic mean free path ($\lambda$) [46]

The Beer-Lambert law describes the intensity of electrons ($I$) emitted from a depth ($d$):

$$ I = I_0 \exp \left(-\frac{d}{\lambda \sin \theta} \right) \quad 3.2 $$

Where $I_0$ is the intensity from an infinitely thick clean substrate, $\theta$ is the electron take-off angle relative to the sample surface. This equation can be used in a number of ways to provide information about overlayer thickness, or to provide a non-destructive depth profile. Further analysis of the equations, show that by considering electrons which emerge at $90^\circ$ to the sample surface, 65% will emerge from a depth of $\lambda$, 85% from a depth of $2\lambda$, and 95% from a depth of $3\lambda$. The fact that 95% of the signal emanates from a depth of $3\lambda$, is a good indication of its surface specificity. As the values of $\lambda$ are in nm, the surface sensitivity of this technique becomes apparent. It is also important to remember that the depth of analytical information varies with electron energy and material.
3.2.4 Spectral Interpretation

The photoemission process described above occurs when the emitted photoelectrons have suffered no loss of energy during transport through the solid. If energy loss does occur during transport through the solid, then the result is the inelastic scattering of photoelectrons, which contributes to the background of the spectrum. 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 further explained 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 [49]). 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.

3.2.4.1 Auger Electrons and Auger parameter

Once a photoelectron has been emitted, the atom must relax in some way. This is achieved by either by the emission of an X-ray photon, or by rearrangement of the remaining electrons, which leads to the emission of an Auger electron (Figure 3.2). The latter of these features can be used to reveal more chemical information of the surface. 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).
Chapter Three:
Choice of Experimental Methods

Figure 3.2 Schematic of the relaxation process in an atom after emission of a core electron

The photoelectron peaks usually display smaller widths than the Auger peaks and are considered to be of much more value in the identification of chemical state. Core-core-core Auger transitions give chemical information but core-valence-valence peaks retain the degeneracy of the valance band and are thus, generally very broad. The Auger electron together with other ordinary peaks, give information on chemical state and species by using a measurement known as the Auger parameter ($\alpha$). When analysing a photoelectron spectrum, the level of accuracy in defining the peaks to given binding energies can be caused by two areas of error:

1) spectrometer calibration and,
2) electrostatic charging of the specimen.

There are many ways in which these inaccuracies can be overcome and the most convenient method is to make use of chemical shift on both the Auger and photoelectron peak in an XPS spectrum and record the separation of the two peaks. This quantity is known as the Auger parameter can be expressed as follows:

\[
\alpha = E_B + E_K - h\nu \quad 3.3
\]

\[
\alpha^* = E_B + E_K \quad 3.4
\]
Chapter Three:
Choice of Experimental Methods

Given that change in chemical state shifts photoelectron lines and also causes similar shifts in Auger lines it seems reasonable that the difference between the kinetic energy of the Auger and photoelectron lines are related to the chemical environment of the ionised atom. All the data obtained are independent of reference level and charging effects and so the unique empirical measurement offers an important source of chemical information.

3.2.4.2 Valence Band

These features can be observed from the low binding energy scale between 0-30 eV, due to the photoemission of the valence electrons. The valence band electrons are involved in bond formation, so the intensity and the energy of the valance peaks depends upon their bonding environment. A useful related technique for the study of the electronic band structures, which cannot be obtained from typical core level analysis, by using UV photons, is the molecular spectroscopy of UPS (ultra-violet photoelectron spectroscopy).

3.2.4.3 Shake-up Satellites

Finally secondary structures, such as X-ray satellites, shake-up/off satellites, plasmon losses and multiple splitting can also be observed in a photoelectron spectrum. The \( \pi - \pi^* \) shake-up satellite is of some interest to organic surface studies, as it is indicative of the presence of aromatic groups. 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, (Lopez et al., 1986) [50]. The shake-up transition produces a discrete energy loss peak on the low kinetic energy, (high binding energy) side of the photoelectron peak. The transition involves the \( \pi \) bonds of a C=C double bond. 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, [51]. The $\pi - \pi^*$ satellite occurs at about 6.7 eV to the low kinetic energy (high binding energy) side of the carbon 1s photopeak, and is between 8-10% of the intensity of the main peak.

### 3.2.4.4 Chemical State Information

Chemical shift is the name given to the observed shift in energy of a photoelectron peak from a particular element when the chemical state of that element changes [52]. Initial state is the ground state of the atom prior to the photoemission process. It is generally assumed that initial state effects are responsible for the chemical shifts, and therefore as the formal oxidation state of an element increases, binding energy of photoelectrons emitted from the element will increase. This assumes that the final state effects such as relaxation, have similar magnitudes for different oxidation states. For most organic samples this assumption is adequate, but it is now widely accepted that it is the final state effects which are responsible for the chemical shift in inorganic solids such as metal oxides.

The interpretation of chemical shift data relies upon the ability to determine peak position with an accuracy of at least ± 0.1 eV. Spectrometer calibration and electrostatic charging of the sample, can cause errors in the measurement of these shifts.

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 fine structure of number of polymer is shown in *High Resolution XPS of Organic Polymers.* (Beamson and Briggs, 1992) [53].
Quantitative information can be obtained from the ratio of the area under the peaks. This means the background used in the scans also of great importance. Therefore the next stage is to subtract a suitable background, an S-shaped background, 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 $\lambda$. The intensity ($I$) of a photoelectron peak from a homogeneous solid can be given, in a simplified form, by:

$$I = J \rho \sigma K \lambda$$

where $J$ is the photon flux; and $\rho$ is the concentration of the atoms in the solid. Provided the X-ray flux remains unaltered for the duration of experiment, the atomic percentages may be calculated as follows:

$$[A] \text{ atomic}\% = \left( \frac{I_A}{F_A} \right) \Sigma \left( \frac{I}{F} \right) \times 100$$

where $I_A$ is the intensity of A and I is the total intensity. Although this quantification method is based on the assumption that, the sample surface is homogeneous within the depth of analysis, it is extremely valuable for comparing similar specimens.

3.2.6 Instrumentation

The spectrometers are based on vacuum systems designed to operate in ultra-high vacuum (UHV). The system consists of vacuum pumping system; sample introduction and manipulation system; an X-ray source; an electron energy analyser and electrostatic transfer lens; electron detection system; and a dedicated data system complete with the relevant software to control the spectrometer and to process data post-analysis. A schematic representation of a typical spectrometer is shown in figure 3.3.
Chapter Three:
Choice of Experimental Methods

Figure 3.3  Schematic of the analysis chamber and analyser of a spectrometer [42]

The technique requires vacua of the order of $10^8$-$10^{10}$ mbar, for its operation. The primary reason for this is directly related to the surface sensitivity of the instrument. Even at $10^{-6}$ a monolayer of contamination can be adsorbed onto the surface in minutes, compared to hours if the pressure is reduced to $10^{-9}$ mbar. Another important factor for the use of ultra high vacuum (UHV) systems is at low vacuum, the probability of the emitted electrons colliding with other molecules before reaching the detector, is extremely high. Finally it can also be said that the ultra high vacuum is a necessity for the satisfactory function of some components, such as X-ray source.
Chapter Three: 
Choice of Experimental Methods

3.2.6.1 X-ray sources

XPS requires the generation of soft X-rays of around 1 keV (i.e. Mg Kα$_{1,2}$ = 1.253 keV and Al Kα$_{1,2}$ = 1.486 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 does not excessively broaden the resultant spectrum. The most frequently used source for the anode are aluminium and magnesium, which are available in a single X-ray gun with twin anodes which provides Al Kα and Mg Kα photons with energies of 1486.6 eV and 1253.6 eV respectively. These systems are equipped with a twin anode X-ray gun, of the type shown schematically in Figure 3.4. Both Al Kα and Mg Kα are utilised for obtaining data presented in this project.

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

**Figure 3.4** Schematic of soft X-ray source with twin anode [54]

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 Al Kα and Mg Kα, whose energies lie between about 1250 and 1500 eV, an accelerating potential of up to 15 kV is required.
Chapter Three: 
Choice of Experimental Methods

The photon flux produced is proportional to the current, so it is necessary to
use as high an electron bombarding current as possible. The maximum power
dissipation is limited to about 1 kW for Al Kα, and 0.5 kW for Mg Kα, before water
cooling becomes an insufficient means of dissipating heat. The sample is shielded
from the anode by a thin, (about 5 μm) window of a material relatively transparent to
X-rays, usually by aluminium foil. This helps prevent material from either the
filament or the anode from being deposited on the specimen [55]. The presence of
this window also helps to reduce the intensity of high energy Bremsstrahlung
radiation from the source as well as eliminating stray source electrons and
contamination from the analytical chamber. When the X-rays pass through the
window, low energy photoelectrons are emitted from the window surface which faces
the sample. These electrons are then directly attracted towards the positively charged
sample, and a small equilibrium potential (<10 eV) is instantaneously established.

Several other materials can be used as X-ray anodes, such as Si Kα
(1739.5eV), Zr Lα (2042.4 eV), Ag Lα (2984.3 eV) and Ti Kα (4510.0). These
higher energy sources would allow access to energy levels unattainable with the
conventional anode materials. For example, the highest K electron available by Al
Kα is Mg 1s electron, whereas if Zr Lα radiation is used the Si 1s electron becomes
available. By use of several of these different energy anodes, it is possible to build up
a depth profile, as they all analyse to different depths, thus monitoring the apparent
changes in composition.

In the course of this work, the use of a monochromated X-ray source is vital
for achieving good spectral resolution. The term X-ray monochromation refers to the
procedure used to reduce the natural X-ray line width, (in Al Kα from 0.85 eV to 0.4
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.
Chapter Three:  
Choice of Experimental Methods

This background is a function of the energy of the electrons from the filament, which strike the X-ray source and the potential of the anode. 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.

The monochromator works by directing the Al Kα radiation into a quartz (orientation 1010) crystal, where the crystal spacing of 0.425 nm, which is appropriate for the Al Kα wavelength of 0.83 nm. The geometry of a rotating anode monochromatised X-ray source is illustrated in Figure 3.5. X-ray monochromators utilise the principles of Bragg’s relationship \( n\lambda = 2d \sin \theta \), with an angle of 78°.

![Figure 3.5](image.png)  
**Figure 3.5**  
Monochromation using Al Kα using a quartz crystal [56].

The area of the sample irradiated depends on the source geometry and the type of electron gun used. The achromatic source generally illuminates a spot size of approximately 1cm². However the monochromated sources which illuminate an area in the order of tens of microns. The VG Scientific Sigma probe XPS at University of Surrey, utilises micro-focussing monochromator and a transfer lens with wide acceptance angle and can achieve spot sizes ∼15µm.
The function of the analyser to filter the electrons emitted from the specimen according to their energy. 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 typical analyser for the XPS instrument is the hemispherical sector analyser (HSA), as it is capable of achieving the resolution for XPS, when combined with a pre-retardation stage. However recently there has been a trend in the manufacturers of Auger instruments to fit HSA-type analysers.

The hemispherical sector analyser consists of two hemispheres of inner radius $R_1$ and outer radius $R_2$, positioned concentrically, (see Figure 3.5). A potential difference $\Delta V$ is 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, and the analyser is isolated from earth [55]. The analyser may then be operated in either fixed analyser transmission (FAT) mode, otherwise known as constant analyser energy (CAE) mode, or in fixed retardation (FRR), alternatively described as constant retardation (CRR) mode.

In CRR mode, 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 the electrons of a specified energy to pass between them. When the photoelectrons reach the focal point of the analyser assembly via a transfer lens, they are retarded electrostatically, prior to entry into 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 in the range of $10 \sim 100\text{ eV}$ are most frequently used in XPS.
Chapter Three:  
Choice of Experimental Methods

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.

![Schematic of HSA](Image)

**Figure 3.5** Schematic of HSA

3.2.6.3 Angle resolved XPS (ARXPS) – Non-destructive depth profile

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 [47]. The non-destructive depth profile is governed by the parameters of the Beer-Lambert equation as shown in Equation 3.2. This can be achieved by altering the geometry of the experiment. Figure 3.6 illustrates how varying the take off angle $\theta$, allows information collected from different depths. It is generally achieved by tilting the samples to the preferred angles. For example $\theta = 15^\circ$ is extremely surface sensitive and at an angle of $\theta = 90^\circ$, the analysis depth moves towards the limiting value of $3\lambda$. The change of angle can also be achieved without turning the sample in the new Sigma Probe instrument at Surrey, for selected angles by the change of operation condition of the Radian lens. A thin overlayer will give characteristic angular distribution predicted by the Beer-Lambert expression, is also given in Figure 3.6. On the other hand, an island like distribution, will show no dependence, and so it is possible to distinguish between these two type phase distribution in this way [42].
Chapter Three:  
Choice of Experimental Methods

In this current work further manipulation of the equation has been carried out as a test for lateral homogeneity. Graphs of lnI_{substrate} versus 1/sin\(\theta\) were constructed for the substrate materials investigated, a straight line was taken as an indication for the uniformity. After taking logs of both sides of the equation 3.2, a graph of lnI_{d} versus 1/sin\(\theta\) may be plotted where \(-d/\lambda\) is the gradient and lnI_{o} is the intercept with the y axis. Thickness of the overlayer can also be estimated (d = -slope x \(\lambda\)).

![Diagram](image)

**Figure 3.6** Angular electron emission (a) sampling depth as a function of electron take-off angle (\(\theta\)), (b) overlayer and intensity versus \(\theta\).

In this project reconstruction of depth profiles using a computer programme ARCTick is also implemented to postulate a compositional depth profile. The method has been classed into four different types of analysis based on various algorithms, and for this work a method called stratification is primarily implemented. This method calculates the average depth of each layer present and the relative quantity of material in each layer [57]. The ARCTick profiles used in the programme have been fully described elsewhere in the literature [58, 59, 60].
3.3 TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (ToF-SIMS)

3.3.1 Introduction

Secondary ion mass spectrometry is well known as a technique for high sensitivity element analysis. In this work the technique has been utilised to analyse complex adhesive systems and interfacial analysis of failure joints. The surface and interfacial chemistry of adhesives and organic coatings can have major effects on their properties and performance. Whilst XPS has been widely employed for adhesion studies, the techniques inherently lack the specificity to provide molecular information that is essential for a full understanding of their interfacial chemistry. Here ToF-SIMS analysis has been fully utilised to determine joint durability, locus of failure, and the role of adhesive and surface components in joint failure. The following review therefore deals with the basic concepts of the SIMS process and instrumentation related to this particular study.

3.3.2 The SIMS Process

SIMS process involves the bombardment of the surface with a high-energy ion beam (10-25 kV), causing material to be sputtered from the surface, and subsequent mass analysis of the ions and ion clusters. Figure 3.7 shows the basis of the mechanism of production of ions and other secondary particles in the SIMS.

![Schematic of SIMS process](image-url)
Chapter Three:
Choice of Experimental Methods

The energy from the primary particles, (e.g. 69 Ga\(^+\) 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 portion of these species becomes ionised and these secondary ions are detected and analysed by a mass spectrometer. Secondary ions may be positively or negatively charged. Although most samples tend to produce either a very strong positive or negative ion yield, it is usual to record both positive and negative ion spectra. Secondary ions detected by a mass spectrometer, are identified on the basis of their mass to charge ratios.

There are two distinct modes of operations in SIMS, named static and dynamic SIMS. In dynamic SIMS a high flux of primary ions is directed at the surface, in order to obtain a very high yield of secondary ions, which are usually elemental ions. In this mode only those mass fragments of interest are monitored and plotted as a function of sputter time. Using this mode it is possible to examine how the composition changes with depth, it is nevertheless not surface sensitive. The fact that ionisation coincides with sputtering causes considerable damage to the surface, and this can be overcome to certain extend by the use of static SIMS technique.

For surface analysis considerations, static SIMS is a much more powerful application. Static SIMS is made possible by reducing the primary ion beam density to very low level, so the secondary ions are emitted from areas not previously damaged, and by the use of high sensitivity pulse counting devices. This enables a high analytical sensitivity. The primary ion beam for this mode is of very low current density (~1nA cm\(^{-2}\)) in order to eliminate sample damage during spectral acquisition. This can be achieved by either using large diameter defocused beam or by rastering a focused beam over the surface, depending on the use of quadrupole or time of flight analyser. The surface chemical analysis by static SIMS lies in its ability to produce mass spectrum of cluster ions as well as elemental ions. Maximum dose of ions into the surface for static SIMS has been calculated as \(10^{13}\) ions cm\(^{-2}\) per analysis, and this is known as static limit (i.e < \(10^{13}\) ions/cm\(^2\)/analysis).
The depth of analysis of fragment ions for static SIMS is significantly lower than that for XPS, under typical operating conditions. Previous studies in sampling depth have estimated the depth to be of the order of 1nm. It is also generally believed that the emission of large molecular fragments is mainly from upper monolayer, as opposed to atomic ions, which come from a much greater emission depth, that can be comparable to XPS. Therefore for SSIMS, the depth for fragment ions (not the elemental ion) is generally thought to be approximately the same as the analysis carried out at $\theta = 15^\circ$ or 1-2 nm in XPS.

3.3.3 Instrumentation

The basic arrangement for the SIMS experiment is shown in figure 3.8. There are three main components; the primary particle source, the mass spectrometer and, since the secondary ions are emitted with a range of kinetic energies, an ion optical system which selects ions within a defined energy band compatible with the capability of the mass analyser.

![Figure 3.8](image)

**Figure 3.8** A schematic representation of a SIMS Instrument [61].
3.3.3.1 Primary Beam

The principle difference between the conventional quadrupole or magnetic sector SIMS and the time-of-flight (ToF) instrument is that the primary ion source is pulsed. The range of types of primary beam source which have been used in SIMS can be classified into four basic types according to their mechanisms of primary beam production: electron bombardment, plasma, source ionisation, and field emission. These sources offer different performance in terms of spatial resolution, ease and speed of use, sensitivity, performance on insulating materials and beam induced damage. The basic components of most types ion beam source, shown in figure 3.9(a) are, the source region/extraction zone, focusing and collimating regions, a mass (Wein) filter beam purification, a pulsing system suited for time-of-flight mass analysis, stigmation/focus lens and finally scan rods.

The mode operation of the primary beam largely defines the type of SIMS information available. For static SIMS the beam is raster scanned across the region of interest. This enables the sensitivity to be optimised by matching the analysed area to the field of view of the collection optics of the analyser.

Figure 3.9 A schematic diagram of (a) the main components of a scanning, focused ion gun (b) Operation of a Wein filter for mass selected ion beam.
3.3.3.2 The Ion Sources

As outlined in the previous section, the basic ion source is based on electron bombardment. These ion sources work upon the principles of using high current density of electrons to ionise the primary beam gas, usually argon or xenon. These sources popular with quadrupole analyser, operate with a variable energy of 0.1-5 keV allowing a range of spot sizes down to 50μm. Sources based on plasma, are rarely used and limited by the electron density which can be generated due to space charge effects. However it has some applications in many semiconductor depth profiling applications. The other source is based on surface ionisation where, the sensitivity to electronegative species is enhanced with an electropositive primary beam. Here, the ion emission is thermally stimulated by warming an adsorbed layer of, for example, caesium on the surface of a high work function metal such as iridium under vacuum condition. There is a drawback of careful handling and operational requirements of the source metal.

The brightest sources used for the surface mass spectrometry are field emission sources, which also produce the highest spatial resolution. These sources operate on the principle of stripping electrons off source atoms situated near to an extremely high electric field. The liquid metal produces the most common form of field ionisation source. Source energies of as high as 10-20 kV, can be produced by a thin skin of liquid metal flowing over a very fine tungsten tip (~5μm) in a region of very high extraction field of about $10^8$ V cm$^{-1}$ (Figure 3.10). This has an effect of distorting the skin towards the exit ring and setting up a conical shape (radius of curvature ~2μm) and ball structure of liquid metal on the probe tip (Taylor cone). Primary ions of the metal are stripped away from the ball.
Figure 3.10  Principle of a liquid metal ion source: (a) source schematic; (b) close up of extraction region.

The source brightness is exceptionally high, but the energy spread is relatively large and depends on the extracted current (5-35 eV for currents of 1-25 μA). Optimum performance for high spatial resolution is therefore achieved at the lowest possible ion current (1μA) and at high extraction voltage (20-30 kV). These are capable of producing a very narrow defined ion beam with a minimum spot size of 50nm.

The most commonly used liquid ion source is based on liquid gallium which relies on field ionising Ga⁺ from a tungsten tip to generate a very bright and highly focusable beam. Although spatial resolutions of 20-200 nm have been realised, it is very difficult to maintain static conditions and obtain sufficient signal at these levels of spatial analysis. In time of flight spectrometry the beam system is adopted for pulsing by the introduction of deflection blanking plates, which rapidly sweeps the ion beam across an aperture. The pulsed version of this type of source also offers the best prospects for molecular ion imaging at high spatial resolution. However it is extremely difficult to maintain the static conditions when these limits are achieved. In general, the spatial resolution is reduced from 200 nm to about 1μm when pulsing.
Chapter Three:  
Choice of Experimental Methods

Gallium has two isotopes $^{69}$Ga (60.1%) and $^{71}$Ga (39.9%), the primary ion beam may also contain cluster ions such as Ga$^3^+$. A *Wein filter* is generally employed between the ion gun and the specimen (Figure 3.9 b), to counter this problem, by providing isotopically separated pure $^{69}$Ga ion beam. A *Wein filter* acts as a mass separator allowing only ions of one m/z into the aperture of the analysis chamber using magnetic and electrostatic forces.

3.3.3.3 Mass analysers

As with the ion sources, the choice of mass analyser depends on the mode of SIMS being employed. For static SIMS it is necessary to maximise the information level achieved per unit of surface damage. The analysis and detection system need to be as efficient as possible for the total yield of secondary ions from the surface. The three most widely used mass analysers are the quadrupole RF mass filter, the magnetic sector, and the time of flight instrument.

Quadrupole mass analysers operate by applying AC and DC 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. These mass analysers are only effective up to masses of about 1000 Daltons, and are restricted by their mass resolution. Above masses of 1000 Daltons, the transmission falls dramatically, making quadrupole analysers unsuitable for the detection of higher mass fragments. It is also a scanning instrument so that it only allows sequential transmission of ions and all other ions are discarded at any particular point in time. The typical field of application for magnetic analysers is dynamic SIMS, i.e. depth profile analysis in most cases combination with imaging. Although it is still in use, the disadvantages lie on their slow mass scanning speed, sequential acquisition, bulky apparatus and the difficulties in generating true UHV.
Chapter Three:  
Choice of Experimental Methods

The ToF mass analyser works on the principle that the time taken for a charged particle such as an ion to travel in a constant electrostatic and magnetic field from its point of origin to a detector is a function of the mass-to-charge ratio of the ion [61]. The pulses of secondary ions are accelerated to a given potential (3 to 8 keV) such that all ions possess the same kinetic energy; they are then allowed to drift through a field-free space before striking the detector.

According to the equation of kinetic energy (Eq.3.1), heavier masses travel more slowly through the flight tube and so the measured flight time, t, of ions of mass-to-charge ratio, m/z, accelerated by a potential down a flight path provides the means for mass analysis.

\[ t = L \left( \frac{m}{2zV} \right)^{1/2} \]  
3.5

The TOF method of analysis requires a sufficiently long flight path (1-1.5 m) and very sophisticated high-frequency pulsing and counting systems to time the flight of the ion to within a few nanoseconds for good mass resolution. The inherent problem with the ToF analyser is the initial energy distribution of secondary ions (ca 20-100 eV), and the subsequent effect on any given mass rising to slightly different velocities. This can be compensated for by an energy analyser in the flight tube. In the Poschenrieder analyser a toroidal electric field produced by electrostatic sectors is interposed between two linear drift tubes (Figure 3.11). In this electrostatic field the secondary ions travel in an arc which are longer for the more energetic ions in such a way that the initial energy variation is compensated.
Figure 3.11  Schematic of Poschenrieder ToF-SIMS mass analyser

In the reflectron analyser an ion mirror performs the same function and is capable of maintaining higher mass resolution at high transmission than the Poschenrieder design. This device consists of a series of precisely spaced rings acting as electrostatic lenses with gradually increasing retarding field. Here the more energetic ions penetrate deeper into the mirror and reflected, and the less energetic ions take a shorter path and will be fine-tuned to collect all the ions of same mass to arrive at the same time at the detector. Finally a Trift™ analyser, is also capable of mass resolution by energy compensation. For this project almost all the data presented were obtained from a Poschenreider energy compensated ToF-SIMS spectrometer.
Chapter Three:
Choice of Experimental Methods

Detection in ToF-SIMS instruments employ single particle counting using a microchannel plate detector. The surface of this flat plate devise consists of an array of channel multipliers of a few tens of microns in diameter. In some cases heavy slow moving ions tend to give low yields on impacting the channel plate. This has been overcome by a variable post acceleration (to 10 keV or more) into the detector immediately prior to detection.

3.3.3.3 SIMS Imaging

The systems equipped with the mass analysers mentioned above and the liquid metal ion source can readily be used in the imaging mode. Rastering the ion beam with the mass spectrometer set to detect certain masses offers the possibility of mapping the distribution of secondary ions. The mapping on the surface elements is obtained by using an unscanned primary ion beam and a mass spectrometer with an ion optical arrangement such that the positional sense of the ions is retained throughout the mass analysis process.

The liquid metal ion beam systems can be operated with beam diameters at the samples down to 50 nm, although the typical range is 200 nm to 1 μm. The beam is digitally rastered across the surface of interest with a chosen number of pixels (for example 256 x 256). Each pixel point is used to image ions of single m/z, of a few specified m/z or a whole mass spectrum, dependent on the detail required and the sophistication of the analyser and data system. Elemental or chemical state images can then be generated of the area of interest. While the analysis of complex chemistry with good spatial resolution is possible, as the magnification increases it becomes more and more difficult to obtain images and still maintain static conditions. As the magnification increases, the number of atoms or molecules in a pixel area decreases.

When considering the sputter yield, ionisation probability and instrumental transmission, the assumption of at least 10 secondary ions per pixel for a major component, lead to the conclusion that for static SIMS analysis below 1 μm² is not really possible.
The secondary ion yield has to be dramatically increased to increase the possibilities of chemical state analysis at high spatial resolution. Recent developments in ToF-SIMS instrumentation indicate that this may soon be realised.

### 3.3.4 Analysis of Polymers

Organic materials are generally difficult to study by surface analytical techniques as they are chemically complex, usually electrically insulating and in the case of SIMS they are also very sensitive to particle bombardment. The major technique used in the past for surface analysis of polymers has been X-ray photoelectron spectroscopy. Although XPS provides multi element and chemical state information, the technique is not adequate for molecular structure studies of polymers, since the chemical state of typical constituent elements (i.e. carbon, oxygen, silicon), do not yield easily resolvable chemical shifts for all chemical environments. XPS also lacks the ability to detect hydrogen and have the photoelectron escape depths averaging over several atomic layers. Applications of SIMS on the other hand, offer high resolution fingerprint mass degree with high signal-to-noise ratio and a sampling depth of only 1-2 atomic layers. However the SIMS has its limitation in organic material analysis. The organic materials tend to have rapid degradation rates under ion bombardment and are susceptible to high rate beam damage and there is also a need for charge neutralisation. These features impose rather stringent experimental restrictions on the analytical set up of the machine.

#### 3.3.4.1 Sample Charging

The use of a positively charged beam as probe species may cause positive charging at the surface of a poorly conducting sample. The surface potential can rise rapidly by hundreds of electronvolts, giving rise to the possibility of the kinetic energy of the emitted ions rising well above the acceptance window of the analyser, and can result in the loss or instability of SIMS spectrum.
In ToF instruments, charge stabilisation can be achieved by irradiating the sample with a pulse of low energy electrons from a flood gun during the period of secondary ion analysis and detection. A carefully balanced beam will compensate for some of the excess positive surface potential, however, excess negative electrons will make the surface potential become negative and positive signal may be lost. It is also possible that the use of electron flood gun will produce problems such as electron-simulated ion emission, which is particularly common in polymer analysis. Also, when the instrument operates in imaging mode with digital scanning, the ion dose per pixel can be high enough to exceed the neutralising electron dose (which covers a very large area). Although in principle only very low energy electrons should be required to provide charge compensation, in practice, it is often necessary to increase the energy, especially for negative ion mode. This is achievable by increasing the energy of the source, or by biasing the sample during the electron pulse. Sometimes the use of a neutral primary particle beam (FAB) can be used as a means for alleviating the problem of charge build-up of a sample surface. In fast ion bombardment the unaffected ions are deflected away, and surface positive charge build up by the loss of secondary electrons, will be compensated by a proportion of those electrons returning to the surface.

It is also a common practice in SIMS analysis to place a metal grid or mesh over the insulating sample and raster the primary beam within a hole in the mesh, to maintain the surface at an appropriate surface potential.

3.3.4.2 Static limit for Sample Damage

Static conditions are usually defined as those, which maintain the integrity of the surface lay within the time scale of the experiment. The processes leading to secondary ion formation, are still destructive, and with the absence of rapid repair mechanisms, the surface will be progressively destroyed, and the spectrum will reflect the change in the structure.
Chapter Three:
Choice of Experimental Methods

The important parameter is therefore the primary particle dose required for acquisition of the spectrum. The ion dose limit for a polymer is $10^{13}$ ions cm$^{-2}$. In practise, doses of $10^{12}$ ions cm$^{-2}$ are preferable to accommodate the fact that some polymers are more damage prone than others. It has been shown [62], that the polymer features can be affected by the ion dose. In particular, the loss of C1s $\pi-\pi^*$ shake-up satellite feature of polystyrene, (a measure of aromaticity of the surface), was monitored after a fluence of $1.6 \times 10^{14}$ ion cm$^{-2}$ at 4 keV. However the C1s satellite feature was observed during the XPS study. Lower ion beam doses would be expected to produce significant changes in the static SIMS spectrum since the information from XPS is averaged over several layers. It is also important, therefore to monitor the surface damage by the decrease of characteristic ions with respect to ion dose, not by the presence of possible rearrangement of fragments.

3.3.5 Spectral Interpretation

In the case of linear or branched polymers at least four types of secondary ions can be observed. Firstly those representing one or more repeat units, where these may be intact, or slightly rearranged to achieve stability. However, in either case a sequence of ions separated by the mass of the repeat unit may be observed. The second group are derived from the repeat unit by simple process, for example the breaking of a single side chain bond, and these are highly characteristic of specific polymer. The third group consists of low mass fragments which are not structurally specific and which include atomic species and simple combinations. The fourth group consists of fragments, which occur over the whole mass range, resulting from processes that lead to ions, which have practically no link with the original polymer structure. A simplified fragmentation pattern for polystyrene, as given by Leggett et al [63], is shown is figure 3.12.

The fragmentation patterns for polymers is dependant on many factors, namely the strengths of the bonds, the stability of the products of the fragmentation, the internal energy of the fragmenting ions and the time interval between ion formation and ion detection.
Chapter Three:  
Choice of Experimental Methods

Figure 3.12  Simplified diagram of the regions in which fragmentation occurs (a) violent fragmentation in impact region, (b) unzipping to give large fingerprint region, (c) simple low-energy fragmentation in monomer region [63].

Since SIMS is a surface mass spectrometry, the fragmentation of ions closely follows the general terminology of mass spectrometry, such as odd and even electron ions, even electron rule, nitrogen rule and quasi-molecular ions. Therefore the understanding of polymer spectra has been largely been encouraged by the comparison of spectra from closely related materials having systematic variations in structure.
3.3.6 Summary

So far the basic theories, experimental details, and interpretation of XPS and ToF-SIMS have been described as they relate to the work carried out in this thesis. Both techniques have been extensively used to analyse the adhesive bonds and their behaviour under environmental exposure. The main priority of this project is to identify the exact locus of the failure following bond failure. The XPS and SIMS are utilised in this adhesive study, with the former being used for quantitative, elemental and chemical state information, and the later for its molecular specificity and for the study of surface segregation effects. In addition these surface analytical methods, Scanning electron microscopy and various other techniques have been used to characterise the bulk properties of the commercial and formulated adhesive resins. The brief details of these auxiliary techniques are given in the following sections.

3.4 SCANNING ELECTRON MICROSCOPY (SEM)

The principle application of SEM is in the study of surface topography. It is a technique particularly suited to this study of the failure surface morphologies of the 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 between 2keV 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 material analysis and more detailed description of the technique is elsewhere in literature [64]. In this work, a variable pressure SEM (Hitachi S-3200N) and a cold field emission high spatial resolution SEM (Hitachi S-4000) have been utilised.
3.5 TENSILE TEST

To compare the performance of the resin in ambient and environmental conditions, with other adhesive systems, a suitable mechanical test was first designed. The choice of mechanical test available was limited by the nature of the properties of both the substrate and the adhesive. The borosilicate glass adherends have a high stiffness and are also extremely brittle. In cases where the adhesive is fairly pliable, tests can be devised where the adhesive coating can be peeled away from the substrate without many difficulties. However, in this case most of the adhesive systems cured to produce highly cross-linked network, which was also relatively brittle. The joint geometry used in this work was a butt joint for its ease of application to the practical optical glass geometry, and for its application in the in-situ fracture experiments. The butt joints were also used as the simplest means of monitoring the decrease in mechanical properties on exposure to a hostile environment, in this case water at 40°C. The stress distribution and energy dissipation mechanisms in the butt joints have been extensively studied by many workers, and the evaluation of those parameters are beyond the scope of this work. The make of the sandwich joint structure, will be further detailed in the section on joint manufacture in the following chapter.

3.6 BULK THERMO-MECHANICAL ANALYSIS

The bulk properties of the materials, were analysed by means of their change of thermo-mechanical properties. Techniques of thermal analysis play a useful role in the characterisation of polymers and of adhesives in particular. In their most common mode, some property of the adhesive is recorded as temperature changes according to a chosen programme, but isothermal operation is usually possible, the property change with time being recorded. Dynamic mechanical analyser (DMA) studies the storage and loss moduli and loss tangent, and differential scanning calorimetry measures the heat flow. The methods used here, were combined to an extent with the surface analysis of failure joints, to make comparisons with the resins.
3.6.1 Differential Scanning Calorimetry - DSC

Whenever a material undergoes a change in physical state, such as melting or transition from one crystalline form to another, or whenever it reacts chemically, heat is either absorbed or liberated. Many such processes can be initiated simply by raising the temperature of the material. The differential scanning calorimeters are designed to determine the enthalpies of these processes by measuring the differential heat flow required to maintain a sample of the material and an inert reference at the same temperature (figure 3.13). This temperature is usually programmed to scan a temperature range by increasing linearly at a predetermined rate. The apparatus can also be used to measure heat capacity, thermal emissivity and the purity of solid samples. In addition, it can be used to yield phase diagram information and to provide kinetic data [65].

![Figure 3.13 Schematic of DSC apparatus](image)

In a DSC system the temperature of the sample and the reference (which is normally an empty sample container), increases at a predetermined rate, and is recorded. If a temperature difference is developed between the sample and the reference (because of exothermic or endothermic reaction in the sample), the power
input is adjusted to remove this difference. Thus, the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal, proportional to the difference between the heat input to the sample and that to the reference, \( \frac{dH}{dt} \), is fed into a recorder. In practice, this recorder is also used to register the average temperature of the sample and the reference.

### 3.6.2 Dynamic Mechanical Analyser - DMA

It may well be impossible to interpret fully a complex DSC trace without resort to results from other experiments such as DMA, which is more sensitive to changes in mechanical properties of the bulk polymer. Dynamic mechanical analysis is a sensitive tool for analysing thermal transitions in solid polymer samples. Thermal transitions are temperature dependent changes in the molecular structure or motion of a material. Thermal transitions are used to determine the impact properties and heat stability of a material as well as to identify the individual components in both copolymers and polymer blends. The RDA II, Rhemetrics Dynamic Mechanical Analyser, has been utilised in this project to measure thermal transitions in formulated and commercial adhesive systems, by means of forced oscillation, of rectangular shaped samples. In a forced oscillation experiment, a sinusoidal deformation at constant frequency and amplitude is applied to the test specimen. This is shown schematically in Figure 3.14, for a torsion experiment.

The motion of molecules in a solid polymer sample is restricted by the interpenetration of the polymer chains. Movement of the polymer backbone can only occur if the thermal energy available (a function of temperature) is greater than the energy required for this movement. The dynamic methods are based on the determination of a mechanical or dielectric loss in the test material. The mechanical loss determines the difference in motion of chain segments in the glassy state or in the melt. The dielectric loss is sensitive to the dipoles of the corresponding chain segment. If mechanical energy is put into a test sample, part of this energy is dissipated irreversibly by the motions of the molecules, i.e. molecule segments, usually as heat.
Chapter Three: 
Choice of Experimental Methods

The mechanical loss goes, as a function of temperature, i.e. the applied frequency, through a maximum at the transition point. Dielectric measurements show the same results for the loss behaviour, due to the difference in the rate of orientation of the dipoles at the transition. These dielectric measurements can only be performed on polymers showing a measurable dipole moment [66].

![Diagram of mechanical testing](image)

**Figure 3.14** Dynamic mechanical testing – forced oscillation [67].

### 3.7 SUMMARY

The analytical and mechanical testing techniques used in this study have been outlined in this Chapter. The project involved the use of a 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 change in the surface morphology to the mechanical performance of the system. The next Chapter will concentrate into the introduction of the materials under study.
4.1 INTRODUCTION TO TEST MATERIALS

In optoelectronic high precision applications, the majority of adhesive joints, are made with the aid of adhesives of having complex polymer chemistry. In this work the use of epoxies are of particular concern due to their extensive application in high reliability optical components. The current adhesion studies are carried out on one of the most extensively used glass substrate (BK-7 borosilicate glass) and on an optical epoxy resin (Tra-Con™ F125). In the first part of this chapter the properties of the materials are presented, while the subsequent sections concentrate on the introduction of the techniques used in this work.

4.1.1 Chemistry and Properties of Epoxy Resins – Tra-Con F125

The chemistry of the epoxy resin used in the current work will only be briefly covered, as standard resin chemistry can be easily obtained from the myriad of textbooks on polymer and adhesion science. However the cure chemistry and formulation of polymercaptan based resins are not well documented, and it is often considered as a `black art' by the manufacturers.
In addition to the major resin components, it is difficult to write an account on all the minor components and their relative amounts in an adhesive system. More problems have been encountered, when trying to obtain formulation related information from the manufacturers. However, the fundamental formulation chemistry of the resin has been identified after an extensive survey on the properties of similar epoxy resins, and with the aid of material safety data sheets.

Therefore, it is intended to describe in this section, the primary components, and the curing, of the ambient fast curing F125 type resin system. The resin is a two-part system, with one part containing the epoxy resin-diluent mixture, and the other containing the curing agent and co-curing catalytic component. The anticipated composition of the F125 two part adhesive, is shown in Table 4.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>1-(2-Aminoethyl) piperazine</th>
<th>~20%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HARDENER</strong></td>
<td>Liquid polysulphide</td>
<td>~80%</td>
<td></td>
</tr>
<tr>
<td><strong>RESIN</strong></td>
<td>Diglycidyl ether of bisphenol A (DGEBA)</td>
<td>~80%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-tert-Butyl-phenylglycidylether</td>
<td>~20%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Composition of Tra-Con F125 system, produced from manufacturers safety data sheets.

The Tra-Con F125 is a two part clear epoxy adhesive. The adhesive has 10 minutes gelling time and the manufacturer recommend the adhesive to be used in fibre optic connectors and other optical bonding applications. Also, some industrial specifications state that the material can be polished in as little as 15-20 minutes [68]. Therefore the material has a very low pot life of about 10 minutes, and has to used immediately after mixing. The general material properties as obtained from the manufacturers data sheet, are given in Table 4.2.
### Table 4.2

Some physical properties of Tra-con F125 adhesive [68].

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature range (°C)</td>
<td>-60 to 115°C</td>
</tr>
<tr>
<td>Viscosity, cps, mixed (after mixing @ 25°C)</td>
<td>15 000</td>
</tr>
<tr>
<td>Hardness, Shore D</td>
<td>76</td>
</tr>
<tr>
<td>Coefficient of expansion (cm/cm³°C)</td>
<td>$6 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The two-part adhesive was supplied in a 2 gram sachet, consisting resin and the hardener. On top of the sachet, a plastic block was used to separate the resin and hardener. Just before application, the plastic block was removed and the two halves of the adhesive were mixed for few minutes, until a clear colour was obtained throughout the sachet. The mix was then immediately applied to the surfaces, to prepare the joint. In the next Chapter the joint preparation method is described in detail.

#### 4.1.1.1 Diglycidyl ether of bisphenol A (DGEBA)

Epoxy resins are a family of ‘pre-polymers’ which contain one or more epoxide groups (oxirane rings). The epoxide group is highly reactive. This is mainly due to the high polarity of this ‘special type’ of ether group and the ease with which this highly strained [69] ring can be opened (the C-O-C angle is approximately 60°).

The application of epoxy resin requires the formation of three-dimensional networks by reaction with suitable polyfunctional hardener, which is discussed later in this section. Many of these curing reactions depend on the reactivity of the epoxy ring, which is much more reactive than the ‘normal’ non-cyclic ethers, R-OR’, where R and R’ are alkyl or aryl groups. In normal ethers the oxygen link is resistant to attack by alkalis, ammonia or amines. Epoxy resins will react with some aliphatic amines at room temperature, and these amines may be used as curing agents at ambient temperatures. This increased reactivity of cyclic ethers is due to the ring strain [70].
Diglycidyl ether of bisphenol-A (DGEBA) is one of the most common types of epoxy resins, made from epichlorohydrin and Bisphenol A. Epichlorohydrin is commercially made from propylene and chlorine in a basic medium while bisphenol-A is synthesised from acetone and phenol. The preparation of DGEBA was patented by Goppel [71] and is outlined in figure 4.1.

Figure 4.1  Production of Epoxy Resins [71]
By varying the length of the average repeat unit (n), there is a marked change in the molecular weight, viscosity and epoxide content. This is achieved by adjusting the epichlorohydrin: bisphenol-A molar ratio. To obtain pure DGEBA, a minimum ratio of 10:1 is commercially used. For example to make very low viscosity epoxides, the bisphenol-A portion of the molecule can be replaced by an aliphatic group. Obviously, there are many variations in formulating epoxies to suit the particular need of the application. The detailed chemistry on DGEBA can be obtained from any textbook on epoxy chemistry [72, 73, 74], and thus including detailed chemistry of the various formulated resins, was deemed as unnecessary in this work.

The epoxy equivalent weight (EEW) is used commercially to characterise the amount of epoxy groups present in the molecule. It is defined as the weight of resin (in grammes) containing 1 g chemical equivalent of epoxide. For DGEBA this is equal to half the molecular weight (i.e EEW = 170). EEW calculations form an important part in the formulation of model epoxy resin adhesive in the later part of this work.

4.1.1.2 Reactive Diluent – p-tert-Butyl-phenylglycidylether

The mono epoxy reactive diluent (Figure 4.2) in the F125 system, allows the diluent to participate, with the resin and curing agent, in the polymerisation and cross-linking reaction thus permitting the diluent to become chemically bound into the cross-linked network. Thus, to a degree, the use of reactive diluent can alleviate some of the debilitating effects found with the non-reactive compounds (i.e. surface segregation of minor components as studied by Taylor et al [75]).

The primary use of reactive diluents is for viscosity control. However, reactive diluents are more often used for more than their viscosity reducing effects. They are incorporated into formulations to improve film flexibility and salt spray resistance [76], but generally they give poorer chemical resistance than a corresponding diluent free system.
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

This is because the material essentially reduces the functionality of the reaction system leading to a decrease in the cross-link density of the cured formulation. Consequently important physical and mechanical properties can be affected, particularly the ability to exhibit a high temperature behaviour. Reactive diluents find only limited usage in adhesives except for speciality application. However, some grades such as F125 epoxy resin contains about 20% of reactive diluent.

![Structure of p-tert-butyl-phenylglycidylether](image)

**Figure 4.2** Structure of p-tert-butyl-phenylglycidylether (CAS-No. 79457-55-9)

Another major criticism of the usage of diluents, especially butyl glycidyl ether, is that, these reactive diluents are biologically active and are readily absorbed by the skin. Great care must be exercised when using them and skin contact must be avoided. Their lower viscosities can make certain types of diluent more hazardous than the higher viscosity liquid epoxy resins, as they flow more easily.

4.1.1.3 Primary Curing Agent - Liquid polysulphide

Liquid polysulphides are usually associated with the manufacture of high performance sealants for the building, construction, insulated glass and transportation industry. For this reason polysulphide polymers used to cure and modify epoxy resins are more often called flexibilisers than hardeners. However in F125 system, it is believed the inclusion is predominantly for its fast cure reactions with epoxy resins.
Within the application areas the adhesion, flexibility, durability and chemical resistance of the polysulphides are well understood and documented [77]. What is not so well known is the effect of mercaptan cure with other resins, namely the polysulphide-epoxy resins. Therefore in this section the general properties and its cure with epoxy resin will be briefly covered.

To understand the properties and how they are obtained requires an examination of the chemical and physical structure of the poly sulphide polymer itself (see Figure 4.3). Chemically, the liquid polysulphides are polymers of bis-(ethylene oxy)methane containing disulphide linkages. The formal or ether linkages in the polymer backbone provide considerable mobility and therefore flexibility to the polymer.

The liquid polysulphides are classified as elastomers and have glass transition temperatures in the range -55°C to -65°C. The saturated nature and the very high sulphur content of the polymer provides chemical resistance to a wide variety of organic solvents, dilute acids, alkalis and water. The absence of unsaturation and carbonyl structures also endows the polymer with good outdoor weathering and resistance to both ultra violet light and ozone. The polymer molecule is terminated with mercaptan groups, which are capable of reacting with a variety of chemical species including the epoxide groups of an epoxy resin. The value of the molecular repeat unit “n” governs the molecular weight of the liquid polysulphide polymer. The value of “n” can be controlled at the manufacturing stage to produce liquid polymers whose molecular weights range from 8,000 to 1,000 [78].

In general the choice of polysulphides as modifiers for epoxy resins has been based on their molecular weight, viscosity, mercaptan content, and functionality. Branching can be introduced into the polysulphide molecule by adding the trifunctional monomer, trichloropropane [79]. This subject will be further discussed in the Chapter on the re-formulated resins.
Chapter Four: The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

The structure of the liquid polysulphide is shown in Figure 4.3. The linearity of the polymer ensures that during co-reaction with an epoxy resin, chain extension rather than cross-linking reactions predominate. Although this can be useful in adding flexibility to the system, an additional curative is needed to obtain a balanced cure network. As stoichiometric loading with liquid epoxy resins is high, this leads to highly flexible products with very low cross-link densities and poor mechanical properties.

In practice however not more than half the stoichiometric quantity is used with the proportion varying according to the degree of flexibility required, and co-curing cycloaliphatic amines and tertiary-amine catalysts are used to upgrade mechanical properties.

![Chemical structure of liquid polysulphide with a disulphide linkage](image)

**Figure 4.3** Chemical structure of liquid polysulphide with a disulphide linkage

4.1.1.4 Co-curing catalytic agent – 1-(2-aminoethyl) piperazine

This higher homologue aliphatic polyamine of (hetero-) cyclic backbone from the ethyleneamine stream of products contains primary, secondary and tertiary amine groups although only the three primary and secondary active hydrogens participate in reaction with epoxy resin (Figure 4.4). Primary amines also react with epoxy resins and in so doing form secondary amines, which are capable of further reaction resulting in the formation of tertiary amines.
Chapter Four: The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

The curing mechanism of the tertiary amines is completely different to that of either primary or secondary amines. The tertiary amine acts as a Lewis base catalyst, and here performs an accelerating function in mercaptan cure.

Although both the primary and secondary amines are involved in the cure reactions, the amine cure is not predominant. It contains only \(-20\%\) of the hardener mixture, which is higher than catalytic amounts but far less for a sole curing agent. While the primary function of the amine is to accelerate the mercaptan cure, it enhances the mechanical properties by the primary and secondary amine cure.

Interaction of the mercaptan groups in polysulphide and the epoxy ring leads to the simple chain extension. However the reaction is accelerated by tertiary amine which may function by either (i) forming mercaptide ions or (ii) opening the epoxide ring (Figure 4.5).

![Figure 4.5](image_url)

**Figure 4.4** Primary and secondary amine cure of 1-(2-Aminoethyl) piperazine with epoxy resins

Tertiary amines can also catalyse interaction between the hydroxyl groups formed and remaining epoxy groups and a cross-linked structure is built up. Therefore the incorporation of 1-piperazine ethanamine in polysulphide epoxy F125, enhances the mechanical properties of the cured system, while accelerating the cure reaction of the mercaptans.
Figure 4.5 The addition reaction of the mercaptan group (-SH) with epoxy resin, from the catalysis at room temperature by amines, which promote production of reactive mercaptide ions [79].

4.1.2 Substrate Material - BK 7 Borosilicate Glass

In optics many simple lenses, prisms and mirror substrates are made of BK 7, grade A fine annealed, borosilicate crown glass (Schott™ Glaswerke, Germany). This material has been extensively used by the opoelectronics industry and also most commonly joined using epoxide adhesives. The material was supplied as a 10mm diameter disc of 3mm thickness.

BK 7 performs well in many rigorous chemical test specifications, and this eradicates the need for special treatment during polishing [80]. It is a relatively hard glass (Knoop hardness = 610), it does not scratch easily and can be handled without special precautions.
Also, the bubble and inclusion content is low and cross-section totals less than 0.029 mm$^2$ per 100 cm$^3$. Another important characteristic of BK 7 is its excellent transmittance, down to 350 nm. The oxide composition of the BK 7 optical borosilicate, is shown in Table 4.3.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Weight percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>60-70</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>10-20</td>
</tr>
<tr>
<td>BaO</td>
<td>1-10</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1-15</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>5-15</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;1</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ti$_2$O$_4$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Sb$_2$O$_3$</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

**Table 4.3** Bulk composition of BK 7 fine annealed borosilicated optical glass [81].

Boric oxide (B$_2$O$_3$), itself a glass former, acts as a flux (i.e., lowers the working temperature) when present in silica and forms borosilicate glass, and the substitution of small percentages of alkali increases the chemical stability. It also exhibits low thermal expansion, high dielectric strength, and high softening temperature.

Borate glasses, free of silica, are of limited practical interest (Lindemann glass). However, boric oxide as a constituent of complex silicate glasses is of great scientific and practical interest, although it affects only a small volume of glass as far as the industry as a whole is concerned.
Chapter Four:  
*The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass*

Schott *et al* [82], found two valuable properties, which B$_2$O$_3$ imparts to a silicate glass, namely improved chemical resistivity and improved resistance to thermal shock. The addition of B$_2$O$_3$ lowers the co-efficient of expansion of alkali silicate glasses so that they become more resistant to rapid changes in temperature. The so-called boric oxide anomaly has been extensively studied, such that the properties of alkali silicate glasses can go through extreme values when varying the concentration of B$_2$O$_3$.

The composition and structures of borosilicates has been explored by many workers [83, 84], and this will not be explored further in this thesis. The following section will briefly explain the procedures involved in the production of optical glass buttons for this project.

4.1.2.1 Production of Glass Substrates

For the manufacture of optoelectronic glass components, two types of objectives are taken into consideration. These differ in their quality requirements and also with respect to their methods of manufacture. There are about twenty different procedures to be carried out, from the supply of material and slitting to the final testing of the finished article. However a special request was made to the manufacturers of the BK 7 glass, to avoid using oil mixtures as cutting lubricants.

The cutting and polishing was carried out by the manufacturers, *Schott Glaswerk*, at a plant in Netherlands. The fabrication of fine, precision glass devices are long and laborious process. The summary of the production procedures are given bellow:

The glass is delivered by the makers in the form of random slabs, then the slabs are cut into slices with a diamond saw. After slitting, the plates will be found to have deep wheel scuffs, and it is necessary to bring them closer to finished button thickness. Using the appropriate grinding tools on a machine with a supply of rough
Chapter Four:
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

abrasive or with a milling machine fitted with a diamond tool, the finished thickness for glass buttons will be achieved. The broken edges of the cut pieces are clear, and it is therefore possible to check them for bubbles and any other inclusions. This normally done with a lamp and with a specialised test apparatus (Shlieren test apparatus [85]). This instrument records the changes in the refractive index distribution of transparent media. The final mouldings are also checked for stress, with the help of a polarising viewer. Test of all optical parts will be carried out according to appropriate national or international standards.

Bubbles are usually only cosmetic defects, particularly when they are neither large nor numerous enough to influence significantly the intensity of light transmitted or scattered by the objective. However strain and stress can not usually tolerated in optoelectronic objectives because they are the result of inhomogeneities and consequently the refractive index is different in different portions of the glass, which adversely affects the transmission quality [86].

After the initial process, more complex procedures of rounding the pieces into cylindrical blocks, obtaining the accurate radii and fine polishing methods will be carried out. However these will not be discussed further in this section.

4.2 MATERIALS CHARACTERISATION

4.2.1 Introduction

The results discussed in this section fall into two major categories: the characterisation of the adherend, and the characterisation of the adhesive. The investigation has drawn on a combination of surface analytical methods, microscopy and mechanical testing techniques.

Later in the thesis, the joint durability and the fracture studies will be carried out. It is therefore important to gain as much information about the adhesive and substrate as possible, before considering the interactions between them.
4.2.2 Characterisation of F125 Adhesive System and the Components

The Tra-Con F125 resin used during the course of this study was a fully formulated, commercially available system, produced by Tra-Con Inc., USA. As precise formulation details are commercially sensitive, some of the formulation chemistry is unavailable. The information necessary for understanding the behaviour of F125 as an adhesive has however been obtained after a survey of similar optical resins. The initial part of this section comprises of characterisation of the individual components of the resin system, and the later part consists of the analysis on the commercial F125 adhesive resin. The adhesive components detailed in this section may not be the exact variants for the commercial F125 system. But, they chemically resemble the individual components of the F125 adhesive. The components were selected after a careful study of their material properties, and these will be later used in the reformulation of the adhesive resins. The selected commercial grades of the four major constituents, DGEBA, diluent, amine and polysulphide, are given below:

i) DGEBA – Araldite 6005/Aldrich

ii) Diluent – 148059/Aldrich

iii) Amine – A55209/Aldrich

iv) Polysulphide – LP 33/Morton Thiokol

4.2.2.1 Analysis of Adhesive Components

Characterisation of the four adhesive components has been carried out by casting a thin layer of solution on to a clean aluminium surface. For the ToF-SIMS analysis, this was achieved by spin casting a controlled volume of the adhesive component solution (1-2% w/w) in acetone, onto a tailor made aluminium ESCALAB type stub (90% aluminium alloy).
This method has produced a uniform layer of material on the surface, with reduced charging problems in SIMS. For monochromated XPS analysis, the ESCALAB stub was covered with an aluminium foil, and the spin casting was done on the foil surface. Then the foil was carefully removed for analysis.

The stubs were ultrasonically cleaned by acetone and then by isopropanol, prior to spin cast. Then the sample stub was mounted on to a simple low-speed rotor (100Hz). Using a Pasteur pipette, few drops of polymer solution were placed on the stub surface and spun for few seconds. This has produced a uniform polymer film on a hard flat substrate, which is not prone to charging problems. The film thickness (~few μm) is sufficient to prevent escape of photoelectrons from the substrates.

4.2.2.1.1 XPS Results

Many variants of the DGEBA are available to the formulation chemist, but this particular grade was selected for its extensive application in commercial adhesive formulations. Except for molecular weight distribution, it is expected that the epoxy resin in the commercial adhesive would have the same chemical structure as Araldite 6005.

As expected the XPS survey spectra of the spin cast DGEBA resin (Araldite 6005), and the reactive diluent (4-tert butylphenyl glycidyl ether) are dominated by just carbon and oxygen photoelectron peaks. However the C 1s high-resolution spectra of these components of the adhesives indicated feature related to their chemical structure. The high-resolution peak fitted C1s spectra obtained with a monochromatic Alkα X-ray source are shown in Figure 4.6 and 4.7.

The peak-fitting of the C 1s was assessed by the plot of the residuals and visual assessment of the quality of the fit. The full width at half-maximum (FWHM) of the individual components of the C 1s spectra were constrained within the range of 0.9-1.5 eV, which enabled the spectra to be fitted in a satisfactory manner. The peak fitted C 1s components are shown in Table 4.4 and 4.5.
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

Figure 4.6  High-resolution C1s spectra of DGEBA.

Figure 4.7  High-resolution C1s spectra of the diluent, p-tert-butyl-phenylglycidylether
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy shift (eV)</th>
<th>FWHM (eV)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-C/C-H</td>
<td>-0.48</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>C-C/C-H</td>
<td>--</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>O-C-O</td>
<td>0.90</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>C-O</td>
<td>1.35</td>
<td>0.90</td>
</tr>
<tr>
<td>5</td>
<td>O=C</td>
<td>1.85</td>
<td>0.95</td>
</tr>
<tr>
<td>6</td>
<td>π - π*</td>
<td>5.23</td>
<td>1.60</td>
</tr>
</tbody>
</table>

**Table 4.4** Peak-fitting data from the C 1s spectra of Araldite 6002 (DGEBA).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy shift (eV)</th>
<th>FWHM (eV)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-C/C-H</td>
<td>-0.60</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>C-C/C-H</td>
<td>--</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>O-C-O</td>
<td>0.55</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>C-O</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>O=C</td>
<td>1.53</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>π - π*</td>
<td>4.70</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Table 4.5** Peak-fitting data from the C 1s spectra of the diluent, p-tert-butylphenylglycidylether.

The chemical structure of the epoxy resin differs from the diluent only by having a repeat unit and a bisphenol structure on its backbone. Therefore all the peaks associated with DGEBA can also be fitted to the C 1s spectrum of the diluent. These are aromatic hydrocarbons, aliphatic hydrocarbons, aromatic ether carbon, aliphatic ether carbon and carbon associated with the epoxy end groups.
The π-π* shake up effects was small in the C 1s of the diluent, and it was found difficult to resolve and quantify in a satisfactory manner.

The apparently symmetrical C1s from the amine is shown in Figure 4.8. As observed from the chemical structure of the 1-(2-Aminoethyl) piperazine, the C1s will possibly have only three peaks. The surface concentration of these three peaks of the C 1s is given below on Table 4.6.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C—N—H</td>
<td>1.15</td>
<td>31.75</td>
</tr>
<tr>
<td></td>
<td>Secondary Amine carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C—N—H</td>
<td>0.47</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Primary Amine Carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C—N—R</td>
<td>1.13</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>Tertiary Amine Carbon</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6 Peak-fitting data from the C 1s spectra of the amine

Figure 4.8 High-resolution C1s Spectra of the amine.
Finally the peak fitting of the C 1s for the polysulphide has been carried out (Figure 4.9). The chemical structure of the polysulphide is that of a simple linear polymer. The resultant C1s high-resolution spectrum indicates the three distinct functionalities, thiol, aliphatic ether and aliphatic diether carbon peaks (Table 4.7). This peak fitting can be confirmed by the theoretical calculations of the number of carbon species in polymer. This also shows similar contribution as identified in the XPS peak fitting.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>Theoretical % Area</th>
<th>Peak fitted % Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 C—S</td>
<td>285.52</td>
<td>1.11</td>
<td>40</td>
<td>45.0</td>
</tr>
<tr>
<td>Thiol Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 C—O</td>
<td>286.67</td>
<td>1.15</td>
<td>40</td>
<td>37.7</td>
</tr>
<tr>
<td>Aliphatic ether Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 O—C—O</td>
<td>288.06</td>
<td>1.15</td>
<td>20</td>
<td>17.7</td>
</tr>
<tr>
<td>Aliphatic Diether Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7 Peak-fitting data from the C 1s spectra of the Polysulphide.

![Figure 4.9](image.png) C1s High-resolution scans of the Polysulphide.
4.2.2.1.2 SIMS Analysis of the Adhesive Components

4.2.2.1.2.1 SIMS of the Epoxy Resin

SIMS analysis was carried out, after spin casting the adhesive components on to a aluminium surface as explained in the previous section. The positive ToF-SIMS spectra of the spin cast DGEBA are shown in Figure 4.10, for the mass range \( m/z = 100-350 \).

![Positive ToF-SIMS Spectra of spun cast Araldite 6005](image)

**Figure 4.10** Positive ToF-SIMS Spectra of spun cast Araldite 6005

The expected fragment ions from epoxy groups (at \( m/z = 57, 191, 252 \) and 269), bisphenol groups (\( m/z = 135, 165 \) and 213) and the oligomer (\( n = 0 \)) at \( m/z = 340 \), are all observed from the Araldite sample. These are in good agreement with the observations made in previous work on commercial materials of this type such as Epikote™ epoxy resins [87]. Assignment of the dominant ions in the spectrum is provided in Table 4.8.
4.2.2.1.2.2 SIMS of the Diluent

As shown in the spectra (Figure 4.11), the fragmentation pattern of the diluent is close to that of the DGEBA, as both have similar chemical structures. However this spectra have some characteristic ion fragments, including that for the molecular ion ($m/z = 206$).

The ion fragments observed from both the diluent and DGEBA material are summarised in Table 4.8. Although some fragment ions of characteristically high intensity are assigned to the diluent, the DGEBA epoxy resin may also have the same ion fragment.

![Figure 4.11 Positive ToF-SIMS Spectra of spun cast 4-tert-butylphenyl 2,3- epoxy propyl ether (Diluent)](image-url)
### Table 4.8 Major positive ion fragments for an uncured epoxy type adhesive.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Source</th>
<th>Fragment/Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>Araldite 6005/Diluent</td>
<td>CH$_3$ - CH$_2^+$</td>
</tr>
<tr>
<td>31</td>
<td>Araldite 6005/Diluent</td>
<td>HO - CH$_2^+$</td>
</tr>
<tr>
<td>43</td>
<td>Araldite 6005/Diluent</td>
<td>CH$_2$ - CH - CH$_2$</td>
</tr>
<tr>
<td>57</td>
<td>Araldite 6005/Diluent</td>
<td>CH$_2$ - CH - CH$_3$</td>
</tr>
<tr>
<td>77</td>
<td>Araldite 6005/Diluent</td>
<td>HO - CH$_2$</td>
</tr>
<tr>
<td>86</td>
<td>Diluent</td>
<td>C$<em>5$H$</em>{10}$O$^+$ or C$_4$H$_6$O$_2^+$</td>
</tr>
<tr>
<td>91</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>115</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>Diluent</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>149</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>163</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>Araldite 6005/Diluent</td>
<td></td>
</tr>
<tr>
<td>206</td>
<td>Diluent [M]$^+$</td>
<td></td>
</tr>
<tr>
<td>213</td>
<td>Araldite 6005</td>
<td>HO - CH$_2$</td>
</tr>
<tr>
<td>252</td>
<td>Araldite 6005</td>
<td></td>
</tr>
<tr>
<td>269</td>
<td>Araldite 6005</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>Araldite 6005[M-CH$_3$]$^+$</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>Araldite 6005 [M]$^+$ (n=0)</td>
<td></td>
</tr>
</tbody>
</table>
Spectra obtained from the analysis of almost all of the adhesive constituents, and from the cured adhesive showed traces of siloxane present (probably poly(dimethyl siloxane), [PDMS] with peaks at m/z = 73 and 147. The confirmatory peaks for PDMS were also found in the negative ion spectrum (m/z = 75 and 149). However the analysis from the bulk adhesive samples (see section 4.2.2.2), have shown a relatively low intensity peaks in comparison to the adhesive ion peaks such as m/z = 91 and 77. PDMS has extremely low surface tension and viscosity, which makes it very mobile on surfaces and thus widely used as a mould release agent. The effect of the contamination is expected to be large on the free surface rather than in the bulk of the material. Therefore it was deemed that the peaks at m/z = 73 and 147 does not play any major role in the characterisation of the fracture surfaces of a joint.

4.2.2.1.2.3 Analysis of Polysulphide Curing Agent by SIMS

Figure 4.12 shows the SIMS spectra obtained from the mercaptan based curing agent of the system. The spectra show the features of a linear fragmentation of the sulphide polymer. The characteristic ion fragments from the polysulphide, m/z = 61, 93, 105, 135, 166, 243, 287 and 334 are shown in Table 4.9. Unfortunately the thin layer of material cast on to the sample stub for this analysis was not contiguous, e.g. Al⁺ at m/z = 27, and this led to signals assigned to aluminium ions to be observed from the spectra.

| +CH₂-SH | 47 |
| +CH₂-CH₂-SH | 61 |
| +CH₂-S-S-CH₃ | 93 |
| +CH₂-CH₂-O-CH₂-CH₂-SH | 105 |
| +CH₂-CH₂-O-CH₂-O-CH₂-CH₂-SH | 135 |
| [S-H-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-S-H][⁺] | 166 (n=0) |
| +CH₂-O-CH₂-S-S-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-SH | 243 |
| S-H-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-S-S-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-S-CH₃ | 287 |
| [S-H-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-S-S-CH₂-CH₂-O-CH₂-O-CH₂-CH₂-S-H][⁺] | 334 (n=1) |

Table 4.9 Major positive ion fragments for the polysulphide curing agent
4.2.2.1.2.4 SIMS of the Amine

As discussed earlier, the amine used in this adhesive system is a cyclic aliphatic piperazine. The fragmentation behaviour resembles greatly that of piperidine and its derivatives. The spectra (Figure 4.13) shows many of the usual amino fragments, such as \( m/z = 30 \) (\( \text{CH}_2\text{-NH}_2 \)), 44 (\( \text{CH}_2\text{-CH-CH=NH}_2 \)) and 56 (\( \text{CH}_2=\text{CH-H=NH}_2 \)). Strong signal from the aluminium foil surface (\( m/z = 27 \)) can also be also observed in the Spectrum. The characteristic ion fragments for the 1-(2-aminoethyl) piperazine, as shown in Table 4.10.
Chapter Four:
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

Table 4.10 Major positive ion fragments of 1-(2-aminoethyl) piperazine.

Figure 4.13 Positive ToF-SIMS Spectra of spun cast of the Amine
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

4.2.2.2 Analysis of cured F125 Adhesive System

In order to characterise the complex F125 resin as a system, static SIMS, and the XPS were both employed to a great extent. With techniques such as XPS and SIMS it was possible to analyse samples of both the cured and uncured resin. So far, the analysis of uncured resin has been carried out. 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. Analysis of fully cured resin is also important, as results of failure analysis will relate to the cured rather than the uncured resin.

4.2.2.2.1 SIMS of the cured F125 Resin System

A comparison of the cured and uncured state of the adhesive was carried out by the analysis of thin films of cured resin. This is achieved by a novel sample preparation as shown in Figure 4.14. This microtoming method involves slicing thin layers of polymer using a clean glass knife. Adopted from a biological specimen preparation method, it produces fresh-clean polymer films of about 10 μm thickness. Such samples reduce the charging problems associated with XPS and SIMS experiments.

Figure 4.14  Schematic of the production of thin adhesive films by microtoming.
Chapter Four:
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

The spectrum obtained from cured resin (figure 4.5), shows the ion fragments from the multi-component resin system which include curing agents, diluent, epoxy resin and may be some other minor components. The characteristic peaks of \( m/z = 77, 91, 103, 115, 165 \) and 178 are highly unsaturated hydrocarbon fragments formed by aromatic compounds, such as the biphenol-A part of the DGEBA. The even ion mass ions of \( m/z = 30, 44, 56, 58 \) and 70 are diagnostics of nitrogen-containing fragments, in particular for this study is the amine curing agent. The ions \( m/z = 57 \) and 59 (\( \text{CH}_2\text{OCHCH}_2^+ \) and \( \text{CH}_3\text{CHOHCH}_2^+ \)) are generally regarded as being characteristic of cross-linked epoxy material, although they can be formed by several other components of the system. Here the \( m/z = 57 \) and 59 are dominant peaks, and in particular peak at \( m/z = 57 \) is an indication of the amount of cure of the resin. However the \( m/z = 59 \) is not very intense in the uncured pure DGEBA, and gives rise to the suggestion that this may have formed from some other oxygen containing material such as a reactive diluent. In addition to epoxy and amine fragments, the spectrum also contain characteristic thiol curing agent fragments (i.e \( m/z = 61 \)), and these are the dominant peaks in the spectrum of the spin cast of unreacted liquid polysulphide.

![Figure 4.15 Positive SIMS spectra of the cured adhesive](image-url)
4.2.2.2 XPS of F125 Adhesive

The survey spectrum obtained from thin film of fully formulated F125 (AlKα), revealed four major peaks, for carbon (69.96%), oxygen (21.61%), nitrogen (6.96%) and sulphur (1.48%) (Figure 4.16 (a)). The high-resolution spectrum of the carbon region is presented in Figure 4.16 (b), (VG Scientific sigma probe spectrometer). On Figure 4.16 (b), attempts were made to resolve its component parts, by peak-fitting. This was initially proved to be quite difficult, as the resin is estimated to have about sixteen different carbon functionalities, attributed to the various components of the resin. Since the resin is fully cured the major components predominantly attributed to the DGEBA type.

In this case the peak fitting has been generalised to fit into five different carbon environments, with the full width half-maximum (FWHM) of the individual components of the C1s spectra constrained within the range of 1.2-1.4 eV. The FWHM for this particular peak fit is not as good as for the XPS of adhesive components, which have produced the widths of up to 0.9 eV, with a monochromatic source, but it is anticipated that subtle variations in the bonding environments of the fully cured resin will give rise to a range of binding energies which will in turn traced to a broader component. The peaks associated with the cured resin, fitted to the C1s spectra, are given in table 4.11.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding Energy Shift (eV)</th>
<th>FWHM (eV)</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-C/C-H</td>
<td>1.35</td>
<td>30.31</td>
</tr>
<tr>
<td>2</td>
<td>O-C-O</td>
<td>1.20</td>
<td>17.83</td>
</tr>
<tr>
<td>3</td>
<td>C-O</td>
<td>1.30</td>
<td>33.87</td>
</tr>
<tr>
<td>4</td>
<td>O-C-C</td>
<td>1.30</td>
<td>13.91</td>
</tr>
<tr>
<td>5</td>
<td>O-C-O</td>
<td>1.30</td>
<td>3.38</td>
</tr>
<tr>
<td>6</td>
<td>π-π* Shake up effect</td>
<td>2.00</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 4.11 Peak fitting data from the C 1s spectra of fully cured F125.
The five peak assignments are attributed to, aromatic and aliphatic hydrocarbon ($\text{C}_1$-$\text{C}_2$-$\text{H}$), aromatic ether carbon ($\text{C}_2$-$\text{O}$), aliphatic ether carbon ($\text{C}_3$-$\text{O}$), carbon associated with epoxy end group and aliphatic diether carbon (O-$\text{C}_5$-$\text{O}$). (Figure 4.16 (b). In addition to the major peak assignments, a small $\pi$-$\pi^*$ shake-up satellite, caused by the bonding-antibonding transition in aromatic organics, was also observed (see detailed discussion on secondary structures, page 36-37). While the first four components are suspected to be derived from the DEGAB based compounds, the fifth, diether, carbon is a common feature among linear polysulphide based curing agents.

Figure 4.16  XPS survey spectra of cured F125 9(a) and high resolution C 1s (b).
4.2.2.2.3 Bulk Analysis by DSC and DMA

The bulk analysis of the cured polymer was used to aid understanding of the physical characteristics, in particular, the glass transition of the polymer. A DSC trace might show some features relate to the enthalpy change of the polymer associated with an endothermic or exothermic change. The use of shape and area of the trace can establish the crystalline melting (endothermic peak), crystallisation and curing in reaction setting adhesives (exothermic peak).

Degradation studies of the adhesives are also possible by the use of exothermic peaks. However the purpose of this analysis is to study the changes in specific heat capacity, and the corresponding deterioration in the mechanical properties.

As shown in Figure 4.17 (a), the step component in DSC trace represents a change in specific heat at a particular temperature (41°C) and this indicates the glass transition temperature of the adhesive ($T_g$). The vitrification is a complex process and very sensitive to the rate of heat and cooling of the test. In this DSC trace the cooling rate of the experiment seems to be slightly higher, as a small bump was observed at the inflection point at 38°C, sometimes termed the 'undershoot' of the curve. However this did not significantly effect the results, as repeated tests confirmed the uniformity of the inflection point. The sample showed no exothermic cure reaction, which is often observed by the dip in DSC curve after the transition point. This indicates a higher degree of cure of the material.

It is sometimes impossible to interpret fully a complex DSC trace without resorting to results from other experiments. In addition, although DSC can measure the Tg of the epoxy, the actual decrease in the mechanical properties can occur prior to the glass transition. In DMA, the absolute value of the generated stress is measured and the glass transition temperature can be obtained from the tan δ value (see Chapter 3). The DMA traces for the F125 system is shown in Figure 4.17(b), and the tan δ for F125 system shows the transition of the polymer lies around 40°C.
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

4.2.3 Characterisation of the Adherend

4.2.3.1 Introduction

An initial study was carried out on the as received borosilicate glass substrate, in order to characterise the adherend surface prior to bonding. This is particularly important, since surface chemistry of many of the substrates used for optoelectronics applications is known to be heterogeneous. Leaching of sodium ions from the glass network [88] and the diffusion of various other species such as silica and magnesia has been studied many workers [89], can result in the production of a chemically heterogeneous and mobile bonding surface. Therefore, surface characterisation is important, in determining the nature and the amount of different chemical species present in the adhering surface.
4.2.3.2 XPS Analysis

4.2.3.2.1 Sample Preparation

The Schott BK-7 borosilicate glass material was supplied by Mellos Griot Limited, in the form of 10 mm diameter buttons of 3 mm thickness. With the exception of a water rinse following the diamond cut process, and the discs received no additional cleaning.

The glass discs were obtained with no antireflection coating, as this is quite often the case for fibre optic terminations. This was also in order to identify the adhesion process between the substrate as accurately as possible. The discs were mounted on sample stubs with double-sided tape prior to analysis by XPS.

4.2.3.2.2 Results of XPS Analysis

The survey spectra obtained from the as received BK 7 material and for the surface cleaned with a solvent cleaning regime, are shown in Figure 4.18. The spectra were obtained from the VG Scientific ESCALAB Mk II electron spectrometer, using an AlKα non-monochromated X-ray source. As expected, the as received borosilicate surface has a significant level of adventitious carbon present, compared to the solvent cleaned glass surface. In both cases, especially in the as received surface, the carbon 1s high-resolution spectrum is a singlet peak with a width of 2.8 eV. This feature is characteristic of substrates used in many technological applications, with a medium to high-level hydrocarbon contamination, with surface concentration of about 40%. This feature will dominate any minor features from the carbon that may be present, and thus make them obscure to assign.
Chapter Four:  
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

The oxygen 1s peak, in both cases is the most dominant, and the remaining species detected included, silicon, sodium, boron, potassium, calcium, fluorine, titanium, nitrogen and barium (Table 4.12). However the surface characterisation result does not show any presence of antimony or zinc as identified from the bulk composition date, supplied by the manufacturers. This may be due their relatively small concentration in the bulk (<1%) and also an indication of surface heterogeneity of the glass.

<table>
<thead>
<tr>
<th>Surface composition/ Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>AS RECEIVED</td>
</tr>
<tr>
<td>45.1</td>
</tr>
<tr>
<td>SOLVENT CLEAN</td>
</tr>
<tr>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 4.12  XPS Quantification of BK 7 Substrate Material.

The cleaning regime of the glass substrates was carried out ultrasonically by a series of washes with acetone and isopropanol. The presence of nitrogen due to surface contamination during manufacturing process has also been removed in the solvent clean sample.

A rigorous cleaning regime may reduce the adventitious carbon even further, but the procedures carried out here resembled the industrial method, and will be continued throughout the project. The more pronounced Auger peaks of FKLL and Na KLL are also observed following the surface cleaning. Chlorine 2p was also detected in some of the as-received surfaces, which can be induced by the use of chlorinated solvents in the final stages of polishing during component manufacture.
Chapter Four: 
The Adhesive Joint System: Characterisation of A Commercial Optical Adhesive and A High Quality Glass

The surface concentration of silicon and carbon are relatively higher in the as-received sample, while silicon is from the glass, which is also typically of the contaminant source poly (dimethyl siloxane) PDMS. This was further confirmed by the ToF-SIMS results, where the PDMS fragments (m/z = 73, 133, 147, 207, and 221) were observed together with some unspecific organic contaminants, for the as received samples.

![Graph](image)

**Figure 4.18** XPS Survey Spectra of Borosilicate BK-7 Glass Surface.
4.2.3.3 Results of Analysis by ToF-SIMS

Positive static SIMS spectra of borosilicate surface obtained, using a VG Scientific Poschenreider type analyser is shown in Figure 4.19. The results show all the characteristic ion fragments, as specified by the XPS spectrum. The Ti\(^{+}(m/z = 48)\), and Mg\(^{+}(m/z = 24)\) show very low intensity peaks, as they are less than 1% in the bulk material.

The other general features include the oxides and hydroxides of some of the inorganic species. The one important observation from this solvent clean sample is that the absence or very low levels of the organic contaminants, and this further reinforces the choice of the application of this cleaning method for the project.

![Figure 4.19 Positive ToF-SIMS spectra of the solvent cleaned BK7 surface](image)

The negative spectra also showed the characteristic inorganic ion fragments of typical borosilicate glass. However traces of chlorine \((m/z = 35)\) have also been observed, and this was reported elsewhere [86, 90], as a possible source of contamination.
4.2.3.4 SEM Results

The scanning electron micrographs were obtained from a BK7 glass disc using a cold field emission SEM. The comparison of the micrographs for a polished BK 7 surface (fine grinding and polish), and a fine polished smooth surface for optical components applications are shown in figure 4.20.

![SEM micrographs of: (a) BK 7 material with standard polish, (b) Fine polished for fibre optics applications.](image)

**Figure 4.20**  SEM micrographs of: (a) BK 7 material with standard polish, (b) Fine polished for fibre optics applications.

On the relatively rough surface, Figure 4.20 (a), the unevenness of the surface varies from 5-15μm, as determined by the SEM. However on the fine polished sample, Figure 4.20 (b), (as used for this project) the surface physical irregularities are difficult to observe even at very high resolution. The slight surface cracking marks observed in the smooth surface are often observed in gold sputter coated surfaces, due to the cracking of the thin film.

Finally the comparison of solvent cleaned and as-received samples are not shown in here, but the results show only surface debris and some other contaminants in the non-solvent cleaned sample, which predominantly resulted from the manufacturers abrasion process.
4.3 SUMMARY

In summary, XPS and SIMS have 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. In addition to the surface techniques, the bulk analysis experiments were also applied to understand the basic physical properties such as glass transition temperature of the adhesive materials. This information is useful to compare the physical characteristics of similar adhesives. Also, an understanding of the nature of the adhesive and the adherend are very useful when analysing the durability of the joints made from reformulated resins (Chapters 8 & 9).

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. Prior to study the effects of hostile environment such as water, on adhesive joints, it essential to evaluate the fracture behaviour of the joints under dry conditions. Therefore the following chapter will concentrate on the dry fracture of joints made from the commercial F125 adhesive.
5.1 JOINT GEOMETRY AND MANUFACTURE

There are limitations associated with any particular joint geometry selected for a mechanical test. In this particular study the joint geometry chosen is a simple butt joint. The main reason for this choice was to enable an existing T-peel stage to accommodate samples, which could be fractured in-situ in the preparation chamber of the ESCALAB spectrometer. In addition, the geometry of the joint resembles that employed in many glass components used for optical applications. It is not the intention of this study to carry out a detailed fracture mechanics study, but the aim is to analyse failure characterisation of joints of having the same geometry, and the effect of varying environmental conditions.

The Figure 5.7 schematically shows the assembly of standard butt-joint and the ESCALAB stubs. The joint assembly comprised of two ESCALAB stubs and 10 mm diameter BK 7 glass discs of the joint, attached to them with three sets of screws by the sides of the platform. This manner of attachment was used in preference to adhesive bonding of the glass to the mounting stubs. Initially it was difficult to obtain an adhesive, which was stronger than the bond strength of the butt joint. Several different adhesives have been tried, but none were found strong enough to hold the glass substrate to the stub base when conducting tensile tests.
Therefore it was decided to modify mechanically the platform of the stub, to accommodate the joint. This was achieved by altering the thickness of the platform (~4 mm), and then machining a recess (~ 10 mm) in the centre of the stub. This modification enabled the joint to be fixed into the hole of the ESCALAB stub (figure 5.9, b). Then the joint was secured by tightening the screws on the sides of the stub platform. This modification was successful with only the occasional cracking of the substrate glass, initiated by the end of the tightened screws.

![ESCALAB sample stub](image)

**Figure 5.7** Schematic of a butt-joint in the ESCALAB stubs.

The substrate material was cleaned using the cleaning regime described in the previous section, immediately prior to bonding to the stubs. The two halves of the joints were secured in a jig, shown in Figure 5.8. This jig assembly consists of a calibrated dial gauge with an accuracy to measure up to 1 μm. The dial gauge was set to zero and the top half of the joint was removed in order to apply the resin.
This was applied directly after mixing the two-part epoxy in the sachet (see Chapter 4 for details). After securing the joint half in the rig, the new reading on the dial was noted, as this gave a value for the glue line thickness of the joint.

The joint was left in the assembly jig for about 2 hours, for sufficient cure (polishability can be achieved in 15 minutes for the Tra-Con F125 adhesive). The final cure adhesive joints had a known bondline thickness ranging from 180 to 200μm.

Initially several attempts were made to fracture the dry joints under UHV conditions in the XPS spectrometer. It was found to be almost impossible to fracture the strong dry joints using the in-situ T-peel stage under in-situ UHV conditions, because the thicker platform hindered the movement of the T-peel fracture stage in the preparation chamber. Therefore all the dry fractures in this work have been carried out in a tensile tensometer in atmospheric conditions.
Chapter Five: Analysis of Interfacial Surfaces of Dry Fracture

On removal from the preparation rig, the sample screw fit stubs were attached to either side of the glass/epoxy resin sandwich. Samples were then located in specially designed grips (see Figure 5.9 a) and the load to failure recorded using a J J Lloyd tensile tensometer, (1kN 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 comparison of the failure stress of the joints could not recorded, as the adherends for the wet joints were secure to the stubs using a separate adhesive (Flexon F215™) which also would dissipate energy during mechanical testing. The values for dry and wet fractures are given in next chapter, but here the nature and the locus of the dry fracture will be examined.

![Figure 5.9](image)

**Figure 5.9** (a) Specially designed grips to locate butt joints in J J Lloyd tensile tensometer (b) Screw stubs for dry fracture
Chapter Five:  
Analysis of Interfacial Surfaces of Dry Fracture

5.2 ANALYSIS OF DRY FAILURES

5.2.1 SEM Results

Scanning electron and optical microscopy studies on the fracture surfaces of the joints fractured in simple tension provided some interesting information. The observations are very similar to the description by Taylor et al [91], in which she found brittle failure of photocured polymers when fractured in tension. The main features of conchoidal fracture surface, based on the observations by Lawn et al [92], are illustrated in Figure 5.10.

![Figure 5.10](image)

**Figure 5.10** Schematic of main features of a conchoidal fracture.

Here the failure is believed to be initiated at defect within the mirror zone; at this stage, crack propagation is rapid giving rise to the smooth mirror zone. At some stage during the fracture the crack starts to divide along its front, to produce a “hackle zone” consisting of tear lines. It is possible in some systems to observe an intermediate region termed the “mist zone” has also been observed [93].
Chapter Five:
Analysis of Interfacial Surfaces of Dry Fracture

Electron and optical micrographs from various areas of the conchoidal fracture surface observed for this particular system, is shown in Figure 5.11. It appears that the failure has occurred very close to the interface within the region of the mirror zone, and moved through an intermediate zone. Then the advancing crack has moved away from the interface, such that the remaining fracture surface visibly cohesive in nature.

Figure 5.11 Schematic of conchoidal fracture surface, scanning electron micrographs of fracture morphology.
5.2.2 Dry Fracture Analysis by XPS

Figure 5.12 depicts the XPS analysis of the fracture surface, carried out on the central region (hackle zone) of the dry failure. The Large area XPS (400µm) analysis carried out in the middle of the joint confirms the cohesive nature of the failure. This spectrum from the middle of the surface is characteristic of adhesive only. The sulphur is present as mercaptan cross-linking agent and the nitrogen is in the system as part of the co-curing catalyst.

![XPS Spectrum](image)

**Figure 5.12** XPS (400µm spot size) taken from the central cohesive failure region of a dry fracture surface (hackle zone).

Quantification of this spectrum shows the presence of about 76% of carbon, which is an indication of a high level of polymeric material on the surface (Table 5.3). In addition the spectrum also shows low levels of oxygen compared to other fracture regions which have the possible oxides residues from the substrate. The spectrum (200µm) obtained from the region identified as mist zone in Figure 5.10 is given in Figure 5.13. In addition to the characteristic sulphur adhesive marker, the spectrum also reveals ~2% silicon, which is the major constituent of the silica glass. This also indicates a relatively thin overlayer of carbon presence in this region.
Chapter Five:
Analysis of Interfacial Surfaces of Dry Fracture

There is a possibility that siloxane contaminants also give rise to the presence of silicon in the surface, however the presence of 2% silicon is unlikely to have been caused from a contamination. Further more, close examination of the high-resolution spectrum of the Si 2p peak, has revealed closer resemblance to the inorganic silicon oxide which has a binding energy at 104 eV.

Figure 5.13 XPS (200μm spot size) taken from the intermediate failure region (mist zone).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mirror Zone (Atomic %)</th>
<th>Mist Zone (Atomic %)</th>
<th>Hackle Zone (Atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>62.5</td>
<td>74.5</td>
<td>75.8</td>
</tr>
<tr>
<td>O 1s</td>
<td>22.4</td>
<td>17.2</td>
<td>16.1</td>
</tr>
<tr>
<td>N 1s</td>
<td>5.3</td>
<td>4.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Si 2p</td>
<td>8.1</td>
<td>1.66</td>
<td>---</td>
</tr>
<tr>
<td>S 2p</td>
<td>1.65</td>
<td>2.31</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Table 5.3 Quantification of the Surface analysis of the spectra shown in figure 5.12, 5.13 and 5.14.
Further away from the mist zone lays the small shiny glass-like mirror zone, where the fracture is assumed to have initiated. The XPS spectrum from this region is shown in Figure 5.14. Quantification of elements from this point of analysis shows very high levels of silicon (~8%), and relatively high oxygen (~63%). This is clearly indicative of the presence of silica from the substrate material.

Figure 5.14 Small area XPS (50 μm spot size) taken from the near interfacial failure region (mirror zone).

However a small amount of sulphur also exists in this region, which confirms the presence of polymer in this initiation zone. The results fall in line with the previously reported observations [91], of initiation of fracture through a near interfacial mirror zone in fully cured brittle adhesives. Expanded spectra of the fracture area for the low binding energy regions are shown in Figure 5.15.

In addition to these results, C1s high resolution spectrum was obtained from these three different regions of the dry fracture. Peak assignments of the C1s indicated the presence of polymer in all three regions.
Although very high concentrations of carbon was detected, due to the lack of molecular specificity in XPS this may also indicate some contribution from hydrocarbon contamination. But the identification of nitrogen and sulphur clearly indicate the presence of residual polymer on the surface. In addition ToF-SIMS has been utilised to analyse the fracture surfaces, which has the potential to overcome the limitations of XPS to provide surface information concerning the presence of the organic phase.

Figure 5.15 Expanded Si 2p/S 2pXPS spectra from fracture regions

5.2.3 Results of the ToF-SIMS Analysis

ToF-SIMS was utilised to monitor chemistry as a function of the change in the locus of failure, during dry fracture. SIMS analyses were obtained from five different areas of the surface, and the resultant spectra showed all major characteristic ions observed for the fully cured resin system. Although similar, they are not identical in the observed intensities. Therefore, characteristic ions from the both substrate and the resin materials were selected to monitor the change in intensities at fracture regions. The selected ion species are given Table 5.4.
Table 5.4  Selected ion fragments for peak intensity study.

All peak intensities were normalised to total ions (m/z = 5 – 400), by dividing individual ion intensities by the total. Here the molecular specificity of SIMS is apparent, with definite traces of characteristic polymer ions identified even at the mirror zone. However the SIMS ion yield is very sensitive to the surface topography. If changes in surface topography are not taken into account, acquired data is not dominated by elemental effects but by topographic effects. Whilst there is no standard method of dealing with topographic issues, normalising peak assignment produced very good data, and has also been used elsewhere [94]. Figure 5.16 depicts selected ion intensities (normalised), as percentages of the four characteristic ions for ease of comparison.

The normalised intensity graph clearly shows the distinct surface characteristics associated with different areas across the mirror zone and the thick polymer section (hackle zone). As expected this line scan shows high intensity characteristic substrate markers (m/z = 23 and m/z = 28), and presence of polymer at the mirror zone. When the analysis is moved away from the initiation area, the adhesive markers (m/z = 57 and m/z = 61), becomes very distinct. However the presence of silicon at the thick polymer section, is due to localised contamination from the poly(dimethyl siloxane) in polymer rich regions (i.e m/z = 73, 133, 147, 207 and 221). The Na\(^+\) (m/z = 23) ion fragments were found to be high in concentration at the mirror zone, but XPS data shows no presence of sodium in the dry fracture surfaces.
Chapter Five:
Analysis of Interfacial Surfaces of Dry Fracture

This can be attributed to the higher surface sensitivity of SIMS towards Na+ ions (i.e. higher ionisation cross-section of the element). At this point no efforts will be spent on detailed analysis on the contribution of individual ions such as, from amine and the diluent, as the results are further examined in the chapter on the durability of the systems.

![Graph](image)

**Figure 5.16** Positive ToF-SIMS scan across the dry fracture surface, with selected ion masses.

5.2.4 Failure Mode for Dry Failure

The detailed studies by scanning electron microscopy, XPS and ToF-SIMS, of the fracture surface have provided valuable information, which enables a failure mechanism to be proposed. In this case a physical defect, most likely a void or polymer cavity is responsible for crack initiation. During fabrication of joints, it was found that avoiding entrapment of gas is almost impossible, due to the high viscous nature of the resin. The presence of a defect can concentrate stresses sufficiently to cause initiation of an interfacial-type failure, but the crack does not have to travel a great distance before becoming unstable.
Chapter Five:
Analysis of Interfacial Surfaces of Dry Fracture

After initiation the crack runs very close to the interface for a distance about 2-4 mm. Then the crack moves away from the interface, and the remaining area of the conchoidal fracture surface failed cohesively within the bulk of the adhesive. Taylor and Watts [91], in an earlier study have also reported similar observations, and reported that it is energetically unstable for the crack to remain interfacial after initial propagation. The possible route of the crack in this study is illustrated in figure 5.17.

In addition, the surface irregularities of the adherend will possibly not allow a predetermined regular failure path, and the application of simple load could be transformed into more complex modes of loading due to the irregularities of the interface. The combination of these factors can contribute to the unstability of the cracks after initiation.

![Figure 5.17 Failure path of the dry joint fracture.](image)

5.3 SUMMARY

The initial aim of this work, (i.e. characterisation of both the resin and the 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 ToF-SIMS.
In the next section of the work, investigation of how the two materials interact, without the added complication of an aggressive environment being present, has also been completed. Finally the results from this area of work 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. In the following Chapter the durability and surface nature of these joint under water will be fully investigated.
CHAPTER SIX
EFFECT OF WATER ON DURABILITY OF THE ADHESIVE JOINTS

6.1 BACKGROUND LITERATURE

The weakening of structural adhesive joints subjected to service conditions has obvious industrial importance and has been studied by many workers. A variety of environments may affect the durability of adhesive joints, in which water is undoubtedly the major and most common hazard. The development of adhesives with long-term durability is probably still one of the greatest challenges faced by adhesive formulators. The ability of a joint to resist moisture is critical when the material is being used to bond or coat a component or device, which is vulnerable to moisture, as in many fibre optic applications. Several possible mechanisms have been suggested to explain the particularly detrimental effect that water has on joints. As it has already been proposed in the adhesion theories mentioned in Chapter 2, several of these mechanisms could be occurring concurrently, although at any one time, only one of the mechanisms will tend to predominate.

Many research groups have studied the damaging effect of humid air or water on various adhesive systems. The majority of the work has been concentrated on identifying the precise mechanism by which attack occurs, that they might be able to design a system capable of withstanding wet or humid conditions. Kerr et al [95] in 1967 established that the presence of water is the dominant factor in the environmental deterioration of joints.
Chapter Six: 
Effect of Water on The Durability of Adhesive Joints

Storing lap joints in vacuum, dry oxygen, dry ethanol or water vapour showed that the only specimens, which significantly decreased in strength, were those exposed to water. Mostovoy et al [96] has reported that the applied stress can accelerate water induced weakening. Since then comprehensive reviews of the experimental data obtained from the durability studies have been published, [21, 97]. Therefore, in this section only a brief overview of the proposed mechanisms will be included.

The interfacial region of a joint has been identified as the area most vulnerable to attack by moisture. One suggestion for this susceptibility to attack, is that this is often a region of lower crosslink density [98]. Kerr et al [98] proposed that water will tend to accumulate in sites near the interface, interfering with either secondary polymer-polymer or metal-polymer bonds, and suggested that failure of the metal-polymer bonds was more likely. This proposal was modified in the light of later experiments when partial recovery of joints kept under vacuum for 24 hours, following exposure to water, was observed. These and many other similar durability studies have indicated a move from visible cohesive failure in dry conditions, to near interfacial failure in the presence of water [99]. True interfacial failures are rare, and near interfacial failure with usually a polymer of the order of nanometres remaining on the fracture surface is generally the case [100]. The instability of the joint in the presence of water can be attributed to four main reasons: (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 or other form of mechanical weakening.

Thermodynamic work of adhesion calculations are often used to evaluate the stability of an interface, which can withstand comparatively high stresses when initially prepared, and then weakens in the presence of third phase. Generally water (though equally, fuel or any other solvent likely to come into contact with the adhesive) may be chosen for such calculations. For an adhesive/substrate interface the work of adhesion value, in an inert atmosphere or dry air, usually have a positive value, indicating thermodynamic stability of the interface.
Chapter Six:
Effect of Water on The Durability of Adhesive Joints

However, the introduction of the third liquid phase, can lead to a negative $W_A$ value being obtained, and indicate the dissociation of the unstable interface. Although such calculations give no indication of the kinetics of disbandment, 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 the anodic dissolution occurs), has been reported for a number of different systems, [101]. A more frequent event however, tends to be the loss of adhesion associated with the formation of cathodic sites, (i.e cathodic disbandment). Although there is no universal mechanism of cathodic disbandment, it is widely accepted that in many cases, corrosion of the adherend occurs as a post, rather that as previously thought, a precursor to the failure event.

The third mechanism relates to the hydration of oxide layers, and the role it plays in the durability studies. Much of the literature on durability is devoted to investigation of the oxides on metallic substrates, rather than bulk inorganic oxides in glass or ceramics substrates. Much of the work also concentrated on aluminium oxides, as this critical in aerospace applications. Some early evidence [102] suggested that the hydration may lead to the mechanical weakening of the oxide film, though this may in fact be a post failure event. However it is also less likely to occur in the case of bulk, inorganic glass type oxides.

The role played by other ions present in an oxide layer has been suggested by Kinloch et al. He reported a correlation between poor durability and high magnesium content in the oxide in a study of aluminium-magnesium alloys [103]. However in a later work by Poole and Watts [104], no such correlation was apparent. They had further suggested that this apparent variation was due to the formation of friable magnesium oxide in non grit blasted surfaces. Taylor et al. has also reported the possibility of preferential segregation of sintering aids such as magnesia on alumina substrate, during durability studies [105]. There is also a wealth of evidence in the literature to suggest that the magnesia preferentially segregates to the free surface during sintering [106, 107].
However there is no evidence to suggest that such friable oxides exists in bulk inorganic network such as glass. Nevertheless Watts et al. has reported sodium ion diffusion in a series of dry adhesion studies of glass, and attributed this phenomenon to acid-base interactions [108].

The final mechanism, that of polymer swelling, clearly warrants some attention. In addition to swelling, the residual stresses may arise as a result of differential contraction between two bonded materials when they are cooled from a higher temperature, or from the contraction of the polymer as cross-linking proceeds. In the same way that unreasonably high shrinkages on cure reduce the force necessary for debonding, it is not unreasonable to suggest that stress arising from polymer swelling will produce a similar effect. A more detailed discussion on the movement of water in adhesive joints is included below. It can therefore be concluded that failure in the presence of third phase (i.e. water), is extremely complex and may be due to a combination of interrelated factors.

6.2 EFFECT OF WATER IN THE JOINT

Several mechanisms have been proposed to explain how the ingress of water occurs in adhesive joints. Comyn et al. have suggested a combination of four main routes by which water is likely to enter a joint [109]. Water may enter a joint by: (i) diffusion through the adhesive, (ii) "wicking", in which the water transported along the interface, (iii) by capillary action, through defects in the coating itself, (e.g. cracks, crazes, or reinforcements) and finally, (iv) if the substrate itself is permeable, then this will allow water to reach the interface.

The process of diffusion has been studied for many years and several comprehensive texts have been published addressing the mathematics governing diffusion [110]. If water diffuses into a joint, then it is possible to model the process using Fick’s law of diffusion and to obtain values for the diffusion coefficient of water in the adhesive. Brewis et al., reported a general tendency in the increase of diffusion coefficient with the concentration of water, on account of the plasticising action of the mobile component in the adhesive [111].
Fickian diffusion is generally characterised by the linear uptake of water and is typical of polymers above glass transition temperature (i.e. rubbery state). Not all the polymers display Fickian behaviour, and glassy polymers tend to show non-Fickian water uptake, with non-linear water uptake curves [112]. 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, and the second stage will not necessarily have the same rate of water uptake as the initial stage [113]. In some instance, leaching of components in the formulation can make it appear as if no water uptake is occurring, (i.e. if the material leached out exceeds the quantity of water taken up by the adhesive). This may be ascertained by the careful use of gravimetric methods. Gledhill et al. used this model as the basis for a computer programme to solve for concentration in a joint at a given time. They used a simple epoxy adhesive with mild steel substrates and found good agreement between predictions from the model and experimental measurements.

Thermodynamic work of adhesion calculations predict that such a system will be unstable in the presence of water, hence as water progressively diffuses into the joint, the proportion of interfacial failure increases and the subsequent joint strength decreases. This was observed in their work of Gledhill et al [114]. In addition they found no reduction of joint strength when the samples are stored in a relative in a 55% relative humidity prior to testing, and concluded “there must be a critical level of water concentration in the adhesive layer, below which environmental attack is precluded”. 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 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 % (Figure 6.1). Although this idea is not universally accepted, it has been applied successfully to a number of systems.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints  

In addition to the bulk diffusion processes, there is much debate as to the actual route of the water penetration. As it has already mentioned in Section 6.1, enough evidence exists to suggest an enhanced diffusion either at the interface/interphase or at anomalous regions within the adhesive such as pores or sections of low cross link density. Shanahan et al. suggested that the diffusion coefficient is higher in bonded joints than in bulk polymer [115]. This is ascribed to an effect which they termed “capillary diffusion”, and is thought to occur at the metal (oxide)-polymer interface due to an interfacial tension between wet adhesive, dry adhesive and metal oxide. However this mechanism has not been verified fully and it is also likely that other factors such as residual stress play a part in enhanced diffusion.

Taylor and Watts have suggested a reduction in the performance due to wet adhesion, is likely to be caused by water segregating within a region close to the adhesive-adherend interface adjacent to highly ordered interfacial bonds (Figure 6.2) [116]. They have also identified segregation of a minor component would generate a hydrophilic interface ~ 1nm into the adhesive. In this ‘wet adhesion’ phenomenon, the water-induced damage is partially reversible, but when the bonds are broken the strength is not retrieved on the subsequent drying of the system.
Chapter Six:
Effect of Water on The Durability of Adhesive Joints

Figure 6.2  Schematic model showing the formation of a diffuse interphase region that often remains on the substrate following wet adhesion [117].

6.3 MECHANICAL TESTS

During this work, extensive studies have been carried out on the effect of water in adhesive joints. In order to achieve this, series of joint have been prepared using the method described in Chapter 5, and fracture analysis has been carried out both in in-situ UHV vacuum conditions, and in a tensometer. The water source used in durability studies is important, as the presence of any water impurities directly affects the XPS and SIMS 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 water purification process, which therefore precluded its use in the study of many materials, especially those which corrode. De-ionised water should also be monitored, as contamination from the ion exchange beads sometimes occurs. For this study multiply distilled milli-Q water was used. Here the water is de-ionised and passed through a series of 4 different filters to remove the various organic and inorganic contaminants. Water purity is checked with the conductivity meter fitted to the filtration system and when the conductivity rises above a specified level (10 Ωm.S), the filters are changed.
Values of load to failure for a series of fabricated butt joints are shown in Figure 6.3. The results clearly show an initial high strength for dry fracture, and then substantially reduced values for the joints just after few hours in water. The comparison is striking when the joints are left in water for few days and the initial strength has been completely reduced. The strength values show almost a plateau like pattern after about 40 days in water.

During the test it was observed that the joints had gained some strength as result of drying in the time taken for preparation and test. A considerable amount of time (~5-10 minutes) had elapsed between the time the glass/epoxy sandwich was taken from the milli-Q water and to be attached to the stubs. Obviously some time has also been spent, during the setting up the joint assembly to the tensile tensomer for fracture.

**Figure 6.3** Load to failure versus immersion time for a series of borosilicate butt joints, (time axis is not linear).

Therefore to avoid drying of the joints during test and preparation, the bond-line of the joint was covered with a wet tissue, and was wetted using a syringe throughout the test procedure.
6.4 VISUAL ASSESSMENTS BY OPTICAL MICROSCOPY

Optical photomicrographs have been obtained from both halves of butt-joints exposed to water at 35° C for between 0-270 days. These results were obtained after the surfaces have been analysed by XPS and ToF-SIMS. Three different modes of failure were observed, which depended upon the period of immersion in water. As it has already been explained in Chapter 4, the dry fracture surfaces (zero time in water), showed conchoidal type of fracture surface morphology. Figure 6.4 illustrates the other two fracture surface morphologies as optical microscope photos. Joints immersed in water for less than twenty days, displayed a mixed mode of failure, with patches of polymer remaining on both sides of joint.

Figure 6.4 Effect of water immersion on the morphology of the failure surface (a) mixed and (b) visually 'adhesive' failure (10 Days Water immersion).
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

The photomicrographs in Figure 6.4 (a) depict the morphology of the surfaces of a joint failed after ten days immersed in water. The long-term exposure (120 days) surface shown in Figure 6.4 (b), produced a visibly 'adhesive' failure joint. At about 35 days of exposure, the joints have almost lost all of their strength, but still had sufficient residual joint strength for it to avoid the joint to fall apart on removal from water. However all the joints exposed more than 35 days, had little or no strength to keep both halves of the joints together.

6.5 ANALYSIS OF FRACTURE SURFACES

Early results from the environmental studies on borosilicate butt-joints were carried out in the conventional VG Scientific ESCALAB Mk II instrument available at that time. However in the later part of the experimentation the VG Scientific Sigma Probe equipped with a monochromated X-ray source was utilised, and has further enabled the possibility of identifying the true locus of failure, especially at the glass side of the fractured joint.

It was observed in the early experiments that the Cls spectra recorded from the glass sides of the failure, were broad and featureless, with no evidence of functional groups characteristic of 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. In this section, the effect of short and long term exposure of water to the ex-situ fracture butt joints are analysed by means of XPS and SIMS. Analysis has been carried out on samples soaked in water from 2 hours to 270 days with varying time intervals. However for the ease of comparison with visual inspection, 10 days water soak (mixed mode), and 120 days (visually adhesive failure) water soaked samples are discussed in detail here.
6.5.1 **XPS Fracture Surface of 10 days Water Soak**

A large area survey spectrum taken from the fracture surfaces of the 10 day water immersion sample is shown Figure 6.5 (a) and (b), allows characteristic peaks to be identified. XPS results from the side of the predominantly ‘glass’ side of the failure revealed a C1s peak which is identical to the C1s peak of the predominantly ‘polymer’ side of fracture. In addition the shape of the background also indicates the presence of polymer in this visibly glass surface.

On the polymer side (Figure 6.5 (b)), no characteristic glass components were observed in the spectrum, instead four major elements of the adhesive, C1s, O1s, N1s and S 2p are observed. Although the polymer side has a small “glass” area, the survey spectra did not exhibit any characteristic glass elements. It may be that the remaining small glass surface of the polymer side is covered with thicker organic overlayer than any polymer layer left on the large clear area of the glass side. Although this observation is not conclusive from XPS alone, a schematic of the fracture corresponding to the photographs on Figure 6.4 is given in Figure 6.6.

![Figure 6.6](image)

**Figure 6.6** Schematic of 10 days water immersed fracture surfaces (a) glass side with a small polymer area (b) Polymer side with small glass area.

The quantitative analysis on the glass side of the fracture (Table 6.1), revealed, the characteristic glass components, Si (2.11%), Na (1.3%) and Ca (0.2%). In addition the O 1s has shown slightly higher intensity than for the polymer, as this is expected from to the contribution of the substrate oxides.
Chapter Six:
Effect of Water on The Durability of Adhesive Joints

<table>
<thead>
<tr>
<th>Element / atomic %</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Si</th>
<th>S</th>
<th>Na</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>'glass'</td>
<td>58.6</td>
<td>29.0</td>
<td>8.7</td>
<td>2.1</td>
<td>--</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>'polymer'</td>
<td>63.3</td>
<td>27.1</td>
<td>8.6</td>
<td>0.4</td>
<td>0.7</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 6.1  Quantitative surface analysis of the spectra shown in Figure 6.5.

![Figure 6.5](image_url)

Figure 6.5  Comparison of both survey and Cls XPS spectra for 10 days water soaked mixed mode failure (a) predominantly 'glass' surface (b) predominantly adhesive side.
One interesting result from the quantification is that the amount of nitrogen present on the wet failure is almost doubled (~8.5%) from the dry fracture quantification. There is no other known source for the nitrogen, except for the polymer itself. The migration of the amine component of the adhesive is the only possibility for this unusually higher presence on the fracture surface.

In addition to the quantification, the high resolution spectrum of the N 1s revealed identical, and symmetrical shaped peaks on both halves of the joint. This type of nitrogen has also been previously observed from the cured and uncured state of the resin itself.

6.5.2 XPS of 120 days Water Soaked Fracture Surfaces

As already mentioned, the fracture surfaces of 120 days water immersion joints have shown ‘interfacial’ failure, and the ‘glass’ side visibly has no polymer left on the surface.

The long-term samples have lost almost all of their strength, and here a thick adhesive film was left on the polymer side. With the aid of clean tweezers, this polymer film was peeled off from the polymer side. The peeled polymer layer was then sandwiched between two metal aperture plates, used for SIMS experiments. The four surfaces to be examined from this fracture and the polymer film in the aperture plates are illustrated schematically in Figure 6.7.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

Figure 6.7  Fracture surfaces for in 120 days water immersion surface analysis; (a) direct tension (Glass side 1 and polymer side 1) and peeling (glass side 2 and polymer side 2), (b) adhesive film for surface analysis by ToF-SIMS.

After long term exposure in water it is expected that, the two glass-adhesive interfaces are equally weakened by the environment. However as a result of the slight variations of the stress distribution in the joint, one of the sides failed first in the direct tension. Induced stresses at loading in the Instron can weaken one side more than the other. On removal from the tensometer, the peeling of the adhesive layer has been carried within few minutes. However this has allowed some drying and the peeling side could have regained some of its original adhesive strength. The XPS survey spectra of the surfaces, which depict the variant natures of the fracture, are shown in Figure 6.8. The quantitative analysis of the elements is also tabulated in Table 6.2.
Table 6.2  Quantitative surface analysis of the spectra shown in Figure 6.8

As expected the polymer side 1 and 2 show the characteristic sulphur signal and the remaining elements were predominantly carbon and oxygen. This is not surprising as the adhesive formulation consisted mainly of hydrocarbon components. About 3.5% surface concentration, of nitrogen was also observed. The only component in the mercaptan cured resin system that contained nitrogen was the amine co-curing catalysing agent. Therefore, the presence of nitrogen in low concentration is evidence of the presence of the catalytic amine at the interface. XPS analysis of the S2p is consistent in the entire wet, dry fracture and bulk surface analysis. In dry fracture, and the bulk analysis of the resin in the previous chapter, showed about 2.5 atomic %. Sulphur is the part of primary curing agent in this adhesive system, and the consistency in the concentration can be attributed to the strongly bound sulphur in the cured resin network. It can also be argued that there are no excess polysulphides present in the system, which segregate to the interface (i.e. efficient stoichiometric amounts of mercaptans are used in the commercial resin).
Figure 6.8 120 Water immersion fracture surfaces (a) tensile fracture polymer side, (b) tensile fracture 'glass' side, (c) peeled polymer side and (d) peeled 'glass' side
One obvious observation from the visibly glass interfacial surfaces is the variation of C:O ratios, on the peeled and tensile fracture surfaces. The tensile fracture side (Figure 6.8 (b)), has a much lower surface concentration for carbon signal and comparative to peeled side, shows higher oxygen signal (Table 6.2). The relatively low intensity of the carbon peak indicates an interfacial failure, where only small residues of the adhesive remains on the glass surface.

The nitrogen peaks on the visibly glass surfaces (peeled and tensile fractured) show higher and similar surface concentration, than in the adhesives sides. As it has been already explained the nitrogen is only associated with the amine component of the adhesive, and higher presence at the glass sides can be due to the segregation of amine at the interface. Also, the presence of sulphur signal, indicative of mercaptan curing agent, is completely absent from this side. The peaks associated with sodium and zinc are characteristic of the glass substrate, although zinc surface concentration was only observed in long-term durability fracture surfaces.

On the peeled 'glass' side, the C:O ratio is much higher, leading to the suggestion that the polymer residues on this side are much larger than in the direct tension fracture side. However the nitrogen concentration is identical to the other glass side, and characteristic adhesive signal, sulphur, also observed in this side. In addition the fracture side shows much lower concentration of silicon signal (4.7%), which is characteristic of silicate glass substrate. Also, sodium and zinc presence observed in this surface. The background associated with the zinc LMM Auger peaks has a small positive slope, suggesting that the zinc may be buried.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

The peak-fitting regime is complex, due to the different functional groups present for the various known and unknown components of the resin system. Although the C1s high-resolution spectrum shown in Figure 6.10 is not fitted to their possible components, it illustrates the nature of C1s spectrum from all the fracture surfaces. From these spectra, the presence of almost identical, organic carbons in all fracture surfaces is established.

![C1s high-resolution spectra of the surfaces from the different fracture modes for the 120 days water immersion test sample.](image)

**Figure 6.10**  C1s high-resolution spectra of the surfaces from the different fracture modes for the 120 days water immersion test sample.

6.5.3 Small Area XPA Analysis of the 120 days Water Soaked sample

On the ‘glass’ side of the tensile fractured joint, small area XPS with 100μm spot size analysis has been carried out. The glass side of the direct tension fracture showed a feature of circular boundary as viewed by the optical microscope. The point analysis on three different areas along this feature is shown in Figure 6.11. The area three encircles the major part of the fractured surface.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

Figure 6.11  The Small Area XPS of the 'Glass' Side of the Tensile Fracture: area 1 and 2 - 200µm, area 3 - 20µm

136
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

By analysing the different regions of this fracture surface, two distinct observations have been made, on the basis of the surface chemical composition. Firstly the change in C:O ratio and secondly the change in intensity of silicon signal. The surface quantification of the elements is shown in Table 6.12.

<table>
<thead>
<tr>
<th></th>
<th>Area1</th>
<th>Area2</th>
<th>Area3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>61.03</td>
<td>47.43</td>
<td>46.83</td>
</tr>
<tr>
<td>O1s</td>
<td>27.49</td>
<td>36.73</td>
<td>33.78</td>
</tr>
<tr>
<td>Ni1s</td>
<td>3.67</td>
<td>4.16</td>
<td>3.67</td>
</tr>
<tr>
<td>Si2p</td>
<td>6.08</td>
<td>11.52</td>
<td>11.63</td>
</tr>
<tr>
<td>Na1s</td>
<td>0.12</td>
<td>0.16</td>
<td>0.8</td>
</tr>
<tr>
<td>Zn2p</td>
<td>1.35</td>
<td>0</td>
<td>3.28</td>
</tr>
<tr>
<td>B1s</td>
<td>0.27</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.3 Surface Concentration of Elements from the Three Different Areas of the 120 Days Water Immersion Sample.

At the area 1, the major section of the fracture, C:O ratio is much higher than the other two analyses. In addition the presence of silicon in this surface area also lower than the other two results. Area 3 and intermediate section area 2 analysis, are almost identical with the exception of zinc signal (3.28%) on the 20 microns (area 1), analysis. Zinc is a minor component of the substrate material (see Section 4.2.3.2.1), and this presence is although not frequent, very occasionally observed in long term durability studies. These results indicate possible zinc diffusion from the glass in water.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

These results tend to suggest that the fracture have a mixed locus of failure, of adhesive failure on the edges and a cohesive fracture in the middle of the surface. However the carbon high-resolution spectra from all three regions are similar to the large area results shown in Figure 6.10. Therefore the locus of failure is still interfacial for the entire surface, but in comparison the larger part of the surface is a polymer rich area, than the edges, where the environmental exposure is at maximum.

In order to establish the nature of silicon present in the glass surface the Auger parameter values also calculated. This is done by recording the chemical shift on both the Auger and photoelectron peak in the XPS spectrum (See section 3.2.3.1 for details). Initially the position of the silicon high intensity peaks was about 104 eV, is indicative of SiO\textsubscript{2}. The values obtained for Si2p and Si \textit{KLL} transition for the tensile fracture glass surface is shown below:

<table>
<thead>
<tr>
<th>'Glass' surface of the tensile fracture</th>
<th>( E_k(Si\text{ KLL})/eV )</th>
<th>( E_B(Si\text{ 2p})/eV )</th>
<th>( \alpha/eV )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1607.12</td>
<td>104.57</td>
<td>1711.69</td>
</tr>
</tbody>
</table>

This calculation of the Auger parameter (\( \alpha \)) for the silicon confirms the presence of only silicate at the surface and not the contamination from PDMS as occasionally observed in some fracture surfaces.

6.5.4 SIMS of fracture surface of 120 days water soak specimen

ToF-SIMS analysis of the four fracture surfaces from the two different modes of failure has been carried out, and the corresponding positive ion SIMS spectra are shown in Figure 6.12 and 6.13. The resultant spectra from all the surfaces show the characteristic ion fragments from the four major components of the adhesive resin, described in Chapter 4. The results show almost identical surfaces, but the comparison of ions present between tensile and peel fracture surfaces, show variations in their intensities. The ion intensities from the diagnostic of epoxide are much lower in the tensile fracture glass side than in peeled glass surface. It is also noticed that the amine contributions (\( m/z = 30, 44, 56, 70, 99 \)), for the weaker side of the joint (tensile glass surface), is higher than the peeled glass side.
Chapter Six:
Effect of Water on The Durability of Adhesive Joints

Figure 6.12  Tensometer tensile fracture ToF-SIMS spectra for 120 days water immersion sample.

Figure 6.13  Peeled surfaces ToF-SIMS spectra for 120 days water immersion sample.

Although all the major characteristic ions in Figure 6.13 can be easily identified, in order to examine the role of minor components, three ion fragments are selected as such to include the epoxy resin, amine, sulphide and an unsaturated hydrocarbon fragment for comparison of intensities in each surface.
Chapter Six:
Effect of Water on The Durability of Adhesive Joints

Initial observations without resort to this comparative study shows, the intensity of amine ion fragments are almost identical in intensities on all fracture surfaces with no significant variations. Since the spectra were already normalised to the total ions, it is possible to see the relative changes in intensities of selected masses. Characteristic peaks selected for this study are given in Table 6.5.

<table>
<thead>
<tr>
<th>Source</th>
<th>Ion Fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/Amine</td>
<td>$^+\text{CH}_2\cdot\text{NH}_2$</td>
</tr>
<tr>
<td>61/Mercaptan</td>
<td>$^+\text{CH}_2\cdot\text{CH}_2\cdot\text{SH}$</td>
</tr>
<tr>
<td>77/Unsaturated</td>
<td><img src="https://example.com/image" alt="Unsaturated Hydrocarbon" /></td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td></td>
</tr>
<tr>
<td>86/Diluent</td>
<td>$^+\text{C}<em>5\text{H}</em>{10}\text{O}$</td>
</tr>
<tr>
<td>135/Bis Phenol A</td>
<td><img src="https://example.com/image" alt="Bis Phenol A" /></td>
</tr>
</tbody>
</table>

Table 6.5 Selected ion fragments for surface study of 4 months water immersion samples

The typical amine mass fragment ($m/z = 30$), and contributions from the adhesive resin $m/z = 77$, 135 the contribution from the primary curing agent, mercaptan ($m/z = 61$) and the diluent ($m/z = 86$) were selected for this study. The graphical representation of the distribution of above fragments is shown in Figure 6.14. ToF-SIMS of the peeled and tensile fracture (both glass and polymer) surfaces shows some significant variation in the intensities in all areas analysed. From this analysis it is clearly shown that on the glass side of the tensile fracture the amine fragments dominate, and on the other polymer side the epoxy and mercaptan fragments show the higher intensities. The two ToF-SIMS analyses from areas one and three on the tensile fracture glass side, corresponds to the positions in the schematic shown for the XPS (see Figure 6.11).
From the XPS on position one, it was earlier deduced, that it was a silicon rich area, but there was not much difference in the surface concentration of the nitrogen in the three areas. However the ToF-SIMS results show a small increase in the amine concentration in the silicon rich area (analysis area 3), to suggest a depleted amine at the near interfacial area of the joint. The two random analysis from the polymer side of the tensile fracture show no significant variation in the their intensities.

**Figure 6.14** Comparison of normalised intensities for the selected ion masses for (a) tensile fractured and, (b) peeled 120 water immersion surfaces.
Chapter Six:  
*Effect of Water on The Durability of Adhesive Joints*

The other positions marked in Figure 6.14 are just random analysis along different positions in the fracture surfaces. These are presented to show any localised variations in the samples. ToF-SIMS of the peeled fracture (both glass and polymer) surfaces also shows significant localised variations in the intensities. Since this is not a well-controlled test the results are not surprising, and yet it shows strong presence of amine, diluent and sulphide on one of the analysis areas from the glass side. By comparison the peeled ‘glass’ side have higher percentage of epoxy related fragments ($m/z = 77$ and 135) than the corresponding polymer side. But no such variations can be found in the glass and adhesive tensile fracture surfaces. It should be noted that the peeled side is slightly stronger than the tensile side, and the higher epoxy presence on the peeled glass side can be attributed to this observation.

### 6.5.5 ToF-SIMS Imaging of 120 Days Tensile Fracture Glass and Polymer Surfaces

Peaks of interest for mapping of the fracture surfaces as follows:

| $^{28}\text{Si}^+$ and $^{23}\text{Na}^+$ | Inorganic substrate markers |
| $m/z = 43$ | Epoxy/Diluent marker |
| $m/z = 56$ | Amine marker |

The images obtained from the glass surface shows the localised regions of sodium, while it also shows the polymer concentration in one part of the surface.

The patchy sodium also observed in the uniformly distributed silicon signal. The interfacial failure of the joint has been further confirmed from these results, though distribution of the organic ions on the ‘glass’ is concentrated on one part of surface.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

**Figure 6.15** Glass side (a) Positive ToF-SIMS image highlighting the polymer rich areas ($m/z = 43$ and $56$) with patches of Na$^+$ (showed in blue $m/z = 23$) (b) Patches of sodium on a uniformly distributed silicon($m/z = 28$)

**Figure 6.16** Polymer side (a) Positive ToF-SIMS image highlighting the polymer rich areas ($m/z = 43$ and $56$) with patches of Na$^+$ (showed in blue $m/z = 23$) (b) Patches of sodium on a scattered weak distribution of silicon($m/z = 28$)
6.6 ANGLE DEPENDENT XPS ANALYSIS

Further in this study, the technique of angle resolved electron spectroscopy has been applied to the failure surfaces generated by the fracture after water immersion tests. As explained earlier in Chapter 3, this was achieved in XPS by varying the electron emission angle, the maximum depth of analysis being achieved normal to the sample surface and the minimum depth at grazing incidence.

The spectra obtained for the 10 and 120 days samples, at 45° take-off angle analysis has already been discussed in the previous section. Unfortunately the comparative angle resolved analysis these time scales was not carried out, however analysis for 35 and 240 days water immersed fracture surfaces will be discussed in this section. These would be expected to reveal the nature of the fracture surfaces of the joints after relatively short and long term exposure to water. The spectra were recorded, at electron take-off angles of 15°, 25°, 35°, 45°, 60° and 90° relative to the sample surface. In order to minimise the 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. The sample degradation is also monitored with a 45° angle analysis, and no such damage was observed. The resultant surface concentrations of the elements are presented in Table 6.6.

As seen on the earlier fracture surfaces, the results from the depth profiling indicate that one side of the fracture surface has low level of polymer present. The spectra from the two extreme angle of analysis for the 35 and 240 days samples are also shown in Figure 6.17 and 6.18.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

<table>
<thead>
<tr>
<th>Glass Side – 35 Days</th>
<th>Polymer Side – 35 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>C 1s</td>
</tr>
<tr>
<td>15</td>
<td>65.8</td>
</tr>
<tr>
<td>25</td>
<td>61.9</td>
</tr>
<tr>
<td>35</td>
<td>53.9</td>
</tr>
<tr>
<td>60</td>
<td>38.5</td>
</tr>
<tr>
<td>75</td>
<td>34.7</td>
</tr>
<tr>
<td>90</td>
<td>32.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Glass Side – 240 Days</th>
<th>Polymer Side – 240 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>C 1s</td>
</tr>
<tr>
<td>15</td>
<td>65.2</td>
</tr>
<tr>
<td>25</td>
<td>64.0</td>
</tr>
<tr>
<td>35</td>
<td>53.6</td>
</tr>
<tr>
<td>60</td>
<td>36.8</td>
</tr>
<tr>
<td>75</td>
<td>33.5</td>
</tr>
<tr>
<td>90</td>
<td>33.0</td>
</tr>
</tbody>
</table>

**Table 6.6** Quantification of elements as analysed from angle resolved XPS.

As expected as the analyses carried out closer to the substrate on the glass side show a strong presence of Na. This was also reflected by the large Na KLL Auger line in the 90° take-off angle analysis of the glass sides. Depletion of C 1s and N 1s signals from glass side with the increase in depth of analysis indicate that the failure was occurring near interfacial with a thin polymer layer left on the glass substrate. An increase in the C:O ratio at the glass sides of the 35 and 240 days can also be monitored from these results. This result possibly indicates a lower level of polymeric presence in the glass side of the long-term water immersion fracture.
Figure 6.19 High-resolution spectra of Si 2s and S 2p at varying take-off angles – 240 days glass side

Also, the S 2p signal is an indication of the presence polysulphide adhesive in the substrates. An analysis of the results from the glass side of the 240 days sample indicates the level of polymeric present in the surface. For analysis recorded in the more surface sensitive mode the S 2p component of the spectrum is clearly seen (Figure 6.19)

In order to estimate the depth of distribution of elements present on the fracture surfaces, further manipulation of the angle resolved results using a method developed by Cumpson et al [57], has been carried out and this is given in the following section.
Figure 6.17 Angle resolved analysis of 35 days water immersion fracture surfaces.

Figure 6.18 240 days water immersion fracture surfaces
6.6.1 **ARCtick Compositional Depth Profiling**

The quantified data from the angle resolved experiments have been further evaluated using a stratification method. This computer methodology was carried out using the **ARCtick** spreadsheet, which was developed by the National Physical Laboratory. It makes the use of the intensity obtained from two angles, in this case $15^\circ$ and $90^\circ$. This means that the amount of detailed information required by the computer is minimised, thus simplifying the calculations involved. Instead of an entire plot of concentration vs. depth, the stratification method calculates the average depth of each layer. This method allows the inclusion of all the species, which are found on the surface. The results are plotted in a form analogous to a chromatogram. Coloured bars represent the average depth of each layer, while the area represents the relative quantities of each species.

Such stratification plots for the 10, 35 and 240 days water immersion joint fracture XPS analysis, are shown in Figure 6.20, 6.21 and 6.22. When the joint was exposed to a relatively short term (10 and 35 days), the bars representing carbon and oxygen are clearly distinct from each other, with carbon being closer to the surface than the oxygen at the glass side of the fracture. However the polymer side of the fracture shows the oxygen as being close to the surface. This feature probably represents the nature of the bulk polymer. Also on all glass sides of the fracture surfaces, the C:O ratio is higher than the polymer sides due to oxides from the inorganic glass. However, in the 240 days the oxygen is closer to the surface as observed for the polymer sides. During fracture of this very long-term water exposure sample, it was observed that this sample has literally fallen apart in the Instron. This has created a visually clear glass side, but as observed by XPS left with a thin overlayer of polymer. Therefore the oxides from the chemical constituents of the glass may have dominated to produce this result.
Chapter Six:  
Effect of Water on The Durability of Adhesive Joints

Figure 6.20  Stratification of XPS angle resolved data for the 10 days water immersion fracture surfaces

Figure 6.21  Stratification plot for 35 days water immersion, joint fracture surfaces

Figure 6.22  Stratification plot for 240 days water immersion joint fracture surfaces.

As expected, on the polymer side traces of sodium and silicon closer to the surface where it has close contact with the glass. However the sodium is not closer to the surface in the 35 days, and in the 240 days sample, it is even further away from
the surface. One possible explanation for the observation is that, as time progress softening of the polymer may also allow the sodium to diffuse into the bulk through the 'underside' glass of the joint. And possibly the near surface sodium from the opposite glass side have dissolved into the water during long term exposure. Strong presence of sodium in the polymer side of 240 days sample also represents this explanation.

The interesting feature observed from these plots is the position of nitrogen. Nitrogen in the glass sides is almost uniformly placed closer to the surface. This can be due to the suspected phenomenon of amine segregation at the interface proposed earlier. These results are corresponding the earlier finding from SIMS experiments for the 120 water soaked samples (See section 6.5.5).

6.7 THICKNESS OF POLYMER OVERLAYER

Further to the stratification analysis, it was intended to summarise all the XPS data obtained from the fracture surfaces. By manipulating all the standard 45° take-off angle analysis, it is possible to compare the level of organic layer present in the glass sides of the fracture. Castle et al. [118] has demonstrated that the depth of analysis can be calculated by simply re-arranging the well-known Beer-Lambert expression (see section 3.2.3 for details). Based on an approach adopted by Watts et al. to calculate the organic overlayers remaining on the steel substrate, the polymer overlayer remaining on the glass substrate were calculated and compared with time of exposure to water [119]. The intensities from the C1s from the polymer side of the fracture were taken as $I_o$, and from the glass side as $I_a$. This approach was only applied to the layers of reduced thickness (i.e presence of Si 2p in the analysis). It means that this approach cannot be applied to the cohesive failure surfaces such as dry fracture. The re-arrangement of the equations used for this calculations are shown below:
Chapter Six:  
*Effect of Water on The Durability of Adhesive Joints*

\[ I_d = L_\infty \left(1 - \exp\left(-\frac{d}{\lambda \sin \theta}\right) \right) \]  
\[ I_d/L_\infty = 1 - \exp\left(-\frac{d}{3.25}\right) \]  
\[ 1 - I_d/L_\infty = \exp\left(-\frac{d}{3.25}\right) \]  
\[ d_{\text{carbon}} = -3.25 \ln \left(1 - I_d/L_\infty\right) \]  

**Figure 6.23**  Polymer overlayer thickness on the glass side of the fracture surfaces and average joint fracture strengths.

The calculated results along with the average fracture strengths of the joints are shown in Figure 6.23. As already mentioned the samples from 0, 2 and 5 hours water immersion, did not show interfacial failures, and thus were not be included in Figure 6.23. However evidence of decrease in the polymer overlayer thickness on the glass sides with the increase of exposure time in water can be clearly seen in the rest of the samples.
Although the plot was not following a well-defined relationship, a clear trend in reduction in polymer presence and their corresponding loss in bond strength is clearly evident from these results. The reduction in polymer overlayer is not so dramatic as the reduction in bond strength. Also the prolonged water exposure of joints of more than 100 days, the remaining polymer layer is very small but it is consistent with about 2 nm. This implies that the remaining polymer on the surface does not play any significant part to the strength of the joint.

This is more evident on the 120 days water immersion sample. When the polymer layer is peeled from the polymer side (see section 6.5.1 for details), the peeling was carried out after about 30 minutes of tensile test. This has allowed an increased polymer thickness to regain some of its adhesion thus, shown a higher presence of polymer on the peeled surface. This was probably due to the partial recovery of the original strength during drying.

6.8 SUMMARY

In this chapter a comprehensive study of the durability of the joints in water has been carried out. The locus of failure of the joints with varying amounts of time of exposure to water has also been studied. The results so far clearly showed the better bond strength of the adhesive in dry conditions and its susceptibility to water even at a relatively small amount of time.

The results obtained here indicated possible amine migration at the interfaces. However a detailed understanding of the formulation chemistry is required to identify the exact nature of the minor components of the adhesive. Therefore a reformulation work based the fundamental chemistry of the commercial resin was carried, and details of this are following on in the next chapter.
CHAPTER SEVEN

EFFECTS OF FRACTURE METHODS ON XPS ANALYSIS RESULTS

7.1 INTRODUCTION

The failure analysis of the joints has been evaluated by comparing the loci of failure as a function of exposure time for the joints in water prior to fracture. So far the experimental results have been obtained from the fracture of the joints in ambient condition by an Instron tensometer. In this section the effect of fracture within UHV (ultra high vacuum) conditions and changes in fracture mode will be examined. Further into this chapter the angle resolved analysis of the XPS would be fully utilised, to evaluate the exact locus of the fractured joints.

7.2 IN-SITU FRACTURE JOINT DESIGN

The requirement to carry out in-situ fracture tests in the XPS preparation chamber restricted the choice of mechanical test to be carried out. However as described in chapter four, the chosen joint design was a simple butt-joint geometry. Although it is preferred for the current investigation such a test has limitations in the assessment of bond strength.

Initially the problem associated with this type of test is the accurate monitoring of the glue line thickness of the joint. The reduction of fracture stress and resultant decrease in butt-joint strength with the increasing glue line thickness, has been studied by many workers [21].
Modelling the stresses in several joint geometries by finite element analysis suggests that joint strength will increase with a corresponding increase in bondline thickness. Experimental results by many workers however indicate the reverse is true. This phenomenon was reported for acrylic adhesives by Meissner et al in 1948 [120]. An early equation by Kendall, that accounts for this phenomenon, agreed well with experimental data [121]. This equation (Eq. 6.1) indicates that the breaking force required is not limited by the strength of the adhesive. This may also account for the peculiarity that a butt joint may in fact be stronger than the adhesive, which holds it together.

\[
F = 2\pi a^2 \left( \frac{2K\gamma}{t} \right)^{1/2} \quad \text{...Equation 6.1}
\]

Where

- \( F \) = Adhesive force, (strength of butt-joint)
- \( a \) = Radius
- \( K \) = Bulk elastic modulus
- \( \gamma \) = Adhesive energy
- \( t \) = Glue line thickness

The adhesives used during the course of the current study cure to 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 amorphous, or as a glassy polymer rather than a crystalline one. The mechanical behaviour of the amorphous polymers, below their glass transition temperature, can be categorised as semi-brittle materials [92]. The strength of amorphous materials such as glasses is known to be determined by the size of defects such as cracks within the material [122]. 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 studies by finite element analysis often do not account for the possibility that such defects exist, therefore predicting higher rather lower joint strengths.
Chapter Seven:  
Effect of Fracture Methods on XPS Analysis Results

On the initial inspection, the stress in a butt-joint might appear uniform across the adhesive 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 [123].

In addition to carrying out mechanical testing in ambient conditions, there is 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 practically possible, the conditions that the component will experience in service. Care should be taken not to exaggerate the test conditions too much [9].

In this work, the test was to be used primarily to create new fracture surfaces without exposure to the atmosphere, so it is believed that this was a reasonable choice. As explained earlier in chapter four the problems associated with the in-situ fracture of dry joints, there are also problems associated with long term water exposed butt-joints.

7.2.1 In-situ Fracture

In order for the 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. The modification is based on an earlier work by Taylor et al. at the University of Surrey [41]. It was re-designed by amputating the existing T-peel jaws replacing it with two new sets of jaws, which could accommodate the poker-chip joints.
Chapter Seven:  
Effect of Fracture Methods on XPS Analysis Results

The alterations were carried out in such a way that the two sets of jaws are now interchangeable to accommodate, both T-peel specimens and butt-joints. Detailed description of the XPS *in-situ* fracture assembly is given elsewhere in literature and will not be discussed further [91]. However when the assembly is fixed inside the preparation chamber of the spectrometer, the movement of the jaws is very much restricted and thus only allows joints made from thin substrates (~1 to 5 mm). The opening of the jaws in restricted by the diameter in the flange (35 mm) on which the fracture stage is mounted (see figure 7.1). It is a problem for this particular work, as the glass substrates are about 10 mm in thickness. Therefore to allow few more millimetre of additional movement in the assembly, the ESCALAB stubs for the *in-situ* tests are modified to have very thin platforms. This modification has allowed the maximum travel of the jaws in the fracture stage without the need for altering the substrate thickness. The fracture is carried out by a gentle twisting of the control screw. Following fracture, both halves of the joints can be recovered and loaded into the analysing chamber for further study.

The Figure 7.1 schematically shows the assembly of standard butt-joint and the ESCALAB stubs in the fracture stage. The joint assembly comprised of two ESCALAB stubs, which were modified, and 10-mm diameter BK 7 glass discs bonded to them with a Premabond toughened acrylic adhesive (Flexon™ F215).

![Control Screw](image)

**Figure 7.1**  Schematic of modified T-peel stage at preparation chamber for *in-situ* UHV fractures.

156
Chapter Seven: 
Effect of Fracture Methods on XPS Analysis Results

The manufacture of joints is otherwise identical to the joint preparation for the \textit{ex-situ} tensometer fracture (see Chapter 4). Therefore the bondline thickness (180\textmu m) was maintained in all the fracture experiments. As soon as the fracture was initiated, the vacuum pressure in the preparation chamber indicated a sudden drop of $10^{-1}$ to $10^{-2}$ Torr, but achieved the required pressure (~$10^{-8}$ Torr) within few minutes. This is due to the release of water molecules present in the joints into the UHV system on fracture.

7.3 RESULTS OF IN-SITU FRACTURE XPS ANALYSIS

Figure 7.2 is a survey spectrum from a butt-joint immersed in water for 20 days, which was fractured \textit{in-situ}. There is a strong C 1s signal from the polymer, but the sodium signal from the glass surface can also be identified. On the apparent glass side (side 1), all the characteristic glass components and a strong presence of carbon are present. The minor components of the bulk glass such as barium and calcium were also observed in side 1. However on the glass side of the fracture the sulphur from the curing agent was completely absent. Unfortunately the \textit{in-situ} analysis was not carried out under a monochromatic source. This is due to the constraints to fracture \textit{in-situ} in the Sigma Probe XPS spectrometer. Therefore the carbon peaks are not very well defined and have almost symmetrical peaks. However, the removal of hydrocarbon contamination in the \textit{in-situ} fracture enabled to visualise the true nature of the fracture surface. The fracture without the influence of the atmosphere clearly shows a near interfacial failure with a thin layer of polymer, that does not contain sulphur left on the glass surface.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Element/ Atomic % & C & O & N & Si & Na & S & Ca & Ba \\
\hline
\textbf{Side 1} & 45.0 & 39.3 & 4.8 & 7.43 & 2.13 & --- & 0.12 & 1.26 \\
\textbf{Side 2} & 62.3 & 29.0 & 3.5 & 2.02 & 1.48 & 1.68 & --- & --- \\
\hline
\end{tabular}
\caption{XPS Quantification of \textit{in-situ} fracture 20 days water immersion sample.}
\end{table}
In order for this fracture to be compared with other ambient fracture analysis, further experiments of ex-situ nature were devised for joints immersed in water for exactly same conditions (i.e. 35°C and milli-Q water). The comparison between similar 20 days water immersion joints of different fracture conditions, are given below:

(a) In situ fracture of the sample in the XPS preparation chamber using XPS fracture stage, and the surfaces were analysed without the exposure to the atmosphere.

(b) In-situ fracture of the sample in the preparation chamber, but the surfaces were exposed to atmosphere before analysis.

(c) Ex-situ fracture of the sample using the aid of XPS fracture stage.

(d) Ex-situ fracture, using a J J Lloyds tensile tensometer.
The test (b) has been devised in order to identify the effect of ultra high vacuum (UHV) conditions on the fracture surface chemistry. Therefore the joint was \textit{in-situ} fractured and exposed to atmosphere before analysis. Then the modified fracture stage of the spectrometer was removed, and the fracture was carried out at atmospheric conditions using the fracture stage (test (c)).

The jaws of the \textit{in-situ} 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. In order to verify this possibility a direct tensile fracture of the joint, the test (d) was carried out. Tensometer conditions are same as for all the other tests in this work (i.e 1kN load cell and 1mm/min pulling rate). The spectra from these different fracture surfaces are summarised in Figure 7.3 and 7.4

By comparing the results obtained from all the fracture surfaces, the ‘glass’ sides of the joint clearly have polymer present in every mode of fractures. However the level of organic presence in the substrate varies with the chosen mode of fracture. In the glass side of the \textit{in-situ} fracture a lower level of carbon presence is expected, due to the absence adventitious carbon. However the surface concentration of carbon in \textit{in-situ} fracture is higher than the other fracture samples. Although adventitious carbon is absent in \textit{in-situ} fracture, the interfacial fracture side (side 1) clearly indicate a thicker layer of organic polymer than the other fracture modes. This can also be related to the shape of the spectrum, which is different from the other three fractured ‘glass’ surfaces, indicates a thicker layer of polymer present. Higher polymeric presence in the \textit{in-situ} fractured glass side can be further identified by the higher nitrogen surface concentration due to the presence of the amine curing agent. Components of the glass such as silicon and sodium are substantially lower, in addition to the non-existence of boron in the \textit{in-situ} glass surface.
Figure 7.3  The apparent 'Glass' sides of the joints fractured under different conditions.
Chapter Seven: Effect of Fracture Methods on XPS Analysis Results

Figure 7.4 The 'Polymer' sides of the joints fractured under different conditions.
Chapter Seven:
Effect of Fracture Methods on XPS Analysis Results

The surface concentrations of all respective elements on the fracture surfaces are shown in Figure 7.5. When the *in-situ* fractured samples were exposed to atmosphere before analysis, the spectra resembled that of the other *ex-situ* fractured samples. In addition the polymer side contains the signal iodine. The source for this presence is unknown, but deemed as a contamination. Also, the iodine presence was never observed in any of the other analytical studies.

![Figure 7.5](image)

*Figure 7.5* Comparison of the surface concentration of elements from the different modes of fracture surfaces, (a) glass side, (b) polymer side.
7.4 SUMMARY

Studies of various fracture modes to determine the effects on the locus of failures have clearly shown the role of UHV conditions. Although the in-situ fracture is interfacial failure, it is not close to the interface as the ex-situ fracture stage fracture or the ex-situ tensile fracture. Water being rapidly removed in UHV conditions, could have also contributed to this result. However an interesting result was obtained from the analysis of in-situ surfaces after exposed to atmosphere. This failure shows much closer to the interface than the in-situ fracture. Also, these studies have indicated that the loci of failure for the ex-situ fracture in fracture stage and the Instron have no significant variations. Therefore the overall observations from this study can be summarised as follows:

i) In-situ fracture is more likely to show an interfacial failure mode with the existence of thicker polymer overlayer, than the joint fractures carried out in the atmosphere.

ii) Failure surfaces obtained from the scissor like jaw action of the in-situ fracture stage does not have any variations to the tensile fracture from an Instron (i.e. similar locus of failures).

Unfortunately these results could not be confirmed by the dry fracture of adhesive joints. In addition to the constraints explained for the in-situ fractures in section 7.2.1, the dry in-situ fractures of joints made from F125 were found to be very difficult due to its strong bond strength. It was found that it was virtually impossible to secure the joint into ESCALAB stub with an even stronger adhesive.
8.1 INTRODUCTION

So far all the experimental work described in this thesis has been carried out on a commercial resin readily available for optical precision bonding. Such commercial resin formulations are known to contain many unknown organic and inorganic components. It is a cumbersome process to identify and determine the role of these individual resin components. Therefore it is intended to carry out reformulation of the commercial resin, based on the knowledge of fundamental formulation chemistry gained earlier in the studies of F125 resin system. In this way the reformulated resins will contain only the components required for curing and catalytic reactions to form a polymer network. Hence, minor components added to enhance shelf life, flame retardancy and the like will not be considered.

During the work described in this Chapter, the effects of formulation chemistry on the physical and performance characteristics of reformulated resins are analysed. It is intended that, as a result of these experiments, it will be possible to identify the role of individual components on the durability of the adhesive resins. In this chapter the characterisation of the reformulated resins using bulk and surface analytical methods and the chemistry of the reformulated adhesive, will be examined.
8.2 SELECTION OF ADHESIVE COMPONENTS

At this stage of the work the prototype formulation of the adhesive resins was achieved, using the four major chemical components of the commercial F125 resin system (see Chapter 4 for details). These are the epoxy resin, diluent, polysulphide and an amine. The suitable chemicals were selected, after careful consideration of their chemical properties. The other fully formulated resin properties such as pot life and heat resistance properties were not considered as significant in this process, as the main aim was to mimic the commercial adhesive based on its fundamental resin chemistry. This would aid the study of resins without the involvement of possible presence of minor components in the system.

8.2.1 Selection Epoxy Resins

There are virtually thousands of molecular weight and viscosity variant epoxy resins available for selection. From this range four well know types of DGEBA type epoxy resins, previously used in other commercial adhesive systems, are selected. Theses resins are obtained from Fluka (D.E.R 330) and Sigma (Araldite) Chemical divisions of the Sigma-Aldrich Company Ltd., UK.

i) D.E.R 330
ii) Araldite 506
iii) Araldite 502
iv) Araldite 6005

D.E.R 330 is a low epoxide equivalent weight (EEW) non-crystallising liquid resin especially processed to give very low viscosity (Brookfield Viscosity < 500 cps at 25° C) without the use of reactive diluent. The Brookfield instrument is a well known type of rotational spindle viscometer and is the subject of several standard test methods for polymers in the liquid state [124]. Initial trials proved that this resin grade flows very easily, and it is very difficult to control the formulations within a joint. Fillers could be used to consolidate its flow properties, but again this may complicate this work further.
Besides, it was decided that the diluent effects are one of the main areas of study in this work, and this could not be achieved by the use of this resin. Araldite 506 is also a low viscosity modified epoxy resin (500-700 cps at 25°C), with an EEW between 172-185 [125]. This resin also flowed easily at room temperature and the formulation within the joint could not be controlled without the aids of fillers. In addition, after several communications with the manufacturers, they did not provide a more precise EEW number for the resin. Although there are other characterisation methods available to identify the number of terminal epoxy groups, this was deemed as unnecessary and time consuming in this formulation study. The third resin, Araldite 502, is a medium viscosity modified epoxy resin (2100-3600 cps at 25°C). This is marginally better than the other two low viscosity resins, and has sufficient flow during mixing. However the addition of diluent was found to be increasing the flow of the material dramatically, and the final mix has a very low viscosity to be formed as an adhesive. In addition, the wider range of EEW number (232-250), will make it difficult to achieve an accurate stoichiometry with the curing agents.

Finally the Araldite 6005 resin has been selected in this reformulation study. It is a high viscosity resin (7000-10000 cps at 25°C), with a precisely quoted EEW of 175. Initially the resin was very thick and did not flow with ease. However with the addition of diluent in several trials, eventually provided the desired stable resin mix suitable for the fabrication of adhesive joints. Therefore Araldite 6005, the DGEBA based epoxy resin has been chosen for the formulation work in this thesis.

8.2.2 Selection of Reactive Diluent

The diluent used in the commercial adhesive system is p-tert-butylphenylglycidylether. This diluent material is obtained from the Aldrich Chemical Division of the Sigma-Aldrich Company Ltd., UK. It is a colourless clear liquid, about 98% pure as analysed by Gas chromatography [125]. This family of epoxy reactive diluents are biologically active and hazardous to the skin. The viscosity reduction capability and the skin irritation tendency of these diluents are directly related to molecular size.
With larger molecules the skin hazard potential is lower, but the viscosity reducing efficiency is also lower. In a review by Oldring et al [71] on the classification of diluent hazards, he tabulated p-tert-butyl-phenylglycidylether among the most skin irritant diluent types and extreme care must be taken to avoid any form of skin contact. During formulation of adhesives described in this thesis, a respirator mask, chemical-resistant gloves, safety goggles and other protective clothing were worn. Minimal contact with the diluent material was maintained and all the formulation work has been carried in a mechanical exhaust.

8.2.3 Selection of Mercaptan Curing Agent

The mercaptan terminated liquid polysulphides were obtained from Morton International Limited, U.K. The three grades of polysulphides which can be used in epoxy curing reactions, LP-3, LP-33 and ZL-1400C have been kindly supplied by Mr Tom Reeves of Morton International Limited. The lower molecular weight LP-3, LP-33 and a newly developed ZL-1400C polymer are used as elastomeric modifiers and curing agents, particularly for epoxy coatings and adhesives. The choice of LP-3, LP-33 and ZL-1400C as curing agents for epoxy resins has been based on their molecular weight, viscosity, mercaptan content, and functionality.

As a result of their low molecular weights LP-3, LP-33 and ZL-1400C have the lowest viscosities of the commercially available polysulphides [78, 79]. Viscosities of less than 2 Pas at 25°C make the polymers extremely easy to handle and incorporate into an epoxy resin. Table 8.1 illustrates two more important parameters, namely the mercaptan content and branching.
Chapter Eight
Reformulation of New Adhesives and their Characterisation

<table>
<thead>
<tr>
<th>Typical Properties</th>
<th>LP-3</th>
<th>LP-33</th>
<th>ZL-1400C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Molecular Weight</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Repeat Unit ‘N’ value (See Chapter 4)</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Average Viscosity at 25°C (Pas)</td>
<td>1.2</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Mercaptan Content (%)</td>
<td>6.8</td>
<td>5.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Trichloropropane (mole %)</td>
<td>2.0</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 8.1**  Properties of liquid polysulphides used in this work for the production of epoxy adhesives [126].

After a paper study of several similar polysulphides it was found that these three liquid polysulphides are the most reactive polymers for the manufacture of mercaptan cured epoxy resins. Branching by trichloropropane is preferred in the formulation, as this has also been introduced in the commercial F125 system. Therefore the ZL-1400C polymer has been excluded from the formulation studies, as it is a linear polymer with exactly two mercaptan groups per molecule.

The LP-3 and LP-33 products are almost identical in their chemistry, have a similar amount of molecular branching and contain 6 wt% mercaptan groups per molecule. After the initial formulation trials, it was found that both polymers could be used in the formulations with adjustments to the molar concentrations. However verbal communications with the commercial F125 resin manufacturers [127], has confirmed that their resin contain between 2 to 5 % of trichloropropane in their polysulphide. Therefore the LP-3 polysulphide has been selected for the work in this thesis. As the manufacturers have incorporated the cross-linking agent during the synthesis of polysulphide, this will not effect the mole calculations for the new adhesives. Although the LP-3 polymer is not 100% linear as the non-branching ZL-1400C variant, the branching is minimal and forms a near linear material.
8.2.4 Selection of Amine

Amine has to be introduced in the formulation to catalyse and/or accelerate the speed of the curing. This was reflected in case of commercial F125 resin, where the adhesive can be handled and polished within about 30 minutes of mixing. In addition the polysulphide cure mechanism is dominated by chain extension reactions rather than cross-linking. The cross-links formed by the reactions from the amine will also be able to reduce the flexibility attained from the chain extension. The selected amine is the same type of amine as in the F125 system: 1-(2-aminoethyl) piperazine. The amine was obtained from the Aldrich Chemical divisions of the Sigma-Aldrich Company Ltd., UK. It is a clear colourless liquid with about 99% pure as analysed by gas chromatography [125]. It is also biologically active, as is the diluent, and care was take during formulation as the amine will be readily absorbed through skin in contact.

8.3 FORMULATION OF THE RESINS

The formulation comprises of two sections. The first group of formulations is based on the variations in the diluent concentrations, and the other is based on variations of amine concentrations. Each group consists of three formulations, and thus six different adhesive resins were manufactured for this current work.

8.3.1 Diluent Variant Formulations

The commercial F125 adhesive consists of 20% diluent in its resin half and posses resin to hardener ratio of 1:1 (see Table 8.1). The reformulation of the diluent variants are formulated with 0%, 10% and 30% w/w of the diluent in the resin half of the two-part adhesive. The selected diluent concentrations will aid the identification of its effect with lower, higher and no diluent. When formulating in this way the hardener component (polysulphide and amine) has been kept constant as the commercial resin ratio (i.e. 80% polysulphide and 20% amine).
Chapter Eight
Reformulation of New Adhesives and their Characterisation

The 1:1 ratio between resin and hardener cannot be maintained in the reformulated systems, as the stoichiometry of the adhesive is different to the commercial resin. Stoichiometry in the hardener between the amine and the polysulphide was maintained by matching the molar concentrations. The ratios between the different components in adhesive systems allows the identification of the adhesives as follows:

i) Diluent Free formulation (0% w/w of the resin) – DF

ii) Lower Diluent formulation (10% w/w of the resin) – LD

iii) Higher Diluent formulation (30% w/w of the resin) – HD

<table>
<thead>
<tr>
<th>Commercial Adhesive System - F125 (Resin : Hardener = 1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>Diglycidyl ether of bisphenol A (DGEBA) = ~80%</td>
</tr>
<tr>
<td>p-tert-Butyl-phenylglycidylether = ~20%</td>
</tr>
</tbody>
</table>

**Table 8.1** The adhesive component ratios of the commercial resin

8.3.1.1 Diluent Free Formulation (DF)

Diluent free resins have been formulated by carefully matching the epoxy equivalent content of the DGEBA and the diluent, to the reactive free hydrogen contents of the mercaptan (-SH) from liquid polysulphide and the amine (-NH). The molar calculation for this formulation is described below in Table 8.2.
Chapter Eight  
Reformulation of New Adhesives and their Characterisation

RESIN HALF OF THE DF ADHESIVE

<table>
<thead>
<tr>
<th>Weight of the Diluent</th>
<th>= 0.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of the DGEBA</td>
<td>= 350 g</td>
</tr>
<tr>
<td>Thus the quantity of epoxy rings</td>
<td>= (\frac{350}{175 \text{ (EEW)}}) = 2 mole</td>
</tr>
</tbody>
</table>

HARDENER OF THE DF ADHESIVE

AMINE

The number of \(-\text{NH}\) groups from a primary and a secondary amine = 3
Molecular weight of the 1-(2-Aminoethyl) piperazine = 129.21 g
For a nominal amount of 63.5 g of amine, the amount of reactive hydrogens = \(\frac{63.5}{129.21} \times 3\) = 1.474 mole.

POLYSULPHIDE

If 20 wt % of amine is 63.5 g the 80 wt % polysulphide = 254 g
The weight % of the mercaptans \(-\text{SH}\) in a polysulphide = 6.8
The molecular weight of a mercaptan group = 33 g
Therefore the number of mercaptans in the hardener = \(\frac{254 \times 6.8}{33 \times 100}\) = 0.523 mole
Thus total reactive hydrogens = 2 mole

Table 8.2  Formulation of the DF adhesive

When changing the diluent content in the formulations, the weight percentage of the hardener components, the polysulphide and amine was maintained as in the commercial adhesive. In other words, 80 % polysulphide and 20 % amine was constant in all diluent variant formulations.

171
The calculations shown in Table 8.2 will allow one to formulate any amount of DF adhesives by applying the appropriate ratios of the mole percentages. A 20 g of DF adhesive formulation is shown in Table 8.3. However the mixing ratio between the resin and hardener halves of the adhesive was changed from 1:1 in commercial adhesive to 1:0.907 in the DF adhesive.

<table>
<thead>
<tr>
<th>Resin : Hardener</th>
<th>1.000 : 0.907</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (g)</td>
</tr>
<tr>
<td>DILUENT(0%)</td>
<td>0</td>
</tr>
<tr>
<td>EPOXY(100%)</td>
<td>350</td>
</tr>
<tr>
<td>AMINE(20%)</td>
<td>63.5</td>
</tr>
<tr>
<td>SULPHIDE(80%)</td>
<td>254</td>
</tr>
</tbody>
</table>

**Table 8.3** Summary of Diluent Free Formulation for a 20 g adhesive

8.3.1.2 10% Diluent (LD) and 30% Diluent (HD) Adhesive Formulations

The formulation method is similar to the DF adhesive, but as the name implies 10% and 30% diluent was incorporated in the resin half of the adhesive. The resin half of the LD and HD formulations contain p-tert-butyl-phenylglycidylether with a molecular weight of 206.9 g. The diluent also contains one epoxy group in its chemical structure. Therefore the calculations molar quantities were made accordingly to accommodate the relevant reactive groups in the hardener and the resin. Summary of the final formulation of 20g of LD and HD adhesives is shown in Table 8.4 (a) and (b).
Chapter Eight
Reformulation of New Adhesives and their Characterisation

(a)

<table>
<thead>
<tr>
<th>Resin : Hardener</th>
<th>Weight (g)</th>
<th>Epoxy cont.</th>
<th>Mole</th>
<th>20 g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>DILUENT(10%)</td>
<td>206.29</td>
<td>1</td>
<td></td>
<td>1.06</td>
</tr>
<tr>
<td>EPOXY(90%)</td>
<td>1856.61</td>
<td>10.61</td>
<td>11.61</td>
<td>9.50</td>
</tr>
<tr>
<td>AMINE(20%)</td>
<td>369.15</td>
<td>8.57</td>
<td></td>
<td>1.89</td>
</tr>
<tr>
<td>SULPHIDE(80%)</td>
<td>1476.61</td>
<td>3.04</td>
<td>11.61</td>
<td>7.56</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Resin : Hardener</th>
<th>Weight (g)</th>
<th>Epoxy cont.</th>
<th>Mole</th>
<th>20 g Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>DILUENT(30%)</td>
<td>206.29</td>
<td>1</td>
<td></td>
<td>3.21</td>
</tr>
<tr>
<td>EPOXY(70%)</td>
<td>481.34</td>
<td>2.75</td>
<td>3.75</td>
<td>7.50</td>
</tr>
<tr>
<td>AMINE(20%)</td>
<td>119.26</td>
<td>2.77</td>
<td></td>
<td>1.86</td>
</tr>
<tr>
<td>SULPHIDE(80%)</td>
<td>477.04</td>
<td>0.98</td>
<td>3.75</td>
<td>7.43</td>
</tr>
</tbody>
</table>

Table 8.4 (a) 10% Diluent reformulated adhesive compositions (b) 30% Diluent formulation.

8.3.2 Amine Variant Formulations

The method of formulating the amine variant adhesives is similar to diluent variant adhesives. Here the resin components, the diluent and DGEBA, are kept at 20 and 80 wt % respectively as in the commercial F125 adhesive. Then the amine concentration was varied to form amine free, 10% amine and 30% amine-containing hardeners for the adhesives. However there were some problems encountered in the formulation of the lower amine adhesives. It was found that the lower amine formulations took a considerable long time (more than 20 days) to achieve maximum cure at room temperature. The resultant cured adhesives showed noticeably higher flexibility, and often showed thixotropic behaviour. The lower amine percentage in the hardener composition is obviously not suitable for use as a load-bearing adhesive application.
However after several trials with varying amount of amine in the formulation, it was found that the minimum concentration of amine that could be used was about 10 wt % of the hardener. Below this concentration the resin-hardener mix took longer time to cure and would have no practical application as adhesive. Therefore the amine free formulation was not included in this study. However a 100% amine cured or mercaptan free formulation was included as an additional adhesive for this work. The final three adhesive in this groups are listed below:

i) Mercaptan free (100% amine or 0% Polysulphide) formulation – SF
ii) 10% amine formulation – LA
iii) 30% amine formulation – HA

The final calculations of molar quantities for these three formulations are shown in Table 8.5 (a), (b) and (c).

<table>
<thead>
<tr>
<th>(a)</th>
<th>Resin : Hardener</th>
<th>1.000 : 0.234</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (g)</td>
<td>Epoxy cont.</td>
</tr>
<tr>
<td>DILUENT (20%)</td>
<td>231.50</td>
<td>1</td>
</tr>
<tr>
<td>EPOXY (80%)</td>
<td>926.00</td>
<td>5.29</td>
</tr>
<tr>
<td>AMINE (100%)</td>
<td>270.67</td>
<td>6.29</td>
</tr>
<tr>
<td>SULPHIDE (0%)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b)</th>
<th>Resin : Hardener</th>
<th>1.000 : 1.300</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (g)</td>
<td>Epoxy cont.</td>
</tr>
<tr>
<td>DILUENT (20%)</td>
<td>231.50</td>
<td>1</td>
</tr>
<tr>
<td>EPOXY (80%)</td>
<td>926.00</td>
<td>5.29</td>
</tr>
<tr>
<td>AMINE (10%)</td>
<td>150.53</td>
<td>3.50</td>
</tr>
<tr>
<td>SULPHIDE (90%)</td>
<td>1354.77</td>
<td>2.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(c)</th>
<th>Resin : Hardener</th>
<th>1.000 : 0.646</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (g)</td>
<td>Epoxy cont.</td>
</tr>
<tr>
<td>DILUENT (20%)</td>
<td>231.50</td>
<td>1</td>
</tr>
<tr>
<td>EPOXY (80%)</td>
<td>926.00</td>
<td>5.29</td>
</tr>
<tr>
<td>AMINE (30%)</td>
<td>224.44</td>
<td>5.29</td>
</tr>
<tr>
<td>SULPHIDE (70%)</td>
<td>523.69</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 8.5 (a) Mercaptan free adhesive composition (SF), (b) LA formulation, (c) HA formulation.
8.4 ANALYSIS OF THE REFORMULATED RESINS

The cure and thermo-mechanical characteristics of the adhesives were carried out using differential scanning calorimetry (Perkin-Elmer DSC-7) and dynamic mechanical analysis (Rheometrics RDA II) available at the University Surrey. In order to aid the fracture studies of the joints in the following chapter, the reformulated adhesive materials were also analysed using ToF-SIMS and XPS.

8.4.1 Measurement of Cure Reactions

What is of concern is the formulation of new adhesives is the understanding of the cure reaction. It is important to know at which temperature and how long a prepolymer should be heated, in order to obtain the product possessing the desired properties in a quick and reproducible manner.

DSC is used to identify the cure reactions of the resins by heating a small amount (0.004-0.008 g) of the uncured, freshly mixed adhesive and the cured resin into an aluminium heater pans. The cured resin was scraped off, using a clean scalpel and measured accurately. A relatively slower rate of temperature increase (5°C/min) was used, allowing the thermal energy to be distributed uniformly throughout the sample. A very slow scan rate should improve resolution, but the size of the peak will decrease. With an increasing scan-rate the size of the peak will increase and thus provide ease of measurement but only to the detriment of resolution. However, for any scan-rate the area under cure should be the same, i.e. if an exothermal peak is observed the amount of energy exerted will remain constant for any scan-rate.

The DSC runs were carried out on all six reformulated adhesives at different time intervals after the initial mixing. Then the exothermic peaks in the DSC traces were carefully monitored for the change in the dissipated energy. It is expected that a fully cured adhesive should not show a high exothermic peak after glass transition step in the thermograph. As an example, analysis from the 10% diluent-containing adhesive (LD) is shown in Figure 8.6, 8.7 and 8.8.
Figure 8.6 (a) A temperature scan of the LD adhesive that has just been mixed, (b) after 1Hr 30min at ambient (~20° C), (c) for 2hours and 30minutes at ambient (~20° C).
The Figure 8.6 (a) for the freshly mixed adhesive shows a glass transition at \(37^\circ\text{C}\), and the exothermic peak, which is the heat generated by the curing reaction of the non-crosslinked portion of the polymer in this case was \(-51.06\ \text{J g}^{-1}\). This exothermic heat output can be easily calculated using the software of the instrument.

Then the adhesive mix was left to cure for 1 hour and 30 minutes at an ambient temperature, about \(-20^\circ\text{C}\) (Figure 8.6 (b). The glass transition was detected at \(37^\circ\text{C}\), and the exothermic peak of curing reaction was observed at \(95^\circ\text{C}\) with a \(\Delta H\) of \(-45.20\ \text{J g}^{-1}\). This sample is partially cured but the degree of cure achieved at room temperature is very small. This could be observed with the enthalpy change between the two results shown in Figure 8.6 (a) and (b). In the samples shown in Figure 8.6 (a) and (b), only a \(\Delta H\) of \(-5.86\ \text{J g}^{-1}\) has occurred in 1 hour and 30 minutes at ambient temperature. The total \(\Delta H\) for the full cure of 10% diluent adhesive is \(-51.06\ \text{J g}^{-1}\).

In the Figure 8.6 (c), for the sample cured at \(20^\circ\text{C}\) for 2 hours and 30 minutes, the \(T_g\) was observed at \(38^\circ\text{C}\). The exothermic peak of curing reaction was observed at \(90^\circ\text{C}\) with a \(\Delta H\) of \(-39.58\ \text{J g}^{-1}\). This time scale also not sufficient for the complete cure of the material. In addition to the exothermic peak, a peak at above \(200^\circ\text{C}\) was also detected for the three results shown in Figure 8.6. This can be related to either the melting of the non-crosslinked part of the resin or degradation. A rerun with a sample encapsulated should show if it is volatilising or melting, but unfortunately no high-pressure sample pans were available at the time of testing.

Finally, Figure 8.7 (a) and (b) shows the results of DSC measurement for the long-term cured sample. The \(T_g\) was detected at \(45^\circ\text{C}\) for the 6 hours at \(40^\circ\text{C}\) cured adhesive (Figure 8.7 (a)). The exothermic reaction is hardly detectable, but was confirmed as \(\Delta H\) of \(4.01\ \text{J g}^{-1}\). The sample is nearly completely cured and nearly every crosslink has reacted. This is further confirmed by the disappearance of the peak attributed to melting. This can now be confidently ascribed to the melting of the non-cross linked components of the resin as described above.
Chapter Eight  
Reformulation of New Adhesives and their Characterisation

The Figure 8.7 (b), is the result of the DSC measurements of the epoxy resin cured for 7 days at 20°C. The $T_g$ step for this trace is hardly observed, as it has blended in with the start of the trace. The $T_g$ for this almost completely cured resin is 45°C. The sample showed virtually no exothermic cure reaction and that indicated that only residual cure remains. The high temperature peak also completely disappeared and this indicates either the crosslinked sample has reduced the volatiles to zero or melting now occurs at higher temperatures.

\[
\Delta H = -4.01 \text{ J g}^{-1} \\
t = 480 \text{ min.}
\]

\[
\Delta H = -2 \text{ J g}^{-1} \\
t = 10.08 \times 10^3 \text{ min.}
\]

**Figure 8.7** (a) LD Sample cured $-40^\circ \text{C}$ for 6 hours, (b) the cure profile for the epoxy cured for 7 days at ambient.
Chapter Eight
Reformulation of New Adhesives and their Characterisation

By plotting the relationships between the temperature of the $T_g$ against the cure time, it should be possible, to estimate the degree of curing. However as the $T_g$ is not a sensitive measure for all materials, the enthalpy can be used.

Figure 8.8 shows the relationship for remaining cure energy per gram against time. It clearly shows the relationship between the decreasing cure energy and increasing cure. The data point marked with a square is estimation, assuming an exponential decay, of the cure time if the sample had been at ambient and still had a residual energy per gram of 4.01 Jg$^{-1}$. It was assumed, that when a cure reaction occurs near the room temperature, a temperature increase of 10°C approximately double the rate of reaction (i.e. Arrhenius rate law [128, 129]).

It has been identified from literature [65], that it is common to determine the degree of cure using isothermal heating. This technique requires constant temperature for long time and re-evaluation at several temperatures. However this was not possible in this study due to time constraints.

![Remaining cure as a function of cure time for LD epoxy adhesive.](image)

**Figure 8.8** Remaining cure as a function of cure time for LD epoxy adhesive.

It is very cumbersome to perform the cure energy plots for all the six reformulated adhesives in this study. Therefore DSC runs for estimated two or three time intervals, has been carried out to identify the minimum remaining cure for the other five reformulated adhesives.
Table 8.6 summarises the results of thermal analysis for all resins and the selected cure time for the materials. As the amine concentration increased the glass transition temperature is slightly increased and the cure time is very much reduced. The adhesive cured with just amine (0% polysulphide) shows the highest transition temperature for the reformulated resins. It is due to the absence of or the reduction of more flexible polysulphide from the formulation. Also, high functionality amine provides the fastest curing schedule by comparison. However, the effects of diluent are not very clear, but the diluent free formulation exhibits a faster curing time, with a higher glass transition temperature.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>$T_g$ (°C)</th>
<th>Cure Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Amine</td>
<td>31</td>
<td>~6 days at 40°C</td>
</tr>
<tr>
<td>F125</td>
<td>41</td>
<td>~2 hours at 40°C</td>
</tr>
<tr>
<td>30% Diluent</td>
<td>44</td>
<td>~7 hours at 40°C</td>
</tr>
<tr>
<td>10% Diluent</td>
<td>45</td>
<td>~7 hours at 40°C</td>
</tr>
<tr>
<td>30% Amine</td>
<td>46</td>
<td>~2 hour at 40°C</td>
</tr>
<tr>
<td>0% Diluent</td>
<td>48</td>
<td>~4 hour at 40°C</td>
</tr>
<tr>
<td>0% Polysulphide</td>
<td>53</td>
<td>~20 minutes at 20°C</td>
</tr>
</tbody>
</table>

Table 8.6 Summary of thermal analysis and selected cure time for reformulated resins.

8.4.2 DMA of Adhesives

Dynamic mechanical analysis was utilised by means of forced oscillation experiment, a sinusoidal determination at a constant frequency and amplitude applied to the specimen (see Chapter 3). The absolute value of the generated stress in the sample is measured and rectangular shaped samples (10 x 30 x 1.5 mm) were used in these experiments.
The test specimens were prepared by curing adhesive mixtures into specially made brass moulds with the required size. The edges of the brass mould were coated with a PTFE release agent, and then the resin was cast into the mould. This has enabled the once cured solid adhesive to be removed easily from the mould.

Figure 8.9 shows the position of tan \( \delta \) peak maxima for the reformulated adhesives and for the commercial resin. The glass transition temperature values are almost identical to the observations from the DSC analysis. On the 10% amine formulation, there is higher proportion polysulphides present, and this reduces the value of the tan \( \delta \). The 0% diluent, 30% amine and 10% diluent formulations all show higher \( T_g \) values than the commercial F125 adhesive.

**Figure 8.9** DMA results for diluent free resin formulation
Chapter Eight
Reformulation of New Adhesives and their Characterisation

The 10% diluent resin have similar shape of the peak as for the commercial adhesive, with a slight increase in the glass transition. Using DSC analysis it has already been identified that the $T_g$ of polysulphide free formulation were the highest among the reformulated resins. However the DMA analysis was not possible on this adhesive due to its high brittle nature. The rectangle samples made for this analysis were too fragile and the analysis could not be completed. This is an indication that a right proportion of all ingredients are needed for the formulation of an adhesive with optimum properties.

8.4.3 XPS of the Adhesives

The resin and the hardener contents of the reformulated adhesives were mixed according to the mixing ratios shown earlier and poured into a mould and left to achieve the maximum cure. The cured resin was then removed from the mould, and the top layer of adhesive was scraped with a clean scalpel, in order to remove the contaminants. Then the cured block of resins was microtomed into thin wafer strips for XPS analysis using the sigma probe spectrometer (see Chapter 4 for details).

8.4.3.1 Results of XPS Analysis

The survey spectra for the reformulated resins are shown in Figure 8.10. All four elements from the reformulation components, carbon, oxygen, nitrogen and sulphur are observed. As expected the mercaptan free formulation did not contain any sulphur. The concentration of elements from the quantitative analysis also shown in Table 8.7.

Here the diluent free formulations have no significant difference in the surface concentration of the element. However the higher amine containing resins, as expected show higher concentration of nitrogen.
Chapter Eight
Reformulation of New Adhesives and their Characterisation

<table>
<thead>
<tr>
<th>Reformulated Adhesives</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C 1s</td>
</tr>
<tr>
<td>30% Diluent Formulation</td>
<td>76.71</td>
</tr>
<tr>
<td>10% Diluent Formulation</td>
<td>73.50</td>
</tr>
<tr>
<td>Diluent Free formulation</td>
<td>76.95</td>
</tr>
<tr>
<td>30% Amine Formulation</td>
<td>74.99</td>
</tr>
<tr>
<td>10% Amine Formulation</td>
<td>77.60</td>
</tr>
<tr>
<td>0% Polysulphide Formulation</td>
<td>78.51</td>
</tr>
</tbody>
</table>

**Table 8.8**  Quantitative Surface analysis results from the six reformulated resins.

**Figure 8.10**  XPS analysis of the reformulated adhesives.
8.4.4 ToF-SIMS of the adhesive formulations

The resin formulations contain the fragmentation patterns for the four major components: DGEBA, 4-tert butyl phenyl epoxypropyl ether, 1-(2-Aminoethyl) piperazine, polysulphide and the relevant fragmentation of the cured epoxy as already discussed in Chapter 3. Therefore in this section, variations in quantified concentration for selected fragment ions will be discussed. The selected ions and their corresponding normalised concentration plots are shown in Figure 8.11. As the diluent and DGEBA are almost identical in their molecular fragmentation behaviour, a common fragment m/z = 57 was selected for this study.

In the amine variant formulations, amine to epoxy ratio increases with the amount of amine inclusion in the hardener. The 100% amine cured adhesive (SF) has the strong signal for m/z = 56. On the diluent variant adhesives the selected three ions fragments have almost similar intensities. However a small change in m/z = 56 is observed with reduction of diluent. Although it is not clear, it could be due small variations in the degree of cure in the resins.

![Figure 8.11](image)

**Figure 8.11** Relative abundance of three selected fragment ions for the reformulated resins.
Chapter Eight
Reformulation of New Adhesives and their Characterisation

8.5 SUMMARY

The results discussed in this chapter shown a methodology for formulating adhesive based on a commercial resin. The reformulated resin so far indicated that by changing the composition resins with improve physical properties can be obtained. This observation is based on the thermal analysis of the adhesives. These results are useful, but do not reveal the long durability of the adhesive systems. Therefore the surface analyses of the adhesives were also carried out, to facilitate the fracture analysis of the joints described in the following chapter.
9.1 INTRODUCTION

After the successful reformulation of the commercial adhesive it is now intended, to analyse the durability of joints fabricated using these resins in hostile conditions. The experimental approach is similar to the earlier durability studies of the commercial F125 adhesive resin. Dry and wet fracture of the joints and the effects of water on the different formulations have been analysed using XPS and ToF-SIMS. The reformulation of the adhesive has produced six different variations, and thus the following sections consist of the durability studies of these new resins. All the joints made from the reformulated resins were left in water for a fixed time of ten days. This would enable a meaningful comparison between materials to be made. The various re-formulated resins are described together, with a list of abbreviations used to identify them in this chapter, in Table 9.1.

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Generic Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% diluent formulation</td>
<td>Diluent Variants</td>
<td>DF (Diluent Free)</td>
</tr>
<tr>
<td>10% diluent formulation</td>
<td>LD (Lower Diluent)</td>
<td></td>
</tr>
<tr>
<td>30% diluent formulation</td>
<td>HD (Higher Diluent)</td>
<td></td>
</tr>
<tr>
<td>100% amine formulation</td>
<td>Amine Variants</td>
<td>SF (Sulphide Free)</td>
</tr>
<tr>
<td>10% amine formulation</td>
<td>LA (Lower Amine)</td>
<td></td>
</tr>
<tr>
<td>30% amine formulation</td>
<td>HA (Higher Amine)</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.1 Abbreviation and group naming of the re-formulations
9.2 FRACTURE STRENGTH OF JOINTS MADE FROM REFORMULATED RESINS

After the bulk characterisations of the resins as described in the previous Chapter, dry and wet tensile fractures of the adhesive joints were carried out. The joint manufacturing procedure for this study is identical to the method explained earlier for the joints made from commercial adhesive resin (see Chapter Five). The fracture strengths of the dry and ten days water immersion samples were recorded using the J J Lloyds tensile tensometer (Figure 9.1).

![Fracture strengths of the reformulated resins as measured by a Tensile Tensometer.](image)

**Figure 9.1** Fracture strengths of the reformulated resins as measured by a Tensile Tensometer.

The results clearly show the substantial reduction in the fracture strengths of all the joints, exposed to water. However none of the dry and wet fracture strengths of the joints made from reformulated adhesives were higher than that of the commercial Tra-Con F125 adhesive (see Chapter 6 for additional details). On the diluent variant formulations, there is no significant difference between the formulations for the dry and wet tensile tests.
There may be some marginal difference between the three diluent variant samples, but this cannot be confirmed by testing just two joints of each resin. However the amine variant adhesive joints have significant differences between their loads to failure values. The sulphide free (SF) samples and the lower amine (LA) samples have very low dry failure values. During bulk characterisation it was observed that the SF has a relatively high modulus with brittle behaviour. Here the joints made from SF formulation have broken at a relatively low load. The LA formulation on the other hand has a very low glass transition temperature, and joints made from this formulation were simply not very strong. Finally the joints from both diluent variant and amine variant formulations have little resistance to water, and show very low load to failure values.

9.3 ANALYSIS OF DRY FRACTURE OF DILUENT VARIANT FORMULATIONS

9.3.1 SEM Analysis of dry fracture joint surfaces of diluent variant adhesives

The fracture surfaces of the joints from all reformulated adhesives were analysed by ToF-SIMS first, XPS and then SEM. However in order to describe the morphology of the fracture surfaces, the results from SEM will be discussed first in this section. The surface morphology of the dry fracture surfaces of the joints made from 10% diluent formulation (LD) is presented in Figure 9.2.

The LD dry fracture surfaces did not show any features related to brittle fracture. However it was found from the SEM micrographs that one side of the fracture surface had craters, and the other side had corresponding polymer fragments. Closer look at these features further also revealed a possible ductile fracture rather than brittle failure (Figure 9.3). However, the reason behind the presence of large number of these features along the fracture path is not clear.
Figure 9.2  SEM micrographs of the dry joint fracture surfaces of the LD formulation.

Figure 9.3  SEM micrographs showing features related to tearing in the dry LD joint fracture.
Similar features were also observed in the dry fracture of the diluent free (DF) joints. However, the craters and corresponding dimples are less frequent and observed to be localized in a small circular area on the fracture surfaces. Here it appeared that that the craters are deeper on one side, and the corresponding side showed identical features of fragments, from the LD dry fracture. What is interesting from the diluent variant formulations is the featureless nature of the HD dry fracture. The higher diluent (HD) formulation provided a dry fracture surface, which has no defined features as observed in the other two diluent variant surfaces. These results are shown in Figure 9.4.

**Figure 9.3** SEM micrographs of the dry joint fracture surfaces of the DF formulation.
Chapter Nine
Durability Studies of the Reformulated Adhesives

Figure 9.4  SEM micrographs of the dry joint fracture surfaces of the HD formulation

9.3.2  XPS Analysis of dry joint fracture surfaces of diluent variant adhesives

The XPS analysis of the dry fracture surfaces of the respective diluent variant joint samples is given in Figure 9.5. The surface concentrations of elements are also presented Table 9.1.

<table>
<thead>
<tr>
<th>Surface Composition / Atomic %</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DF</strong></td>
<td>40.29</td>
<td>41.43</td>
<td>5.41</td>
<td>12.87</td>
<td>---</td>
</tr>
<tr>
<td>Side 1</td>
<td>75.28</td>
<td>15.77</td>
<td>6.80</td>
<td>---</td>
<td>2.14</td>
</tr>
<tr>
<td>Side 2</td>
<td>50.93</td>
<td>31.89</td>
<td>7.28</td>
<td>9.90</td>
<td>---</td>
</tr>
<tr>
<td>LD</td>
<td>50.93</td>
<td>31.89</td>
<td>7.28</td>
<td>9.90</td>
<td>---</td>
</tr>
<tr>
<td>Side 1</td>
<td>75.77</td>
<td>16.31</td>
<td>5.88</td>
<td>---</td>
<td>2.04</td>
</tr>
<tr>
<td>Side 2</td>
<td>77.72</td>
<td>15.90</td>
<td>3.44</td>
<td>---</td>
<td>2.93</td>
</tr>
<tr>
<td>HD</td>
<td>77.51</td>
<td>15.68</td>
<td>4.16</td>
<td>---</td>
<td>2.65</td>
</tr>
</tbody>
</table>

Table 9.1  XPS quantification of diluent variant dry fracture surfaces.
Figure 9.5  XPS spectra of diluent variant dry fracture surfaces.
The XPS data for LD and DF formulations indicates a clear ‘polymer-glass’ interfacial failure. On the Side 1 of both of these dry fractures, higher concentrations of oxygen and silicon, and the disappearance of sulphur was observed. This indicates a predominately glass on this half of the fracture. However the significant amount of carbon in the Side 1 of DF and LD fracture surfaces also indicate presence of polymer. With the absence of sulphur which is characteristic of the polymer, surface contamination following failure is also another possibility for the presence of carbon. It can also be observed that the amount of carbon presence in DF Side 1 is substantially lower than on LD Side 1. Together with the reduction of carbon, the diluent free Side 1 indicates higher amount of silicon and oxygen.

It reasonable to assume that the features observed in the SEM of DF and LD Side 1 surfaces can be attributed to residual polymer. The lower carbon surface concentration in DF Side 1 also related to the suspected localised polymer, as observed in SEM. The quantification of analysis from HD fracture surfaces however, features almost identical surface concentration of carbon, oxygen, nitrogen and sulphide, which is characteristic of mercaptan curing agent. The 30% diluent dry fracture shows fracture through the bulk of the adhesive. The ToF-SIMS analysis of all these dry fracture surfaces will help further to evaluate the mode of failure, and these results are discussed in the following section.

9.3.3 ToF-SIMS of the dry joint fracture surfaces of diluent variant adhesives

The SIMS analysis has been carried out all the dry surfaces from the diluent variant joint fractures. The SIMS of DF fracture surfaces are shown in Figure 9.6. Initial observation of the analysis, confirms the presence of characteristic ion fragments from the bulk adhesive on both halves of the surfaces. Epoxy ion fragments (at m/z = 57 and 191), bisphenol groups (m/z = 135 and 165) and unsaturated hydrocarbon fragments (at m/z = 77 and 91) are all can be identified from these analyses (see Chapter 4 for details). Also, a series of amine related fragments such as C_2H_4N^+ (m/z = 42), C_3H_6NH_2^+ (m/z = 56), C_4H_8N^+ (m/z = 70), C_4H_7N_2^+ (m/z = 83), C_7H_13N_2^+ (m/z = 125) and C_8H_14N_3^+ (m/z = 152), are very intense on the both fracture surfaces.
On Side 1, however presence of Na\(^+\) (\(m/z = 23\)) and relatively high K\(^+\) (\(m/z = 39\)) and Si\(^+\) (\(m/z = 28\)) can also be observed. This result gives an indication the polymer layer on Side 1 is more closer to the glass substrate. Also, comparatively strong presence of typical organic ion fragments such as CH\(_3\)\(^+\) (\(m/z = 15\)) and CH\(_3\)CH\(_2\)\(^+\) (\(m/z = 27\)) and strong epoxy fragments such as C\(_3\)H\(_5\)O\(^+\) (\(m/z = 57\)) and C\(_9\)H\(_{11}\)O\(^+\) (\(m/z = 135\)) identifies Side 2 as a polymer rich fracture surface. These observations are in line with the results obtained from the XPS analysis, where silicon containing Side 1 and sulphur containing Side 2 surfaces were earlier identified.

![SIMS spectra for Side 1 and Side 2](image)

**Figure 9.6** Positive ToF-SIMS analysis of DF dry fracture surfaces.

The SIMS spectra from the LD fracture surfaces are presented in Figure 9.7. The results are closely related to the XPS investigations, where Side 1 has been identified as the 'glass' side containing higher surface concentrations of Si 2p and O 1s. Here, the SIMS analysis also shows characteristic fragments from the glass substrates such as Na\(^+\) (\(m/z = 23\)), Si\(^+\) (\(m/z = 28\)), K\(^+\) (\(m/z = 39\)), Ba\(^+\) (\(m/z = 137\)) and BaOH\(^+\) (\(m/z = 154\)). However the Side 1 spectra also show organic ion fragments containing epoxy ring (\(m/z = 43\) and 57) and bisphenol A (\(m/z = 135\)).
Other fragment ions present on this side include, SiOH$^+$ or CH$_2$CH$_2$OH$^+$ ($m/z = 45$) and aromatic ion series ($m/z = 77, 91$ and $115$). Source of the $m/z = 69$ and $71$ are not clear. However, a study by Van Ooij et al, states that these are only formed by under-cure epoxies following exposure to moisture and are, therefore considered to be fragments diagnostic of hydrolysis products. They are linear fragments of C$_4$H$_5$O$^+$ and C$_4$H$_7$O$^+$ respectively, which differ by one $-\text{C-C}-$ vs $-\text{C=C-}$ bond. The Side 2 surface however, closely resembles the bulk polymer, with little or no characteristic ion fragments of the inorganic glass substrate.

![Figure 9.7](image)

**Figure 9.7** ToF-SIMS analyses of LD dry fracture surfaces.

The ToF-SIMS spectra obtained from the HD dry fracture surfaces show identical patterns ion fragments originated from the adhesive (Figure 9.8). The typical ion fragments observed from the bulk adhesive are repeated in these two sides. The XPS spectra for these surfaces have also previously revealed similar results (see section 9.3.2).
Figure 9.8 ToF-SIMS analyses of HD dry fracture surfaces.

9.4 ANALYSIS OF WET FRACTURE OF DILUENT VARIANT FORMULATIONS

9.4.1 SEM Analysis of wet fracture joint surfaces of diluent variant adhesives

The diluent variant joint samples were fractured after an immersion time in water of 10 days. The SEM results on the fracture surfaces for LD formulation are given in Figure 9.9, 9.10. The results are interesting when compared to the micrographs obtained for the dry fracture.

During dry fracture analysis of the LD joint, it was confirmed that the fracture creates a polymer side, and a glass side with polymer residues. Here the wet fracture of the LD joint has created an apparent polymer side and a glass side with layer of polymer left on the surface. The apparent polymer side (Side 1) depicted in Figure 9.9 appears to have complex features on its surface. The micrograph shows non-uniformity, containing craters and valleys like features along the surface. The Side 2 (Figure 9.10) also has the similar features, but it was observed that a non-continuous layer of polymer was left on the surface.
The analysis at 25 μm field of view of Side 2 indicates the possibility of a thin residual layer is left right next the glass surface (Figure 9.10, (c)). However SEM alone cannot confirm these features without resorting to other surface sensitive techniques. It is also interesting to note that the localised peeling of polymer show larger peeled skin at the surface, while in the dry fracture peeling is small, regular shaped and uniformly distributed along the surface.

It is also possible that the water has a softening effect on the polymer to tear in larger sections. Finally it should be noted that standard optical microscopy is inapplicable due to the highly transparent nature of the reformulated adhesives.
Like the LD wet fracture surfaces, the SEM analysis of the HD wet fracture surfaces show no major difference in their morphology. The micrographs obtained for HD wet fractures are shown Figure 9.11. When the SEM was carried out on DF wet fracture surfaces, peeling features as in LD wet fracture on Side 1, and a non-uniform Side 2 were observed (Figure 9.12)

Figure 9.10 10 day water immersion LD diluent fracture surface – Side 2 (a) 1 mm, (b) 100 μm and (c) 25 μm SEM micrographs
Figure 9.11  SEM images of HD 10 days water immersion fracture surfaces, (a) Side 1, (b) Side 2

Figure 9.12  SEM images of DF 10 days water immersion fracture surfaces, (a) Side 1, (b) Side 2

9.4.2 XPS Analysis of wet fracture joint surfaces of diluent variant adhesives

The XPS spectra of the 10 days water immersion samples are shown in Figure 9.13. The spectra from Side 1 surface of the HD wet fracture indicate presence of silicon and higher surface concentration of oxygen (Table 9.2). The Side 2 has on the other hand shows higher concentration of carbon and sulphur.
The dry fracture of HD has earlier indicated identical fracture surfaces with thick polymer layer remaining on either side. It appears that the fracture interface has moved closed to the glass substrate as the joints were immersed into the water. The interfacial analysis by SIMS in the following section will further aid to identify the chemistry at these surfaces.

The XPS analysis of wet fracture surfaces of the LD joints closely resembles the dry fracture results. SEM micrographs of the Side 2 fracture surface, has also revealed that it contains peeling layers of polymers and large craters along its fracture surface, possibly leaving very little polymer left at localised areas on the substrate. This may have created a mixed fracture mode, after the prolonged exposure of water. On the other hand, XPS spectrum of the wet fracture show Side 1 with very strong silicon and oxygen concentration, and due to this higher concentration, the other half (Side 2) of the fracture also show presence of silicon.

The dry fracture of DF joints also produced 'glass' and 'polymer' side. This may be due to the mixed modes of failure of the joints and this Side 1 surface did also show peeling features during SEM analysis.

<table>
<thead>
<tr>
<th></th>
<th>Surface Composition / Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td><strong>DF</strong></td>
<td></td>
</tr>
<tr>
<td>Side 1</td>
<td>32.56</td>
</tr>
<tr>
<td>Side 2</td>
<td>68.81</td>
</tr>
<tr>
<td><strong>LD</strong></td>
<td></td>
</tr>
<tr>
<td>Side 1</td>
<td>76.19</td>
</tr>
<tr>
<td>Side 2</td>
<td>66.95</td>
</tr>
<tr>
<td><strong>HD</strong></td>
<td></td>
</tr>
<tr>
<td>Side 1</td>
<td>69.12</td>
</tr>
<tr>
<td>Side 2</td>
<td>76.45</td>
</tr>
</tbody>
</table>

**Table 9.2** XPS quantification of diluent variant wet fracture surfaces.
Figure 9.13  XPS spectra of diluent variant 10 days water immersion joint fracture surfaces.
9.4.3 ToF-SIMS Analysis of wet fracture joint surfaces of diluent variant adhesives

ToF-SIMS analysis carried on the DF 10 days water immersion fracture surfaces are shown in Figure 9.13. The fracture halves are almost identical to the fracture surface observed for the dry fracture. As in the dry fracture, one side of the fracture (Side 1), contains strong characteristic ion fragments from the glass substrate. Nevertheless both side are dominated by fragmentation pattern of the resin, with strong amine related peaks. Other difference from the dry fracture ‘glass’ side is the presence of Ba\(^+(m/z = 137)\) and BaOH\(^+(m/z = 154)\) in the wet fracture Side 1. This might be due to a thinner layer of polymer left on the surface in the wet fracture. This can be further confirmed by the comparison between the XPS results from the ‘glass’ sides of the dry and wet fracture. Although the XPS analyses are qualitatively similar, the C:O ratio in the dry fracture ‘glass’ side (40:41) is less than that in the corresponding 10 days water immersion ‘glass’ side (33:46). These results in fall inline with the observations made during the study of durability of F125 adhesive, where reduction of polymer layer thickness on the glass sides was observed in long-term water immersion.

Figure 9.13 ToF-SIMS analysis of DF 10 days water immersion joint fracture surfaces.
Chapter Nine
Durability Studies of the Reformulated Adhesives

The SIMS analysis of the LD wet fracture has also produced a Side 2 which has strong characteristic ions characteristic of the glass (Figure 9.14). However as in the wet fracture of DF resin joints, the apparent glass side also contains a series of fragments related to the components, which make this formulation. A relatively strong presence of a higher ion mass amine fragment on Side 1, \( C_7H_{16}N_3^+ \) \((m/z = 142)\), was also observed. By comparison this feature was not observed in the dry fracture of the joint, where the typically higher epoxy ion fragment, \( C_9H_{11}O^+ \) \((m/z = 135)\) dominated that cluster of ions in the spectrum. This leads to a hypothesis that amine migration may also occur during water immersion of the joints. However this cannot be confirmed without resort to quantification of ion fragments, which will be attempted in the following section.

![Figure 9.14 ToF-SIMS analysis of LD 10 days water immersion joint fracture surfaces.](image)

Also it is interesting to note that the C:O ratio as quantified by the XPS analysis for LD surfaces was, lower in the wet `glass` side (67:19) and higher for the dry `glass` side (51:32). This is an opposite trend to the analysis of the DF joints surfaces.
The SIMS analysis of the HD wet fracture surfaces has shown identical ion fragments in their respective two halves (Figure 9.14). This is also very similar to the spectra obtained for the HD dry fracture surfaces. Side 1 and 2 do not show any characteristic ion fragment related to the substrate, and contains series ions from the bulk polymer. This result also confirms that both the dry and wet fractures are through the bulk of the adhesive. However, one of the surfaces (Side 1) from the wet fracture has showed a marginally higher C:O ratio (69:21) than both halves dry fracture surface (77:16). From these results it can be said that the effect of water on the locus of failure is less in HD joints than the joints made from the other two diluent variant formulations. Although SIMS analysis from both dry and wet fracture surfaces show characteristic ion fragments of the adhesive, the dominance of amine related fragments seen in the wet fracture of LD and DF joints has not observed in the HD wet surfaces.

**Figure 9.15** ToF-SIMS analysis of HD 10 days water immersion joint fracture surfaces.
9.4.4 Comparison of SIMS results from all the fracture surfaces of the diluent variant reformulated resins

The comparison of the entire SIMS spectra from several materials in a matrix experiment such as this, is very time consuming and difficult. Similar to the method explained in Chapter 6 (§ 6.5.5), it is intended here to select the characteristic ion fragments from the four constituents of the reformulated resins, and compare their relative intensities.

The selected ion fragments for this study are given below in Table 9.3. It is however very difficult to select a fragment uniquely originated from the diluent. Although C₅H₁₀O⁺ (m/z = 86) was found to be dominant of the analysis of the spun cast film, this ion can also be generated by the DGEBA molecule. However this ion fragment is included in this study to identify the presence of diluent on the surface.

An ion fragment from the substrate materials such as Na⁺ was not selected for this study. Since the graphs are plotted as percentages, the very high presence of sodium ions in some analysis will give a false impression of very lower organic presence in those surfaces, and the smaller values for the organic ion fragment are very difficult to present in a graphical form. Besides without resorting to this methodology, very high intensity ion fragments from the substrate material can be easily compared from the spectra of the fracture halves. The comparisons of SIMS analysis from the diluent variant joint fracture surfaces are given in Figure 9.16.

<table>
<thead>
<tr>
<th>Source</th>
<th>Ion Fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>61/Mercaptan</td>
<td>+CH₂-CH₂-SH</td>
</tr>
<tr>
<td>70/Amine</td>
<td>C₄H₉N⁺</td>
</tr>
<tr>
<td>77/Unsaturated Hydrocarbon</td>
<td></td>
</tr>
<tr>
<td>86/Diluent</td>
<td>+C₅H₁₀O</td>
</tr>
<tr>
<td>135/Bis Phenol A</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.3 Selected ion fragments for surface study of reformulated joint fractures.
Figure 9.16 Comparison of selected ion fragment intensities from ToF-SIMS analysis for the Diluent variant formulations.

The initial observation from Figure 9.16 shows the HD polymer surfaces to have very similar proportion of ion fragments in both dry and wet fractures. However, a small increase in the proportion of amine intensity can be observed at the Side 1 wet fracture. This result is very much reinforcing the conclusions of the XPS examination of this class of joints, where Side 2 was identified as a 'glass' side of the interfacial fracture.
Also no sodium or any other ions relating to the substrate material was observed in the SIMS or XPS analysis. On the other hand the DF and LD fracture surfaces show some variation in their relative percentages of the ion fragments.

DF dry and wet fracture Side 1 surfaces have already been identified by XPS as 'glass' surfaces and SIMS analysis has also shown a very intense signal for the sodium ion. It is interesting to note the relative percentages of $m/z = 70$ (amine) and $m/z = 61$ (mercaptan) in both halves of the joint. What is considered to be 'glass' side (Side 1) show higher values for $m/z = 70$ with the reduction of intensity for $m/z = 61$. On Side 2, the reverse is true for both dry and wet fracture surfaces. This observation can be attributed to amine migration to the fracture interfaces.

Also on wet fracture Side 1 increased intensity of the $m/z = 77$ (aromatic hydrocarbon) also observed. However the reasons behind this are not clear. The ratio of ion fragment intensities in the LD fracture surfaces show a complex and hard to explain distribution. Although XPS identifies the dry fracture Side 1 and wet fracture Side 2 as 'glass' sides, the SIMS however did suggest a possible mixed mode of failure of the joints. Here, the ion fragment comparison also suggests a non-uniform mixed mode of joint failures.

9.5 ANALYSIS OF DRY FRACTURE OF AMINE VARIANT FORMULATIONS

9.5.1 SEM Analysis of dry fracture joint surfaces of amine variant adhesives

SEM micrographs from the analysis of the dry fracture surfaces of SF joints are shown Figure 9.17. The Side 1 surface show voids along its surface possibly created by the bubbles in the mix. The very fast curing of this resin may have promoted entrapping of more bubbles during cure.
As explained earlier in the bulk analysis of SF adhesive (see Chapter 8 for details), the extremely brittle behaviour of the material was also observed on the fracture surface. The joint fracture was violent with no clear fracture mode and surface was found to be covered with broken pieces and powder of the cured adhesive. The Side 2 of the fracture has matching small peak like features to the holes observed in the Side 1.

**Figure 9.17** SEM micrographs of the dry fracture surfaces from SF formulation.
The LA fracture has however created different type of surfaces. The Side 1 surface (Figure 9.18 (a) and (b)) show lots of tearing and surface splitting like features. Figure 9.18 (c) also confirms a show some signs of surface shrinkage effects.

Since the SEM analysis is the last in the order of surface analysis, possible damage caused by the XPS and SIMS analysis or the UHV environment may have also contributed to these features. This is further aided by the very low glass transition temperature and the higher flexibility of the adhesive. Similar features were also monitored in the Side 2 analysis and the micrographs are thus not produced in this section.

Figure 9.18 SEM micrographs of Side 1 of the LA dry fracture (a) 500 µm view (b) 50 µm view (c) 10 µm view along the tear line.

The HA dry fracture surfaces shown in Figure 9.19, resemble the features observed from the dry fracture of LD, DF and SF resin joints. The voids in Side 1 and the corresponding fragment of polymer on Side 2 can be clearly observed from the SEM micrographs. HA resin also has a faster cure time, and thus may have contributed to entrapping more bubble related voids.
Figure 9.19 SEM micrographs of Side 1 and Side 2 of the HA dry fracture.

9.5.2 XPS analysis of dry joint fracture surfaces of amine variant adhesives

The XPS a spectrum of the SF (100% amine cure resin) Side 1 has higher surface concentration of oxygen and also show presence of silicon (Figure 9.20). On the contrary the Side 2 has no silicon and have higher carbon concentration. This type of near interfacial failures has also been observed, in the fracture faces of the HA joint. As observed in diluent variant adhesives, features related to 'pulled' polymer residues were also observed on the corresponding SEM analysis of the apparent 'glass' sides. The SEM of the 'polymer' sides similarly have showed matching craters like features.
Figure 9.20  XPS spectra of the dry fracture surfaces from amine variant adhesive formulations.
The two fracture surfaces from the lower amine (LA) joint however show very similar spectra. This is an indication the fracture path of the soft LA adhesive joint have gone through the bulk of the polymer. The concentrations of elements at the fracture surfaces are given in Table 9.4. Due to an instrument malfunction Side 2 of the SF dry fracture Side 2 surface was not analysed by the monochromatic source.

<table>
<thead>
<tr>
<th></th>
<th>SF</th>
<th>LA</th>
<th>HA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Side 1</td>
<td>Side 1</td>
<td>Side 1</td>
</tr>
<tr>
<td></td>
<td>Side 2</td>
<td>Side 2</td>
<td>Side 2</td>
</tr>
<tr>
<td>C</td>
<td>78.12</td>
<td>77.93</td>
<td>70.82</td>
</tr>
<tr>
<td>O</td>
<td>12.66</td>
<td>14.20</td>
<td>15.80</td>
</tr>
<tr>
<td>N</td>
<td>9.21</td>
<td>4.50</td>
<td>12.01</td>
</tr>
<tr>
<td>Si</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S</td>
<td>---</td>
<td>3.36</td>
<td>1.27</td>
</tr>
</tbody>
</table>

**Table 9.4** XPS quantification of amine variant dry fracture surfaces.

9.5.3 **ToF-SIMS Analysis of dry fracture joint surfaces of amine variant adhesives**

The examination of the SIMS spectra shown in Figure 9.21 for the SF dry fracture, have shown very similar characteristics ions on both halves of the joint. However as seen in many other dry fracture analysis the Side 2 which is considered to be the ‘glass’ side as analysed by the XPS, shows higher intensities for Na⁺ ion fragments. As expected the analysis SF dry fracture surfaces show dominant ion fragments from the amine, which is the only curing agent for this formulation.
Figure 9.21  ToF-SIMS analysis of SF Dry joint fracture surfaces.

The SIMS analyses from the LA dry fracture surfaces are also shown in Figure 9.22. These results show absolutely no difference at all from the two surfaces, and this result correspond to the XPS investigation explained in the previous section. The lower amine content of the adhesive is also evident with reduced intensities of the amine related peaks, in comparison with SF surfaces.

Figure 9.22  ToF-SIMS analysis of LA Dry joint fracture surfaces.
Analysis from the 30% amine formulation also shows no significant variations between the two fracture halves, except a Na\(^+\) ion on Side 2 (Figure 9.23). It is interesting to note that there are no major differences in the qualitative SIMS analysis between all the amine formulations, but as expected, intensities of the amine related ion fragments were found to be varied according to their formulation stoichiometry.

![Figure 9.23](image-url)  
**Figure 9.23** ToF-SIMS analysis of HA Dry joint fracture surfaces.

### 9.6 ANALYSIS OF WET FRACTURE (10 DAYS WATER IMMERSION) OF AMINE VARIANT FORMULATIONS

#### 9.6.1 SEM Analysis of wet fracture joint surfaces of amine variant adhesives

The HA fracture surfaces shown in Figure 9.24, indicates the features observed in many other reformulated resins, such as craters and peeleing marks. A larger hole can also be observed in the Side 1. The cause for this feature is similar to the one earlier explained in the dry fractures, and is possibly from a void formed by the bubble inclusion.
Figure 9.24  SEM micrographs of the HA wet fracture surfaces.

The SEM results obtained for the LA wet fracture sample has showed cracks and wrinkle marks on the surfaces (Figure 9.25). These features have also been observed in the dry fracture, and the effects of water are not clear from this analysis.

Figure 9.25  SEM micrographs of the LA wet fracture surfaces.

The SF wet fracture Side 1 shown in Figure 9.26, interestingly indicates features of brittle fracture. These types of features were observed in both halves of the joint. As explained earlier in chapter 4, the resin is very brittle and almost becomes powder with a strong applied pressure with the thumb.
Chapter Nine  
Durability Studies of the Reformulated Adhesives

Also, the SF dry fracture earlier showed a fracture closer to the interface, but on the contrary the wet fracture seems to be fracturing through the bulk resin.

![SEM micrographs of the SF wet fracture surfaces.](image)

**Figure 9.26** SEM micrographs of the SF wet fracture surfaces.

9.6.2 **XPS Analysis of wet fracture joint surfaces of amine variant adhesives**

The XPS wet fracture analysis for LA and SF formulations show no significant changes in the analysis between the two fracture halves (Figure 9.27). The spectra from the LA surfaces also are very similar its dry fracture analysis. However the SF wet fracture results are different from the dry fracture analysis. Earlier the dry fracture was identified as a near interfacial failure, but here in the wet fracture, the failure seems to be through the bulk polymer as XPS analysis show identical spectra relating to the bulk resin. The role of water in this no quite clear, but this observation is suspected to have induced by the unpredictable behaviour of the cured SF resin.

The initial observation of the spectra for the HA resin indicated that the fracture behaviour was very similar to its dry fracture. However the quantification of the surface elements from the wet fracture Side 2 indicates presence of higher concentration of silicon (13.2%) and oxygen (38.6%) than the dry fracture (see Table 9.5). This may also indicate that the wet HA fracture have a closer interfacial fracture than the dry failure. This observation is also very similar to the findings from the commercial F125 adhesive.
**Figure 9.27** XPS spectra of the wet fracture surfaces from amine variant adhesive formulations.
Chapter Nine
Durability Studies of the Reformulated Adhesives

<table>
<thead>
<tr>
<th>Surface Composition / Atomic %</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF Side 1</td>
<td>78.72</td>
<td>13.01</td>
<td>8.26</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>SF Side 2</td>
<td>78.24</td>
<td>12.99</td>
<td>8.77</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LA Side 1</td>
<td>74.86</td>
<td>17.04</td>
<td>4.86</td>
<td>---</td>
<td>3.24</td>
</tr>
<tr>
<td>LA Side 2</td>
<td>75.66</td>
<td>16.67</td>
<td>3.89</td>
<td>---</td>
<td>3.78</td>
</tr>
<tr>
<td>HA Side 1</td>
<td>76.86</td>
<td>15.34</td>
<td>5.84</td>
<td>---</td>
<td>1.95</td>
</tr>
<tr>
<td>HA Side 2</td>
<td>43.28</td>
<td>38.64</td>
<td>4.83</td>
<td>13.25</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 9.5 XPS quantification of amine variant wet fracture surfaces.

9.6.3 ToF-SIMS Analysis of wet fracture joint surfaces of amine variant adhesives

ToF-SIMS analysis for the SF wet fracture is shown in Figure 9.28. The spectra from both halves clearly dominated by the series of ion fragments originated from the amine-curing agent.

Figure 9.28 ToF-SIMS analysis of SF Wet joint fracture surfaces
The high intensity of the amine peaks at \( m/z = 56 \) and \( m/z = 125 \) are clearly evident with their relative peak height to the adjacent epoxy fragment such as \( m/z = 57 \) and \( m/z = 135 \). Also, this feature appears to be higher than what was observed in the dry fracture. These features will be further examined in a later section with the comparison of the peak intensities between resins.

The LA wet fracture analysis, shown in Figure 9.29 represents two identical fracture halves of the joint. Theses results also correspond to the XPS and SEM of the fracture, where no significant variations between the two fracture halves were found. As expected the dominance of amine related species observed in the other amine variant fracture is very much reduced in these surfaces. Also the spectra are similar to the dry fracture analysis. However a higher intensity of the peak at \( m/z = 86 \) (C\(_5\)H\(_{10}\)O\(^+\)) is observed only in the spectra from both halves of the wet fracture. The peak at \( m/z = 86 \) was earlier identified as a dominant ion fragment from the spun cast analysis of the diluent. Another ion fragment \( m/z = 133 \), also shows a slightly increased intensity in the wet fracture spectra and a strong presence of this fragment was also earlier identified as characteristic to the diluent (see Chapter 4).

**Figure 9.29** ToF-SIMS analysis of LA Wet joint fracture surfaces.
The SIMS spectra shown for the two wet fracture halves of the HA resin (Figure 9.30), clearly corresponds to the results obtained by XPS. The XPS analysis has indicated an interfacial failure with higher oxygen and silicon concentration in Side 2. Similarly the SIMS spectrum for the Side 2 shows higher intensity ion fragments of Na⁺ and Si⁺. Regardless of this difference, the rest of the spectrum shows no significant variation from Side 1.

These results fall in line with most of the fracture analysis from the commercial and the reformulated resins, where a near interfacial failure in water immersion sample with a thin layer of polymer left on one half was observed. However in order to verify the role of different components in the formulations, comparison between the intensities of characteristic ion fragments are important, and thus will be discussed in the following section of this chapter.

**Figure 9.30** ToF-SIMS analysis of HA Wet joint fracture surfaces.
9.6.4 Comparison of SIMS results from all the fracture surfaces of the Amine variant reformulated resins

The manner of comparison of ion fragments is the same as the method used for the diluent variant adhesives. The plot shown in Figure 9.31, does not show any significant variation in dry and wet fracture analysis of the SF resin joints. Although the SIMS identified one side each in dry and wet fracture with Na⁺, the organic fragments shown here are almost at equal ratios. Random fracture of this formulation as observed in other examinations can be attributed to this observation.

*Figure 9.31* Comparison of selected ion fragment intensities from ToF-SIMS analysis for the Amine variant formulations.
The LA polymer fracture surfaces show some variations in the comparison. Although it appears that the ion fragment assigned to diluent seems to be increasing in the wet joint fracture, the reasons behind this feature are not very clear. The surfaces formed by the fracture of LA joints are uniquely different from all the other reformulated adhesives, by having surfaces cracking and possible shrinking related features. Possible diluent segregation can be attributed to this observation, but the results are inconclusive to confirm this.

Strongest of amine variant adhesives, the HA resin, also at first observation shows no variation between ion fragment ratios. However, the ratio between selected amine and mercaptan fragment on the ‘glass’ sides (Side 2) of the fracture seems to be changing, as observed earlier in the DF analysis (see section 9.44). This feature may also be attributed to amine segregation at the interface.

Finally, the thickness of the polymer overlayer remaining on the glass substrate was calculated based on the methodology explained in Chapter 6 (§ 6.7). These results are shown in Figure 9.32. The results are obtained by the attenuated substrate approach (i.e. with reference to samples with Si2p signals).

![Figure 9.32](image)

**Figure 9.32** Polymer overlayer thickness on the glass side of the fracture surfaces and average joint fracture strengths
Chapter Nine
Durability Studies of the Reformulated Adhesives

The polymer overlayer left on the DF samples does not change significantly in the 10 day fracture samples. Although the fractures of both wet and dry fracture of LD samples indicate near interfacial failure, an increase in polymer thickness for the water immersion sample can be observed. As time progress a reduction in polymer left on the fracture surface is expected as earlier observed in the experiments of the commercial F125 adhesive. However series of long-term durability test are required to establish a clear trend in failures towards near interfacial failure with increased time of exposure to water. Besides localised variations in the thickness could also give variations in this result. The HD polymer clearly shows a cohesive failure during dry fracture and a near interfacial fracture with 10 days water immersion.

The SF resin shows a complete opposite modes of failure with interfacial failure during dry fracture and cohesive failure at prolonged water immersion. However it has already been shown that this particular reformulation is extremely brittle and lower load to failure values. This could have produced this random failure mode. The LA formulation produced cohesive failure in both dry and wet fracture, and near interfacial failures were observed in wet and dry fracture of the HA formulation.

9.7 SUMMARY

The reformulation work explained in the last two chapters clearly indicates different types of failure mechanism for the various formulations of the adhesives. A summary of results obtained for the reformulated resins is tabulated with regards to their strength, failure mechanisms (Table 9.6). A crude rating method based on the load to failure plot of Figure 9.1 is used for comparing strength of the joints between formulations. Also a summary containing the evidences collected from the ToF-SIMS analysis for any segregation of adhesive components towards the surface shown in Table 9.7. By analysing all the results so far, although there is no definite proof of segregation on all the reformulations, although there is some evidence suggests amine and diluents migration in certain formulations (see Table 9.7).
Chapter Nine  
Durability Studies of the Reformulated Adhesives

The effects of this on the joint durability are not very clear. However, combining all the analytical work on the reformulated adhesive, a better resin system can be proposed based on their durability and strength.

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Strength</th>
<th>Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tra-Con F125</td>
<td>⚫⚫⚫⚫⚫</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Dry DF</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Dry LD</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Dry HD</td>
<td>●●●●●</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Wet Tra-Con F125</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Wet DF</td>
<td>○●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Wet LD</td>
<td>○●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Wet HD</td>
<td>○●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Dry SF</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Dry LA</td>
<td>●●●●●</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Dry HA</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
<tr>
<td>Wet SF</td>
<td>○●●●●</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Wet LA</td>
<td>○●●●●</td>
<td>Cohesive</td>
</tr>
<tr>
<td>Wet HA</td>
<td>●●●●●</td>
<td>Interfacial</td>
</tr>
</tbody>
</table>

Table 9.6  Summary from test results of the reformulated adhesives

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Evidence of segregation towards surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amine</td>
</tr>
<tr>
<td>Diluent Free (DF)</td>
<td>✓</td>
</tr>
<tr>
<td>10% Diluent (LD)</td>
<td>✓</td>
</tr>
<tr>
<td>30% Diluent (HD)</td>
<td>✓</td>
</tr>
<tr>
<td>Sulphide Free (SF)</td>
<td>---</td>
</tr>
<tr>
<td>10% Amine (LA)</td>
<td>---</td>
</tr>
<tr>
<td>30% Amine (HA)</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 9.7  Evidence of segregation of adhesive components with joint exposure to water - a summary of ToF-SIMS data.
CHAPTER TEN

ADHESION OF EPOXY ADHESIVES TO AN OPTICAL GLASS

10.1 INTRODUCTION

The previous six chapters have documented the work carried out during the course of this study, in an effort to gain an insight into the failure mechanisms and durability of joints fabricated from a high reliability optical adhesive. The progressive experimentation with various methods to understand the commercial resin system, which was explained in the early part of the thesis, is considered to be an important preliminary stage of the work. This work is important to the electronic industry where fast curing mercaptan resins are often employed for bonding optical components. In this work, this understanding of the commercial resin led to the development of reformulated adhesives based on the primary components of the system, and this work has been described in the later part of the thesis. This chapter is presented as a discussion of the experimental work described within Chapters 4, 5, 6, 7, 8 and 9, based on a discussion of long and short term durability and failure mechanisms.

10.2 STUDY OF COMMERCIAL F125 RESIN

Initial studies were primarily aimed at understanding the chemistry and properties of the commercial adhesive. This was achieved by a paper study on the properties of the cured adhesive and the individual components, which form the commercial resin system.
Chapter Ten:
Adhesion of Epoxy Based Adhesives to An Optical Glass

This has revealed considerable information on the general chemistry related to the structure and the cure network. Based on this investigation, the chemistry of four primary adhesive components was analysed using XPS and SIMS. The surface analysis using high-resolution XPS was able to identify the nature of C 1s spectra of the individual adhesive components. Peak fitting of the C 1s spectra was successfully carried out, to understand and evaluate the nature of the cured adhesive. In addition to the XPS study, ToF-SIMS analysis of the spun cast adhesive components revealed very important informations regarding the fragmentation patterns of the chemicals. This study was critical, as it would later aid the characterisation of the interfacial chemistry of the fractured adhesive joints.

Then the experimental investigation was shifted towards the study of the cured adhesive system. Thin adhesive foils have been obtained for the analysis using a novel microtoming method. Clean strips of the cured adhesive were again analysed using XPS and ToF-SIMS. Peak fitting of the high-resolution XPS of C 1s revealed some characteristic peak assignments, although not matching all the assignments observed for the individual adhesive components, this was found to be too difficult to achieve with a high degree of confidence. This was because the number of peak assignments expected from the individual component analysis is too many, and very difficult to fit into the analysis of the cured resin. However the results were satisfactory with six characteristic peak assignments were attributed to the high-resolution C 1s spectra.

The ToF-SIMS analysis of the cured adhesive revealed a combination of the ion fragments expected from the knowledge obtained from the earlier analysis of the individual components. Finally bulk analyses of the cured adhesive were carried out using DSC and DMA. Results have revealed the glass transition temperature, $T_g$, of 41° C for the cured adhesive.
As part of the characterisation of the materials, a paper study of the production process of the substrate material was carried out. Then the substrate materials were obtained without any chemical cleaning or optical coating, as this was often the case for optical terminations. Analyses of the substrate, cleaned with a cleaning regime with acetone and isopropanol has revealed substantial reduction in the adventitious carbon observed in the XPS of the as received material. Therefore this method of substrate cleaning was followed through this work for the purpose of joint manufacture.

Apart from identifying a cleaning regime, XPS was also employed to examine the nature of the glass substrate. A strong O 1s signal from the oxides, which form the glass, and several inorganic species were identified. As expected the SIMS analysis was also confirmed the presence of characteristic inorganic ion fragments, which make the borosilicate glass substrate. A comparative study to evaluate the polishing methods was also carried out using SEM. This has shown a fine polished surface similar to that observed for typical optical components. After this study of both adhesive and substrate materials the work was then concentrated into understanding the fracture behaviour of the dry adhesive joints.

Analysis of the dry fracture surfaces by SEM has clearly indicated a typical conchoidal type fracture of the joints. Initial observations have shown an initiation of the fracture at a defect at the shiny mirror zone. In addition to the mirror zone, a large hackle zone and an intermediate mist zone were observed. The XPS has identified the locus of failure at the mirror zone as near interfacial, and then the rest of the fracture to be more towards the bulk of the adhesive. The SIMS analysis of the surface also supported this observation and reduction in the peak intensities for the characteristic glass ion fragments such as Na\(^+\) and Si\(^+\) were observed with increased distance away from the mirror zone. Followed by the dry fracture analysis on the durability of the joints to exposure to water was extensively studied.
Chapter Ten:
Adhesion of Epoxy Based Adhesives to An Optical Glass

The tensile tests used to evaluate the joint strengths and durability indicated up to 80% reduction in the strength when immersed in water for 10 days. Prolonged exposure to water revealed that the joint strengths had reached a lowest value after few days and there onwards no significant change was observed. The optical microscopic assessment of the fracture surfaces also showed that the joints were failing in a visually mixed mode manner when left in water for 10 days and the prolonged exposure to water has shown visually ‘adhesive’ failures. The XPS analysis of the 10 days sample confirmed the visually adhesive areas to be near interfacial with thin layer of polymer left on the surface.

Specimens exposed to prolonged 120 days exposure to water, were also analysed using XPS. Here the locus confirmed to be near interfacial throughout the fracture surface. Also the thin adhesive layer left on the surface, was readily peeled from the substrate, and this has shown a change in locus of failure with a thicker overlayer of polymer on the apparently “glass” surface.

Although the initial observation of the 120 days joint sample was identified to have failed in a near interfacial manner, localised variation in the surface was also observed. When compared these results with visual observations by optical microscope, it was found that failure was closed to glass substrate near the edge of the sample. SIMS analysis on the same localised areas revealed an amine rich regions near the sample edges. Similar observations were not observed in the peeled side of the same sample. Since the peeling was not simultaneously carried out with the tensile fracture, this result has been confirmed a relationship between amine segregation and weakening of the joints. In order to analyse this phenomenon further, angle dependent XPS analyses were also carried out on several short and long-term water exposed joint fracture surfaces.

Locus of failure close to the interface has been well documented from the results obtained for 10, 35 and 240 days water immersion samples. The conventional montage plots made from changing the electron take-off angles clearly identified the near surface nature of these failures.
In addition to this approach, a depth profiling modelling based on a software programme (ARCtick), also been carried out. The resulting model plots, have shown presence of nitrogen originated from the amine curing agent, close to the interfacial failure surface. Amine segregation at the interfaces is suspected to be the only cause for this observation. After this study, calculation of the polymer overlayer thickness of the interfacial failure surfaces, based on the Beer-Lambert expression was carried out. These results have shown a relationship between the reduction of bond strength with a concomitant reduction in polymer overlayer thickness. However the results from the joints exposed to prolonged water immersion, have shown no significant change in the amount of polymer left on the surface. This correlates well with the very low fracture strength values of the joints of prolonged water exposure. It can be argued that when joints have lost almost all of its residual bond strength, the loci of failure are identical and no significant changes can be observed. Schematic of the locus of failure for dry and wet fracture surfaces are shown in Figure 10.1.

Figure 10.1 Schematic of Fracture surfaces of the Commercial Tra-Con F125.
Finally on the study of the commercial resins, the effect of different fracture methods on the locus of failure has also been analysed by means of XPS. These results have indicated that when fractures are carried out on joints exposed for 20 days to water, in-situ fracture is more likely to have an interfacial failure with a presence of a thicker organic layer. Near interfacial failures with thin overlayer of polymer was observed in the ex-situ fracture modes, such as tensile and T-peel fracture stage failures. Also, it was found that the T-peel stage of the XPS spectrometer had provided identical failure modes to the tensile fracture of the joints.

After this comprehensive study on the durability of the commercial F125 resin, it was intended that the next stage of this work should relate to the role of individual component in the adhesive formulation. This was realised in an extensive work on the chemistry and reformulation of the commercial Tra-Con F125 adhesive, and discussion of this work follows in the next section.

### 10.3 THE STUDY OF REFORMULATED ADHESIVES

After a careful study into the components of the commercial adhesives, the four primary components which make the formulations has been selected based on various physical and chemical properties such as viscosity, epoxy equivalent weight, molecular weight etc. This study is used to make the right choice of materials, which would give an ease of mixing and ideal stoichiometries. The epoxy resin, reactive diluent, polysulphide curing agent and an amine catalytic curing agent has been selected from various manufacturer for the purpose of reformulating commercial adhesive.

Six adhesives were formulated and initially the thermal and surface analyses of the resins were carried out. It has shown clearly a change in the physical properties of the resins with the change in composition of the adhesive components. It has shown the highest glass transition temperature to be for the sulphide free formulation but the material was too brittle and has little use as a structural adhesive. Then the 10% amine formulation found to be having lower transition temperature, and identified as a very flexible adhesive at ambient temperature.
Abbreviations used for the reformulated resins as shown earlier in Chapter 9, are given again below in Table 10.1.

<table>
<thead>
<tr>
<th>Adhesive Type</th>
<th>Generic Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% diluent formulation</td>
<td>Diluent Variants</td>
<td>DF (Diluent Free)</td>
</tr>
<tr>
<td>10% diluent formulation</td>
<td></td>
<td>LD (Lower Diluent)</td>
</tr>
<tr>
<td>30% diluent formulation</td>
<td></td>
<td>HD (Higher Diluent)</td>
</tr>
<tr>
<td>100% amine formulation</td>
<td>Amine Variants</td>
<td>SF (Sulphide Free)</td>
</tr>
<tr>
<td>10% amine formulation</td>
<td></td>
<td>LA (Lower Amine)</td>
</tr>
<tr>
<td>30% amine formulation</td>
<td></td>
<td>HA (Higher Amine)</td>
</tr>
</tbody>
</table>

Table 10.1 Abbreviation and group naming of the re-formulations

Apart from these two formulations the rest of the adhesives, including the commercial F125 have their \( T_g \) values lie between 40 and 50°C. Surface analyses of the cured resin formulations were also carried out by XPS and SIMS, and then butt-joints were fabricated to study the durability of the adhesives.

The durability of the adhesives was initially assessed by comparison of failure load in the dry and after 10 days water immersion. Apart from SF and LA formulations the rest have no variations both at dry and wet fracture. This was due to extremely brittle (SF) and very flexible (LA) nature of the joints. By generalising the results it can be said that none of the reformulated adhesive have superior strength values to the commercial adhesive. However when the joints were tested for their strength after water immersion there was no significant change observed. Therefore this initial study has indicated that the reformulation work is not going to produce an adhesive with superior bond strength to that of the commercial resin. This was not, however, the aim of this part of the work. This work was continued with extensive analysis of the fracture surfaces to determine the locus of failure, and to understand the role minor components in the formulations.
Chapter Ten:
Adhesion of Epoxy Based Adhesives to An Optical Glass

The XPS analysis of the dry fracture of the diluent variant formulations has shown cohesive failure for only to the HD formulation. The other two diluent variant resins (DF and LD) fractured near interfacially at dry condition. The resins are expected to fail cohesively during dry fracture, and this result was little surprising at first instance. The XPS analysis was generally carried out at the centre of the fracture surfaces. It was thought that a larger mirror zone was extending to the middle of the surface possibly due to a low strain fracture. This could have resulted in spectra the characterising the locus of failure as interfacial, as observed earlier in the dry fracture of the commercial resin.

However the SEM analysis of the fracture faces of DF and LD polymers did not show any such features. Instead the SEM images of the interfacial surfaces indicated polymer fragments to be left all along the surface regions. Although there are no variations in the joint strength for DF and LD resins, the results indicate that the joints made from this resin are very susceptible to any form of environmental attack.

Further XPS analysis from the wet fracture surfaces (10 days water immersion) has identified near interfacial failure for all three diluent variant adhesive. A thin overlayer of polymer on the interfacial fracture surface was observed for the DF fracture sample, indicating the change from cohesive failure during dry fracture. This type of comparison cannot be made to the DF and LD adhesive as both dry and wet fracture from these resins showed interfacial failure. However a reduction in polymer thickness on the interfacial side was anticipated, but on the contrary an increase was observed. This can be attributed to localised variations in the surface thickness.

Finally the ToF-SIMS analysis of the wet fracture interfacial sides of the all three diluent variant joints have shown increased presence of ion fragments attributed to amine, when compared to the corresponding ‘polymer’ side. Also the comparison of the interfacial surfaces of dry and wet fractures of the DF and LD polymers clearly showed an increase in the intensities of amine at the interface. This observation was attributed to the amine segregation at the interface at prolonged exposure to water.
Although small, amine segregation at the fracture interface of the HD resins was also observed. However, this type of migration behaviour was not observed for the diluent, which is also a minor component in this formulation. This is possibly because the diluent used is a reactive compound, which would cure to form part of the cross linked network. The amine, on the other hand, will take part in the cured network, and the excessive amine can migrate to the interface. Also, all the adhesive systems analysed here do not, primarily, depend on amine cure, instead mercaptan was used. Although the amine takes part in the cure reaction, it was primarily used here as a catalyst.

It may be difficult to visualise all the different failure mechanisms of the reformulated adhesives. Therefore schematic of the locus of failure for the dry wet fractures of diluent variant formulations are illustrated in Figure 10.2.

During the dry fracture of the amine variant adhesives, the SF and HA resins has been identified as having interfacial failures. But, the wet fracture of the SF failed cohesively, and the HA resin failed interfacially with reduce polymer layer left on the surface. The LA resin joint failed cohesively at wet and dry conditions.

The failure characteristics of the HA (30% amine) adhesive is similar to the observations from the commercial adhesives where reduction of bond strength and near interfacial joint failures in prolonged exposure to water was observed. However interfacial failure of these joints at dry fracture may be an indication of weaker joint. The SEM images of the interfacial dry fracture surface showed clusters of polymer fragments attached to the surfaces. This feature was also observed on the interfacial fracture side of the 10 days water immersion sample. This shows that it is a possibility that regions of surfaces have stronger adhesion levels than the other areas. This may due to segregation of certain adhesive components, which promote adhesion. This view is supported by the ToF-SIMS results, which clearly indicated a higher presence of amine and diluent in both dry and wet fracture interfacial surfaces.
Figure 10.2 Schematic of Fracture surfaces of the Diluent Variant Formulations
The SEM of SF (100% amine) dry fracture interfacial side has indicated a similar feature to the HA analysis. Dominance of these features can be attributed to the interfacial failure during dry fracture. However features relating to the brittle fracture were also noticed in the SEM analysis. This is an indication that a mixed failure mode is acting on this fracture. The reason behind the cohesive failure for the wet fracture of SF joints was initially thought to be due to the politicisation effects of the water on the bulk polymer. However the SEM examination of the surfaces clearly revealed a random brittle failure surface. The localised clusters observed in the dry fracture were not observed in this failure mode. SIMS analysis of the interfacial side of the dry fracture showed marginal increase in the amine and diluent related ion fragments, but on the cohesive wet fracture surfaces, the relationship was not clearly evident.

One should recall that this SF formulation is that it has very little strength as an adhesive on both at dry and wet conditions and this was indicated by the tensile tests of the joints. The surface analysis of the fracture surfaces also shows that although the formulation is not strong, the effect water is minimal at least for the 10 days water immersion.

Finally the cohesive failure mode of the LA (10% amine) adhesive formulation in both at dry wet fractures can be related to its physical properties. The adhesive is very flexible low glass transition temperature polymer, and low load to failure values are already recorded during tensile test of the joints.

The SEM micrographs have also shown thick polymer layer presence in dry and wet fracture surfaces. XPS analysis has further confirmed this observation, and no significant variations between wet and dry fracture surfaces were monitored. The amine segregation was not clear from the SIMS results, but higher intensity diluent fragments on both halves of the wet fracture, was evident when compared with the dry fracture surface analyses. The significant of this increased intensity in the wet fracture on the locus of is not clear, but may have some role in the reduction of bond strength of the wet joints. Summary of locus of failure for all amine variant adhesives are shown in Figure 10.3.
Chapter Ten: Adhesion of Epoxy Based Adhesives to An Optical Glass

Figure 10.3 Schematic of Fracture Surfaces of the Amine Variant Formulations.
CHAPTER ELEVEN

CONCLUSIONS

11.1 INTRODUCTION

A detailed investigation into the durability of a commercial adhesive has been carried out. The investigations were extended into reformulation of the commercial adhesives, and the role of adhesive components and durability were evaluated. The loci of failure and the failure modes of the F125 commercial adhesive have been identified by XPS, ToF-SIMS and SEM. Initially migration of minor components in the commercial adhesive was identified. This was later extended to the study of reformulated resins to identify segregation of minor components, in detail. In this Chapter the conclusions derived from these works will be summarised.

11.2 THE COMMERCIAL TRA-CON™ F125 ADHESIVE

Initial study on the substrate preparation has shown that better cleanliness can be achieved by using a simple ultrasonic cleaning regime with a series of solvents. The dry fracture of the joints made with the commercial adhesive indicated conchoidal fracture with a small mirror zone. The surface analysis of various regions of the surface, has confirmed that the fracture is close to the substrate (near-interfacial) in the mirror zone, and then moving through the bulk of the adhesive layer. The effect of water on the locus of failure has also been established by the analysis of the fracture surfaces of joints immersed in water. The locus of failure for joints at 10 days of water immersion are predominantly near interfacial, but prolonged exposure to water for over 100 days results in near interfacial failure through the entire joint, with a thin polymer overlayer of about 2 nm left on the interface.
Chapter Eleven:
Conclusions

While this work has established the reduction of polymer overlayer thickness with the time the joints left in water, it has also shown that as a result of drying the polymer overlayer left on the surface can be increased. In addition, the thickness of the polymer left on the surface remains almost unchanged between 100 days and the end of the test programme (240 days). Also no reduction in the fracture strength values were observed during this time period. It is clear from the results that the effect of water in prolonged water immersion is constant or at least minimal.

The study of the commercial resin by ToF-SIMS and angle resolved XPS have identified segregation of minor components of the adhesive, such as amine and diluent. Although the migration of diluent in not very clear, the segregation of amine close to the fracture interface was clearly established.

Finally as a part of the study of commercial resins, the effect of in-situ fracture conditions and the different fracture modes were evaluated. It was found that the fracture at in-situ tends to provide near interfacial failure with thicker polymer left on the surface than a sample fractured at atmosphere. Also, no difference in the locus of failure was observed between the tensile and XPS T-peel stage fracture.

11.3 THE REFORMULATED RESIN SYSTEMS

A variety of model formulations have been examined to assess the role of variations in the minor components on the strength, durability and interfacial chemistry of the adhesive joints. It was found that the physical properties could be altered significantly by varying the amounts of components in the adhesives. Perhaps not surprisingly the model adhesives perform any better than the commercial resin. However the aim of this piece of work was to study segregation phenomena at the glass/adhesive interface and relate this to the adhesive formulation. This has been achieved and ToF-SIMS is shown to be a very powerful technique for this purpose.
Chapter Eleven: Conclusions

In the case of the 0 and 10 % diluent containing variant adhesives, increase in the segregation of the amine at the interface for wet fracture (10 days water immersion) samples was identified.

The amine segregation was observed in all the interfacial failures of the diluent variant formulations, except 30% diluent dry fracture, where the locus of failure was identified as through the bulk of the adhesive. The near interfacial failure during wet fracture did show a small increase of amine at the interface. The studies of diluent variant adhesives none the less did not show any significant trend in the change amount of diluent present at the fracture interfaces.

The 100% amine formulations showed no trend in amine segregation both at dry and wet fractures, although as expected higher intensity amine ion fragments were observed at the surfaces. Perhaps the fast curing of this formulation prevented significant migration of the amine to the interface. The only other interfacially fractured joints were dry and wet joints of 30 % amine formulation. These joints showed significant amount amine segregation at the `glass’ sides of the fracture. Only 10 % amine formulation did show signs of diluent migration during wet fracture. Also, joints made from this are very low bond strength both at dry and wet conditions.

Finally there was clear relationship between the reduction in bond strength and the polymer overlayer thickness was identified and this behaviour is similar to the joints made from commercial resin. A trend could be possibly achieved with the aid of more long-term durability studies. The formulations made with pure amine cure (100 % amine) or with higher mercaptan cure (10 % cure) did not provide joints of good bond strength. Although not better than the commercial resin the bond strength of all diluent variant adhesive and 30 % amine cured adhesive have modest amount of bond strengths. Also, only the 30 % diluent variant formulation has the loci of failure similar to the commercial adhesive (i.e cohesive at dry fracture and near interfacial during wet fracture).
Chapter Eleven: Conclusions

The purpose of this project to investigate the failure mechanisms and the segregation phenomena of the minor component, in a commercial adhesive system. Initial work has shown that the failure mechanism of the joints to be cohesive through the bulk and then move towards interfacial failure when the joints were exposed to water. The complexity of the commercial resin led to inconclusive evidence on the segregation of minor components. Therefore formulation of different resin based on the basic chemistry of the commercial resin was carried out. As expected these resins were not superior in bond strength to the commercial adhesive. However a trend in the segregation of minor components during wet and dry fracture of various joints has been identified during this study. Also what is clear from this work is that segregation of minor components of the adhesives does occur, and this could play a major role in the interfacial failure of the joints. The results from this work have identified the importance of minor components, and excessive use in adhesive formulations may weaken the assembled joints.

11.4 FUTURE WORK

The presence of minor components and their role in durability of the adhesive joints has been illustrated. The potential therefore exists to include adsorption related experiments during formulation of the adhesives, to identify any preferential adsorption of individual components on the adherend surface. The groundwork on the effect of water on various formulations has been identified from this work. It would also be interesting to carry out further detailed studies of the interphase region, to discover more about the interphase chemistry of the glass/resins systems.

In order to study the segregation phenomena further, more durability studies of the joints with series of long-term exposure time scales to water are needed. These matrices of experiments would aid to establish a relationship between the stoichiometry of the resin and the locus of failure. It has already been shown in this work that a fast cure adhesive could result in reduced segregation of minor components at the interface.
Chapter Eleven: Conclusions

The cure rate is dependent on several factors such as choice of materials and stoichiometry of the adhesive mix etc. It is impossible to carry out experiments to cover all aspects of adhesive formulation. However it is possible to monitor segregation of minor components by just changing few important parameters.

The cure rate and the study of glass transition temperature are carried out in this work, just to identify the basic physical behaviour of commercial and reformulated adhesive. In order to examine the segregation phenomenon, it is necessary to carry out a detailed study of the kinetics, as well as the thermodynamics of the various systems. Combining these results would undoubtedly aid the determination of precise mechanisms by which diffusion of water occurs in these materials.

In this work, apart from surface cleaning with different solvent, no major effort has been spent on surface treatments or modifications. It would be interesting to see the effects of adhesion promoters such as silanes, on amine segregation from different formulations.
REFERENCES

14) Vasenin, R.M., Adhesive Age, 8(5), p. 21, (1965 (a)).
15) Vasenin, R.M., Adhesive Age, 8(6), p. 30, (1965 (b)).
References

52) Kratos Technology Notes, www.kratos.co.uk
References


References

References


