The attainment of controlled adhesion by incorporation of low level additives in a PDMS-based adhesive

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/7764

Publisher: © Ubu Ana

Please cite the published version.
This item is held in Loughborough University’s Institutional Repository (https://dspace.lboro.ac.uk/) and was harvested from the British Library’s EThOS service (http://www.ethos.bl.uk/). It is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
THE ATTAINMENT OF CONTROLLED ADHESION BY INCORPORATION
OF LOW LEVEL ADDITIVES IN A PDMS-BASED ADHESIVE

By

Ubu Ana

A Doctoral Thesis
Submitted in partial fulfilment of the requirements
for the award of the degree of Doctor of Philosophy of Loughborough
University

4 October 2005

Institute of Polymer Technology & Materials Engineering

Supervisor: Dr Gary Critchlow

© Ubu Ana 2005
Abstract

Stearates are commonly used in polymer technology as slip additives and lubricants. The release properties of stearic acid and its metallic derivatives are extensively manipulated in rubber processing industries where they are used as mold release agents. Previous unrelated studies have shown that increased additions of stearic acid consistently reduced mold sticking. Despite their widespread usage, however, few studies have been directed to study their mechanism of action. In a preliminary study conducted by AWE and Loughborough University, the attainment of low levels of adhesion was studied and in particular the use of stearic acid as an adhesion modifier was studied. It was found that adding minute amounts of stearic acid resulted in dramatic reductions to the strength of aluminium bonded with a PDMS-based adhesive. The cause of this fall-off in adhesion (as measured by T-peel test) was initially attributed to the migration of stearic acid to the surface forming a weak boundary layer. The possibility that stearic acid acts as an inhibitor for the cure reaction was also considered. Surface analysis predominantly with static secondary ion mass spectrometry (SSIMS) and X-ray photoelectron spectroscopy (XPS) was carried out to ascertain locus of failure and the likelihood of stearic acid at the interface. Failure was identified as having taken place in a cohesive, and potentially interphasial, layer near the interface of the joint. No evidence was given to support the WBL theory proposed by most researchers, thus findings from the present study contradicted existing literature. Fourier Transform infrared (FT-IR) spectroscopy in collaboration with differential scanning calorimetry (DSC) was used to investigate the effect of stearic acid on the cure reaction. These studies disclosed a catalytic effect on the curing process of the adhesive. It was suggested that the resultant increase in modulus of the stearic acid modified material in the region of failure was the cause of premature joint failure at low level loads.
Acknowledgements

I am sincerely appreciative of the financial support of the EPSRC and AWE in funding this project.

I thank my supervisors Drs. Gary Critchlow (IPTME) and Malcolm Spence (AWE) for their invaluable support, advice, expertise and guidance. They have skilfully navigated my research so that I have been able to fulfil my own academic requirements and meet the needs of my industrial sponsors. Their own high standards of work have inspired me throughout this research. I am truly grateful to Dr Critchow for his support and understanding when personal matters had to take precedence over this project.

I would also like to thank my other colleagues in IPTME and ISST for their patience and diligence in processing my samples. I am especially grateful to Mrs Pat Crapper and Mr David Hall for generating the extensive XPS and SSIMS data. Special thanks go to Drs. Mike Reading and Gerry Swallowe for their assistance in processing and discussing the thermal kinetic data.

Overwhelming thanks are extended to Mr Furo Jumbo, a fellow final year research student, for the inordinate amount of time spent developing the FE model contained within this research. I thank him also for his tolerance when explaining the FE method to this self confessed novice, especially in the light of his own looming deadline.

Finally, I thank God, my family and my friends for helping me through probably the most stressful period of my life thus far. I am grateful for the comfort and encouragement I have received despite progressively neglecting each relationship as the work load increased. I specifically thank God for blessing me with the opportunity to study for my PhD and for putting into place a network of people to facilitate this process, and my family and friends for their encouragement, their prayers and the joy they have given me over the last three years.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuate Total Reflectance</td>
</tr>
<tr>
<td>AWE</td>
<td>Atomic Weapons Establishment</td>
</tr>
<tr>
<td>CAA</td>
<td>Chromic Acid Anodise</td>
</tr>
<tr>
<td>CAE</td>
<td>Chromic Acid Etch</td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon Fibre Reinforced Polymer</td>
</tr>
<tr>
<td>CHA</td>
<td>Concentric Hemispherical Analyser</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DG</td>
<td>Degrease</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EDXA</td>
<td>X-ray Energy Dispersive Analysis</td>
</tr>
<tr>
<td>EVA</td>
<td>Poly(ethylene-co-vinyl acetate)</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Model</td>
</tr>
<tr>
<td>FPL</td>
<td>Forest Products Laboratory</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GB</td>
<td>Grit-blast</td>
</tr>
<tr>
<td>ISS</td>
<td>Ion Scattering Spectroscopy</td>
</tr>
<tr>
<td>IPTME</td>
<td>Institute of Polymer Technology and Materials Engineering</td>
</tr>
<tr>
<td>ISST</td>
<td>Institute of Surface Science and Technology</td>
</tr>
<tr>
<td>IRE</td>
<td>Internal Reflection Element</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
</tr>
<tr>
<td>MAH</td>
<td>Maleic Anhydride</td>
</tr>
<tr>
<td>MTDSC</td>
<td>Modulated Temperature Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile Butadiene Rubber</td>
</tr>
<tr>
<td>PAA</td>
<td>Phosphoric Acid Anodising</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure Sensitive Adhesive</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl acetate)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>RTV</td>
<td>Room Temperature Vulcanisable</td>
</tr>
<tr>
<td>SAA</td>
<td>Sulphuric Acid Anodising</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SSIMS</td>
<td>Static Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SLS</td>
<td>Single Lap Shear</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TOF-SSIMS</td>
<td>Time-of-flight Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>WBL</td>
<td>Weak Boundary Layer</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>X-SEM</td>
<td>Extended Resolution-Scanning Electron Microscopy</td>
</tr>
</tbody>
</table>
List of Tables

Table 1.0  Surface energy as an indication of bonding capability. 6
Table 1.1  Summary of the main pre-treatment processes for aluminium. 9
Table 1.2  The Physical Characteristics of the Bond Types Attributed to the Adsorption Adhesion Mechanism 33
Table 1.3  Typical components of a silicone adhesive based on hydrosilylation cure system. 63
Table 1.4  A summary of experimental techniques and their uses in the present study 70
Table 1.5  A Comparison of Surface Analytical Techniques 82
Table 2.0  Typical Properties of Sylgard 184 127
Table 2.1  Alloy composition 128
Table 2.2  Physical Properties of Stearates. 129
Table 2.3  Physical properties of Acetic Acid 130
Table 2.4  Material Properties Aluminium adherend 137
Table 2.5  Material Properties for the adhesives 138
Table 2.6  Adhesive Preparations for DSC 144
Table 3.0  Peel strength values for unmodified and stearic acid modified T-peel joints. 149
Table 3.1  Affect of additives on adhesive strength as measured by T-peel test at room temperature and after curing for 24 hours. 151
Table 3.2  Comparison of the effect of joint configuration and surface Pretreatment on adhesive strength. 155
Table 3.3  The effect of stearic acid on the ratio of Al to Si peak Intensity on the metal side of SSIMS spectra of failed T-peel joints. 168
| Table 3.4a | The chemical composition of the polymer and metal side of failure for an unmodified and a joint modified with 0.3 wt% stearic acid. |
| Table 3.4b | The chemical composition of the polymer and metal side of failure for joints modified with 0.4 wt% and 1.0 wt% stearic acid. |
| Table 3.5  | Wavenumber positions of characteristic peaks for Silicones. |
| Table 3.6  | XPS chemical analysis of SLS joints subjected to a variety of surface pre-treatments. |
| Table 3.7  | XPS chemical analysis of T-peel joints subjected to a variety of substrate pre-treatments. |
| Table 3.8  | Chemical composition of polymer side of failed calcium stearate modified joint. |
| Table 3.9  | Chemical composition of metal side of failed calcium stearate modified joint. |
| Table 3.10 | Chemical composition of polymer side of failed zinc stearate modified joint. |
| Table 3.11 | Chemical composition of metal side of failed zinc stearate modified joint. |
| Table 3.12 | Chemical composition of polymer side of failed acetic acid modified joint. |
| Table 3.13 | Chemical composition of metal side of failed acetic acid modified joint. |
| Table 3.14 | Kinetic constants determined using the Kissenger method of analysing thermal data for a variety of adhesive formulations. |
| Table 3.15 | Summary of experiments performed and their aims. |
## List of Figures

| Figure 1.0 | Schematic diagram of interfaces in an adhesively bonded system | 4 |
| Figure 1.1 | The molecular structure of a silicone | 59 |
| Figure 1.2 | Proposed cure reaction for Sylgard 184 | 65 |
| Figure 1.3 | Common joint (a) butt; (b) single lap; (c) wedge; (d) 90° Peel; and (e) T-peel, configurations for adhesive strength tests. | 72 |
| Figure 1.4 | An example of a T-Peel Specimen during a Test. | 76 |
| Figure 1.5 | Area of interest in surface analysis. | 81 |
| Figure 1.6 | An illustration of the operating principle of XPS | 83 |
| Figure 2.0 | Stearates Chemical Formula | 128 |
| Figure 2.1 | Molecular Structure of Acetic Acid | 129 |
| Figure 2.2 | Operating Cycle for standard CAA 40/50V Process | 132 |
| Figure 2.3 | T-peel Joint Configuration; (a) plan view, (b) side view | 133 |
| Figure 2.4 | Dimensions of SLS joints; (a) plan view, (b) side view | 135 |
| Figure 2.5 | T-peel specimen | 139 |
| Figure 2.6 | T-Peel Schematic showing boundary conditions | 140 |
| Figure 2.7 | FE Mesh showing fillet area mesh density | 141 |
| Figure 3.0 | Typical force/extension curves for stearic acid Modified FPL etched, T-peel joints | 148 |
| Figure 3.1 | Effect of stearic acid on adhesive strength. | 149 |
| Figure 3.2 | Effect of alternative additives on adhesive strength. | 151 |
| Figure 3.3 | The effect of SLS joint configuration and surface pretreatment on adhesive strength of unmodified and modified joints | 153 |
Figure 3.4  The effect of surface pretreatment on T-peel strength. 154

Figure 3.5  SEM micrograph of features typical of the polymer surface of failed joints 157

Figure 3.5.1  SEM images of metal side of an unmodified joint 158

Figure 3.5.2  SEM images of metal side of 0.1wt% stearic acid modified joint 158

Figure 3.5.2  SEM images of metal side of 0.2wt% stearic acid modified joint 159

Figure 3.5.2  SEM images of metal side of 0.3wt% stearic acid modified joint 159

Figure 3.5.2  SEM images of metal side of 0.4wt% stearic acid modified joint 160

Figure 3.5.2  SEM images of metal side of 0.5wt% stearic acid modified joint 160

Figure 3.5.2  SEM images of metal side of 0.8wt% stearic acid modified joint 161

Figure 3.5.2  SEM images of metal side of 1.0wt% stearic acid modified joint 161

Figure 3.6.1  SSIMS spectra of the polymer surfaces of (a) an unmodified, (b) 0.3wt% modified, (c) 0.4wt% modified and (d) 1.0wt% modified failed T-peel joint. 164

Figure 3.6.2  SSIMS spectra of the metal surface of (a) an unmodified, (b), a 0.3wt%, (c) a 0.4wt% and (d) a 1.0wt% stearic acid modified T-peel joints. 167

Figure 3.7a-b  Polymer side of unmodified peel joint and metal side of an unmodified T-peel joint 170

Figure 3.7c-d  Polymer side of 0.3 wt% modified joint and metal side of 0.3 wt% modified T-peel joint 170

Figure 3.7e-f  Polymer side of 0.4 wt% modified joint and metal side of 0.4 wt% modified T-peel joint 171

Figure 3.7g-h  Polymer side of 1.0 wt% modified joint and metal side of 1.0 wt% modified T-peel joint 172
Figure 3.8  ATR Absorbance spectrum of the polymer side of a failed, unmodified joint surface  

Figure 3.9  ATR Absorbance spectrum of the polymer side of a failed, 0.5 wt% modified joint surface.  

Figure 3.10  ATR spectra of the metal side of failed unmodified and modified joints.  

Figure 3.11  SEM micrographs of the polymer side of a failed calcium stearate modified joint.  

Figure 3.12  SEM micrographs of the metal side of failed calcium stearate modified joints.  

Figure 3.13  SEM micrographs of the polymer side of a failed zinc stearate modified joint.  

Figure 3.14  SEM micrographs of the metal side of a failed zinc stearate modified joint.  

Figure 3.15  SEM micrograph of polymer side of a failed glacial acetic acid modified joint.  

Figure 3.16  SEM micrograph of metal side of glacial acetic acid modified joint.  

Figure 3.17  XPS spectrum of the polymer side of a calcium stearate modified joint.  

Figure 3.18  XPS spectrum of the metal side of a calcium stearate modified joint  

Figure 3.19  XPS spectrum of the polymer side of a zinc stearate modified joint  

Figure 3.20  XPS spectrum of the metal side of a zinc stearate modified joint  

Figure 3.21  XPS spectrum of the polymer side of a glacial acetic acid modified joint  

Figure 3.22  XPS spectrum of the metal side of a failed glacial acetic acid modified joint  

Figure 3.23a  The effect of stearic acid on conversion rate after curing at room temperature for 72 hours
Figure 3.23b The effect of stearic acid on conversion rate after curing at room temperature for 24 hours.

Figure 3.23c Effect of stearic acid on the final conversion after curing at room temperature for 24 hours and 72 hours.

Figure 3.24 IR spectra showing depletion of vinyl (CH₂=CH₂) and silyl (SiH) groups with time in an unmodified cure reaction.

Figure 3.25 IR spectra showing depletion of vinyl (CH₂=CH₂) and silyl (SiH) groups with time in a cure reaction modified with 0.1 wt% stearic acid.

Figure 3.26 IR spectra showing depletion of vinyl (CH₂=CH₂) and silyl (SiH) groups with time in a cure reaction modified with 0.3 wt% stearic acid.

Figure 3.27 IR Spectra showing depletion of vinyl (CH₂=CH₂) and silyl (SiH) groups with time in a cure reaction modified with 0.4 wt% stearic acid.

Figure 3.28 IR Spectra showing depletion of vinyl (CH₂=CH₂) and silyl (SiH) groups with time in a cure reaction modified with 0.5 wt% stearic acid.

Figure 3.29 The Kissenger analysis of the effect of stearic acid on the kinetics of the cure reaction.

Figure 3.30 Variation of Activation Energy with Extent of Reaction in Sylgard.

Figure 3.31 Kinetic Analysis of an unmodified cure reaction.

Figure 3.32 Friedman analysis of a cure reaction of a modified adhesive (0.3wt% stearic acid).

Figure 3.33 Effect of stearic acid on crosslink density.

Figure 3.34 Effect of stearic acid on tensile properties.

Figure 3.35 The effect of stearic acid on stress distribution.
### Contents

Certificate of Originality
Abstract i
Acknowledgements ii
Abbreviations iii
List of Tables iv
List of Figures v

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>Literature Review</th>
<th>1-126</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>General Introduction</td>
<td>1-4</td>
</tr>
<tr>
<td>1.1</td>
<td>What is an adhesive?</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Factors required for optimised adhesion</td>
<td>4-25</td>
</tr>
<tr>
<td>1.2.1</td>
<td>The importance of wettability</td>
<td>5</td>
</tr>
<tr>
<td>1.2.2</td>
<td>The influence of surface pretreatment on adhesion</td>
<td>7</td>
</tr>
<tr>
<td>1.2.2.1</td>
<td>Aluminium alloy pretreatment methods</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2.1.1</td>
<td>Degreasing</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2.1.2</td>
<td>Grit-blasting</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2.1.3</td>
<td>Chemical and electrochemical treatments</td>
<td>11</td>
</tr>
<tr>
<td>1.2.2.1.3.1</td>
<td>Chromic acid etch (CAE)</td>
<td>11</td>
</tr>
<tr>
<td>1.2.2.1.3.2</td>
<td>Chromic acid anodising (CAA)</td>
<td>12</td>
</tr>
<tr>
<td>1.2.2.1.4</td>
<td>Surface morphology and joint strength</td>
<td>12</td>
</tr>
<tr>
<td>1.2.2.1.5</td>
<td>Corrosion Resistance</td>
<td>14</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Influence of adhesive properties on adhesion</td>
<td>15-20</td>
</tr>
<tr>
<td>1.2.3.1</td>
<td>Types of adhesive</td>
<td>15</td>
</tr>
<tr>
<td>1.2.3.2</td>
<td>Polymer surface chemistry</td>
<td>17</td>
</tr>
<tr>
<td>1.2.3.3</td>
<td>Bulk adhesive properties</td>
<td>18</td>
</tr>
<tr>
<td>1.2.4</td>
<td>Stress distribution</td>
<td>21-25</td>
</tr>
<tr>
<td>1.2.4.1</td>
<td>Stresses in the adherend</td>
<td>21</td>
</tr>
<tr>
<td>1.2.4.2</td>
<td>Stresses within the adhesive</td>
<td>23</td>
</tr>
<tr>
<td>1.2.4.3</td>
<td>Stresses at the interface/interphase</td>
<td>25</td>
</tr>
<tr>
<td>Section</td>
<td>Pages</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>1.3 Theories of Adhesion</td>
<td>28-52</td>
<td></td>
</tr>
<tr>
<td>1.3.1 Mechanical Interlocking</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1.3.2 Physical Adsorption</td>
<td>30-35</td>
<td></td>
</tr>
<tr>
<td>1.3.2.1 Acid-Base Interactions</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1.3.2.2 Chemical Adsorption</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>1.3.3 Diffusion Theory</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>1.3.4 Electrostatic Theory</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>1.3.5 Adhesion Indices</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>1.3.6 Rheological Theory</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1.3.7 Pressure Sensitive Adhesion</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>1.3.8 Co-ordinate Force Bond Theory</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1.3.9 Weak Boundary Layer (WBL) Theory</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>1.3.9.1 The effect of stearic acid on adhesion</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>1.3.10 Summary</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>1.4 Interphase formation and interfacial effects</td>
<td>54-58</td>
<td></td>
</tr>
<tr>
<td>1.5 Silicone chemistry</td>
<td>59-67</td>
<td></td>
</tr>
<tr>
<td>1.5.1 Sylgard 184™</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>1.5.2 Influence of interfaces on rates of crosslinking</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>1.6 Experimental techniques</td>
<td>68-124</td>
<td></td>
</tr>
<tr>
<td>1.6.1 Strength of Adhesive Joints</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>1.6.1.1 Peel test</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>1.6.1.1.2 Peel Force and Energy</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>1.6.1.2 Single Lap Shear Joint (SLS)</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>1.6.1.3 Finite Element Analysis (FEA)</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>1.6.2 Surface Analysis</td>
<td>81-92</td>
<td></td>
</tr>
<tr>
<td>1.6.2.1 X-ray Photoelectron Spectroscopy (XPS)</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>1.6.2.2 Static Secondary Ion Mass Spectrometry (SSIMS)</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>1.6.2.3 Applications of XPS and SSIMS in adhesion studies</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>1.6.3 Attenuated Total Reflectance (ATR)</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>
1.6.4 Fourier Transform Infra-red (FTIR) Spectroscopy 94-96
1.6.5 General Introduction to Differential Scanning Calorimetry (DSC) 96-122
1.6.5.1 Thermal Analysis and Kinetic Measurements 99
1.6.5.2 Reaction Kinetics from Thermal Analysis 100
1.6.5.3 Mechanisms and Kinetic Equations 101
1.6.5.4 Isothermal methods 104
1.6.5.5 Determination of the function of $\alpha$ 105
1.6.5.6 Measurement of Activation Energy, $E_A$ 109
1.6.5.7 Determining the Pre-exponential Factor, $A$ 110
1.6.5.8 Single-Heating Rate Method 111
1.6.5.9 Multi-Heating-Rate Method 113
1.6.5.10 Application of DSC study on silicone rubber cure reactions 116
1.6.5.11 Summary 121
1.6.6 Solvent Swelling 122
1.6.6.1 Theory 123
1.7 General Summary 125

Chapter 2 Experimental Procedures 126-148

2.1 Materials 126
2.1.1 Adhesive 126
2.1.1.1 Unmodified adhesive 127
2.1.1.2 Modified adhesive 127
2.2 Aluminium alloy substrates 127
2.3 Additives 128
2.3.1 Stearates 128
2.3.2 Acetic Acid 129
2.4 Substrate Pretreatment 130
2.4.1 Degrease (DG) 130
2.4.2 Grit-blast (GB) 131
2.4.3 Sulphuric Acid/Chromic Acid Etch (FPL) 131
2.4.4 Chromic Acid Anodise (CAA) 131

2.5 Mechanical Testing 133
2.5.1 Adhesion Tests 133
2.5.1.1 T-peel Test 133
2.5.1.2 Single Lap Shear (SLS) Joint Test 134
2.5.2 Tensile Test 136

2.6 FE Modelling of T-peel Joints 136
2.6.1 Physical Model 136
2.6.1.1 Material Properties 137
2.6.1.2 Finite Element Model 138
2.6.1.3 Mesh Design and Element Performance 140

2.7 Surface Analytical Techniques 142
2.7.1 SSIMS 142
2.7.2 XPS 142
2.7.3 ATR 143

2.8 Kinetic Analysis by DSC 143
2.8.1 Sample preparation 143
2.8.1.1 Kissenger Method 144
2.8.1.2 Friedman Method 145
2.8.1.3 FTIR Spectroscopy 145

2.9 Solvent Swelling 146
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Joint Assessment</td>
<td>147</td>
</tr>
<tr>
<td>3.1.1</td>
<td>T-peel test</td>
<td>147</td>
</tr>
<tr>
<td>3.1.1.1</td>
<td>The effect of other additives on peel strength</td>
<td>150</td>
</tr>
<tr>
<td>3.1.1.2</td>
<td>SLS test</td>
<td>152</td>
</tr>
<tr>
<td>3.2</td>
<td>Failure Analysis</td>
<td>156</td>
</tr>
<tr>
<td>3.2.1</td>
<td>SEM</td>
<td>156</td>
</tr>
<tr>
<td>3.2.2</td>
<td>SSIMS</td>
<td>162</td>
</tr>
<tr>
<td>3.2.3</td>
<td>XPS</td>
<td>169</td>
</tr>
<tr>
<td>3.2.4</td>
<td>ATR</td>
<td>174</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Failure analysis of substrate pretreatments on SLS and T-peel joints</td>
<td>180</td>
</tr>
<tr>
<td>3.2.5.1.1</td>
<td>Degreased SLS joints</td>
<td>180</td>
</tr>
<tr>
<td>3.2.5.1.2</td>
<td>Degreased T-peel joints</td>
<td>181</td>
</tr>
<tr>
<td>3.2.5.2.1</td>
<td>Grit-blast SLS joint</td>
<td>181</td>
</tr>
<tr>
<td>3.2.5.2.2</td>
<td>Grit-blast T-peel joint</td>
<td>181</td>
</tr>
<tr>
<td>3.2.5.3.1</td>
<td>CAE SLS joint</td>
<td>182</td>
</tr>
<tr>
<td>3.2.5.3.2</td>
<td>CAE T-peel joint</td>
<td>182</td>
</tr>
<tr>
<td>3.2.5.4.1</td>
<td>CAA SLS joint</td>
<td>182</td>
</tr>
<tr>
<td>3.2.5.4.2</td>
<td>CAA T-peel joint</td>
<td>183</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Failure analysis of joints modified with alternative additives</td>
<td>186</td>
</tr>
<tr>
<td>3.2.6.1</td>
<td>SEM characterisation</td>
<td>186</td>
</tr>
<tr>
<td>3.2.6.2</td>
<td>XPS Analysis</td>
<td>191</td>
</tr>
<tr>
<td>3.3</td>
<td>Cure Kinetics</td>
<td>198</td>
</tr>
<tr>
<td>3.3.1</td>
<td>FTIR</td>
<td>198</td>
</tr>
<tr>
<td>3.3.2</td>
<td>DSC</td>
<td>207</td>
</tr>
<tr>
<td>3.3.2.1</td>
<td>Kissenger Method</td>
<td>207</td>
</tr>
<tr>
<td>3.3.2.2</td>
<td>Friedman Analysis</td>
<td>208</td>
</tr>
</tbody>
</table>
3.4 Bulk Properties 212
3.4.1 Solvent Swelling 212
3.4.2 Tensile Test 213

3.5 Finite Element Analysis 216

3.6 Summary 218

Chapter 4 Discussion 219-236

4.1 The effect of stearic acid on joint strength 219

4.2 Failure analysis 220

4.3 The effect of stearic acid on cure kinetics 223-228
4.3.1 FTIR 223
4.3.2 Kinetic analysis by thermal methods 224
4.3.2.1 Kissenger analysis 224
4.3.2.2 Friedman analysis 225

4.4 Crosslink Density 227

4.5 Mechanical properties 229
4.5.1 Finite Element Analysis of Stresses 230

4.6 Parametric studies 232
4.6.1 The effect of substrate pretreatment 232
4.6.2 The effect of joint configuration 234
4.6.3 The effect of alternative additives 235

Chapter 5.0 Conclusions 237-239

Chapter 6.0 Further Work 240-241
1.0 General Introduction

The study detailed herein is a collaboration between the Atomic Weapons Establishment (AWE) Aldermaston and Loughborough University aimed at investigating methods for creating controlled levels of adhesion between metal foils using a poly(dimethylsiloxane) (PDMS)-based adhesive. In the first instance, the attainment of low levels of adhesion was studied and in particular the use of stearic acid as a modifier to the adhesive was considered. Other factors such as the influence of other additives and varying the surface treatment have also been investigated. What follows in this section is a detailed review of the science and engineering of adhesion with respect to the factors that influence adhesion, including surface pretreatment, interfacial strength, adhesive properties and stress distribution.

Intuitively, adhesion may be considered as a sum of energy processes where the fracture energy \( G \) will involve a term associated with the energy required for breaking primary or secondary bonds at the interface when the joint fails. This surface energy term will be the thermodynamic work of adhesion \( \mathcal{W}_A \) or of cohesion \( \mathcal{W}_C \), depending on if the joint fails at the interface or adhesively within one phase. To this surface energy term must be added a term \( \mathcal{V} \) representing other energy absorbing processes such as plastic deformation or viscoelastic loss due to stretching of the material. Consequently, on this basis for a particular structure joint strength is influenced by:

- the strength of the interface, \( \mathcal{W}_A \)
- the strength of the adhesive, \( \mathcal{W}_C \)
- the distribution of stresses within the joint, \( \mathcal{V} \)
The factors that affect adhesion are intimately linked with adhesion mechanisms. There are a number of longstanding and newer theories of adhesion and these will be discussed in terms of their relevance to joint formation, particularly in the case of polymer-to-metal bonding. Also of particular bearing to the present study is the theory of abhesion, or poor adhesion, which lends itself to the explanation for lower than expected levels of adherence that sometimes occurs in joints. The focus of the present study is the modification of the adhesion between aluminium substrates using a PDMS-based adhesive. The adherend of choice is 1xxx series aluminium. Also detailed in this section are experimental procedures employed throughout this research. It is recognised that the complexity of adhesion problems requires analytical procedures that will enable scrutiny of the different levels of this phenomenon. Events occurring on a microscopic level often manifest themselves macroscopically. For instance, reduced levels of adhesion in the presence of stearic acid represent a macroscopic manifestation of events taking place on a microscopic scale such as weak interlayer formation at the adhesive/adherend interface. Consequently the techniques, analyses and experiments conducted throughout this study need to encompass this scale of activities. Thus there will be a comprehensive account of adhesion tests, such as single lap shear joint (SLS) and the T-peel; surface analysis techniques like X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS) and attenuated total reflectance (ATR) spectroscopy; bulk adhesive investigative methods, for instance Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

Following the discourse on adhesion, the factors that influence adhesion and the investigative methods commonly employed to address adhesion issues conducted in the literature review in Chapter 1, the experimental procedures will be described in detail in Chapter 2 followed by a presentation of the results and data generated during these experiments in Chapter 3. A thorough discussion of the information accumulated as a result of these experiments will commence in Chapter 4, which will be ensued by the
conclusions drawn from these in Chapter 5. Suggestions of further work will be put forward in Chapter 6.

1.1 What is an adhesive?

Adhesion is a fundamentally molecular attraction exerted between two bodies in contact. This may be with or without the introduction of a third body, i.e. the adhesive. In the present study we are only concerned with adhesion occurring through the introduction of an adhesive, i.e. adhesive bonding.

Early definitions of an adhesive were fairly basic and only made reference to the fact that it bonds two surfaces together. An example of this is the definition put forward by Bikales\(^1\) that an adhesive is a substance capable of holding materials together by surface attachment. This description makes no mention of the structural aspect of an adhesive. This requirement is later incorporated by authors such as Comyn\(^2\) who describes an adhesive as a material which when applied to the surface of materials can join them together and resist separation. A further expansion of the definition has been made to encompass the polymeric nature of most adhesives. So for totality, an adhesive is a polymeric material that when applied to two or more surfaces can join them together to resist separation. By virtue of this definition it maybe interpreted that an adhesive must do two things:

- It must wet the surfaces, i.e. the contact angle $\theta < 90^\circ$.
- Subsequently, the adhesive must harden and form a cohesively strong material.

These criteria form the basis of strong bond formation with adhesives. The factors that affect adhesion fall into one of the two categories. Thus it may be assumed that upon compliance of these two requirements a strong adhesive
1.2 Factors required for optimised adhesion

The definitions of an adhesive and the criteria that must be fulfilled to achieve good adhesion allude to the factors that influence adhesion, namely: the condition of the substrate surface which is determined by pretreatment and possibly the presence of a primer or coupling agent; the bulk mechanical properties of the adherends and the stresses present which relates to joint configuration and; the properties of the bulk adhesive which determines cohesive strength of the adhesive itself.

A bonded system consists of layers of different materials. Figure 1.0 illustrates the typical constituents of an adhesively bonded system. Since it is paramount that intimate contact must be made between the molecules of the adhesive and those of the atoms or molecules of the adherend it also follows that the adhesive must be in close contact with the primer, which in turn must be in close contact with the adherend via its oxide.

**Figure 1.0** Schematic diagram of interfaces in an adhesively bonded system\(^3\).
In the current study the primer application stage is omitted during the formation of the bonded joints so the role of the primer or coupling agent will not be discussed further. Instead in the present study the adhesive is applied directly to the surface of the adherend. Also this case is concerned solely with metal-metal bonding and in particular with the bonding of aluminium. Therefore aspects of polymer bonding have not been discussed in this thesis in great detail.

1.2.1 The importance of wettability

As it is required that an adhesive must wet the surfaces to which it is being applied this means that they are most often in the liquid state. This enables them to spread and make a contact angle $\theta$ approaching zero, thereby providing the conditions for intimate contact between the molecules of the adhesive and those of atoms or molecules in the adherend to take place. Upon application, the adhesive will, generally, be a liquid of relatively low viscosity. Once wetting has taken place there is then the possibility of interfacial interactions occurring. The contact angle is a measure of the extent of wetting as indicated by the angle a single liquid droplet makes with the surface. When a liquid wets a solid to the extent that the contact angle becomes zero the liquid is said to spread. Hence wetting, or the spreading of a liquid on a solid surface, is favourable for any adhesive which makes a contact angle $<90^\circ$.

For adhesion to occur the surface free energy of the solid must be greater than the critical surface tension of the adhesive. The rate and degree of wetting is determined by the surface energies of the adherend and adhesive and surface energies are determined by surface chemistries. All metals in common use have oxide coats which are of high surface energy. For example alumina (Al$_2$O$_3$), which is the natural oxide of aluminium, has a surface energy of 638 mJ m$^{-2}$ compared with 20-46 mJ m$^{-2}$ for most
polymers/adhesives. This means that metals are easy to bond whereas there are greater difficulties associated with bonding some polymers. Table 1.0 gives surface energies of a range of materials, arranged in order of increasing energy and therefore ease of bonding.

It is still possible to bond polymers with low surface energies such as polypropylene and polyethylene but only after such materials have undergone adequate surface pretreatment, for example flame treatment. Such methods chemically modify polyolefin surfaces by introducing new chemical groups that are polar which raise the surface energy of the material. This promotes adhesion by increasing the propensity of the treated surface to form bonds with the adhesive. The same principle is applied when pretreating metal surfaces prior to bonding. This is discussed further in the following section.

<table>
<thead>
<tr>
<th>Solid</th>
<th>$\gamma_s^d$ (mJ m$^{-2}$)</th>
<th>$\gamma_s^p$ (mJ m$^{-2}$)</th>
<th>$\gamma_s$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Difficult to bond/low energy surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>18.6</td>
<td>0.5</td>
<td>19.1</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>30.2</td>
<td>-</td>
<td>30.2</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>33.2</td>
<td>-</td>
<td>33.2</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>35.9</td>
<td>4.3</td>
<td>40.3</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>40.0</td>
<td>1.5</td>
<td>41.5</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>41.4</td>
<td>0.6</td>
<td>42.0</td>
</tr>
<tr>
<td>Rubber modified epoxide *(comyn 1997)</td>
<td>37.2</td>
<td>8.3</td>
<td>45.5</td>
</tr>
<tr>
<td>Amine cured epoxide</td>
<td>41.8</td>
<td>3.3</td>
<td>45.1</td>
</tr>
<tr>
<td>Easy to bond/high energy surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica (SiO$_2$)</td>
<td>78</td>
<td>209</td>
<td>287</td>
</tr>
<tr>
<td>Alumina (Al$_2$O$_3$)</td>
<td>100</td>
<td>538</td>
<td>638</td>
</tr>
<tr>
<td>Ferric oxide (Fe$_2$O$_3$)</td>
<td>107</td>
<td>1250</td>
<td>1357</td>
</tr>
</tbody>
</table>

Table 1.0  Surface energy as an indication of bonding capability$^5$. 
Chapter I Literature Review

1.2.2 The influence of surface pretreatment on adhesion

The bonding of metals is widespread. The most commonly used are bonded steel and aluminium. As mentioned above this study is purely focused on the bonding of aluminium. The extent of intimate contact between the materials that comprise the bonded system (ref. Figure 1.0) is determined by the surface preparation method applied to the adherend. The nature and character of the surface of an adherend is very important in establishing the strength and durability of the adhesion to that surface, as summarised by Critchlow and Brewis.

Among the many factors that affect the durability of adhesively bonded aluminium joints, the choice of surface pre-treatment is crucial in realising the required bond strength and durability. The objective of surface pretreatment of an adherend is the following:

- removal of contaminants or weak boundary layers;
- modification of surface chemistry;
- alteration of surface geometry.

By providing a clean surface wettability is enhanced since contaminants that may impede the ability of the adhesive to spread across the surface of the adherend are removed. This also promotes intimate contact between the adhesive molecules and the atoms or molecules of the adherend.

Surface chemistry is important as it dictates the degree of contact achieved and also the magnitude of the interaction where contact has occurred, i.e. whether chemical bonding, hydrogen bonding or some van der Waals’ force or involved. Whether surface contaminants can be displaced will also depend on the chemistry of the adhesive.
Increased roughness and intrinsic hydrolytic stability of the surface have also been identified as being important for good bondability. A common attribute to good adhesive performance is the concept of mechanical interlocking, whereby the adhesive interlocks around the irregularities of the substrate. The potential bonding area of a rough surface is greater than for a smooth surface. This is especially true if the irregularities are deep and narrow. Furthermore if the intrinsic contact angle of the adhesive is $<90^\circ$, a rough surface will further lower the contact angle so that it wets and spreads across the surface.

The surface preparation of aluminium alloys generally consists of several steps of which are: initial cleaning to remove surface contamination; acid or alkaline etching to remove weak inhomogeneous oxide formed by the thermal exposure during the fabrication process; and a chemical or electrochemical treatment to stabilise the surface and promote adhesion\textsuperscript{7}. Table 1.1 summarises the common pretreatments for aluminium and its alloys. The table lists the large number of available pretreatments for bonding aluminium and its alloys. As illustrated, they range from simple mechanical processes to highly complex and expensive multistage operations.

In the present study the pretreatment methods described below were employed to ascertain their effect on the phenomenon of reduced levels of adhesion in the presence of stearic acid.
<table>
<thead>
<tr>
<th>Pretreatment type</th>
<th>Process</th>
</tr>
</thead>
</table>
| Mechanical        | Solvent wipe or clean by immersion or from vapour phase  
|                   | Alkaline or acid degreasing  
|                   | Abrasion from pads  
|                   | Grit- or sand-blasting or honing, wet or dry  
|                   | Plasma or corona discharge  
|                   | Plasma spray or other PVD methods |
| Chemical          | Acid etching, e.g. chromic, nitric or mixed acids  
|                   | Alkaline etching, usually proprietary solutions based on sodium hydroxide.  
|                   | Conversion coatings |
| Electrochemical   | AC or DC, e.g. in weak chromic, phosphoric or sulphuric electrolytes  
| Others            | Laser ablation  
|                   | CO₂ cryoblasting |

**Table 1.1** Summary of the main pretreatment processes for aluminium⁸.

A number of these pretreatments will be discussed in more detail in the following section.
Chapter 1  

1.2.2.1  

Aluminium alloy pretreatment methods

1.2.2.1.1  

Degreasing

Solvent wiping by hand is the simplest procedure usually encountered to remove poorly adhering particulate soiling and the fabricating oils and lubricants that can be present on "as received" aluminium surfaces. Vapour degreasing is favoured where heavy oil, grease or loosely adhering particle soiling is present. Although this is one of the simplest processes, it is possible to obtain high initial joint strengths from just degreasing the surface of the substrate. Degreasing improves wetting by removing organic contamination from the bonding area. However, the durability of bonds formed in harsh environments is very poor.

1.2.2.1.2  

Grit-blasting

One of the most frequently used mechanical pretreatment methods is grit-blasting. Grit-blasting can be used to remove more adherent soils that may not be readily removed using solvent wiping or vapour degreasing, for example metal fines or corrosion products. It is a mechanical treatment which roughens the surface of the substrate. The peak and valley undulating morphology conferred to the substrate by this process improves adhesion by increasing the surface area over which interactions can occur. It has been found that as long as the intrinsic contact angle of a drop of liquid is <90° then the apparent contact angle will be reduced on a rough surface.

The macro-roughened surfaces produced by mechanical pretreatments were reviewed along with chemical and electrochemical pretreatments. Critchlow and Brewis found that degreasing and blasting the surface produced
satisfactory initial bond strength, but performed poorly in a range of durability tests. The effect of roughening was investigated and it was found that finer particles used for grit blasting improved bond durability between steel and phenolic resin but the initial dry strength was not influenced by particle size\(^7\). This work suggested that a finer surface roughness produced better durability observed for the chemical based treatments. This work performed suggested that macro-roughness was incapable of producing superior durability observed for chemical based etching and anodising processes which imparted a micro roughened surface topography.

### 1.2.2.1.3 Chemical and electrochemical treatments

There are several aims to these types of treatment\(^3\).

a) The removal of potential weak boundary layers.

b) Increase surface roughness (chemical < electrochemical).

c) Alter surface chemistry with consequent changes in the rate and degree of wetting.

d) Produce a more stable oxide (chemical < electrochemical).

#### 1.2.2.1.3.1 Chromic acid etch (CAE)

For adhesively bonded joints requiring high strength and long term durability the cleaned aluminium is typically etched in either a chromic/sulphuric acid etch or a dichromate/sulphuric acid etch. The former is predominantly used in Europe and the latter, which is also known as the FPL (Forest Product Laboratory) etch or optimised FPL etch, is used predominantly by the North American aerospace industry. The FPL etch oxide consists of a network of shallow pores and protrusions, or whiskers 50 Å thick\(^{11}\), on top of a thin
barrier layer. Protuberances seem to be spaced about 300 Å apart and rise 50 Å at a concentration of about $10^{10}/cm^2$. Venebles, et al.\textsuperscript{12} claim that the presence of the whiskers and the mechanisms of mechanical interlocking is crucial for enhancing the durability of joints with FPL etch adherends.

1.2.2.1.3.2 Chromic acid anodising (CAA)

Chromic acid anodising (CAA) has been the aluminium electrochemical pre-treatment of choice of the European aerospace manufacturers for over 60 years\textsuperscript{13}. This process includes a chromic/sulphuric acid etch followed by CAA. This specification entails a stepwise process where the voltage is increased from 0V to 40V in 40-50 minutes. In the final stage the voltage is ramped to 50V. Depending on the alloy the thickness of the coating can range from 2-6 microns. The inherent CAA cell morphology, without prior FPL etching or other pretreatment, is a dense structure of tall columns. The outer surface is quite smooth with fine pores running through most of the oxide layer at the junction of the column walls. FPL etch type pretreatment before CAA processing further enhances the morphology of the outer surface of the CAA oxide resulting in a surface with FPL cell and whisker morphology. Other anodising treatments that can be used on aluminium adherends include sulphuric acid (SAA) and phosphoric acid (PAA); CAA is generally thought to be best suited for adhesive bonding of aluminium.

1.2.2.1.4 Surface morphology and joint strength

Hennemann and Brockmann\textsuperscript{13} conducted a study on surface morphology and its effects on adhesion. Their studies on clad 2024 aluminium alloy revealed significantly higher peel strengths for anodised adherends compared with FPL etched adherends. From the work performed they concluded that pore size
and, in particular, the structure of the oxide layer were important for strength and durability of adhesive bonds. The correlation between surface morphology and bondability was only true in so far as the adhesive was able, after wetting the surface, to invade the oxide morphology. The barrier layer at the bottom of the honeycomb morphology associated with anodised surfaces represents a greater surface area for wetting, and adhesive penetration, than the morphology of etched surfaces. Work by Gent and Lin\textsuperscript{14} on apparent strength of adhesion of an elastic layer adhering to a porous substrate explained the increased measured adhesion as initially being due to the roughness of the surface itself. In their study the strength of adhesion was increased twenty fold as a result of surface roughness. When an elastic adhesive layer penetrated a rough rigid substrate, extra work was expended in debonding the layer because the material in the pores is stretched as it is pulled out. The extra work was proportional to the fractional area of surface occupied by pores, and to the ratio of depth. In the same study it was found that when the pores were interconnected, like the pores in CAA oxide, the strands of adhesive within them were broken rather than pulled out, as in the previous scenario. The extra work from this process was several hundred times the work of detachment from a smooth substrate. In this case the additional work was proportional to the depth of pores. However, it must also be remembered that with etched and anodised adherends the surface chemistry has been altered so as to promote the rate and extent of wetting. Therefore in addition to the mechanical keying effect described above there are also contributions to joint strength from surface chemical interactions. These interactions contribute significantly to joint strength especially where primary chemical bonding takes place, as with primers and coupling agents\textsuperscript{11}.

Based on the studies discussed above it is generally believed that to produce a durable adhesive bond a nano- or micro-rough surface topography is beneficial. This may be achieved through mechanical roughening or electrochemical treatment. In the case of micro-roughened surfaces the exact nature of the effect of surface topography is a matter of some debate. One school of thought places importance on the mechanical interlocking theory, for example Venables\textsuperscript{15}. Others suggest the enhancement of energy dissipative
mechanisms causing plastic deformation of the adhesive make a contribution. Thus, chemical pretreatments improve joint strength by a combination of enhancing $W_A$ through the formation of primary bonds at the interface which facilitate transmission of stresses, $\psi$, from the interface to the bulk. The micro-roughness characteristic of chemical pretreatments also alters the way that the stress is distributed when the joint is loaded. This can increase the energy dissipation which occurs during fracture.

1.2.2.1.5 Corrosion Resistance

For completeness the importance of corrosion protection for adhesively bonded metal joints must be mentioned. This aspect of joint performance is particularly important where the service environment is harsh, for example in a marine environment. Here the issue of joint durability outweighs initial joint strength. The durability of adhesive bonded aluminium joints is markedly affected by surface pretreatment. Durability is poor if adherends are only degreased and/or mechanically abraded but is much improved if adherends are etched or anodised. A more in-depth discussion of the effect of pretreatment of aluminium alloys on durability is given by Poole.

A metal surface awaiting the application of an adhesive can be protected from corrosion by applying a primer. Primers are sometimes used either as an alternative or as an addition to a pretreatment. Figure 1.0 shows a primer layer between the adherend/oxide and adhesive layer. Some primers are chemisorbed to the metal oxide and therefore cannot be readily displaced by moisture and so provide protection in this way. Furthermore, by incorporating corrosion inhibitors, such as strontium chromate, the durability of the joint can be improved. Since the present case study is concerned primarily with initial joint strength the subject of durability will not be discussed further. Consult Wake for more information on primers and their use in bonding metals.
1.2.3 Influence of adhesive properties on adhesion

Initial joint strength is determined by the magnitude of physical and chemical interaction between adhesive and adherend at the interface. However, maximum adhesive performance hinges on a number of additional factors working in concert with good adhesion, for instance whether the joint is tested in a static, quasi-static or creep or fatigue conditions. Some other factors are: gross joint geometry; topography at the interface; chemical nature of the materials present in the total joint; mechanical responses of the solids present; the presence of viscoelastic phases involved; strain rate; and the temperature and environmental exposure conditions in service, or test conditions. The properties of the selected adhesive can have relevance to most or all of these variables.

1.2.3.1 Types of adhesive

It has been established that in the first instance an adhesive must wet the surfaces to which it is being applied and secondly it must harden to form a cohesively strong solid so that it can withstand applied stresses. With reference to the latter, pressure sensitive adhesives represent the exception as they remain permanently tacky so are only required to resist modest stresses. The first criterion governs the initial strength of the bond and is controlled by the chemistry of the polymer surface. The second criterion dictates the quality of the final bond. Adhesives are most commonly classified in terms of the way in which the transition from liquid phase to solid phase takes place, as in the present case, or by the chemical nature of the adhesive itself. There are four main types of adhesives which harden by the following mechanisms:
a) Solvent-based adhesives harden by evaporation of solvent. Contact adhesives are typical and well known examples of solvent-based adhesives.

b) Emulsion adhesives harden by evaporation of the dispersion medium which is normally water, an example of which is poly(vinyl acetate) (PVA).

c) Hot melt adhesives are essentially thermoplastics and hardening occurs when the adhesives cool between the adherends. Polyolefins, polyesters and polyamides are among the polymers types that have been used as bases for hot melt adhesives.

d) Reaction setting adhesives harden because a monomer or resin has undergone an addition or condensation reaction. Depending on the functionalities of the molecules either thermoplastics or thermosets are formed. Common examples of this type of adhesive include polyurethanes, epoxies, phenolics, acrylics and silicones. The silicones are of specific relevance to the present study, particularly two-part addition cure products.

The adhesive groups described show that all adhesives either contain polymers or polymers are formed within the adhesive bond and that they are the source of cohesive strength of adhesives. Thus the influence of the adhesive on joint strength is governed both by polymer surface chemistry and bulk adhesive properties. The contribution of each factor on adhesion is subsequently discussed in greater detail.
1.2.3.2  Polymer surface chemistry

Adhesion is a surface phenomenon so the chemistry of the adhesive surface is equally as important as that of the adherend. In both cases their surface energies will be determined by their chemistry. In turn these relative surface energies affect the rate and degree of wetting\(^3\).\(^4\).\(^5\). As stated earlier, for complete wetting of a liquid on a solid surface to occur the surface energy of the solid must be substantially greater than the critical surface tension of the liquid. This condition ensures that interfacial forces acting between the molecules of the liquid and the atoms or molecules of the solid supersede the cohesive forces acting between the molecules of the liquid. The surface chemistry of the adhesive and adherend not only affect the degree of contact achieved, but also the magnitude of the interaction where contact has occurred, i.e. whether chemical bonding, hydrogen bonding or some van der Waals' force is required\(^3\).\(^7\).

The wetting and spreading processes described above are influenced by the geometrical features of the surface and by the presence of chemical functionalities. These chemical functionalities dictate the type of chemical interaction that takes place between the adhesive and adherend and consequently the strength of the interface. As the interface is usually the site of premature debonding it is important to maximise the bonding in this region. For example Baier, et al.\(^{21}\), using the concept of critical surface tension \(\gamma_c\) have measured on several structurally related series of solids including unbranched polyethylene, and chlorinated and fluorinated analogues of polyethylene. They correlated these empirical measurements of surface energy "with respect to the most probable exposed atoms". In the same work, Baier, et al.\(^{21}\), concluded that in order to get good adhesion the adherend surface should be kept free from low surface tension organic films. They predicted that substituent groups such as \(-\text{OH}, -\text{SH}, -\text{COOH},\) and \(-\text{NH}\) at the outermost surface, would increase the adherence of the surface; whereas low
energy, less polar groups, such as $-\text{CH}_3$ or $-\text{CH}_2-$, would decrease the bondability of the surface.

1.2.3.3 Bulk adhesive properties

It has been established that interfacial forces play an important role in developing initial joint strength rather than during subsequent mechanical loading of the joint. In this respect, bulk properties of the adhesive are among the many factors that influence the ultimate strength of the adhesive joint. If it is assumed that interfacial strength has been maximised, and that the adherends are rigid and strong, it may be concluded that the strength of the joint is completely determined by the bulk properties of the adhesive.

The polymeric nature of adhesives means their mechanical properties are also dependent on glass transition temperature ($T_g$) of the polymer. The mechanical properties of uncrosslinked and unfilled polymers change dramatically around this temperature. The most often illustrated property is the effect on modulus; it can decrease $10^4$ fold as the polymer is heated from below to above the $T_g$. At temperatures far below the $T_g$ the glassy polymer cannot elongate to a large extent when stressed and generally breaks at very low extensions$^{22}$.

As most adhesives are polymers the strength of their intermolecular bonds is significant in controlling the cohesive strength of the adhesive. Adhesives comprise a mixture of compounds which interact with the surface and each other during the bonding procedure. This process, referred to as adhesive curing, involves the provision of energy to the adhesive system which causes a reaction of the adhesive mixture. As curing proceeds the viscous mixture becomes a rigid solid as the compounds react and cohesively link the adhesive, often referred to as crosslinking. This process enables strength to be established between the joined adherends. In this thesis consideration is
restricted to a PDMS-based room temperature vulcanisable (RTV) adhesive that cures via an addition reaction to form a three-dimensional (3D) network structure. The primary bonds that hold together a network polymer cannot be easily disrupted by heat, solvents or mechanical forces. The impact of crosslinking can be effectively demonstrated by vulcanising natural rubber. Natural rubber is soft and sticky but a typical rubber used in car tyres contains about 5% sulphur which produces about 500 carbon atoms. Forty per cent sulphur produces many more crosslinks and results in a hard rigid plastic. This example shows what a dramatic effect the degree of crosslinking has on the properties of the polymer.

The rheology of an adhesive also has great bearing on the strength of adhesion and cohesion. The large effects of rate and temperature on adhesion and cohesion of simple polymeric solids are due to viscoelastic processes. Viscoelasticity is concerned primarily with polymer deformation and its importance in adhesion processes lies in the fact that deformation that accompanies adhesive fracture can make an important contribution to the overall joint strengths. Strength properties are greatly enhanced by viscous resistance to internal motion, or more generally, by energy losses. In general, adhesives are applied in the liquid state and strength is developed during the subsequent solidification stage by a number of mechanisms the most relevant of which is the formation of a crosslinked polymer. However, although PSAs, such as the one used in the current study, do not change their physical states they must also wet the surface of the adherend like a liquid and sustain loads like a solid. This conflict is resolved by the dependence of mechanical strength on viscoelasticity. For engineering purposes the properties of an adhesive should be dominated by the elastic properties. PSAs have large viscous components which can be reduced by crosslinking. Increasing the rubbery response of an adhesive tends to improve joint strength. Shih and Hamed found that wax increased the poly(ethylene-co-vinyl acetate) (EVA)-rich phase portion of a heterogeneous EVA/rosin blend resulting in a higher rubbery response. The T-peel fracture energies of EVA/tackifier/wax blends bonded to polypropylene film were controlled by two factors: (1) a WBL, which has a deleterious effect on bonding; and (2) on the
other hand, an increased rubbery response in the stick slip region, which tends to strengthen joints.

From the polymeric nature of adhesives it is possible to assign the same mechanical properties as polymers. For example, modulus, strength in all its forms, such as tensile, fatigue, adhesive, creep resistance, toughness, and so on. However difficulty arises when attempting to specify optimum values for these properties. As with any polymer, these properties depend on factors such as service conditions, application, and type of adhesive, amongst others. For example, structural adhesives are normally the only load-bearing components of the structural assembly, and as such the demands and requirements of structural adhesives are greater than for most other adhesive types. A high performance structural adhesive should provide both rigidity for high tensile strength and the toughness and flexibility to resist high peel and impact forces of the service environment\textsuperscript{26}. On the other hand pressure sensitive adhesives do not require any load bearing capacity.

Mechanical properties of the bulk adhesive may also be manipulated by incorporating additive into the matrix of the material. For most commercially produced adhesives a range of fillers, antioxidants, and other additives are present that may provide additional toughening or crack arrest. Adhesives formed by polymerisation or crosslinking reactions are often brittle, glassy solids with poor resistance to impact and peeling forces. Impact and peel resistance can be improved by addition of a rubber toughener to the adhesive formulation. Improved impact resistance is achieved by introducing rubbery domains into the polymer morphology. Improved fracture toughness is attributed to the ability of the rubbery domains to absorb and dissipate energy associated with propagating cracks. In the simplest case this involves the dispersion of small rubber particles in a glassy polymer matrix. There are numerous examples of such toughening mechanisms and their impact on mechanical properties, including adhesion, in the literature\textsuperscript{27, 28, 29, 30}. In our case, adhesive properties were modified by incorporating small amounts of stearic acid into the silicone matrix. However, contrastingly, deterioration in
adhesive strength was observed. A more detailed consideration of the silicone chemistry is given in Section 1.5.

1.2.4 Stress distribution

The strength of a joint is determined by a number of different material characteristics, namely force, stress, strain, ultimate tensile strength, modulus, toughness, and brittle, elastic and plastic behaviour. The distribution of stresses within the system can be considered on different scales. For instance, on the largest scale the flexibility or rigidity of the adherends will determine the array of stresses operating in this region; from here the distribution of stresses within the bulk of the adhesive represents an intermediate point in the scale; and finally interfacial stresses correspond to the smallest area of consideration.

1.2.4.1 Stresses in the adherend

The ultimate method of testing the strength of adhesive joints is to measure the force or energy required to break a joint. Single lap shear joints (SLS) are easy to make and test but the distribution of stresses complicates their behaviour. Volkersen was the first to attempt to analyse the pattern of stress distribution. They are commonly used for testing joints made from rigid adherends and adhesives. The bending moments in SLS joints mean the adherends are no longer in simple tension but are bent. Goland and Reissner analysed the bending moments of the overlap region and found that the mean shear stress was concentrated very near the ends and that conversely the central region bears virtually no load. When the joint breaks, cracks will be initiated where stresses are greatest, and they will then propagate through the joint. Other configurations of the lap joint, such as the double lap shear
joint, are largely designed to improve load-transfer so that stress concentrations and peel are minimised.

Where at least one adherend is flexible, peel tests are conducted where the flexible member is peeled from the rigid adherend at a defined angle. The T-peel configuration is used where both adherends are flexible. Peel stresses are to be avoided at all costs by the joint designer. Hinopoulos and Broughton\textsuperscript{32} used finite element analysis (FEA) to investigate the effect of adherend properties and geometric parameters, amongst others, on joint performance as measured by T-peel. Studies on the specimen geometry showed that stress distributions were sensitive to adherend material properties. In general, stresses were reduced when changes in specimen geometry resulted in smaller joint displacements for the same load. Whereas the adhesive in lap joints at low loads is largely in shear, peel configurations experience predominantly transverse, tearing loads. For this reason peel joints are not intended to bear loads. There are many energy dissipating processes associate with peel such as work of adhesion ($W_a$) or cohesion ($W_c$), plastic deformation of the adhesive close to the fracture surface, viscoelastic dissipation as the peel front advances causing the adhesive to be stressed and then relaxed and for plastic and/or viscoelastic losses in bending the freed strip through the peel angle. Jayota, et al.\textsuperscript{33}, used finite element modelling (FEM) to illustrate stress distribution in the peel arms of a T-peel test configuration.

The stress concentration present in the end regions of the overlap of the adhesive layer in bonded lap shear joints when they are loaded can be relieved by methods such as tapering of adherends and/or using large fillets of adhesive. However, these can be costly to incorporate into component design or may not be practical due to possible damage to the adherends during machining. Also large fillets of adhesive are not easily controlled during manufacture and cure, especially when using a low viscosity adhesive or where access is limited. One technique is to utilise an adhesive bondline with variable modulus. In the past this has been tackled by either slightly
toughening the adhesive at the ends of the bond overlap or by using two
different adhesives. Both methods affect a step change in bondline modulus.
Fifton and Broughton\textsuperscript{34} investigated the behaviour of a graded modulus
bondline consisting of high and low modulus adhesives using finite element
modelling (FEM). The variable modulus bondline was modelled by assigning
different adhesive properties to specific regions of the bondline. The work
undertaken by these authors showed that variable modulus bondlines were
effective in reducing stress concentrations. In the present research FEM was
used to model our T-peel joint configuration in order to investigate the
influence of change of modulus on the measured adhesion.

1.2.4.2 Stresses within the adhesive

The requirement for an adhesive is that it is strong enough to withstand
stresses to which the object is normally exposed. In the event of a failure it is
preferable for the joint to break within the adhesive itself or at an interface
between the adhesive and adherend. In addition there is the conflict between
the need for the adhesive bonding to be strong enough to do its job and to
last, yet weak enough to be dismantled should there be a need to take the
joint apart. If it is assumed that bonding conditions are such that joint strength
is determined solely by bulk adhesive properties, it is commonplace to find
tremendous discrepancies between the strength of a joint and the bulk
properties of the adhesive. For example, the tensile strength of a butt joint
may be many times as great as the tensile strength of the adhesive. Alternatively the joint strength may be much less than the strength of the
adhesive\textsuperscript{35}.

When a joint is subjected to a mechanical loading the adhesive layer exhibits
a complicated pattern of nonhomogeneous multiaxial stress. The fact that
stress is not spatially uniform implies the presence of stress concentrations in
some regions. The consequences of localised stress concentrations can be
particularly severe in the case of hard brittle adhesives, which in addition often exhibit localised shrinkage stresses before any mechanical load is applied to the joint. The peak local stress in a brittle adhesive can be many times as great as the joint load per unit joint area, and can lead to failure at an extremely low level of the joint load\textsuperscript{35}.

With rubbery or viscous or plastic adhesives, the factor of localised stress concentration can be markedly alleviated by local stress relaxation, but the multiaxial character of the stress within the adhesive layer remains significant. For example, a simple tensile load on a butt joint translates into a nearly completely balanced triaxial stress, or hydrostatic tension, within the thin soft adhesive layer. Since the bulk modulus of an elastomer can be $10^3$ or $10^4$ times the Young’s modulus and since a viscous liquid can flow in response to a uniaxial tensile stress but not in response to a hydrostatic stress, it is clear that the uniaxial tensile behaviour of the adhesive material and the behaviour of the adhesive in a loaded joint are two completely different matters. Thus where the strength of a joint is indeed determined by the bulk properties of the adhesive, i.e. joints with rigid adherends and strong bonds across the interface, a meaningful development between bulk properties in terms of the complete pattern of response to multiaxial stresses; not merely the tensile strength of the adhesive material is suggested\textsuperscript{35}.

The thickness of the adhesive layer is of importance in most adhesive joints and should be controlled in tests of adhesion. Adams, \textit{et al.}\textsuperscript{36} investigated the influence of bondline thickness on the strength of structural adhesive joints with sheet steel and a rubber modified, aluminium filled single component epoxy adhesive, in lap joint under three point bending and tension and, in T-peel joints under tension, over a range of glue line thicknesses between 0.1 mm and 3.0 mm inclusive. A correlation was found between the bending moment induced across the overlap and the failure load. The thickness of the adhesive layer increases or decreases the joint strength depending on the type of joint involved. In shear, the adhesion level increases with decreasing glue line thickness\textsuperscript{37}, whereas peel strengths increase with increasing thickness\textsuperscript{38} as a sufficient quantity of adhesive is needed to dissipate energy.
Most joint designs seem to expect uniform adhesive, however, in some situations this is not always optimal. The works of Bryant and Dukes\textsuperscript{39, 40} investigates stress effects due to variation in bondline thickness. These investigators inserted copper wires in the centre of the bondline of joints to precisely control the bondline thickness and found no negative effect on the joint strength as compared to equal thickness bondlines without the wires. It might have been expected that such an inclusion would have introduced some altered stress effects changing the measured strengths. In some situations slightly thicker adhesive layers in high stress or strain regions can relieve stress concentrations. Adams, \textit{et al.}\textsuperscript{41} proposed that the adherends of a lap joint should be profiled so that the adhesive thickness can be varied along the length of the overlap while leaving the adherend thickness essentially constant. In general, however, excessively thick bondlines are to be avoided as they normally result in poorer strength. Kline\textsuperscript{42} found for adhesive thicknesses comparable to or greater than the adherend thickness, increasing adhesive thickness increased the peak stresses as a result of the increase in bending moment.

1.2.4.3 Stresses at the interface/interphase

For any particular structure, the attainment of an apparently strong adhesive bonded joint depends critically on the distribution of stresses within the bonded system. Many studies have shown that the interface should be more accurately considered as a three dimensional region, within which the properties differ from those of the bulk phases, termed an interphase. This accent redirects attention from the previous focus on forces across the interface towards the influence of the interphasial regions on the bonded structure as a whole. The three dimensional nature of the interfacial region means that a simple bonded joint can be thought of as a composite in the sense that its properties are the sum of the interaction between those phases joined and the interface between them. This viewpoint was instigated by
Good\textsuperscript{43} when he applied the Griffith-Irwin crack theory of fracture to a joint comprising a bond between two phases\textsuperscript{44}. The fracture stress, $\sigma_f$, is given by

$$\sigma_f = k(EG/l)^{1/2} \text{ (MPa)}$$

(1)

where $k$ is a constant, $l$ is the length of the critical crack and $EG$ is the product of the modulus and fracture energy. The modulus, $E$, arises in the Griffith theory as its value determines the amount of elastically stored energy at a given strain. It is this stored energy which is released providing fracture energy, $G$, when fracture occurs. Within the adhesive joint $E$ and $G$ are semi-local properties and fracture will occur where the term $EG/l$ is lowest, whether at or near the interface or within one of the cohesive phases. Therefore factors which alter $E$ or $G$ or $l$ locally within the joint may alter its strength.

Stress distribution at the interface has been attributed to low adhesion of a silicone containing polymer in some studies. In an investigation conducted by Amouroux \textit{et al.}\textsuperscript{45} the adherence of an acrylic tape on silicone elastomers containing various quantities of a silicone MQ resin by an instrumented peel test was studied. Their work was based on the findings of Bi-min Zhang Newby, \textit{et al.}\textsuperscript{46, 47}.

Newby and Chaudhury\textsuperscript{46} initially reported experimental results which confirmed that viscoelastic adhesives do slip on segmentally mobile organic surfaces during the peeling of a viscoelastic adhesive from a solid substrate. Evidence of slip was obtained from the interfacial displacements of small fluorescent particles when the adhesive was peeled from various substrates. A large slip was observed on segmentally mobile tethered chains of PDMS. The unusually low adhesion of silicone-containing polymer was attributed to the propensity of huge slippage exhibited by such materials.

Following on from this study, it was shown by Amouroux and colleagues\textsuperscript{45} that slippage exhibited was related to the composition of the elastomer in MQ.
resin, namely small silica-like particles inserted into the elastomer. High slip amplitudes were associated with low MQ resin content and resulted in weak shear deformations in the adhesive. Thus, depending on the composition of the elastomer the peel energy was dominated either by frictional losses associated with slip at the interface, low MQ resin content, or by viscous dissipation due to shear deformations distributed in the volume of the adhesive, in the case of high MQ resin content. Where the MQ resin content was low the ascribed mechanism led to a reduction in peel strength, thereby leading the authors to conclude that the associated affect on peel strength could be attributed to interfacial slip. The fact that the stresses generated in the interfacial region differed from those generated in the bulk indicates the role of stress distribution in controlling adhesion. A more detailed consideration of the physical and chemical environment within the interphasial region is given in Section 1.4.
1.3 Theories of Adhesion

Interactions occurring across an interface range from weak physical dispersion forces to hydrogen, covalent, and ionic bonding. Moreover, surface roughness can allow for a mechanical contribution to the observed joint strength. The type of interaction(s) occurring in a system depends upon the chemical constitution of the adhesive and the substrate, and the topography of the adherend surface. In the previous section the mechanical and chemical contributions to adhesion have been alluded to; however, there are several more existing theories for adhesion.

The following section is a discussion of established and newer theories for explaining the mechanism of adhesion. The traditional theories of adhesion are: mechanical interlocking\textsuperscript{12}, adsorption\textsuperscript{11} which is often sub-divided into the following categories: acid-base, physical and chemical, diffusion\textsuperscript{48}, and electrostatic\textsuperscript{49}. The weak boundary layer theory (WBL) is often grouped with these theories\textsuperscript{50}. Although not strictly a theory of adhesion, it does provide an explanation for why joints fail. It must be noted that physical adsorption is always present when there is intimate contact between molecules. In addition to these well-known theories there are some more recent models for adhesion. These include the rheological model, reviewed by Fourche\textsuperscript{51}; adhesion indices model put forward by Iwamoto 1995\textsuperscript{52}, the pressure sensitive model as discussed by Allen\textsuperscript{53} in a recent review of contemporary adhesion theories, the co-ordinate theory by Ye et al.\textsuperscript{54}; and Chung's\textsuperscript{55} unified theory.
1.3.1 Mechanical Interlocking

This theory provides the oldest explanation of adhesion phenomenon. The theory of mechanical interlocking puts forward the suggestion that adhesion occurs as a result of adhesive penetration into surface irregularities. Subsequent mechanical keying or interlocking of the adhesive is the major source of joint strength. Despite the prevalence of examples relating joint strength and durability to increased surface roughness in the literature, the theory is not universally applicable since good adhesion occurs between smooth surfaces, such as the adhesion that occurs between wet glass microscope slides. Also, it has been observed that increased roughness can result in lower joint strengths.

Mechanical interlocking can make a significant contribution towards the joint strength if the adherend surface geometry is specifically fabricated to enhance adhesive penetration. It is still debatable whether the increase in joint strength can be directly related to a mechanical interlocking mechanism or to secondary mechanisms such as an increase in specific surface area for chemical bonding or improved kinetics of wetting.

Adhesion by mechanical interlocking requires that the adhesive penetrates geometric irregularities on the adherend surface. Evidence of thermosetting adhesive penetration into the pores of an anodic oxide was presented by Hennemann and Brockmann. Penetration of the pores on aluminium anodic oxide surfaces by thermoplastic adhesives has also been demonstrated.

Penetration of the polymer into the oxide pores depends upon the wettability of the surface and the shape of the pore. Pore filling occurs until the pressure of the trapped gases equals the capillary pressure. It has been suggested that the shape of the pore, cylindrical versus ink bottle, is a crucial factor in controlling the pore filling process. Penetration of the adhesive into pores on the surface can contribute significantly towards high joint strengths, since it is
believed that the failing of ligaments of the adhesive or primer that enter the pores requires considerable plastic deformation, and thus high fracture energy. More recently, Packham and Johnston\(^{57}\) were able to vary the porosity of a ceramic by varying the firing temperature, and showed that the bonding strength of polyethylene to the fired ceramic was a function of the degree of porosity of the ceramic. In the same work, the authors conceded that adhesion by mechanical interlocking or keying is a contribution to the observed adhesive strength, and "at the very least, London dispersion force interactions between the adhesive and substrate" also exist.

Gent and Lin\(^{58}\), using uniformly perforated aluminium plates bonded with a vulcanised rubber adhesive, showed that when an elastic adhesive layer penetrates the pores, extra work, of up to 20% more than with planar aluminium adherends is required to cause de-bonding in a 90°-peel or a T-peel configuration. The extra work is due to the viscoelastic deformation of the adhesive in the pores as adhesive is pulled out. When the perforations were interconnected, extra work by as much as several hundred times was required to fail the joint. In the interconnected situation, the chemical bonds in the adhesive had to break for the joint to fail; this was reflected in the observed increased joint strength.

### 1.3.2 Physical Adsorption

Adhesion by this mechanism is attributed to surface chemical forces, and the chemisorption or physisorption of atomic and molecular species\(^{11}\). The attractive forces working across two surfaces include weak dispersion forces and stronger forces attributed to hydrogen, covalent, and ionic bonding\(^{59}\). Work conducted by Zisman and colleagues\(^{21, 60}\) demonstrated that van der Waals dispersion and polarisation forces are more than adequate to account for the observed strengths of adhesive joints. The types of bonds formed between two surfaces depend upon the chemical structure of the interface. In order for chemisorption or physisorption processes to occur across the
interface it is imperative that the adsorbate wet the substrate. In general, for spontaneous wetting, the surface energy of the solid must be greater than that of the liquid.$^2$

When these criteria are fulfilled then the thermodynamic work of adhesion between the solid and the liquid were expressed by Young as:

$$W_A = \gamma_s + \gamma_L - \gamma_{SL}$$  \hspace{1cm} (2)

where $\gamma_s$ is the surface energy of the solid, $\gamma_L$ is the surface tension of the liquid, and $\gamma_{SL}$ is the solid/liquid interfacial tension. It has been proposed that the surface free energy can be generally expressed by two terms corresponding to dispersion forces and to polar forces:

$$\gamma_s = \gamma_s^D + \gamma_s^P$$  \hspace{1cm} (3)

Carré and Schultz$^6$ using a two liquid contact angle method developed for high-energy solids, determined the surface energy of aluminium that had received various pre-treatments. By measuring the contact angle of water on the solid, in the presence of a non-polar liquid, they were able to demonstrate that surface pre-treatments affect the dispersion and polar components of the surface energy. A sulphuric acid anodised sample was found to have both a high dispersive component, and a high polar component of surface energy. This surface, in turn, exhibited a low resistance to corrosion. A chromate-phosphate conversion coated sample had a high dispersion component, but a lower polar component of surface energy. The chromate-phosphate coated specimen was found to be highly corrosion resistant. Carré and Schultz$^6$ concluded that for good “dry” adhesive joint strength, and for good durability in the presence of moisture, the surface should have a high dispersive component of surface energy, $\gamma_s^D$ and a low polar component, $\gamma_s^P$. The contribution of dispersion and polar components can then be used to predict
interactions at the interface. It was postulated that the work of adhesion, $W_A$, can be correlated to the measured joint strength$^{61}$.

Ahagon and Gent$^{62}$ showed that the observed adhesion of poly (butadiene) to organosilane treated glass increased by 35 times when the silane was vinylsilane, compared to ethylsilane. This was attributed to the formation of chemical bonds at the interface. However, adhesion to the ethylsilane and the vinylsilane treated glass was 25% greater than predicted by $W_A$ arguments. These higher than predicted values in joint strength were attributed to the energy absorbing, viscoelastic effects associated with polymer deformation, such as chain stressing and sliding. Table 1.2 illustrates the magnitude of the chemical and physical bonds involved in the adsorption theory of adhesion. It is evident that these bonds operate over short distances, hence the importance of wetting and intimate contact in bonding. This also highlights the importance of surface cleanliness as any contamination present on the surface of the adherend will obstruct these short range bonds.
Chapter I

Table 1.2 The Physical Characteristics of the Bond Types Attributed to the Adsorption Adhesion Mechanism\textsuperscript{59}.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Bond energy (kJ mol\textsuperscript{-1})</th>
<th>Equilibrium length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td>600-1200</td>
<td>2-4</td>
</tr>
<tr>
<td>Covalent</td>
<td>60-800</td>
<td>0.7-3</td>
</tr>
<tr>
<td>Secondary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>~ 50</td>
<td>3</td>
</tr>
<tr>
<td>Dipole</td>
<td>~ 2-21</td>
<td>4*</td>
</tr>
<tr>
<td>interactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>London</td>
<td>~0.08-42</td>
<td>&lt;10*</td>
</tr>
<tr>
<td>dispersion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Dipole interactions (also known as Polar forces) and Dispersion forces are often referred to collectively as van der Waals forces.

As mentioned earlier, the wetting and spreading processes are influenced by the geometric features of the surface, and by the presence of chemical functionalities that can alter the surface energy of the substrate. Using contact angle measurements, Lee\textsuperscript{63} determined the wettability of silica surfaces primed with reactive silanes. The wettability was determined by the conformation of the organic portion, R, of the silane molecule: R-Si(OR\textsuperscript{3}). Lee classified various silanes into three groups based on polarity of the R group. For example, if the R group was vinyl, the silane treated surface was classified as having low polarity, for amino- groups, the silane treated surface was classified as having medium polarity, and for glycidoxy- groups, the surface was classified as having high polarity.
1.3.2.1 Acid-Base Interactions

A number of authors have suggested that acid-base interactions may be, to a certain extent, responsible for the intrinsic adhesion forces at inorganic/polymer interfaces\textsuperscript{21}. Fowkes\textsuperscript{64} extended the viewpoint of bases as electron donors and acids as electron acceptors to the understanding of adhesion of polymers on inorganic surfaces, by proposing that the thermodynamic work of adhesion ($W_A$) could be separated into components of: London dispersion ($W_A^d$) forces, hydrogen-bond ($W_A^h$) forces, acid-base ($W_A^{ab}$) forces, dipole-dipole ($W_A^p$) interactions, and induced dipole-dipole ($W_A^i$) interactions.

Namely:

$$W_A = W_A^d + W_A^h + W_A^{ab} + W_A^p + W_A^i$$

In a later study Fowkes demonstrated that hydrogen bonding is a subset of the acid-base reactions. Using the Drago E and C constants and equations\textsuperscript{65}, Fowkes calculated the enthalpies of acid-base interaction between various hydrogen bonding liquids, and compared these calculated values with measured enthalpies of interaction. The calculated acid-base enthalpies agreed well with the measured interaction enthalpies, giving rise to Fowkes' claim that hydrogen bonds are a subset of acid-base interactions and that the work of adhesion between a polymer and an inorganic substrate could be accounted for by dispersion forces and acid-base interactions so that:

$$W_A = W_A^d + W_A^{ab}$$

Fowkes\textsuperscript{66} also submitted that it is possible to improve adhesive joint strengths by enhancing the interfacial acid-base interactions through proper surface modifications, including the use of organosilanes. Fowkes\textsuperscript{67} provides a review
of techniques that can be used to quantitatively characterize the acid-base properties of liquids, polymers, and inorganic surfaces.

In a metal/polymer system, both the polymer and the metal substrate can exhibit amphoteric behaviour. Bolger\textsuperscript{68} assessed that the only forces worth considering, in addition to dispersion forces, were hydrogen bonding forces, and used an acid-base mechanism to predict the relative magnitude of the hydrogen bonds. Since under ambient conditions, metal oxide surfaces are generally hydroxylated, the hydroxyl group can act as either an acid or a base.

The overall nature of acid-base interactions with solid surfaces in terms of electrostatic, charge transfer, exchange, polarization, and dispersion components was described by Lee\textsuperscript{70}. Among these, Lee considered the electrostatic (or ionic) and charge transfer (or covalent) to be the major components. Lee also described acid-base interactions in terms of density-functional theory, and provided an equation for the number of transferred electrons for solid interactions involving metals or polymers. Jensen\textsuperscript{70} provides a thorough review on the current theories of acid-base interactions with relation to surface chemistry and adhesion.

**1.3.2.2 Chemical Adsorption**

Adhesion involves all kinds of chemical bonding: covalent, hydrogen, van der Waals, metallic and ionic. However, only the first three types are relevant in organic coatings. A common example of metallic bonding is soldering. Ion implantation or plating in the electronics industry may involve ionic bonding\textsuperscript{55}.

As stated above only covalent bonding, hydrogen bonding and van der Waals interactions are present in organic coatings. Of the three types of bonds, chemical covalent bonds correspond to the highest interaction energies (60-
700 kJ mol\(^{-1}\)) and van der Waals, or physical bonds, interactions produce the weakest bonds (2-40 kJ mol\(^{-1}\)). Based on this information any adhesion due to the formation of chemical bonds at the interface will be strong. There are a number of examples where adhesive bonding has been shown to include primary chemical bonding in addition to secondary van der Waals interactions. This mechanism is demonstrated in the rubber-brass (Cu 70%-Zn 30%) adhesion. Polysulphur bonds appear between copper and elastomer vulcanised with sulphur. Chemical bonds also occur in bridging mechanisms, through coupling agents such as silanes, in glass-adhesive bonding\(^{51}\). However, this type of bonding is notoriously difficult to cultivate and requiring special conditions to do so.

It is intrinsically difficult to investigate chemical interactions because all the relevant information has to be collected from the surfaces exposed when joints have been broken\(^{53}\) and because only a small number of molecules are involved in chemical interfacial reactions\(^{51}\). However, the advent of surface analytical techniques such as XPS and SSIMS has produced clear evidence in a growing number of examples for covalent bonding and other interactions. The most extensive exploration in this area has been in connection with coupling agents particularly instigated by the composite industry where good bonding between the reinforcing fibres and the polymer matrix in which they are embedded is imperative\(^{53}\).

Adhesion by chemical bonding is frequently the foremost adhesion mechanism in the case of polymer-metal interfaces. From a structural point of view, the creation of such interfaces involves the passage from a crystalline metal structure to a complex molecular polymer structure. Chemical bonds are formed at the interface, usually as a result of a charge transfer from the metal to the polymer. For example in the case of aluminium deposited onto polyimide, Pireaux et al. established the existence of a C-O-Al complex followed by the formation of Al-O and Al-C bonds. The existence of C-O-metal complexes by the charge transfer from the metal to the polymer has been observed on Cu, Cr, Co, Ti, Ag, Au, and Pd, and seems to be a general characteristic of this type of interface\(^{53}\).
Boiziau and Lecayon\textsuperscript{53} emphasised the role played by a local electrical field in the activation and improvement of interfacial reactions. The grafting on a metal, such as Ni, Al, Pt, of a polymerisable organic molecule such as acrylonitrile, operates in various manners, depending on the polarisation of the metallic surface: grafting by terminal carbon for a negative polarisation; flat, in the absence of polarisation; and by nitrogen for a positive polarisation. In all cases covalent bonds are formed between the molecule and the metallic surface. However, a polymerisation reaction is only possible in the case of a negative or positive polarisation. In summary, Boiziau and Lecayon demonstrated that the establishment of a strong metal-polymer bond results from Lewis acid-base reactions activated by the interfacial electrical field.

1.3.3 Diffusion Theory

This theory characteristically applies to polymers when they show self-adhesion, or autohesion, and when they adhere to each other. The diffusion theory takes the view that polymers in contact may interdiffuse, thereby eliminating the interface\textsuperscript{48}. Such interdiffusion will only occur at temperatures above the glass transition temperature where the polymers are mobile. Furthermore, the polymers must be compatible, i.e. mutually soluble. However, as most polymers, including those with similar chemical structures such as poly(ethylene) and poly(propylene) are incompatible, i.e. have dissimilar solubility parameters; the theory is generally only applicable in bonding like rubbery polymers. For example, when surfaces coated with contact adhesives are pressed together, and in the solvent welding of thermoplastics.

In addition, since this theory requires that the adhesive and substrate are mutually soluble and possess significant mobility, the mechanism does not directly apply in metal-to-polymer adhesion\textsuperscript{11} except perhaps when primers are used. Allen\textsuperscript{68} argues that the penetration of polymers into interstices of a
metal surface involves a diffusion mechanism, although he admits that this is an extreme interpretation of the original proposals of Voyutskii\textsuperscript{48} that deal with the interdiffusion of polymers.

1.3.4 Electrostatic Theory

It is important to distinguish this from the mechanisms involving electron interactions involved in the discussions on physical and chemical adsorption theories of adhesion. Deryaguin and colleagues\textsuperscript{49} considered the adhesion and separation of a pressure sensitive tape from a rigid substrate. It was put forward that when these two substances of different electronegativity are in intimate contact, an electrical double layer will be formed at the interface. Thus, according to this theory, adhesion arose as a result of electrostatic effects arising from contact potential at the adherend/adhesive interface\textsuperscript{59}. Consequently, electron transfer is expected to occur between the adhesive and the substrate due to a difference in their electronic band structures. It was hypothesised that this transfer led to the formation of an electrostatic double layer at the interface, and subsequently to adhesion due to the attractive forces inherent in the double layer. Therefore, in order to separate the two layers, the electrostatic attraction of the double layer has to be overcome and this produces a potential difference between the two which will increase until there is an electric discharge\textsuperscript{53}.

In this theory the adhesive-substrate system is treated as a plate capacitor whose plates consist of the electrical double layer which is thought to occur between a polymer and a metallic substrate when they are brought into contact with one another. The energy of adhesion of the system is equal to the energy of separation of the two capacitor faces:

$$W = \frac{\delta^2 h}{2 \varepsilon}$$  \hspace{1cm} (6)
where $\delta$ is the surface charge density, $h$, the distance between the charge planes, and $\varepsilon$ the dielectric constant of the medium. The conditions for this theory are based on Paschen’s Law which says that the potential to initiate a spark discharge depends upon the quantity of gas between the electrodes, which is the product of the gap length and gas pressure. The distance $h$ is calculated from this law and connects $h$ to the discharge potential and to the pressure of the gas medium in which the discharge occurs. Deryaguin assumed that the energy of the capacitance is equal to the energy of adhesion and proceeded to show good agreement between these. In his experiments he compared the results obtained using a peel test to measure the energy of separation of a glass-poly(vinyl chloride) assembly with the discharge energy of a capacitor and found the results were in good agreement.

In 1982 Wake showed that the method used by Deryaguin to determine the values of the various terms in the calculation were circular and flawed. In addition, attempts to repeat Deryaguin’s measurements were unsuccessful, thus, largely discrediting this theory. Furthermore, the difficulty of proving the existence of an electrical double layer with the adhesive bond intact led many authors to believe that the electrical effect was a consequence rather than the cause of adhesion. However, the direct evidence of an electrical double layer at the interface without rupture of the assembly was confirmed by Possart’s experimental works on a low density polyethylene-aluminium assembly using scanning electron microscopy (SEM). This author also provided calculations for the electrostatic contribution to the total work of adhesion which showed that these contributions were quite small. Possart’s work succeeded in restoring the legitimacy of Deryaguin’s theory to a certain extent.

The interpretation of adhesion according to the electrical theory is only applicable in the case of incompatible materials and, despite the unpopularity of this theory, is considered the basis for adhesion for aluminium-grafted polyolefin assemblies obtained by melting, under pressure, the polymer in contact with the metal. Subsequently, a good correlation is observed between
electrical properties and adhesive strengths. Although the mechanism is likely to occur in metal/polymer systems, researchers have calculated, from charge densities at surfaces, that the electronic contribution to the thermodynamic work of adhesion ($W_A$) is small compared to the contribution from chemical interactions$^{72,73}$.

1.3.5 Adhesion Indices

The adhesion indices model put forward by Iwamoto$^{52}$ offers an alternative perspective of the adhesion phenomenon in terms of general dielectric components. He found that despite the wealth of studies which aim to explain both the mechanical and non-mechanical mechanisms and the specific interacting sites, it has been more difficult to correlate directly experimental results with these theoretical calculations$^{52}$. As a consequence of the contributing factors to adhesion, as discussed in Section 1.2, the adhesion indices model provides a general perspective of the adhesive bond in terms of dielectric indices and predictions of adhesive trends that are based on experimental results taken from literature values rather than absolute strengths determined by Iwamoto. He presented a perspective of adhesion using average property indices such as dielectric constant, dipole moment, and thermal conductivity. These indices were derived by comparisons of dielectric theories of adhesion and cohesion with comparisons to literature-based experimental data. The author applied his indicial theory to examples he termed, dielectric-dielectric and metal-dielectric, which may be translated as polymer-polymer and metal-polymer adhesion respectively.

In the first instance, dielectric-dielectric example, an energy term for the model for two components at the interface was stated as:

$$E \approx -\frac{1}{2} \mu_a \cdot R_a - \frac{1}{2} \mu_b \cdot R_b - \left( -\frac{1}{2} \mu_a \cdot R_b - \frac{1}{2} \mu_b \cdot R_a \right)$$  (7)
where $\mu = $ dipole moment; $R = $ reaction field; subscripts $a, b = $ components $a$ and $b$. This expression seeks to describe the interaction energy of various components at an interface. This expression was extrapolated from the simpler cohesive case where cohesion is proportional to $-1/2 \mu R$. This extrapolation was found to be qualitatively similar to quantum mechanical derivations in which the dispersion energy is proportional to the polarisability tensor and the electric field tensor. However, here moment is used instead of polarisabilities.

In the case of metal-dielectric adhesion the metal was not treated as a polarisable entity. However, the metal-dielectric interactions may be simplified since the metal has an additionally important mechanism due to the accessible conduction bands that reflect the associated electronically polarisable nature of the possible pathways. Theoretically such mechanisms contribute to the energy pathways of the metal-dielectric interface.

In the metal-dielectric example it was assumed that electric field interactions would describe the basic adhesive event. Based on electronic principles and average properties, the metal-dielectric surface can be considered analogous to a capacitive circuit. Thus, the energy loss within this system upon charging can be related, before and after, introduction of the dielectric to the following expression:

$$\Delta E = \left(\frac{1}{2}\right)C_0 V_0^2 - \left(\frac{1}{2}\right)CV^2$$

where $C = $ capacitance $= \varepsilon C_0$; $V = $ field strength with dielectric $= V_0/E$; $\varepsilon = $ dielectric constant; $C_0 = $ free space capacitance $= \varepsilon_0 A/D$; $V_0 = $ applied field without dielectric; $\varepsilon_0 = $ free space permittivity; $A = $ area of capacitor surface; and $D = $ distance between the capacitor plates. For adhesion, this model can be visualised using a discontinuous surface so that upon metallization, the metal-dielectric interaction can be considered as a series of capacitors. The surface interactions can then be extrapolated from analogous circuit
elements, assuming that the surface field is an extension of the bulk reaction field (R). The energy loss mechanisms can then be analogously extrapolated from the circuit properties so that the energy E at the target element (n) is:

\[ E(n) \propto -\left(\frac{1}{2} CV^2\right) \]  

Expanding this to the electric equivalents gives:

\[ E(n) = -(1/2)i^2pt = -(1/2)\frac{q^2}{p} \omega = (-1/2)C^2r^2p\omega \]

\[ = (-1/2)e^{2A/d}R^2p\omega \]

\[ = (-1/2)e^{3\varepsilon_0[A/d]}R^2\omega L/K \] (10)

where \( i = \) current; \( p = \) resistivity; \( t = \) time in seconds; \( A = \) area of surface dipole "capacitor" element; \( d = \) distance between dipole surface moments; \( \omega = \) angular frequency; \( R = \) reaction field of the dielectric; \( \varepsilon = \) dielectric constant of dielectric; \( \varepsilon_0 = \) permittivity constant; \( L = \) Wiedman-Franz constant of the metal; \( K = \) thermal conductivity of the metal; \( q = \) coulombs. Equation (10) will be related to the energy loss of the system as a whole. This simplistic model suggests that the adhesion of a dielectric to a metal surface will be related to the dielectric constant and inversely proportional to the thermal conductivity of the metal.

1.3.6 Rheological Theory

In his review of adhesion mechanisms Fourche\textsuperscript{51} relates the rheological properties of the adhesive to the adhesion of an assembly as measured by a peel test. He notes the variation of peel strength with separation rate and temperature and concludes that adhesion is closely dependent on the...
rheological characteristics of adherates; namely, their bulk properties. An expression relating the failure energy of an assembly, $W$, to two terms was developed and is as follows:

$$W = W_0 f(V, T)$$

(11)

where $W_0$ is the Dupré's reversible energy of adhesion depending on the surface properties of adherates, and $f(V, T)$ is a function of the separation rate, $V$, and the temperature, $T$. This factor accounts for the dissipation of energy resulting from the irreversible deformation of the viscoelastic solid adhesive during the failure propagation and only depends on the bulk properties of the adhesive.

From studies on the adhesive properties of model aluminium-elastomer assemblies, $g(M_c)$, a molecular dissipation factor has been introduced in equation 11 to account for the irreversible deformation of bonds in the chain between crosslinks or entanglements and depends on $M_c$, the molecular weight between two crosslinks of elastomer. The adhesive or cohesive failure energy is then stated as:

$$W = W_0 g(M_c) f(V, T)$$

(12)

The product, $W_0 g(M_c)$, represents the limit value of the measured failure energy in absence of viscoelastic losses (i.e. under conditions close to thermodynamic equilibrium). This relation explains quantitatively the variation of the adhesive and cohesive properties of elastomers with their degree of crosslinking (which is very sensitive to the surface treatment of the substrate, especially near the interface).

Equation 12 enables the quantitative connection of the failure energy and the reversible energy of adhesion, and also separation of the contributions of the
bulk and surface properties of adherates in the failure energy. This model is considered to be an improvement on the adsorption model of adhesion.

1.3.7 Pressure Sensitive Adhesion

In his discourse on the progress of developments in the adhesion science over the last forty years Allen\textsuperscript{53} reviews the theories of adhesion and their current status. Included in his review of the established theories of adhesion is a brief account of the mechanism by which pressure sensitive adhesives (PSAs) form strong bonds with the material with which they are in contact.

Pressure-sensitive adhesion is determined by the degree of wetting and by the energy of deformation of the viscoelastic adhesive until rupture or separation from the surface occurs. Adhesion can be enhanced by contact time and contact pressure. Both increase the area of wetted sections kinetically by flow of the adhesive. This is especially important for rough surfaces and crosslinked adhesives.

The role of deformation energy is best demonstrated by peeling a pressure sensitive tape from a rigid adherend\textsuperscript{45-47,74-77}. The modes of failure and peel strength are both affected by pulling rate and temperature\textsuperscript{74}. For example, cohesive failure tends to take place at low rates or high temperatures, with a transition to adhesive failure at higher rates and lower temperatures. Here the magnitude of the peel force is influenced by wetting. At still higher rates where the adhesive is pulled from the backing, the peeling force is dramatically lower and becomes independent of the pulling rate.

PSAs are well-known as adhesive tapes for domestic and commercial purposes. Unlike other adhesives it is imperative that they do not undergo curing or crosslinking so as to maintain their high viscosity liquid state. In these types of adhesives bond strength is imparted by the pressure used to
force the high viscosity fluid to flow thereby bringing it into intimate contact with the adherend surface. In the event that crosslinking takes place the adherate becomes hard and brittle, the bond ceases to exist in turn weakening the adhesive\textsuperscript{53}

### 1.3.8 Co-ordinate Force Bond Theory

The co-ordinate force theory is not a new theory in itself as it has its roots in Fowkes’ acid-base interaction theory\textsuperscript{54}. Furthermore, the theory of co-ordinate bonds was used by Zhou\textsuperscript{78} in studying the adhesion phenomena of PTFE and Li. The concept of co-ordinate forces was used to interpret selected adhesion phenomena that were difficult to explain using conventional theories. In this particular paper the authors used co-ordinate forces to explain why the adhesion strength of grafted-PE is significantly larger than ungrafted-PE\textsuperscript{54}.

In this study\textsuperscript{54} MPE, the grafting product of low density poly ethylene (LDPE), and MAH (maleic anhydride) were used to bond Fe and Al substrates. It was found that low levels of grafting exerted a huge influence on adhesion strengths despite the fact that such low grafting percentages did not significantly change the polarity of the PE. The authors attributed the high adhesion strength to the formation of co-ordinate forces and this was supported by data retrieved by XPS. The new chemical bonds formed in the interface of the adhesive and the metals were illustrated by XPS analyses of the bulk MPE and aluminium. The species of interest were oxygen in the bulk MPE and Al in the bulk. This information was compared to the same data collected from interfacial MPE and Al. Under suitable conditions, the lone pair of electrons of oxygen atoms are able to form co-ordinate bonds with the empty orbitals of metals such as Fe or Al. The binding energy of this type of bond (40-600 KJ mol\textsuperscript{-1}) is much higher than the force of van der Waals interactions (1-20 KJ mol\textsuperscript{-1}). By examining the chemical states of oxygen and
aluminium in the bulk and comparing these to their chemical states at the interface it was possible to identify the formation of co-ordinate bonds\textsuperscript{54}.

Following analysis of the interface of MPE new peaks at higher binding energies were found in addition to the peaks that were originally in the bulk. The authors attributed this to a change in the electron distribution and a reduction in electron negativity of some of the oxygen atoms in the interface. The formation of the co-ordinate bonds between the oxygen and the empty orbitals in the aluminium were believed to be the reason for the change of the peak positions. This assumption was proved by the shifting of the 2p peak of interfacial Al to a low energy position. Aluminium has two 2p peaks, one associated with the ion \textit{Al}^{3+} and the other with \textit{Al}. Since the \textit{Al}^{3+} ion has empty orbitals, the oxygen atoms in MPE will first co-ordinate with it resulting in a shift to a low energy position. Since the neutral \textit{Al} atoms have a relatively low electron negativity the transfers of electrons will be from the outer shell electrons of \textit{Al} to the oxygen atoms and hence to the carbon atoms resulting in the high field shifting of the 2p peak position of neutral \textit{Al} atoms. It was the formation of these energy bonds that caused the resultant increase in adhesion strength.

### 1.3.9 Weak Boundary Layer (WBL) Theory

Thin interfacial layers of low mechanical strength were predicted by Bikerman in 1967\textsuperscript{50}. In this theory, true interfacial failure would never occur, but the locus of failure in metal-polymer adhesion would be in a thin layer whose cohesive strength is low for some reason. As intimated this theory does not advance our knowledge of adhesion between materials but it does provide some insight as to why joints fail.

Some coatings or joints fail prematurely for a variety of reasons. Some of the reasons for this are listed below\textsuperscript{55}:
At times such failure can be attributed to inadequate surface preparation leading to contaminated or non-polar surfaces. Poor wetting or spreading prevents intimate molecular contact.

Structural defects such as air bubbles, voids, crevices, and other flaws may act as areas of stress concentration causing a joint to fail at stresses far below its mechanical strength. These voids, etc may also prevent intimate contact of the adhesive to the substrate surface.

A rigid molecular structure is present whereby there is not enough mobility for alignment to bonding sites may also contribute to loss of adhesion.

The inefficient distribution of polar groups, for example located on side chains or their uneven spacing, can lead to premature failure. In this position such groups only impose secondary effects on adhesion. In his study Chung⁵⁵, notes that polar groups in the polymer backbone gave higher adhesion than as pendant groups on the main polymer chain.

Internal stress/strain due to thick adhesive layer, high shrinkage, and non-uniform thermal expansion, corrosion in harsh environments heat, cold, water, salt, radiations, and fumes, amongst others.

The introduction of a WBL as a result of segregation and migration of low molecular weight material to the interface⁷⁹. In principle, all industrial polymers that contain a molecular weight distribution or low molecular weight additives (such as plasticizers, antioxidants, or stabilisers) are susceptible to this effect. Also in systems which have to be cured following application, the curing agent could be reduced in concentration due to specific adsorption on or chemical reaction with the metal (oxide) surface. This effect is very metal specific and may lead to a reduced crosslink density of a thin polymer film and hence to a reduced modulus or cohesive strength of the polymer adjacent to the metal.

Although interfacial failure probably occurs if adhesion is solely governed by surface energetic factors, it has become apparent that WBL formation occurs
very frequently in metal-polymer bonding. Its existence in many bonding systems has been demonstrated conclusively by XPS analysis of the interface\textsuperscript{79}. The Bikerman model is simple and was subject to criticism in the past\textsuperscript{61}. Nevertheless, as a consequence of surface analysis techniques it is now admitted that many cases of poor adhesion can be attributed to these weak interfacial layers.

The present study is concerned with Al/polymer adhesion but more specifically why this assembly fails at reduced loads when stearic acid is added to the adhesive mixture. Although there are numerous theories expounding the mechanisms required for a strong adhesive bond, only the WBL theory addresses the issue of poor bond strength and why it occurs.

1.3.9.1 The effect of stearic acid on adhesion

The release properties of stearic acid and its derivatives are very well established. Consequently, this property is frequently exploited in the polymer industry where stearates are commonly employed as mould release agents, slip additives and processing aids\textsuperscript{80}. Furthermore, stearic acid is used extensively in rubber compounding where, along with zinc oxide, it acts as an activator\textsuperscript{80}. In the light of the popularity of these materials it is surprising that very little investigation has been undertaken to elucidate the mechanism by which they operate\textsuperscript{81}. As a result, the cause of their release-property effects still remains something of a mystery. Despite this seeming lack of interest, a few authors have ventured to obtain an answer to this question. This present study is one of them, seeking to furnish the reader with a suitable answer. It must be stressed that the context here is the effect of stearic acid on a PDMS-based adhesive, thus any explanation supplied for this system may or may not apply to other adhesives. However, the following provides a summary of these studies. Firstly it is necessary to understand the role of stearic acid in polymer technology.
As mentioned earlier, a disproportionate amount of work has been undertaken to ascertain the origin of the release property of stearic acid. One such study by Schneberger and Nakanishi\textsuperscript{81} centres on the behaviour of fatty acids and selected fluorinated compounds applied at controlled surface concentrations, as release agents for polyurethane from cold rolled steel. The authors sought to determine which compounds were effective as release agents, in what concentration and the location of the release agents after demoulding. A variety of acids were chosen for the study, among them stearic acid. Stearic acid was used because it is a commonly used mould release agent; lower fatty acids were used to ascertain the effect of chain length on release behaviour. The investigations carried out by Schneberger and colleague revealed that saturated aliphatic acids exhibited release behaviour only above a chain length of 10 or 12 carbons and that the fatty acids were effective at lower surface concentrations as their chain length increased. Furthermore, it was established that stearic acid possessed an optimum level of operation in that stearic acid release increased only marginally above 0.034 micrograms/cm\textsuperscript{2}. Experiments were conducted to establish whether stearic acid formed a layer at the interface. Infrared studies of de-moulded eluted surfaces indicated that stearic acid at the interface was the cause of the observed enhancement of release properties, as it provided a WBL.

More than a decade later Packham et al.\textsuperscript{80} investigated the influence of carboxylic acid residues on adhesion, with particular reference to interfacial layers formed during the moulding of nitrile butadiene rubber (NBR) compounds. The sources of carboxylic acids were stearic acid, lauric acid; caprylic acid, arachidic acid, and their salts acid were zinc stearate and zinc laurate. The authors identified that the mould release of NBR was strongly influenced by residues from the polymer and compounding ingredients were demonstrated to form an interfacial layer during moulding. The carboxylic acid residues that comprise an important part of this layer were attributed to two potential sources: emulsifier residues in the base rubber and stearic acid added during compounding. Generally, it was found that mould adhesion decreased as the carboxylic acid concentration increased and those residues from longer chain acids such as stearic acid reduced adhesion to a greater
extent than those from shorter chain acids such as lauric acid. This was thought to be due to the propensity of the longer chain fatty acids to form films that were more prone to shearing. The interfacial evidence of this was obtained by XPS and SIMS. Both techniques provided evidence of carboxylic acid residues migrating to the interface. However, the evidence provided by XPS analysis was indirect as this technique was unable to directly identify the carboxylic acid residues. Instead the presence of zinc and oxygen on the rubber side of the interface were taken as rough surrogates for carboxylate residues such as zinc soaps. In essence these authors also attributed the deterioration of adhesion with fatty acid content to the formation of a weak boundary layer at the interface.

A few years later Packham in collaboration with other researchers\textsuperscript{82}, again investigated the effect on adhesion of additives on commercial composite films based on PVA. These were investigated by using SEM with other surface analytical techniques, such as X-ray diffraction, extended resolution scanning electron microscopy (SEM/X-SEM), XPS and thermal analysis. The results of this study led the authors of this report to conclude that in the absence of stearic acid pretreatment CaCO\textsubscript{3} filler particles bonded well to the PVA composite matrix. This observation suggested good adhesion and consequently enhanced mechanical properties in the absence of stearic acid pretreatment of filler particles. In addition, the surface energy of stearic acid treated CaCO\textsubscript{3} particles was reduced in comparison to untreated particles, thus lowering the work of adhesion between the matrix and the filler. This was attributed to be the cause of strain induced failure and the resultant particle de-wetting from the PVA matrix. The process of de-wetting was found to be instigated by an agglomeration of particles which acted as regions of stress concentration.

To date the most effective internal mould release agents have been found to be the metallic salts of carboxylic acid, specifically, zinc stearate and calcium stearate\textsuperscript{83}. An examination of the mechanism by which stearates act as internal mould release agents in matched metal die RP mouldings attributed this property to formation of a weak boundary layer by the stearate at the
interface of the mould surface and the fibre-glass part. Fletcher questions the common preconception that the stearates operate by migrating to the surface of the part to form a fatty monolayer between the part and the metal mould. His doubts are based on the propensity of the stearates to migrate to any significant extent during the relatively short cycle times in today’s processing environment. As a result of extensive investigations using SEM and X-ray energy dispersive analysis (EDXA) to determine whether statistically significant migration took place, it was possible to conclude that zinc stearate was present throughout the moulded polyester matrixes in an approximately homogenous manner. This result led the author to assert with confidence that the mechanism by which zinc stearate acts as an effective mould release agent was not explained by the migration and WBL theory. Instead, it was proposed that the zinc stearate operated by changing the surface force by a surfactant type alignment of the zinc stearate. To expand, the zinc molecule embeds itself in the polyester matrix and the fatty end of the molecule arranges itself between the surface of the polyester part and the mould.

It is clear, from the examples provided, that where investigations have been conducted into the release mechanism of stearic acid and its derivatives the formation of a weak boundary layer by migration to the interface has been identified as the principle culprit for its deleterious affect on adhesion. Although work by Fletcher has cast doubt on this explanation, by suggesting a change in molecular orientation at the surface. The release property of stearic acid can be considered to be analogous to adhesion or, more aptly, poor adhesion. The authors cited employed a variety of techniques to reach this consensus, illustrating that adhesion problems cannot be solved conclusively by any one method but that a combination of advanced surface analytical techniques is required. A number of the aforementioned techniques have also been used in the present study; details follow.
Adhesion is a complex phenomenon which cannot be interpreted using a single model to explain bonding given the broad range of both processes and materials which may be used in the bonding system. The main and established theories, put forward by various authors, for explaining the adhesion phenomenon are; mechanical interlocking; diffusion; physical adsorption; chemical adsorption; the acid-base theory, often all grouped together under the umbrella of adsorption theory; electrostatic; and weak boundary layer. The WBL theory does not explain adhesion but it does supply knowledge towards understanding why adhesively bonded joints fail prematurely. More recently developed theories include the use of properties such as dielectric constant, dipole moment, and thermal conductivity to derive the adhesion indices model. Then there are the coordinate model of adhesion; the pressure sensitive model of adhesion; and the rheological model of adhesion.

The theories discussed appear to differ from one another; however, there are premises that bind them all together. It has been stated that in order to obtain a strong adhesive bond intimate molecular contact must be achieved through spreading and wetting and also electronic interactions such as chemical bonds must be established. The latter condition ensures the formation of strong cohesive and interfacial bonds, thus, all of the theories discussed aim to fulfil these two pre-conditions. These theories are interrelated to a certain extent. For example it is a well established view that hydrogen bonding is a sub-set of acid-base theory and both of these models are considered to belong to the category of co-ordinate forces. These models may also be considered to be related to the physical adsorption theory in that thermodynamic characterisation of the solid surface by contact angle measurements provides their surface energy in terms of the dispersive and non-dispersive, including Debye, Keesom, and acid base interactions, components of this energy. The rheological model may be inserted here as
this theory seeks to determine the contribution of bulk and surface properties to adhesion energy. The adhesion indices model and the electrostatic model can be linked to each other by the fact that both models treat the materials as capacitors and assess the adhesion phenomenon from the perspective of its general dielectric components. In a broader sense these two theories may be related to chemical and physical adsorption theories by virtue of the electronic interactions that takes place in each of the theories.

Moreover, these theories generally agree that adhesion occurs by a synergistic combination of two or more mechanisms. For example, increasing the adherend roughness may contribute to mechanical adhesion, but because of capillary forces could also result in increased wettability of the substrate by the adhesive. The increased surface area could result in an increased number of total primary or secondary bonds between the adhesive and adherend, per geometric area. The synergism of adhesion mechanisms is illustrated by the work of Arrowsmith, et al. in the authors attempt to develop a new surface treatment for aluminium.
1.4 Interphase formation and interfacial effects

In classical thermodynamics the term interface is used to designate an interfacial region within which properties differ distinctly from the bulk phases or where there is a gradient in property change. The terms interphase or mesophase have recently been employed to emphasise the three dimensional nature of this region. The interphase is thought to play an important role in adhesive bonding. It is believed that many important factors in the performance of adhesive bonds depend on the nature of interphases. These include amongst other things transfer of stress. Since as previously discussed it can be concluded that the interphase region is the most critical in determining the effectiveness of adhesive bonds, a great deal of research effort has been made to understand, control and modify its properties.

The physical formation of an interphase has been demonstrated, for example, by Arayasantiparb et al. who used electron energy-loss spectroscopy and electron microscopy to provide evidence of pore penetration on phosphoric acid anodised aluminium surfaces. The formation of such nano-composite structures led Lee to describe interphases in terms of fractals. In detailing interatomic interactions for a number of adhesive/metal combinations, the presence of a weak layer at the interphase was mentioned by Lee. Packham has also described the nanometre-scale features of the interphase in terms of fractals but has argued that these features lead to a redistribution of stresses within the bondline leading to increased energy dissipation by the joint. An early realisation of the ability of surface roughness to redistribute stress leading to a larger volume of plastic deformation of the adhesive was reported by Evans and Packham with polyethylene bonded to chemically or electrochemically roughened copper, steel and zinc. Attempts to determine the mechanical properties of the interphasial polymer by in-situ monitoring have been carried out by a number of workers. Kim and Hodzic, for example, applied a range of techniques including; stereoscopic displacement analysis, nanoindentation and nanoscratch testing along with a number of...
atomic force microscopy (AFM) based methods to the study of the modulus and hardness of the interphasial material in glass-polymer composite materials. Phase imaging AFM was found to be particularly useful providing the necessary spatial resolution for such studies. In these studies the interphase was shown to be both softer and harder than the matrix depending upon the matrix/fibre/size combination chosen. Similarly, Cross et al.\textsuperscript{93} used FTIR and tapping mode AFM to investigate the interphase between glass fibres and Epon 828/NMA system. Phase imaging AFM showed the epoxy/NMA interphase extending to approximately 2.5 microns with this material not being fully cured (~75% cured only). In contrast, Zheng and Ashcroft\textsuperscript{94} used depth sensing nanoindentation across the bondline on epoxide bonded carbon fibre reinforced polymer (CFRP) joints. In the study by Zheng and Ashcroft no change was observed in the modulus and hardness indicating that there was no noticeable change in these parameters in the interphasial polymer. The authors do, however, point out that their measurements were limited by the lateral resolution of the tests performed.

The chemistry and cure reactions incorporating the interphasial polymer have been studied by a number of workers\textsuperscript{95-105}. For example, Bouchet and Roche\textsuperscript{95} discuss the topic of interphases, particularly those formed with epoxides. In this study, dicy monomer adsorbed onto the acid proton of the aluminium oxide. Diglycidylether of bisphenol (DGEBA) was adsorbed through opening of the oxirane ring. A 5754 alloy used with a DGEBA: diamine ratio of 1:1. Thin films were generated by varying the cure conditions to replicate the interphase so this could be more directly observed. Pure DGEBA created no chemical reaction. In contrast, two diamine monomers were studied. In both cases chemical sorption of the amine created partial dissolution of the oxide or hydrated oxide metallic ions then diffused within the monomer mixture to form organometallic complexes. Above a solubility limit chelates are crystallised forming a needle-like structure. During cure these crystals are not yet formed leading to phase separation and a new epoxy network. Interphase formation reduces practical adhesion by introducing residual stress. Similarly, Bracho-Troconis\textsuperscript{96} and Shanahan\textsuperscript{97} used DGEBA/dicyandiamide (DDA) system (1:1 ratio) in
epoxy/steel joints where the peel arm is degreased carbon steel bonded onto a stiff adhesive block. Also DGEBA/4,4'-diaminodiphenyl sulphone (DDS) in 1:1 ratio. 180 degree peel test used. For cure temperatures of 100 to 120 degrees variable cure times were used prior to contact with the steel. With contact times of 30 minutes or greater crosslinking occurred in contact with the steel. With measured energy of adhesion values independent of T at ~22 J.m-2. For lower times the energy is dependant upon the amount of unreacted DDA available.

Initial observations were made by Allen et al.98 and Sharp99. In a study reported in 1972 Allen et al noted thin glassy layers remaining on titanium alloy lap joints after testing, free from the filler and pigmentation associated with the bulk of the adhesive. Also at that time Sharpe commented upon the fact that the components within a bonded system were treated as discrete entities, that of two substrates and an adhesive when, in fact there are many more layers present in a bonded joint. Citing earlier work by Bikerman on weak boundary layers he expanded upon these arguments by reviewing work conducted upon polyethylene and their tendency to form such boundary layers. He acknowledged the existence of boundary layers in many types of joints but was reluctant to use the term weak for all instances.

Since then, many other workers have begun to study the interphasial chemistry between the adhesive and adherend. For example, Fondeur and Koenig100 conducted FTIR microscopy studies on aluminium substrates coated with an epoxide adhesive. They found that there was a variation of the dicyandiamide concentration within the thickness of the adhesive layer. Studying both the nitrile and carbonyl peaks they found that for untreated aluminium substrates there was a comparatively high level of dicyandiamide near to the substrates surface that coincided with a high level of carbonyl material. The opposite was observed for the CAA where the dicyandiamide content was at a minimum at the same distance from the substrate.

Nigro and Ishida101 conducted FTIR reflectance absorption spectroscopy on epoxide resin Epon 828 with a BF3-monoethylamine catalyst system applied
to polished 1008 Drawing Quality steel substrates. They studied the degree of conversion of the oxirane (epoxide) ring as a function of depth and found that epoxy conversion rates were higher closest to the steel substrate. The epoxy prepolymer was also applied onto the steel surface without hardener and the same phenomenon was still observed. They suggested that the steel might, in some way, interact with the epoxide adhesive causing homopolymerisation of the epoxide resin at the surface of the substrate.

Roche et al.\textsuperscript{102} studied the resultant interphases of a DGEBA epoxide when combined with either an aliphatic, aromatic or cyclic diamine curing agent and then applied onto aluminium or titanium surfaces. They found differences through the thickness of the adhesive layer; the $T_g$ was lower at the interphase for both substrates. The stochiometric ratio was higher nearer to the substrate with an amine:epoxy ratio of 1.2 as opposed to 1 within the bulk region. Placing the DGEBA and IPDA individually in direct contact with the aluminium and titanium substrates, they found that dissolution of the metal oxides occurred in the basic IPDA liquid. Taking samples of the reacted IPDA liquor and combining them with DGEBA, they measured the $T_g$, Young's modulus and the epoxide amine ratio. They compared this with the properties of the interphasial regions and bulk polymer regions. What they found was that the modified IPDA system had the same properties as the thin layer samples with reduced $T_g$, increased a/e ratio and differing Young's moduli.

Safavi-Ardebeil\textsuperscript{103} conducted experiments upon FPL etched A1100 aluminium substrates bonded with an epoxide adhesive, Hysol EA-9346. Sectioning the joints at various angles they were able to examine the bondline with nanoindentation. Nanoindentation revealed that there was a gradient of the Young's modulus, which increased by approximately 13\% in the interphasial region when compared to the values obtained within the bulk of the bondline. The concept of an interphase with a modulus intermediate to the reinforcement and matrix has been suggested. This is hoped to minimise stress concentrations which occur at interfaces between phases with drastically different moduli. Kardos et al.\textsuperscript{104} tested this hypothesis by preferentially crystallising the matrix in the vicinity of the reinforcing fibre.
surface in short graphite fibre/polycarbonate composites. It has been suggested that a restrained layer with higher modulus than the matrix is required for maximum bonding and hydrothermal stability\textsuperscript{104}.

Kollek\textsuperscript{105} used FTIR diffuse reflectance analysis to study the absorption chemistry of epoxide and phenolic resins on aluminium substrates. He observed that both the curing agent and the epoxy resin monomer were adsorbed on the aluminium oxide surface. They found that the Dicy monomer was adsorbed by the oxide layers of the substrate and was attributed to the acid proton of the aluminium oxide reacting with and reducing the observed nitrile peaks. For the epoxy monomer, less adsorption was observed and it was suggested that this occurred by the opening of the epoxide ring. Significantly, any anomalous physicochemical properties of this material could result in a reduction in joint strengths compared to what may be predicted considering bulk material properties.

Thin film studies can be conducted using DRIFT (Diffuse Reflectance Fourier Transform infrared) or by specular reflectance. ATR techniques can be used to study liquids by placing them on a crystal through which the infrared radiation is passed. In these studies, the ATR technique was employed to evaluate the chemistry of the adhesives as well as the near interfacial chemistry of the adhesive bonds.
1.5 Silicone chemistry

The term silicone is not used consistently. On occasion it is used to generically designate all monomeric and polymeric organosilicon polymers containing Si-C bonds and sometimes as a collective term for organosilicon polymers containing Si-O-Si bonds, therefore the term silicone, as adopted in the present study refers to polymers with the following structure

\[
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\text{Si-O-Si-O-Si-O-Si-O-Si-O-Si-O} \\
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R}
\]

Figure 1.1 The molecular structure of a silicone

where \( R = \text{Me} \). This is poly(dimethylsiloxane) (PDMS), the most commonly encountered silicone. Other groups can be substituted for the methyl groups along the chain, for example phenyl, vinyl or trifluoropropyl.

Note that "polyorganosiloxanes" is deemed to be a more precise term for these compounds rather than silicones; however, the name silicone continues to be used for simplicity of speech and because of an adherence to the older usage, which it would now be almost impossible to abandon. This terminology is, therefore, used throughout this report.
From the definition of silicones provided, these compounds can be characterised according to their general structural principles in the following manner\textsuperscript{106}:

- Silicones are polymeric and therefore possess the typical structural features of organic macromolecules.

- They contain Si-O bonds so are fundamentally identical with the units of silicic acids and silicates.

- They contain hydrocarbon radicals combined directly with silicon, therefore, structural units and bonds relate them to organic, especially organometallic and organosilicon chemistry.

It is possible to prepare silicone polymers ranging from low viscosity fluids to rigid cross-linked resins. So, as intimated silicone polymers can be categorised an unreactive fluids and resins and reactive functionalised polymeric monomers. The latter react to form silicone rubbers.

Silicone fluids are colourless fluids with viscosities ranging from very low to very high viscosity (0.1x10\textsuperscript{-6} to 1.0 m\textsuperscript{2} s\textsuperscript{-1})\textsuperscript{107}. This class can be further sub-divided into two classes: (a) dimethylsilicone fluids and (b) other fluids. As a class dimethylsilicone fluids are colourless, odourless, and practically non-volatile and non-toxic materials characterised by relatively high stability at high temperatures and are capable of maintaining their physical properties over a wide temperature range (-70°C to 200°C). The fluids have reasonably good chemical resistance but are attacked by concentrated acids and alkalis. In general, the dimethylsilicone fluids are soluble in aliphatic aromatic hydrocarbons and chlorinated hydrocarbons, which is to be expected from the low solubility parameter of 14.9 MPa\textsuperscript{1/2}. They are insoluble in acetone, ethylene glycol; and, water as these possess higher solubility parameter. The silicone fluids are very poor solvents, the poly(dimethylsiloxanes) being the worst\textsuperscript{107}.
Silicone resins are prepared batch-wise by hydrolysis of a blend of chlorosilanes. In order that the final product shall be crosslinked a quantity of trichlorosilanes must be incorporated into the blend. Their crosslinked nature means that they have very good heat resistance but are mechanically much weaker than the corresponding organic crosslinked materials. This weakness may be ascribed to the tendency of the polymers to form ring structures with consequent low crosslinking efficiency and to the low intermolecular forces. The resins are good electrical insulators, particularly at elevated temperatures and under damp conditions\textsuperscript{107}.

Silicone rubbers are formed as a result of reactions between polymeric monomers consisting of a variety of functional groups such as hydroxyl, vinyl, silyl, methyl, amongst others. Mechanical strength is imparted by the addition of suitable inorganic fillers and the characteristic elastic properties are obtained as the result of intermolecular crosslinking in the presence of an oxidising curing agent\textsuperscript{108}. Dimethylsilicone rubbers consist of very high molecular weight linear gums crosslinked after fabrication. The type of rubber obtained depends on the functionality of the monomer used. For example a mono-functional material will limit the molecular weight of the final rubber; a di-functional monomer will produce a high molecular weight linear gum; and a tri-functional monomer will lead to crosslinking\textsuperscript{107}. The important properties of the rubbers include their temperature stability, retention of elasticity at low temperatures and good electrical properties. Silicone rubbers are widely used in many applications where flexibility at extremes of temperature, beyond the limits of other synthetic or natural rubbers, is desirable\textsuperscript{109}. These rubbers also boast outstanding resistance to high temperatures and are unique in retaining their flexibility at temperatures as low as -80°C. However, at normal temperatures their physical properties such as tensile strength, maximum elongation and tear resistance are inferior to those of other rubbers. Compared with organic rubbers the silicones have a very high air permeability being 10-20 times as permeable as the organic rubbers. Thermal conductivity is also high, roughly twice that of natural rubber\textsuperscript{107}. 
As detailed, the silicones can be classified as unreactive fluids, crosslinked resins and reactive functional polymeric monomers that form rubbers. The class of interest in this study is the silicone rubbers. Although the rubbers possess a number of properties which make them attractive to a wide range of industries, it is its adhesive properties that are of particular interest in this study. The silicone rubber used in this report, namely Sylgard 184™, is a two-part RTV adhesive manufactured by Dow Corning.

1.5.1 Sylgard 184™

Sylgard 184™ (hereafter referred to as simply Sylgard 184) is designed to be a two-part medium viscosity liquid silicone rubber which, when cured, form flexible rubber encapsulants giving environmental protection and electrical and physical stability designed for use as potting encapsulants. In two-part systems the polymer base and crosslinker system are packaged separately. The catalyst, inhibitor, fillers and other additives, including the adhesion promoter are formulated with one or the other parts of the package depending; on their chemical reactivity (in this case the catalyst is formulated with the crosslinker). Overall a silicone adhesive formulation based on the hydrosilylation reaction may contain several components (Table 1.3). This reaction is described in the following section.
<table>
<thead>
<tr>
<th>Component</th>
<th>Polymer/additive</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>Alkenyl functionalised PDMS</td>
<td>Backbone of silicone cured network</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>Si-H functionalised polymer PDMS</td>
<td>Crosslinks alkenyl PDMS</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum-based complex</td>
<td>Fast and controlled cure at room or elevated temperature</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>Various organic or organosilicone type</td>
<td>Delays cure at room temperature and increases pot or bath life</td>
</tr>
<tr>
<td>Inorganic or organic filler</td>
<td>Silica, carbon black</td>
<td>Reinforces mechanical strength</td>
</tr>
<tr>
<td>Pigment</td>
<td>Various metallic oxides</td>
<td>Colour/thermal stability</td>
</tr>
<tr>
<td>Adhesion promoter</td>
<td>Various silanes and proprietary complex compounds</td>
<td>Enhance adhesion of silicone to specific substrates. Prolonged durability.</td>
</tr>
</tbody>
</table>

| Table 1.3 | Typical components of a silicone adhesive based on hydrosilylation cure system. |

Sylgard 184 is cured by an organometallic crosslinking reaction. The siloxane base oligomers contain the reactive vinyl groups. The crosslinking oligomers contain at least three silicon hydride bonds each. The curing agent contains a proprietary platinum-based catalyst that catalyses the addition of the SiH bond across the vinyl groups, forming Si-CH₂-CH₂-Si linkages. The vinyl groups are usually placed at the end of the polymer base chains and the SiH groups are usually placed in a combined structure within the crosslinker. The multiple reaction sites on both the base and crosslinking oligomers allow for three-dimensional crosslinking. One advantage of this type of addition
reaction is that no waste products, such as MeOH, EtOH, H₂, are generated. The final product can be modified by varying the ratio of curing agent to base oligomer, for example increasing the ratio of curing agent to base a harder, more crosslinked rubber results. Heating will also accelerate the cross-linking reaction again producing a harder more crosslinked elastomer.

The cure process for this product is via an addition, or hydrosilylation, reaction. The following mechanism, entailing the oxidative addition of the =SiH on the Pt, followed by H (hydrogen) transfer on the double bond in the β-position, and finally reductive elimination of the product. The main steps of this process, as proposed by Dow Corning, are illustrated below:

\[
\begin{array}{c}
\text{=Si-CH=CH}_2 \\
\cdot \\
\cdot \\
\cdot \\
\text{Pt} \\
\downarrow \\
\text{=Si-H} \\
\text{⇌} \\
\text{=Si-CH}_2-\text{CH}_2-\text{Pt-Si⇌} \rightarrow \text{=Si-CH}_2-\text{CH}_2-\text{Si⇌} \\
\text{=Si} \\
\text{H} \\
\end{array}
\]

D. J. Campbell et al. used Sylgard 184 in their study and proposed the following molecular structure for the base and cross-linking oligomers. In their study the authors also put forward a possible cure reaction for this PDMS-based elastomer. Both the base and cross-linking oligomers along with the proposed cure reaction are illustrated in the figure below:
Chapter 1

Literature Review

**Figure 1.2** Proposed cure reaction for Sylgard 184\(^{111}\).

The product of this reaction is a crosslinked 3D network structure. Other crosslinking routes available to silicone polymers are by condensation and with radicals. As these mechanisms exceed the bounds of this study, they will not be discussed further.

The hydrosilylation reaction is notorious for the side reactions frequently observed during the process of crosslinking\(^ {112}\). However the crosslinking reaction is the primary route\(^ {113}\). Simpson et al.\(^ {113}\) studied the addition reaction and associated side reactions for a hydrosilylation reaction of a terminal vinyl with a silyl polysiloxane crosslinker from Dow Corning. These reactions are shown below:

The primary addition reaction:

(Crosslinker) \(-\text{Si-H} + \text{CH}_2=\text{HC-Si- (Polymer)}\)

(Pt Catalyst + heat) \(\rightarrow\text{Si-CH}_2\text{-CH}_2\text{-Si- (3D network)}\) \(\text{(13)}\)
Chapter I Literature Review

The first of the secondary reactions is the catalysed hydrolysis of SiH groups as follows:

\[
\sim \text{-Si-H} + \text{H}_2\text{O} (\text{Pt Catalyst + heat}) \rightarrow \sim \text{-Si-OH} + \text{H}_2 \quad (14)
\]

The newly formed silanol group (SiOH) then catalytically reacts with remaining SiH groups to form a type of crosslinking via Si-O-Si bonds:

\[
\sim \text{-Si-H} + \text{HO-Si} \sim (\text{Pt Catalyst + heat}) \rightarrow \sim \text{-Si-O-Si-} \sim + \text{H}_2 \quad (15)
\]

Another secondary reaction is the condensation of two silanol groups formed via the catalysed hydrolysis of SiH (see above)

\[
\sim \text{-Si-OH} + \text{HO-Si} \sim (\text{heat}) \rightarrow \sim \text{-Si-O-Si} \sim + \text{H}_2\text{O} \quad (16)
\]

The platinum catalysed reactions in equation 14 and 15 are slower than the primary crosslinking reaction (equation 13). It is expected that silanol condensation reaction (16) is even slower than the SiH reactions (14) and (15). Reactions (14) and (16) are jointly referred to as post cure reactions. These reactions produce crosslinks in a siloxane network when they occur between different molecules.

1.5.2 Influence of interfaces on rates of crosslinking

Many industrial applications require fast curing silicone systems that homogeneously crosslink throughout the bulk of the material\textsuperscript{113}. Systems that rely on hydrosilylation reactions effectively satisfy this need. The reaction is controlled by variables such as temperature, level of catalyst and the molar ratio of the crosslinker to the reactive group. All of these parameters enable control of the final performance of the silicone product.
Many applications rely on the elasticity imparted by the 3D silicone network. The performance of a coating especially its mechanical and adhesion properties is governed by the extent of crosslinking and by any residual chemical groups in the bulk material and at interfaces. There are numerous methods for measuring reaction rates in bulk crosslinking polymer networks but they cannot be easily applied to thin films and coatings. As a result, knowledge of crosslinking kinetics and mechanisms in PDMS is mainly drawn from studies of the bulk material with much less work being performed on thin films\textsuperscript{114}.

Over the past few decades the profundity of the impact of interfaces on polymer structure and dynamics has been discovered. The two major reasons for why the coating-substrate interface might influence the kinetics of crosslinking and curing in thin silicones coatings are surface segregation and chemical reactions with a substrate\textsuperscript{114}.

To lower the interfacial energy, a reactive component in a silicone formulation might segregate to the interface. Consequently, there will be an excess of the component at the interface and depletion in the bulk. Silicones typically contain a catalyst and an inhibitor to control catalysis rate. If this fine balance is upset by surface segregation of either, the rates of the reactions are likely to be affected. On the other hand, the presence of an interface with a substrate opens up the possibility of reactions that will compete with the silicone crosslinking reaction. Silyl groups contained in the crosslinker are known to be reactive with silanol (SiOH) or hydroxyl groups on a substrate. It has been found that SiOH chain ends will bond to interfacial hydroxyl groups, which in turn will restrict the transport of molecules at the interface\textsuperscript{114}.

In the present study modification of the bulk adhesive with stearic acid has resulted in a substantial reduction in joint strength of an aluminium bonded adherend. It is possible that stearic acid inhibits the formation of crosslinks via the primary reaction (13) by promoting the ordinarily much slower side reactions. It is also possible that migration of stearic acid to the interface of the joint upsets the fine balance of catalyst and inhibitor which determine the
rate of the crosslink formation. Either mechanism would result in a reduction in bulk cohesive strength and subsequently adhesion.

1.6 Experimental techniques

A variety of factors affect the quality of adhesively bonded joints, for example surface preparation and the strength of the adhesive itself, thereby underscoring the need for a medley of analytical techniques when attempting to solve adhesion problems. In a survey conducted by a large number of analytical techniques were identified, which have been applied to adhesion studies with aluminium alloy adherends. It has been identified that the interface plays an important role in determining joint strength. In addition the contribution of bulk adhesive properties, with respect to cure kinetics, has been recognised. The experiments carried out within this study have been chosen to enable maximum characterisation of the contribution of both aspects of the problem.

Initially, the strength of the adhesive with and without stearic acid will have to be measured and compared, and this will be achieved primarily using the T-Peel test. This test was also used as a way of inducing failure in the joint so that surface studies of the two types of joint could be carried out. With particular regards to this the surface effects of stearic acid will be investigated using two main surface analytical techniques. These are static secondary ion mass spectroscopy (SSIMS) and X-ray photoelectron spectroscopy (XPS). However, these will be accompanied by complementary surface analysis techniques such as scanning electron microscopy (SEM), and attenuated total reflectance (ATR) spectroscopy. ATR will also be applied to identifying any differences in bond formation in the locus of failure. As far as investigating the effect of stearic acid on cure kinetics, differential scanning calorimetry (DSC), both conventional and modulated temperature (MTDSC), in the modified and unmodified case will be used. Fourier Transform infrared (FTIR)
spectroscopy will be used to follow the progress of the cure reaction and the extent of conversion measured and compared, and in addition solvent swelling methods will be used to measure the crosslink density of the adhesive. The experimental techniques outlined above will be described in greater detail in terms of their basic principles, advantages and limitations, and their use in this study. Table 1.4 summarises the purpose of each experiment.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-peel test</td>
<td>Measure adhesive strength</td>
</tr>
<tr>
<td></td>
<td>Generate failure surfaces</td>
</tr>
<tr>
<td>Single lap joint (SLS)</td>
<td>measure for adhesion strength</td>
</tr>
<tr>
<td>Surface analysis</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Failure mode analysis</td>
</tr>
<tr>
<td>SSIMS</td>
<td>Failure mode analysis, qualitative surface analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>Failure mode analysis, quantitative chemical analysis</td>
</tr>
<tr>
<td>ATR</td>
<td>Failure mode analysis, identification of chemical/molecular groups</td>
</tr>
<tr>
<td>Kinetic analysis</td>
<td></td>
</tr>
<tr>
<td>Differential scanning calorimetry</td>
<td>Determination of effect of stearic acid on kinetic constants E and A</td>
</tr>
<tr>
<td>FTIR</td>
<td>Study effect of stearic acid on cure reaction rate</td>
</tr>
<tr>
<td>Solvent Swelling</td>
<td>Determine effect of stearic acid on crosslink density</td>
</tr>
<tr>
<td>Tensile test</td>
<td>Effect of stearic acid on bulk adhesive mechanical properties.</td>
</tr>
<tr>
<td>FEA</td>
<td>Comparison of unmodified adhesive mechanical properties with modified adhesive properties on stress distribution</td>
</tr>
</tbody>
</table>

**Table 1.4** A summary of experimental techniques and their uses in the present study

What follows is a detailed description of these techniques in the order they were carried out in this research.
1.6.1 Strength of Adhesive Joints

The aim for any adhesive is to give joints that are fit for their intended purpose. The ideal test for adhesive strength is to measure the force or total energy needed to break a joint. Bonded materials are subjected to various stresses\(^9\), so to fully evaluate a bonded system a number of different test methods are necessary to gauge the relative durability of both the materials and the processes used. A number of them are described by Kinloch. The most common test configurations in the adhesives industry are the single lap joint, the double lap joint, the cylindrical butt joint and the peel joint. These configurations are the subject of standards documents. Tod\(^{116}\) lists five main purposes for adhesion tests:

1. to check the quality of an adhesive to see if it falls within defined limits;
2. to determine the effectiveness of a surface pretreatment;
3. to gather data for the prediction of joint performance;
4. to select an adhesive from a group for a specific application;
5. to evaluate the effect of ageing.

The selection of a particular configuration must consider the nature of the adhesive; a test suitable for a rigid structural material is unlikely to be useful for an elastomeric system such as an adhesive tape\(^{117}\).
Figure 1.3 Common joint (a) butt; (b) single lap; (c) wedge; (d) 90° Peel; and (e) T-peel, configurations for adhesive strength tests\(^9\).

The T-peel was the primary test method for adhesion in this study as both adherends were flexible Al foil and the adhesive was pressure sensitive. However, for comparative purposes the single lap joint (SLS) was used in addition to the T-peel test results.

### 1.6.1.1 Peel test

The results of a peel test are defined as the average peel force per unit width of the strip peeled. In a peel test, the force is applied so that a flexible member is peeled either from a rigid plate or a second flexible member. The force recorded gives a measure of adhesion. There are many variations on this test, two of which are depicted in Figure 1.3, (d) and (e). In peel tests the substrate is more often rigid and the flexible member is peeled at a defined angle. It is obvious that the 'peel angle', which may be present at 90° or 180° or variable, is a formal angle between the lines of action on the substrate and
the peeled strip, cannot be the actual angle at the point of fracture: for any given formal angle this will vary according to the bending stiffness of the peeled member.\(^{118}\).

The advantage of the peel test over other adhesion tests is that each strip peeled yields a trace which shows how the force varies along the whole distance peeled, whereas other adhesion tests only give a single estimate of strength from each piece tested, for instance, the ultimate stress at failure in shear tests and tensile tests. Peel strength at a particular angle is determined in the following way:

\[
P_{\pi/2} = F/b \quad \text{at } 90^\circ \quad (17)
\]

and

\[
P_\pi = 2F/b \quad \text{at } 180^\circ \quad (18)
\]

Taking an average in peel tests enables deviations from the mean and any systematic variation along the sample to be easily seen.\(^{118}\).

Generally, designers and materials engineers see peel tests as a measure of toughness.\(^{45}\) It is now known that peeling viscoelastic materials involves several dissipative mechanisms, localised in different zones relative to the fracture tip. At the fracture tip, the work of adhesion \(W_a = \gamma_1 + \gamma_2 - \gamma_{12}\), where \(\gamma_1\) and \(\gamma_2\) are the surface tension of the adhesive and of the substrate, respectively; and \(\gamma_{12}\) is the interfacial tension between the adhesive and the substrate, is necessary to separate the two bodies and create new free surfaces (Duprê). In the case of viscoelastic materials, substrate-adhesive-air contact line is not straight but forms a periodic wave pattern due to instability analogous to the meniscus instability in hydrodynamics. This periodic structure leads to the formation of columns of adhesive that are elongated in the direction of the peel force. The corresponding work of adhesion may form an important part of the peel energy. Some work may also be dissipated far
from the fracture tip inducing a compression which in turn gives birth to a shear stress field. The resistance of the interface to shear stress could indeed have an important effect on the final peel force. Work by Amouroux et al.\textsuperscript{45} demonstrated that for a silicone elastomer the possibility of slip motions at the interface was an important factor affecting peel strength. For small amounts of silicone resin content in the PDMS matrix, interfacial slip was found to be extensive and the peel energy was low compared with high amounts of resin where the peel energy was higher. Thus the control of slip at the interface was found to be an efficient way to adjust the peel force.

1.6.1.1.2 Peel Force and Energy

It is evident that, to peel one layer of substrate from the other, energy must be provided in the form of external work. This external work can be distributed between several deformation and failure processes\textsuperscript{119} in the following way:

\begin{equation}
G_A = \frac{1}{B} \left( \frac{dU_{ext}}{da} - \frac{dU_s}{da} - \frac{dU_{dt}}{da} - \frac{dU_{db}}{da} \right)
\end{equation}

where $G_A$ refers to the adhesive fracture toughness, $U$ is an energy term and the suffixes ext, s, dt, and db refer to external, strain, dissipation in tension and dissipation in bending. The adhesive fracture energy can be determined from the peel forces using the well established relationship

\begin{equation}
G = \left( \frac{P}{b} \right) (1 - \cos \theta)
\end{equation}

Many factors contribute to adhesive strength including peel angle, peel rate, adhesive rheology and surface energy of the substrate. However, all these factors have been investigated previously using stiff substrates such as glass or steel. When Steven-Fountain et al.\textsuperscript{120} used equation 20 to convert the peel
forces obtained from peel tests on rubber (flexible) substrates to $G$ different results were obtained. In particular the influence of the peel angle on peel strength was reversed. The authors attributed this result to the omission of the effect of substrate extensibility. In essence equation 20 was deemed to be inappropriate for the case where the substrate is flexible. Data obtained in the study showed that misleading results could be obtained even when the assumptions of equation 20, these being no tensile deformation of the peeling arm, no bending stiffness and no irreversible deformation in the arm, are being obeyed. Subsequently, it is foreseeable that erroneous results will be obtained if equation 20 is applied to situations where there is some tensile stretching of the arm or bending resistance or irreversible deformation in the leg. Consequently, the authors concluded that adhesive fracture energy should not be calculated using equation 20 in experiments where the substrate is flexible even when the pertinent assumptions are satisfied experimentally.

Moore and Williams\textsuperscript{119} define $G^{db}$ as a strain energy release rate and a complex function determined by using elastic-plastic large displacement theory. In order to determine the adhesive fracture toughness without neglecting any of the elastic or plastic deformations it is essential to conduct a peel test whereby the peel angle is controlled and tensile stress/strain measurement of the peel arm up to fracture.

In the present study a T-peel test has been conducted on the specimens in order to obtain a value for the adhesive strength of the silicone rubber adhesive. Figure 1.4 shows an example of a T-peel joint where the two peel arms are made from different materials. In this situation the stiffness of the two materials will differ so that the peel angles will be $\phi$ and $\theta$ (rather than 90\textdegree)\textsuperscript{119}. However, in the current work the adherends are both aluminium and are the same dimension, i.e. width, length and thickness, so there is no difference in stiffness. Also in this test the angle of each peel arm was 90\textdegree.
In their analysis of the T-peel test geometry, Moore and Williams initially considered both peel arms. However, since the two peel arms in the current work are the same, and their peel angles are also the same symmetry can be applied allowing only one peel arm to be considered in the analysis. This enables the following energy terms to be reduced to one overall expression (2000):

\[ G_A^1 = (G_A^{Eb})^2 - (G_A^{db})^2 \]  \hspace{1cm} (21)

\[ G_A^2 = (G_A^{Eb})^2 - (G_A^{db})^2 \]  \hspace{1cm} (22)

\[ G_A = G_A^1 + G_A^2 \]  \hspace{1cm} (23)

In the current example \( G_A^1 = G_A^2 \) as the adherends are from the same material so \( G_A = G_A^1 = G_A^2 \).
The two terms for the dissipated energy expressions (equations 21 and 22) arise as a result of the differing peel arm materials. Aside from this the peel toughness terms are similar to those for the fixed peel arm test.

1.6.1.2 Single Lap Shear Joint (SLS)

Single lap joint testing was chosen as it is one of the simplest joint configurations and also one of the cheapest for process control and in the evaluation of processing variables. Although single lap joints are straightforward to build and test, the arrays of stresses that arise during this test are shear and direct both of which are exceedingly non-uniform\textsuperscript{118} causing rotation of the overlap, thereby, rendering their behaviour complicated and difficult to interpret. As a result of the joint configuration, during loading the substrate can undergo severe bending which results in the applied strain not being equal over the length of the bonded area. This causes the shear stress to be higher at the ends of the debonded area, perpendicular to the applied load and be reduced near the centre of the bonded area. This means that the shear stress is never as simple as the load divided by the bonded area. Consequently, the test does not measure any true shear stresses. Despite these complications, the single lap joint test remains widespread because of its simplicity and the commonality of its joint configuration\textsuperscript{121}. It is used in the current research as a comparative tool to the peel test to investigate whether measured reduction in adhesion with stearic acid addition can be reproduced in another test where the distribution of stress differs.

1.6.1.3 Finite Element Analysis (FEA)

FEA is a well established means for mathematically modelling stress analysis problems and many other problem types. A comprehensive review of the
FEA technique is given by Adams, Comyn and Wake\textsuperscript{121}. FEA is a numerical analysis technique for obtaining approximate solutions to a wide variety of engineering problems. This method of analysis arose because many problems in engineering are solved using traditional analytical methods which are generally restricted to simple geometries and simple loading. However, complex problems lead to mathematical problems which are not capable of solution by analytical methods. In the past the problem was reduced via simplifying assumptions, thus turning it into one which did have an analytical solution. Sometimes the assumptions required were so gross that the solution obtained was virtually worthless. With the advent of the computer, it became possible to obtain accurate approximate solutions for these previously ‘unsolvable’ problems using numerical methods of analysis. In FEA an approximate solution is attempted by assuming that the behaviour of the continuum, the adhesive in this instance, can be represented by a \textit{finite} number of unknowns. In the continuum the field has a value everywhere so there are effectively an infinite number of unknowns. The FEA method reduces the number of unknowns to a large, but finite value by dividing the continuum into a number of individual elements, and expressing the unknown as an approximating function over each element. Approximating function values are calculated at nodal points and nodal values become the new finite set of unknowns. The great advantage of this technique lies in the fact that the stresses in a body of almost any geometrical shape under load can be determined. The method is well suited for analysing adhesive joints as it avoids approximations of the closed form theories, for example Volkersen's Analysis, where the strain energy of certain stresses within the joint are neglected, thus enabling more accurate answers to be found outside the bounds of such closed form analyses.

With FEM it is possible to conduct three dimensional\textsuperscript{122-126} or two dimensional analyses\textsuperscript{120, 127-129} of any joint configuration. Although more accurate solutions are obtained to the structural assessment of adhesive joints with a converged three-dimensional analysis than a two-dimensional analysis, however, the use of three-dimensional solid elements in complex structural analysis research problems has a number of disadvantages\textsuperscript{129}. For example,
considerable increases in computer processing time, mesh generation and results processing time make three-dimensional analyses less favourable despite their advantages. A two-dimensional analysis can be used for comparative studies where a series of finite element models are required without losing out on too much accuracy\textsuperscript{128-129}. Hinopoulos and Broughton\textsuperscript{129} used a converged two-dimensional T-peel analysis in a comparative study to assess the viability of the T-peel method in an industrial environment. The finite element method was employed to perform a series of non-linear stress and deformation analyses of multiple T-peel joints under tensile loading. The solutions obtained using this technique were compared with experimental values and were found to give an accurate prediction of joint stiffness when plasticity of the adhesive and adherends was taken into account.

Successful adhesive bonding relies on the transfer of load through the assembly. For this reason joints are configured to improve load transfer in order to minimise localised stress concentrations\textsuperscript{121}. A common use for FEA is to predict joint behaviour at given loads and it is therefore important to understand the critical factors which influence this analysis, i.e. loading system, magnitude of loads, structural geometry, mechanical properties of the adhesive and adherends. Cotofana et al.\textsuperscript{130}, successfully used FEA to optimise a model for a new plastic package for optical sensors. FEA was used to compare stresses in a variety of designs, the results of which were able to determine the optimal choice for a reliable low-cost product. Two and 3D finite element models were used by Gilchrist and Smith\textsuperscript{131} to predict stresses within the adhesive bonded and weld-bonded T-peel joints. The epoxy adhesive was modelled as a homogenous layer providing a perfect bond between aluminium adherends. This work elucidates the regions of cohesive crack propagation with a typical adhesive bonded and weld-bonded T-peel joints, the subsequent direction of crack propagation and the relative duration of the different stages of fatigue crack growth, up to final fracture. Jayota, et al.\textsuperscript{33} make use of finite elements to study interfacial fracture in T-peel tests. In this analysis the T-peel test was used to probe adhesion. Where the polymer was a viscoelastic elastomer, it is shown that this approach may be used to identify conditions for peak viscous dissipation at
the largest length scales in the peel arms. This section describes the FEA of T-peel joints as a means of validating experimental results. Numerous authors have also used FEA to study single lap joints$^{36,130-135}$. In the present study FEA is being used to perform stress analyses of unmodified and modified T-peel joints. It is thought that modification causes changes in adhesive properties, such as tensile modulus, which may exert an effect on stress distribution in the adhesive layer. FEA will be used to model the changes induced in the material properties of the adhesive when stearic acid is added. This change will initially be ascertained by conducting bulk mechanical tests such as tensile tests. The data will then form the basis of a FEA investigation. However this method will be used in a purely supportive role. Fitton and Broughton$^{34}$ used a simple FEA model to investigate graduation in bondline modulus of a high and low modulus adhesive in the SLS geometry. The variable modulus bondline was modelled by assigning different adhesive properties to specific regions of the bondline. From this simple analysis the effect of adhesive properties on the distribution of stresses was illustrated.
1.6.2 Surface Analysis

Surface analysis is the use of chemical and physical probes that give information about the surface region of a sample. The area probed may be the extreme top layer of atoms or it may extend up to several microns beneath the sample surface, depending on the technique used. The analysis is performed to provide information on such characteristics as the chemical composition, the level of trace impurities or the physical structure of the sampled region. Figure 1.5 demonstrates the transition from bulk to surface analysis.

![Image of bulk and surface analysis]

**Figure 1.5** Area of interest in surface analysis.

The most commonly used surface analytical techniques for chemical analysis are X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS). Surface topography or texture is most usually studied using electron microscopy (SEM, STEM or TEM) or atomic force microscopy (AFM). Related techniques such as
profilometry can also be used to provide quantitative data over a macroscopic area.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AES</th>
<th>XPS</th>
<th>SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Excitation source</strong></td>
<td>Electrons</td>
<td>X-rays</td>
<td>Ions</td>
</tr>
<tr>
<td><strong>Species detected</strong></td>
<td>Electrons</td>
<td>Electrons</td>
<td>Ions</td>
</tr>
<tr>
<td><strong>Spatial resolution</strong></td>
<td>100nm</td>
<td>100µm</td>
<td>1µm (SSIMS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10µm (imaging)</td>
<td>20nm (imaging)</td>
</tr>
<tr>
<td><strong>Sampling depth</strong></td>
<td>2-5nm</td>
<td>2-5nm</td>
<td>0.1nm (SSIMS)</td>
</tr>
<tr>
<td><strong>Depth profile</strong></td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Quantitative</strong></td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Compound information</strong></td>
<td>Limited</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Sensitivity</strong></td>
<td>&gt;0.1%</td>
<td>&gt;0.1%</td>
<td>0.1% (SSIMS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ppm (DSIMS)</td>
</tr>
<tr>
<td><strong>Elemental range</strong></td>
<td>Li-U</td>
<td>Li-U</td>
<td>H-U</td>
</tr>
<tr>
<td><strong>Sample types</strong></td>
<td>Metals, ceramics,</td>
<td>All solids</td>
<td>All solids</td>
</tr>
<tr>
<td></td>
<td>flat glasses,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>limited data from</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>polymers</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.5: A Comparison of Surface Analytical Techniques

The principle techniques employed in this research are static SIMS (SSIMS) and XPS, although SEM was used for preliminary examinations of failure surfaces. Attenuated total reflectance (ATR) was employed as a collaborative technique.
1.6.2.1 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface analytical technique that is a very important tool in adhesion science. It has been particularly useful in investigating the causes of poor adhesion in plastic surfaces, such as polyolefin’s.

![Diagram of XPS](image)

Figure 1.6 An illustration of the operating principle of XPS

XPS depends on ultra high vacuum technology (UHV). In Figure 1.6, the sample surface is irradiated with soft X-rays (usually Mg Kα or Al Kα with energies of 1253.6 and 1486.6 eV, respectively). Thus, an X-ray flux is used to excite electrons from the surface of the sample. The photoelectrons emitted are then analysed in terms of their kinetic energy ($E_K$) giving rise to a spectrum depicting the binding energy of the electrons detected. In this study, an unmonochromatised Al Kα X-ray source was used to produce all spectra. The kinetic energy is related to the binding energy $E_b$ by the equation below:
where $h\nu$ is the quantum energy of the X-rays and $\psi$ is the work-function. $E_b$ is the usual diagnostic parameter allowing elemental identification to be made by reference to data compilations in the literature and defines the binding energy of the electron.

Generally, instruments can be operated in a broad scan spectrum, where electrons are detected from a wide energy range, typically 0 to $\sim1250$eV; or, alternatively, high energy resolution data can be obtained. The broad scan spectrum provides surface elemental identification. All elements in the range Li to U have at least one XPS peak within the energy range detailed above. In the current work a broad scan was initially carried out to ascertain the general nature of the joint surfaces exposed post joint failure to determine failure modes$^{136, 138}$.

Quantification is achieved by the use of relative sensitivity factors appropriate to the instrument being used. These may be theoretically or experimentally derived and allow surface compositions to be determined, usually expressed in atom percent terms. The detection limits for most elements in XPS are in the range $\sim0.1$ to 1%. The relative intensity ratios of the detected elements are proportional to the concentrations of the surface atoms$^{136, 138}$.

The precise value of $E_b$ for any given element is also dependent upon its chemical environment. More intimate chemical information can be determined by accurately measuring the discrete chemical shifts caused by localised electron-electron interactions. This high resolution mode is therefore the other method of operating the XPS spectrometer. To obtain this information the energy resolution of the spectrometer is increased by decreasing the pass energy of the CHA. Curve fitting or peak deconvolution is commonly carried out on high energy resolved data to identify the relative amounts of different components of an elemental peak. These procedures were not carried out in this report. A narrow scan of the C1s peak in the
modified joint was undertaken in order to establish the presence of stearic acid at the surface. A shift of approximately 4eV in this peak would be expected should stearic acid be detected\(^{140}\).

XPS is surface sensitive because in order for the emitted electrons to be identified, they must escape without losing energy. This condition is only fulfilled when the ejected electrons come from the surface of the sample. Electrons with energies in the region of interest (100-1500eV) have inelastic mean free paths, \(\lambda\), of \(~0.5-3\text{nm}\). Sampling depths are approximately \(3\lambda\) and are a function of the particular peak under scrutiny; hence the sampling depth is given by\(^{138}\):

\[
d = 3\lambda \cos \theta
\]

where \(d\) is sampling depth and \(\theta\) is the angle between the energy detector and the sample surface. Increasing the angle between the energy detector and the sample surface reduces the sampling depth and this angular sensitivity forms the basis of angle resolved XPS.

The main strength of the technique is its ability to elucidate surface chemical bonds. The presence of adjacent atoms in a molecule causes atoms to shift in their binding energies (chemical shifts) due to perturbations induced by chemical bonding within the valence electrons of an atom. Chemical shift information is beneficial in understanding the chemical state of any surface and the functional groups present, although this can be ambiguous. These chemical shifts are well documented in literature\(^{140}\). It should be emphasised that for insulating surfaces, including thick oxide layers on metallic samples, surface charging effects can also lead to peak shifts; in this case all the peaks in the spectrum shift to the same extent. In this situation, some kind of energy calibration must be applied or the charging neutralised by a flood of low energy electrons, for measured binding energies to be meaningful. In this study surface charging effects were combated by referencing the binding energies with respect to the C1s peak which occurs at 285eV.
The principle advantages of XPS are its low radiation damage rate, even for sensitive organic materials. All kinds of materials in almost any physical form can be examined. The principle drawback is the poor spatial resolution. Typically the area observed is several mm² but more recent instruments allow selected area analysis with a spot diameter of ∼200µm. A particular problem in the analysis of complex polymeric surfaces concerns the identification and quantification of specific functional groups. This is frequently necessary when investigating the effects of surface pre-treatments, which generally introduce a range of functionalities. Derivatisation by specific reactions to introduce distinctive labels is a possible way around this problem\textsuperscript{136,138}.

1.6.2.2 Static Secondary Ion Mass Spectrometry (SSIMS)

Secondary ion mass spectrometry (SIMS) is described, by Swift and Vickerman\textsuperscript{141}, as the mass spectrometry of atomic or molecular particles which are emitted when a solid surface is bombarded by energetic primary particles (sputtering). Those primary particles are commonly ions or neutral species which, upon striking a solid surface, induce a series of atomic collision cascades within the surface layers of the sample. The primary beam can be O\textsubscript{2+}, O\textsuperscript{−}, Cs\textsuperscript{+}, Ar\textsuperscript{+}, Xe\textsuperscript{+}, Ga\textsuperscript{+}, or any of a number of other species\textsuperscript{142}. This process initiates the ejection of neutral and ionised (positive or negative) secondary species from the uppermost surface of the solid. These are detected using a mass spectrometer. Many species are formed by the interaction of the beam with the sample, but the positive and negative secondary ions are the species of interest for SIMS. The secondary ions are extracted by electric fields and energy and mass analysed. Detection is by electron multiplier, Faraday cup, or ion sensitive image amplifier for imaging\textsuperscript{142}. 
The key components of the SIMS experiment are the primary particle beam and the mass spectrometer and each component can be varied depending upon the nature of the information required and hence the type of SIMS mode employed. Three types of SIMS experiment are possible; (1) dynamic SIMS; (2) static SIMS and (3) time-of-flight SIMS (ToF-SIMS), which is really a sub-set of SSIMS. The present study is focused on SSIMS so the other experiments will not be mentioned further. However, for a more detailed study of these alternatives consult Briggs and Briggs and Seah.

In SSIMS the primary ion dose is kept very low (<10\(^{13}\) ions cm\(^{-2}\)). Under SSIMS conditions beam induced surface damage is negligible since, under such low fluence conditions, less than a monolayer is removed in the time required for analysis. The SSIMS mode is extremely surface specific, with more than 95% of the spectral information generated from the top two atomic layers of the sample. The spectral data obtained from SSIMS not only provides unequivocal identification of surface elemental species but invariably contains peaks at high mass as a consequence of the emission of cluster or molecular ion fragments from the surface. The interpretation of these high mass peaks provides unique chemical structure and bonding information about the surface. Also in SSIMS the emphasis is on maximising the molecular information (cluster ion intensity) in the spectra and minimising information depth. Typical SSIMS conditions would be 3 keV \(Ar^+\) at 1 nA cm\(^{-2}\), and an information depth of 1 nm.

A variety of ion gun types is used in SSIMS and these give rise to the range of primary ion/energy combinations which are encountered. This variety is due to the different requirements for guns which allow work at high level or low spatial resolution in addition to the constraints imposed by the type of mass spectrometer employed, either quadrupole, requiring a continuous beam, or time of flight, requiring a pulsed beam. The most important ion source parameters are brightness, extractable current and energy spread. These parameters will determine the final current/spot size characteristics of the beam at the sample surface. The SSIMS instrument used in this study...
has a duoplasmatron ion gun using negative oxygen at 12.5 KeV. The mass spectrometer is magnetic sector.

Although SSIMS can be a very sensitive technique, the major problem is quantification. SSIMS has two unique advantages in surface and interface analysis, namely that H is detected directly, and that isotopes are distinguished. As with traditional mass spectroscopy, a secondary ion mass spectrum provides a chemical fingerprint of the sample being bombarded. The identification of an unknown compound relies on the availability of very large databases and accurate interpretation of the spectra is often a skilled process\textsuperscript{141,144}.

In summary operation in the UHV regime is even more important in SSIMS than in XPS. As SSIMS is inherently more surface sensitive so surface contamination by adsorption causes more problems; not only is the available surface for analysis reduced but also the spectrum of the contaminating material has a much greater impact on the acquired spectrum in SSIMS than would be the case for the equivalent XPS experiment. XPS, on the other hand, is an extremely important tool in adhesion studies because of its wide applicability. In particular it has proved decisive in investigating the reasons for the poor adhesive properties of many plastic surfaces such as polyolefin's, and the role of surface pre-treatment processes used to overcome these fundamental problems.

1.6.2.3 Applications of XPS and SSIMS in adhesion studies.

XPS and SIMS have been used in the analysis of a variety of surfaces. These techniques have been used in a complementary manner with one another or in conjunction with other surface analytical techniques, such as SEM. This section will now focus on their uses in the study of polymeric
surfaces and polymer/metal interfaces in reference to locus of failure studies in adhesion.

The adhesive used in the current study is a PDMS-based material. Dong et al.\textsuperscript{145}, used time-of-flight secondary ion mass spectrometry to characterise PDMS. In the first of their two studies, the effects of molecular weight and the end group on fragmentation were investigated. In later work Dong et al.\textsuperscript{146} studied the effect of functional group changes on polymer fragmentation mechanisms. The studies conducted by Dong and his colleagues\textsuperscript{145, 146} showed that the distinctive fragmentation patterns obtained by ToF-SIMS can be used as a means of identifying polysiloxanes. Swift and Vickerman\textsuperscript{141} cite the use of SSIMS as a powerful tool for the direct characterisation of chemically similar materials. The ability of this tool to directly distinguish backbone structure and the significant functionalities that make compounds different is of particular benefit in the field of polymer science.

The sensitivity of XPS and SSIMS experiments is an important factor to consider as relatively small amounts of stearic acid are incorporated into the adhesive. These techniques will be required to establish whether this relatively low molecular weight material is present at the interface of the joint. The ability of XPS to identify many chemical species has long been one of the advantages of this technique. Recently, Long et al.\textsuperscript{147} used XPS in this capacity to quantify the surface chemical composition of polypropylene containing terminal unsaturation modified with a hydride terminated PDMS. XPS analysis revealed a complicated surface with the presence of various oxides. Bes et al.\textsuperscript{148} also used XPS to determine chemical compositions at the surface of poly(methyl methacrylate-dimethylsiloxane) (PMMA) tri block copolymers. This technique proved to be sensitive enough to analyse low levels of PDMS fluid (1.5-2.0%)\textsuperscript{149}. In addition, it could differentiate between different forms of silicone\textsuperscript{150}.

Although both secondary ion mass spectrometry and XPS may be used independently of each other, they can be used in a collaboratory manner without compromising the information gathered from either technique.
Gardella and Hercules\textsuperscript{151} illustrate this point in their work. The authors specifically look at the analytical capabilities of the two techniques for the analysis of poly(methacrylates) where the pendant ester group is varied in length and functionality. From the results of their study they concluded that although both methods were able to clearly differentiate between small alkyl ester groups pendant in the poly (methacrylate) polymer series, they found it difficult to analyse isomeric side chains by XPS in comparison to SSIMS which provided simple direct analysis of isomeric side groups through pattern analysis and analysis of spectral base peaks. Probably their most fundamental conclusion was that SSIMS spectra were able to provide important complementary data to XPS for polymer analysis; moreover, in some cases providing information where XPS analysis was not definitive.

In adhesion studies it is important to understand the conditions required to attain high joint strengths. However, locating areas of joint failure is equally as essential, especially when premature failure at significantly lower strengths occurs. As highlighted in earlier sections adhesion is a complex phenomenon and thus employs a number of techniques for its assessment. In work conducted by Davis and Watts\textsuperscript{152}, XPS and ToF-SIMS were used to study the failure surfaces of lap shear joints exposed to an aggressive environment, namely water at 30\textdegree C. The aim of their work was to use these surface analysis methods to provide analytical data, from which they hoped to deduce the interfacial chemistry of failure and provide a comprehensive model of the chemistry and electrochemistry that contribute to the observed reduction in joint strength. The failed lap shear joints were studied with XPS and ToF-SIMS was utilised to provide further details regarding the organic material remaining on the metal side of the failed joint. The high sensitivity of this technique coupled with the ability to detect fragments of the adhesive system enabled SSIMS to be used to fingerprint the adhesive. The combination of these two techniques enabled the authors to identify the mode of adhesive failure, detect the presence of contaminants and to produce plots showing the spatial distribution of species present within the failure regimes. To surmise,
they successfully used XPS and SSIMS conditions in a complementary manner to study a complex system.

The role of the interface in joint strength is a running theme in this research. XPS and SSIMS have been used to great effectiveness to identify the polymer/metal interface as the determining factor when assessing joint strength. Interest in the chemistry of this region has arisen because the nature of chemical bonding at and near the interface is thought to be responsible for the adhesive strength of joints\textsuperscript{153}. Developments in these surface analysis techniques for characterisation of polymer surfaces have made it possible to investigate the interfacial chemistry in polymer/metal systems in more detail\textsuperscript{154}. The study conducted by van Ooij and colleagues\textsuperscript{154} concluded that SSIMS and XPS are powerful and highly complimentary techniques for the study of adhesion and corrosion phenomena. Although SSIMS was deemed a more surface sensitive technique than XPS, a limitation of SSIMS was that many characteristic fragment ions of certain components are also formed by other components thus imposing a certain level of ambiguity on spectral interpretation and peak identification.

Since adhesion is a surface event, the sensitivity of the chosen technique in this region becomes important. In a study into paint/metal interfaces surface analysis techniques combining variety and sensitivity were employed\textsuperscript{154}. XPS, SSIMS and ToF-SIMS were used as it was thought that a better understanding of the paint/metal interfacial chemistry would shed more light on the possible correlation between paint adhesion and corrosion performance.

As a large proportion of SSIMS experiments are performed on insulating samples\textsuperscript{143} it is important for the surface potential of such samples to be stabilised so that emitted ions have the correct energy for analysis by the mass spectrometer\textsuperscript{155}. The quality needed for this stabilisation depends on the width of the energy band pass of the mass spectrometer. In SSIMS it is important to control this effect as variations in energy spectral widths
influences the intensity of the energies accepted by the mass spectrometer and will change as the surface potential of the surface changes.

In this study a Cameca ims 3f instrument was used to study the failed surfaces of the metal/polymer joints. Chew and Sykes document the use of this instrument in adhesion studies. They reported that the requisite removal of <1% of the outer monolayer renders the choice of primary species immaterial as the analysis is performed well within the pre-equilibrium region and the probability of events occurring more than once at the same site is low. Furthermore, the primary ions will penetrate and become buried well below the outer monolayer and at the low doses used did not influence the surface chemistry of the sample. The authors conducted analyses using negative ions and the sample charging was compensated for by setting the magnet to a commonly observed molecular peak and adjusting the sample potential to maximise the signal. In the current study a low current negative ion beam was used to perform analyses, consequently surface charging was not an issue. This was compounded by the fact that high mass resolutions were not employed, mass resolution >250.

The literature illustrates plainly that the inherent complexity of adhesion problems cannot be resolved singularly by any one type of surface analytical technique. It is better to employ a combination of techniques so that a more complete picture can be constructed, i.e. quantitative capability of XPS in conjunction with the qualitative nature of SSIMS. The techniques of XPS and SIMS have been described and their applications in polymer technology discussed. XPS has been found to be more quantitative and probes the functional groups present at the surface whereas SSIMS is a qualitative technique which can provide a more detailed picture of the molecular structure of polymer molecules at surfaces. These techniques find applications as research tools and also as routine analytical techniques for problem solving.
1.6.3 Attenuated Total Reflectance (ATR)

ATR is used for analysis of the surface of materials. It is also suitable for characterising materials which are either too thick or too strongly absorbing to be analysed by transmission spectroscopy. For the bulk material or thick film, no sample preparation is required for ATR analysis.

In ATR, the infrared radiation is passed through an infrared transmitting crystal with a high refractive index, allowing the radiation to reflect within the ATR element several times. The sampling surface is pressed into intimate optical contact with the top surface of the crystal such as ZnSe or Ge. The infrared radiation from the spectrometer enters the crystal. It then reflects through the crystal and penetrates into the sample a finite amount with each reflection along the top surface via the so-called evanescent wave. At the output end of the crystal, the beam is directed out of the crystal and back into the normal beam path of the spectrometer.

Classical examples of ATR include the determination of optical constants, analysis of thick polymer surfaces. Recent advancement of ATR spectroscopy to the analysis of thin films on metallic substrates has added a new dimension to this technique. ATR spectroscopy is an ideal technique for analysing the surface of crosslinked elastomeric materials. Ductile materials can form excellent optical contact with the surface of an ATR prism\textsuperscript{157}. Reproducibility of the ATR spectrum of these samples is sufficiently good to allow the application of the subtraction technique to enhance the difference between samples. Chen and Gardella\textsuperscript{158} manipulated the versatility and surface sensitivity of the attenuated total reflectance technique to establish a procedure for the quantitative surface analysis of binary polymer blends having a complex compositional depth gradient. The quantification was based on calibration by transmission FTIR measurements. The validation of the quantification method was done by recording ATR spectra of die cast films on the internal reflection element (IRE) of homogenous polymer PS and
comparing the corrected ATR spectra of polymer blend samples and direct-cast samples of the homogenous polymer PS on the IRE with their transmission spectra. These comparisons showed good precision of this quantification in most cases after these corrections. ATR was used in conjunction with XPS and SSIMS to study comprehensively the full range of surface segregation process of the polymer blend.

The following sections discuss the experimental methods used to investigate the cure kinetics of the hydrosilylation reaction. Firstly the use of FTIR is discussed, followed by a variety of thermally based kinetic analyses, with a primary focus on differential Scanning calorimetry (DSC).

1.6.4 Fourier Transform Infra-red (FTIR) Spectroscopy

FTIR is sensitive to the presence of chemical functional groups in a sample. Once the wavenumber positions of the bands of a functional group are known, this information can be used to identify that functional group in many samples via literature of appropriate data compilations. FTIR spectra can also be used to confirm molecular identities. This involves comparing the spectra of two samples to each other to determine whether the samples have the same composition. Finally, the peak intensities in an infrared spectrum are proportional to concentration, so FTIR spectra can be used to measure concentrations$^{157,159}$.

The capability of FTIR to detect chemical functionalities makes it a useful technique in adhesion studies especially when investigating joint durability. In such case studies where many functionalities maybe present, as a result of hydration or due to the presence of coupling agent or primer that sustain adhesion in adverse conditions, FTIR has proved to be invaluable. Stralin and Hjertberg$^{160}$ used it to better understand the adhesion mechanism.
between Al and ethylene copolymers obtained by hydration of the Al surface. FTIR facilitated this by enabling identification of functional group interactions at the interface which made it possible to identify the locus of failure. Metals are often chemically pretreated so that joints are able to sustain their strength in adverse conditions. These pretreatments enhance bonding by chemically modifying the surface of the adherend. Fondeur and Koenig\textsuperscript{161} used FTIR to characterise the surfaces of Al after various pretreatments. FTIR was able to distinguish between the different forms of oxide produced by the pretreatments. Using specular reflectance FTIR molecular composition and orientation of anodic Al films were investigated and characterised.

FTIR spectra can be plotted in transmission or absorbance. However, for spectra being used in quantitative analysis, such as measuring concentrations, absorbance must be used. This is because Beer's Law states that absorbance and concentration are linearly proportional. Transmittance and concentration are not linearly proportional, making transmittance spectra ill-suited for quantitative analysis\textsuperscript{162}. In this study, FTIR absorbance spectra has been used to follow the progress of the adhesive cure reaction in order to determine the effect of stearic acid on the system.

As the strength of the absorption is proportional to the concentration FTIR can be used for quantitative analysis. By maintaining constant sample geometry and keeping the infrared optics the same for all measurements, a linear relationship can be observed between the infrared absorption and the concentration of the sample. A further requirement for quantification is that the intensity of the infrared radiation is within the linear range of the detector. Where these criteria are fulfilled, the Beer-Lambert law holds between the absorbance, $A$, and the concentration of the sample transmission spectrum\textsuperscript{157}. The Beer-Lambert law relates absorbance and concentration in the following way

$$A = \varepsilon lc$$

(26)
where $\epsilon$ is specific absorptivity, $l$ is thickness and $c$ is concentration. The linear relationship of the intensity of IR spectrum as a function of concentration has been reported for other spectroscopic sampling methods, including ATR. The criteria for quantitative analysis, such as constancy of sample geometry and infrared optics, still apply to these techniques. Therefore, in order to make quantitative comparisons among various techniques sophisticated analysis using exact optical theory is required. The software necessitates definition of the optical path, optical properties of the sample, and the number of sample phases, the thickness, and the concentration. So by using computer software based on exact optical theory, it is possible to compare the transmission spectrum, ATR spectrum, and external reflection spectrum of the same sample\textsuperscript{157}.

1.6.5. General Introduction to Differential Scanning Calorimetry (DSC)

DSC is a technique used to study the thermal transitions of polymers. DSC experiments measures how much more heat has to be supplied to a sample material in order to maintain a constant rate of heating between the sample material and the reference. In the most common DSC design, two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path. The polymer sample goes in one pan. The other pan is known as the reference and is left empty. The experimental conditions, such as heating rate and temperature are then programmed into the computer, which turns on the furnace. So the computer turns on the furnace, and tells it to heat the two pans at a specific rate, usually at 10$^\circ$C per minute. The computer can maintain a constant heating rate throughout the experiment. But more importantly, it ensures that the two separate pans heat at the same rate as each other. DSC is used to determine thermodynamic properties of polymers, such as heat capacity, glass transitions, melting, and crystallisation.
temperatures. It can also be used to detect kinetic processes such as cure and physical aging.

A variation of the DSC technique is modulated temperature differential scanning calorimetry (MTDSC). In this experiment the conventional linear heating programme is modulated by superimposing a modulation term to the linear part of the temperature-time function\(^{164}\). The most common MTDSC experiment uses a sinusoidal wave of small amplitude on the linear rise. Portions of each cycle then involve heating while other portions involve cooling. The overall trend, however, remains a linear change in average temperature with time. The resultant heat flow signal is analysed to separate the response to the perturbation from the response to the underlying heating programme.

The modulated heating programme may be of the form:

\[
T = T_0 + \beta t + B \sin(\omega t)
\]  

Where \(T_0\) is the starting temperature, \(\beta\) the heating rate, \(B\) the amplitude of the modulation and \(\omega\) its angular frequency \((= 2\pi f\), where \(f\) is the frequency). The contributions to the resulting heat flow can be written in the form:

\[
\frac{dq}{dt} = C_{p,s}(dT/dt) + f(t,T)
\]

Where the heat flow into the sample is \(dq/dt\), \(C_{p,s}\) is the heat capacity of the sample and \(f(t,T)\) arises due to the heat flow arising as kinetically hindered event. Combination of these two equations (27) and (28) gives:

\[
\frac{dq}{dt} = \left\{ \beta C_{p,s} + F(t,T) \right\} + \left\{ \omega B C_{p,s} \cos(\omega t) + D \sin(\omega t) \right\}
\]

**Underlying component** **cyclic component**
Where \( F(t, T) \) is the average of \( f(t, T) \) over the interval of at least one modulation, \( D \) in the cyclic component is the amplitude of the kinetically hindered response to the temperature modulation. Both, \( C_p, t \) and \( D \) will be slowly varying functions of time and temperature but can be considered effectively constant over the duration of a single modulation. So the kinetically hindered responses are usually assumed to show Arrhenius-type behaviour. The amplitude of temperature modulation is usually restricted to a degree or less so that the kinetic response can be considered to be linear.

Therefore the signals derived from a MTDSC experiment are: (i) the underlying signal, which is equivalent to conventional DSC; (ii) the in-phase cyclic component from which heat capacity of the sample can be calculated, and (iii) the out-of-phase signal \( D \) which pertains to the amplitude of the kinetically hindered response to the temperature modulation. Multiplying the heat capacity by the heating rate gives (iv) the reversing contribution to the underlying heat flow. Subtraction of the reversing contribution to the underlying heat flow signal gives (v) the non-reversing heat flow.

Aside from the frequently used sine wave form other modulations may be superimposed on the linear rise of the conventional DSC programme. These alternatives include the quasi-isothermal mode, the heating-cooling mode, the heating only mode, the heating-iso mode, the saw-tooth or square wave mode (modes used by Perkin-Elmer and Mettler-Toledo respectively) and the step-scan mode. As only a sinusoidal waveform is used in this study these alternatives are not mentioned further.

There are many advantages to using the MTDSC technique. For example, the use of appropriate experimental conditions, i.e. frequencies and amplitudes of modulation, allows separation of reversing processes, such as \( T_g \), from non-reversing processes, i.e. cure reactions. It is easier to distinguish between baseline effects and real transitions as the baseline curvature on the cyclic signal is generally very low. The signal-to-noise ratio (S:N) of the cyclic measurement of heat capacity is generally greater,
because all drift of noise at frequencies other than that of the modulation is ignored by the Fourier transform analysis. Resolution of processes can be improved because very low underlying heating rates can be used.

1.6.5.1 Thermal Analysis and Kinetic Measurements

Thermal analysis encompasses a family of measurement techniques, such as DTA, DSC, TGA, that record the response of a material to being heated or cooled\textsuperscript{165}, so making it possible to characterise both kinetic and thermodynamic events with these techniques. The dependent variable is usually temperature, but may also be time, as is the case in kinetic variables studies. Several of the thermal analysis techniques are briefly summarised below, together with the material responses detected.

Thermal analysis techniques are relatively simple and easy, thus enabling their use in a wide range of experiments. In this study differential scanning calorimetry has been employed to study the cure kinetics of the unmodified and modified (with stearic acid) adhesive. The equations used to perform the kinetic analysis were derived from thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry techniques. These methods were used to study a range of systems from simple chemical solutions\textsuperscript{166} to more complex thermoset cure reactions of epoxies and polyurethanes.

The kinetic expressions and relationships established by these methods stemmed from investigations into solid decomposition reactions. The assumptions made from these studies were extrapolated so that they could be applied to other types of chemical reactions, for example cure reactions. The following section details the origins of the kinetic expressions used in the current analysis and their application in determining the kinetic constants of Arrhenius chemical reactions, namely the activation energy \( E \) and pre-
Chapter I Literature Review

exponential constant A. The various types of DSC experiment will also be described, in addition to, the means by which these methods enable the determination of kinetic constants. The classes of DSC experiment are isothermal and non-isothermal. The non-isothermal method can be subdivided into two further methods, namely single heating rate method and the multi-heating rate (or dynamic) method.

In the following sections the use of thermal analysis for kinetic investigations will be reviewed, and where possible particular reference to silicone rubber reaction systems will be made. Some of the techniques described in the following sections were used to investigate the effect of stearic acid on the cure reaction as a possible explanation for measured adhesion; was thought to be a reduction in the cohesive strength of the adhesive a result of cure inhibition by the additive.

1.6.5.2 Reaction Kinetics from Thermal Analysis

The main reasons for measuring rates of reaction are: (i) to obtain information about the reaction mechanism; (ii) and/or to determine values of kinetic parameters. These two aims are closely related because the reaction mechanism, which is used here in the sense of the detailed chemical steps involved, can usually only be inferred from the overall picture constructed from the kinetic model and as much complementary evidence (e.g. spectroscopy, chemical and structural analysis, etc) as possible.

Kinetic analysis includes: determination of the mechanism or appropriate kinetic equation for the system being analysed, and; the measurement of reaction orders n, activation energies E and frequency/pre-exponential factors A of the reaction. One purpose of kinetic analysis may be to model cure behaviour. Another may be to characterise the cure, ageing, or degradation of thermosetting polymer systems. Still another may be for comparison
purposes, for example, to compare, different resins or matrices, to compare the effects of fillers, additives, and environmental factors\textsuperscript{164}.

The rate equations documented further in this section are based on studies conducted on solid decomposition reactions of the form:

\[ A \rightarrow B + C \]  \hspace{1cm} (30)

This general equation can apply to both homogenous and heterogeneous reaction systems. In thermal analysis experiments the reactions studied are almost always heterogeneous reactions involving at least one initially solid reactant and the reaction temperature is usually increased or decreased linearly according to a set programme\textsuperscript{164}. The rate equations, which are likely to apply in heterogeneous reactions, are considerably different from those in homogeneous kinetics and programmed temperature experiments, require a different approach to kinetic analysis, often referred to as non-isothermal kinetics\textsuperscript{164}. The principles developed for non-isothermal kinetics analysis have been applied to homogenous kinetics, but because of the influence of thermal analysis techniques and their main use in studying initially solid samples, there has been greater emphasis on heterogeneous systems\textsuperscript{164}.

1.6.5.3 Mechanisms and Kinetic Equations

A kinetic study involves the measurement of the extent of reaction or chemical conversion, \( \alpha \), either as a function of time \( t \), at constant temperature, or as a function of temperature, \( T \), which is increased according to some heating regime (usually linear), the heating rate \( \beta = \frac{dT}{dt} \). The isothermal method, \( \alpha \) against \( t \), corresponds to the curve of concentration against \( t \) familiar from homogenous kinetics, while the dynamic method, \( \alpha \) against \( T \), is the basis of thermal analysis\textsuperscript{164}.
It has been agreed by Malek\textsuperscript{167}, that all kinetic models start with the basic rate equation that relates the rate of conversion at constant temperature, $d\alpha/dt$, to a function of the concentration of reactants, $f(\alpha)$, through a rate constant, $k$:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (31)$$

where $\alpha$ is the chemical conversion or extent of reaction, $k$ is the rate constant, $f(\alpha)$ is the differential form of the mathematical expression of the kinetic model. Furthermore, $f(\alpha)$ is assumed to be independent of temperature.

The aim of the kinetic analysis of thermal data is to find the most probable kinetic model which gives the best description of the studied process and allows the calculation of reliable values for the parameters $A$ and $E$.\textsuperscript{167} Maciejewski\textsuperscript{168} goes further by stating that a reaction must be described by a kinetic triplet ($E$, $A$, and $f(\alpha)$ or $g(\alpha)$, where $g(\alpha)$ is the integral form of the mathematical expression of the kinetic model). Knowledge of only one of the Arrhenius parameters is considered insufficient to characterise the kinetics of a reaction. The purpose of this section is to characterise the kinetics of thermoset cure from data obtained by thermal analysis techniques.

In general there are two typical models for thermoset cure: nth-order and autocatalytic\textsuperscript{165}. At this juncture, it should be noted that curing is not necessarily limited to one chemical reaction, and the kinetics may be those of an overall process when the chemical reactions occur simultaneously. Curing by two or more consecutive reactions is also possible.

For thermosets that follow nth-order kinetics, the rate of conversion is proportional to the concentration of unreacted material (reactant concentration), so that

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (32)$$
where $n$ is the reaction order. Autocatalysed thermoset reactions are observed in reactions where one of the reaction products is also a catalyst for further reaction\textsuperscript{165}. Autocatalysed thermoset cure reactions are characterised by an accelerating isothermal reaction rate. The kinetics of autocatalysed reactions are described by equations of the form:

$$\frac{da}{dt} = k\alpha^m(1 - \alpha)^n$$

(33)

where $m$ is also the reaction order.

Earlier, it was stated that temperature is, usually, the dependent variable in thermal analysis. As a function of temperature, the rate constant $k$ is associated to the dependent variable via an Arrhenius relationship

$$k = Ae^{-E/RT}$$

(34)

or

$$k = AT^n e^{-E/RT}$$

(35)

where $E$ is the activation energy, $R$ the gas constant, $T$ the absolute temperature, and $A$ the pre-exponential or frequency factor. By combining equations (31) and (35) the complete rate equation is given

$$\frac{da}{dt} = f(\alpha)Ae^{-E/RT}$$

(36)

The curing of most thermosets can be sufficiently described by these simple, chemically based models, thereby, suggesting that chemical reactions control the rate of most cure processes\textsuperscript{165}.
1.6.5.4 Isothermal Methods

The isothermal method is a thermal analysis technique used to measure the time dependence of curing at constant temperature\textsuperscript{169}. Isothermal methods are recommended for complete characterisation and modelling of the cure process\textsuperscript{165}. In the main, isothermal methods can best distinguish between different reaction mechanisms and they give the most accurate and reliable description of adhesive cure. Methods are described for determining the reaction processes and for measuring rate constants and activation energies.

The isothermal method, $\alpha$ against $t$, corresponds to the conventional curve of concentration against $t$ familiar from homogeneous kinetics\textsuperscript{164}. The main approaches used in kinetic analysis of isothermal data are all based on the initial assumption that a single conversion function and a single set of Arrhenius parameters, $A$ and $E$, apply over the full range of $\alpha$\textsuperscript{164}. Any deviations can be indicated by curved Arrhenius plots.

For thermal analysis using the isothermal method, the two basic parameters, $d\alpha/dt$ and $\alpha$, are required and can be obtained from DSC exotherm/endotherm data. The reaction rate is obtained by dividing the peak height, $dH/dt$, at time $t$ by the total heat of reaction $\Delta H_0$\textsuperscript{164}.

\[
\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \quad (37)
\]

The value $\alpha$ is determined by measuring the partial heat of reaction $\Delta H_p$ up to time $t$, and dividing by the total heat of the reaction

\[
\alpha = \frac{\Delta H_p}{\Delta H_0} \quad (38)
\]
Chapter 1

1.6.5.5 Determination of the function of $\alpha$

It is sometimes found that a given set of $\alpha$-time observations are obeyed with equal accuracy by two different rate equations and the kinetic analysis resolves itself into a test of distinguishing applicability of the alternative functions of $\alpha$. Four general approaches have been used in kinetic analysis \(^{170}\), all based on the assumption that a single conversion function and a single set of Arrhenius parameters apply to the full range of $\alpha$. The main approaches that have been employed to analyse isothermal kinetic data, for decomposition and other reactions, are described below \(^{170}\).

When the temperature of a decomposing compound is maintained constant it is possible to express the influence of temperature on the reaction rate (Equation 35) in the form of a constant $k$, the specific reaction's rate constant. Thereby, enabling the shape of plot of $d\alpha/dt$ against $\alpha$ to be determined by $f(\alpha)$. Data for isothermal experiments are often stated in an integral form derived in the following way:

$$\frac{d\alpha}{dt} = f(\alpha)k \quad (39)$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = k \int_0^t dt = kt \quad (40)$$

when

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) \quad (41)$$

we may write

$$g(\alpha) = kt \quad (42)$$
Thus the shape of a plot of $\alpha$ against $t$ is determined by $g(\alpha)$

In determining the function of $\alpha$ for isothermal experiments consider equation 42. As mentioned earlier the influence of temperature on $k$ is that it becomes constant so enabling the study of the form of $g(\alpha)$ without knowing $E$ or $A$.

The main approaches that have been used in kinetic analysis of isothermal data include (i) testing the linearity of plots of $g(\alpha)$ against $t$; (ii) a reduced-time method; (iii) comparison of measured $(d\alpha/dt)$ against $\alpha$ or $t$ with master curves; (iv) linearity of plots of $d\alpha/dt$ against $f(\alpha)$. These methods are described below:

(i) One method is to test the linearity of plots of $g(\alpha)$ against $t$. The function that gives a good straight-line fit may be assumed to be the correct function. The slope of the line is then $k$ and the reaction rate is constant. A series of experiments carried out at different temperatures should all fit the same $g(\alpha)$, but yield different values for $k$. Thus, a series of values of $k$ with corresponding values of $T$ are obtained. From equation 35 we obtain

$$k = AT^n e^{-E/RT} \quad (35)$$

$$\therefore \ln \left(\frac{k}{T^n}\right) = \ln A - \frac{E}{RT} \quad (43)$$

A plot of the left side of equation 43 against $1/T$ should give a straight line from which $E$ and $A$ may be determined. If $n = 0$, equation 43 is simplified to

$$\ln k = \ln A - \frac{E}{RT} \quad (44)$$

This is the classical method of evaluating the parameters $A$, $E$, and $g(\alpha)$. 
(ii) A reduced time method can also be used to analyse isothermal data. Plots of $\alpha$ against measured values of reduced-time are compared with plots calculated for the rate equation\textsuperscript{164}. Taking the time elapsed to $\alpha = 0.9$ to be $t_{0.9}$ it is possible to get

$$\frac{g(\alpha)}{g(0.9)} = \frac{t}{t_{0.9}} \quad (45)$$

A series of master plots of $\alpha$ against $g(\alpha)/g(0.9)$ may be drawn for the different $g(\alpha)$'s. It is possible, then, to superimpose the experimental reduced time plots of $\alpha$ against $t/t_{0.9}$ upon these master plots. The equation that gives the closest fit is then selected. The advantage of this method is that data from experiments carried out at several different temperatures may be collected onto a single plot, thereby, enabling any variations in $g(\alpha)$ with temperature to be discerned. An inherent disadvantage of this technique is that it involves the comparison of curves. A modified version of this method plots $\frac{g(\alpha)}{g_{0.9}}$ against $\frac{t}{t_{0.9}}$.

When experimental data are in good agreement with the theoretical expression they should produce a straight line with a slope of unity that passes through the origin. The most prominent problem in the use of any of these methods is the accurate evaluation of $t$ when allowance is made for an induction period. Similar methods based on the differential form of the isothermal rate equation

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (31)$$

are possible by using the quantity reduced rate instead of the reduced-time. Taking the rate of reaction at $\alpha = 0.9$ to be $\left(\frac{d\alpha}{dt}\right)_{0.9}$ we may write
\[
\frac{\frac{d\alpha}{dt}}{\left(\frac{d\alpha}{dt}\right)_{0.9}} = \frac{f(\alpha)}{f(0.9)}
\]

(46)

This approach has the advantage that it overcomes possible errors due to the presence of an induction period. However, for it to be effective, very high quality data must be available before it can be employed.

An inherent disadvantage of the reduced time method of analysis is that it involves the comparison of curves. A widely used alternative method of preliminary identification of the rate law providing the most satisfactory fit to a set of data is through a plot of the form \( \ln\left(\ln(1 - \alpha)\right) = n \ln t + \text{const.} \)

(iii) Another method of determining the function of \( \alpha \) is through the comparison of measured \( (d\alpha/dt) \) against \( \alpha \) or \( t \) with master curves, although very accurate values of \( \alpha \) are required for satisfactory application of this differential approach\textsuperscript{170}.

(iv) The linearity of plots of \( d\alpha/dt \) against \( f(\alpha) \) can be used to determine the appropriate rate equation\textsuperscript{164}. The deviation of a set of experimental points from the calculated regression line can be quantified by various standard statistical criteria. For example, the correlation coefficient, \( r \); the standard error of the slope of the regression line, \( s_b \); or the standard error of the estimate of \( g(\alpha) \) from \( t \), \( s_{yx} \). However, the use of a single parameter to express the deviation of the data from the least squares line does not reveal whether deviations are systematic or approximately random. Brown and Galwey\textsuperscript{172}, however, assert that the magnitudes and directions of such deviations and their variations with \( \alpha \) can be useful in identifying the most appropriate rate equations, and plots of residuals, \( [g(\alpha)_{\text{expt}} - g(\alpha)_{\text{predicted}}] \), against time have been suggested. It is then possible to identify each kinetic model within similar groups with the alternative model with which it is most likely to be confused.
Once a satisfactory fit has been obtained for a rate equation, the value of $k$ and its standard error, $s_b$, may be determined from the slope of the plot. If the form of the conversion function $g(\alpha)$ does not change with temperature, the values of $k$ at a series of isothermal temperatures, $T$, can be used in a conventional Arrhenius plot to calculate values for $E$ and $A$.

1.6.5.6 Measurement of Activation Energy, $E$

Dollimore and Reading\textsuperscript{171} put forward two main methods for measuring the activation energy. Namely, jump methods and non-jump methods. Both methods were based on mass loss measurements as the means of reaction rate measurement. The jump methods are categorised as the temperature jump method and the rate jump constant rate thermal analysis. The isothermal method and the constant rate thermal analysis method comprise the sub-divisions of the non-jump methods. The former is of specific relevance to this section and is discussed below.

From equation 35 it may be written

$$\ln\left(\frac{d\alpha/dt}{T^n}\right) = \ln[f(\alpha)A] - \frac{E}{RT}$$  \hspace{1cm} (47)

If the same extent of reaction is taken for each experiment then the first term on the right side of equation 47 becomes constant. It is then possible to produce a plot of the left side of this equation against $1/T$, the slope of which should give a straight line, from which $E$ can be determined. Assuming $n$ to be zero simplifies the equation to

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[f(\alpha)A] - \frac{E}{RT}$$  \hspace{1cm} (48)
Alternatively, the integral form of equation 42 can be taken for isothermal experiments, such that

\[ g(\alpha) = kt \]  \hspace{1cm} (42)

where \( k = AT^n e^{-E/RT} \) \hspace{1cm} (35)

\[ \therefore g(\alpha) = tAT^n e^{-E/RT} \] \hspace{1cm} (49)

when \( T \) is constant,

\[ \therefore -\ln(T^n) = \ln \left( \frac{A}{g(\alpha)} \right) - \frac{E}{RT} \] \hspace{1cm} (50)

Again take the same extent of reaction in each experiment to render the first term in the right side of equation 50 a constant. Thus plot the left side of this equation against \( 1/T \) again giving a straight line the slope of which allows \( E \) to be determined.

If \( n \) is assumed to be zero equation (50) can be simplified to become:

\[ -\ln(t) = \ln \left( \frac{A}{g(\alpha)} \right) - \frac{E}{RT} \] \hspace{1cm} (51)

the above form of the equation can be applied to isothermal experiments when the experimental data is in an integral form, as is often the case for mass loss measurements, and accurate differential data is unavailable.

1.6.5.7 Determining the Pre-exponential Factor, \( A \)

\( A \) is the measure of the effects of both the integral degrees of freedom of the reacting species and the necessary redistribution of that energy so that
reaction ensues. The pre-exponential factor is, almost certainly, a function of temperature as suggested by its relationship to the Boltzman energy distribution, but to a first approximation it may be considered a constant\textsuperscript{171}. Although the physical significance of this parameter is not well understood, it is, however, useful to ascribe some formal value to this quantity. Methods based on the differential form of the rate automatically give values for, $E$, $f(\alpha)$ or $g(\alpha)$, and $A$ when the correct $f(\alpha)$ or $g(\alpha)$ is selected on the basis of the criteria outlined from analysis of single non-isothermal data (section 1.6.5.8). The use of equations 50 and 51 gives as the intercept the quantity $\ln[A/g(\alpha)]$. When $g(\alpha)$ has been determined, using the methods described in section 1.6.5.6, a plot of $g(\alpha)$ against $g(\alpha)/A$ should give a straight line with a slope of $1/A$; thus, $A$ may be determined. Methods based on equations 47 and 48 give as the intercept the quantity $\ln[f(\alpha)A]$. Once $f(\alpha)$ has been determined using one of the methods described above (section 1.6.5.5), a plot of $f(\alpha)$ against $f(\alpha)A$ should give a straight line with a slope of $A$. Similarly, methods based on equations derived from constant rate thermal analysis (CRTA) give as their intercept the quantity $\ln[AR/Eg(\alpha)]$, at the same time giving a value for $E$ from the gradient of the plot. The intercept gives the value of $A/g(\alpha)$. Once $g(\alpha)$ is determined, a plot of $g(\alpha)/A$ against $g(\alpha)$ should give a straight line with a slope $1/A$; thus, $A$ may be determined. At this point it must be emphasised that it is not possible to ascertain the value of $A$ without knowing $f(\alpha)$ or $g(\alpha)$.

1.6.5.8 Single-Heating Rate Method

This is the beginning of the section on non isothermal kinetics. In this section experiments are divided into single heating rate methods and multi-heating rate methods. The advantages and disadvantages of both types of experiment are discussed.
Borchardt and Daniels\textsuperscript{166} were the first to describe the application of dynamic DTA and DSC to the study of reaction kinetics. They derived equations relating the shape of the DTA curve to the reaction kinetics giving rise to the curve. Equivalent equations for the DSC experiment were also derived\textsuperscript{165}. The equations were based on reactions occurring in stirred solutions where heat capacities and heat transfer coefficients of sample and reference are almost identical\textsuperscript{173}. By assuming the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time and that only one reaction occurs, they arrived at equation 37.

Single heating rate data are most frequently analysed according to equation 36 with \( f(\alpha) = (1-\alpha)^n \), assuming nth-order kinetics\textsuperscript{165}. From equations 34 and 36, it follows that

\[
\ln\left(\frac{d\alpha}{dt}\right)/(1 - \alpha)^n = \ln k = \ln A - E/RT
\]

Where \( n \), \( \ln A \), and \( E \) may be experimentally determined from a single-heating-rate DSC experiment. Taking logarithms of equation 36 gives

\[
\ln(d\alpha/dt) = \ln A - E/RT + n\ln(1 - \alpha)
\]

Solving equation 53, using multiple linear regression, enables \( A \) and \( E \) to be obtained from the intercept and slope of the regression line. This method was used by Park, et al.\textsuperscript{169} to obtain accurate kinetic parameters for simple reaction systems. However, for the bulk of thermoset cure reactions it consistently overestimates the activation energy and frequency factor when compared to values obtained from isothermal experiments.

The single-heating rate method is attractive because in principle, one experiment can provide what would otherwise require several lengthy experiments. Despite this obvious advantage, however, the single-heating-rate method has been found to yield inconsistent and unreliable results when used to predict the route of a reaction over a wide time-temperature range.
Chapter 1 Literature Review

The criterion for judging the dynamic experiment is usually its ability to describe and predict accurately the isothermal behaviour\textsuperscript{165}. Following years of debate about whether the form of $f(\alpha)$ or $g(\alpha)$ and the magnitudes of $E$ and $A$ can be obtained from measurements from a single programmed temperature experiment, Criado, et al.\textsuperscript{174}, clearly showed that the same TG curve could be generated using three different kinetic models with different Arrhenius parameters. Vyazovkin and Lesnikovich\textsuperscript{175} emphasize that all non-isothermal data have ambiguous solutions that arise from attempts to determine too many unknown constants from limited data, or when a set of data can be alternatively described by different models and kinetic constants\textsuperscript{164}. On this subject Malek\textsuperscript{167} has given an account of the correlation between kinetic parameters and the kinetic models from which they are derived. As a consequence of the correlation between $E$ and $A$, a thermal analysis (TA) curve can be described by a kinetic model with an associated apparent $E$ value, instead of the true model and true $E$ value. From this point of view single heating rate experiments can be deemed as problematic.

1.6.5.9 Multi-Heating-Rate, or Isoconversional, Method

It has been suggested that data from several dynamic experiments at different heating rates $\beta$ are the only acceptable norm for kinetic investigations using thermal analysis techniques, other than sets of $\alpha$-t data at a series of different but constant temperatures (temperature-jump method), or constant rate studies\textsuperscript{165}. When data from several dynamic experiments at different heating rates, $\beta$, are available the approach is usually to temporarily eliminate the unknown form of the model $f(\alpha)$ or $g(\alpha)$ by comparing measurements made at a common value of $\alpha$ under the different heating rate conditions. This approach is known as isoconversional kinetic analysis\textsuperscript{164}.
Isoconversional methods are based on the assumption that the rate of reaction at constant extent of reaction $\alpha$ is only a function of the temperature, i.e. that $f(\alpha)$ is independent from the degree of reaction $\alpha$:

$$d \ln \left( \frac{d\alpha}{dt} \right)_\alpha / dT^{-1} = -E_a / R$$

(54)

where the subscript $\alpha$ indicates the values at that extent of reaction. From integration of equation 52 we get

$$\ln \left( \frac{d\alpha}{dt} \right)_\alpha = -E_a / RT + \text{constant}$$

(55)

A plot of $\ln \left( \frac{d\alpha}{dt} \right)_\alpha$ against $T^{-1}$ is the basis of the Friedman method$^{164}$. If the investigated reaction is a single step reaction the lines for the different degree of reaction are parallel and have slopes $(-E_a / R)$ and intercepts $\ln[Af(\alpha)]$. Otherwise the slopes are different. The exponential factor can only be determined if $f(\alpha)$ is known$^{176}$.

Like other differential analysis techniques measurements of instantaneous rates are very sensitive to experimental noise, so use of an integral method is recommended, based on a more general form of integration of the equation:

$$g(\alpha) = \int_0^T (A/\beta) \exp(-E/RT) dT$$

$$= A \int_0^\alpha \exp(-E/RT(\alpha)) dT$$

(56)

Where $T(t)$ is the heating programme. For linear heating programmes, one of the many approximations for the temperature integral may be used$^{177}$. This leads to relationships of the form:

$$\ln(\beta) = \text{cons tan} t - (-E_a / RT\alpha)$$

(57)
Plots of $\ln(\beta)$ versus $1/T_\alpha$ are the basis of the methods of Flynn and Wall\textsuperscript{164} and Ozawa\textsuperscript{178,179}, both of which are integral methods.

There are numerous approaches involving the use of the second derivative of equation

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \left( \frac{d\alpha}{dt} \right) = \frac{A}{\beta} \exp\left( -\frac{E}{RT} \right) f(\alpha)$$ \hspace{1cm} (58)

Or the version with $f(\alpha) = (1-\alpha)^n$, with respect to temperature or with respect to time, despite the problems of obtaining accurate values of second derivatives\textsuperscript{164}. Using

$$\left( \frac{d\alpha}{dT} \right) = \frac{A}{\beta} \exp\left( -\frac{E}{RT} \right) (1-\alpha)^n$$ \hspace{1cm} (59)

gives

$$\left( \frac{d^2\alpha}{dT^2} \right) = \left( \frac{d\alpha}{dT} \right) \left[ \frac{E}{RT^2} - n \left( \frac{d\alpha}{dT} \right) (1-\alpha) \right]$$ \hspace{1cm} (60)

and because this second derivative must be zero at the point of inflexion of a TG curve and at the maximum of a DSC peak\textsuperscript{164}:

$$\frac{E}{RT_{\text{max}}^2} = \left( \frac{d\alpha}{dT} \right)_{\text{max}} (n(1-\alpha_{\text{max}}))$$ \hspace{1cm} (61)

from which $E$ maybe calculated if $n$ is known and $T_{\text{max}}$, $\left( \frac{d\alpha}{dT_{\text{max}}} \right)$ and $\alpha_{\text{max}}$ are measured. Combining equations. 59 and 61 gives\textsuperscript{164}:

$$\left( \frac{A}{\beta} \right) \exp\left( -\frac{E}{RT_{\text{max}}} \right) n(1-\alpha)^{n-1} = \left( \frac{E}{RT_{\text{max}}^2} \right)^n$$ \hspace{1cm} (62)

and because $(1-\alpha_{\text{max}})$is constant for a given value of $n$, the Kissinger\textsuperscript{180} method of obtaining a value for $E$ is to plot $\ln\left( \frac{\beta}{T_{\text{max}}^2} \right)$ against $\frac{1}{T_{\text{max}}}$ for a series of experiments at different heating rates $\beta$, the slope of which is $-\frac{E}{R}$. 
The Ozawa treatment is also applicable to derivative curves and is similar to the Kissinger method whereby $\ln \beta$ is plotted against $1/T_{\text{max}}$ and the slope is again $-E/R$\textsuperscript{164}.

Studies of the effects of sample mass and particle size on the determination of kinetic parameters from DSC runs using the methods of Kissinger and Ozawa, found that the two methods gave similar values for $E$ with slightly lower precision for the Kissinger method. It was suggested that value for $\alpha = 0.5$ be used in place of $T_{\text{max}}$.

1.6.5.10 Application of DSC study on silicone rubber cure reactions

DSC, DTA and TG have been used in the past to study the cure kinetics of thermosetting polymers, mostly thermosetting polymers such as epoxies, polyurethanes and unsaturated polyester compounds. As intimated there are comparatively fewer such studies on silicones\textsuperscript{113}.

As silicones are found in many industries it is important to understand how their structure affects their properties in order to improve processing techniques, for example, so that it may be possible to engineer the desired properties. Understanding structure-property relationships is important for other reasons as well. For instance, in the present study it was initially thought that the addition of stearic acid to the adhesive may cause an alteration of the structure of the adhesive by acting as an inhibitor for the hydrosilylation reaction responsible for producing a crosslinked rubber material. Should this reaction be inhibited the final yield of crosslinks would be affected. Fewer crosslinks produce a mechanically weaker material in terms of cohesive strength; it is this property that lends itself to the maximum potential strength of the adhesive. The development of a crosslinked polymer network determines processing behaviour, viscosity, gel point and crosslink
density. These parameters in turn affect the final properties of the network including modulus, ultimate strength and permeability\textsuperscript{184}.

The Kissenger method was used to investigate the kinetics of a two-part liquid silicone rubber (Dow Corning Q3-9590 A/B) by Macosko and Lee\textsuperscript{184}. This product is a flowable silicone elastomer specifically designed for liquid injection molding applications. Polymerisation in this compound results from a hydrosilylation reaction between vinyl terminated poly(dimethylsiloxane) (PDMS) and a multifunctional silane crosslinker. Using data obtained by isothermal and non-isothermal (dynamic) DSC a reaction model based on first order kinetics was proposed:

\[ dp_a = \bar{k}(1 - p_a) \]

where \( p_a = \alpha \) the extent of reaction (see equation 32 in Section 1.6.5.3).

In order to obtain the activation energy of polymerisation \( E_p \) and the frequency coefficient or pre-exponential constant \( A_p \), the Kissinger method was applied to data collected from DSC experiments. For this purpose it was assumed that the rate constant \( \bar{k} \) was Arrhenius temperature dependent throughout the entire cure, so that

\[ \bar{k} = A_p \exp\left(-\frac{E_p}{RT}\right) \] (63)

The Kissinger method entails plotting \( \ln \bar{k} \) against \( 1/T \) to yield a straight line where the slope gives the activation energy of reaction, in this instance the activation energy of polymerisation, and the intercept gives the frequency coefficient (again for polymerisation in this particular case).

The problem with this method has been identified by a number of authors. For example in a later study into the same silicone rubber material the inadequacy of the first order reaction mechanism chosen to describe the
polymerisation reaction was realised. The authors asserted that the first-order reaction mechanism attributed to this system would only be valid if the polymerisation took place as a single reaction between the vinyl terminated PDMS and the silane curing agent at the active catalyst site. It was found that this reaction is more complex one with several reversible reactions in parallel and in series. They identified that the deficiency of the first-order equation in modelling the true reaction mechanism lay in the anomalous concentration-dependant activation energy and rate constant.

By using isothermal and non-isothermal DSC data the rate of cure was examined and the initial first-order model mechanism was improved upon by determining the rate constants at several isothermal temperatures and fitting the data to reaction kinetic parameters. An Arrhenius plot was used to find their activation energies.

The initial model mechanism was improved upon by determining the rate of conversion by dividing the rate of exothermic heat release \( q(t) \) by the total heat of reaction,

\[
\frac{d\alpha}{dt} = \frac{q(t)}{m\Delta H_r}
\]

where \( m \) is DSC sample mass and \( \Delta H_r \) is the total heat release during a dynamic experiment. Then isothermal curing data was used to fit reaction kinetic parameters and the dynamic data tested the kinetic model under non-isothermal conditions. The resulting model is the revised version of the original first-order mechanism:

\[
\frac{d\alpha}{dt} = k_1(d - \alpha)(t - t_z)
\]

To test this new model under non-isothermal conditions, predicted conversions for the dynamic DSC run were compared to experimental data. It
was shown that the model slightly over estimated the inhibition time. The slightly lower precision with dynamic method has been documented\(^{164}\). These errors in the Kissinger method probably arise from the omission of the effect of the material between the specimen and the heat source, which invariably influences the heating of the specimen, in evaluating shapes of peaks and the relation of these shapes to the order of reaction kinetics\(^{183}\).

Kissinger set up expressions for quasi-steady state heating so that at the centre of the reference heating was represented by:

\[
T_r = T_0 + \phi t - \frac{\phi p c a^2}{4k}
\]  
(66)

and at the centre of the sample:

\[
T_s = T_0 + \phi t - f\left(\frac{dq}{dt}\right)
\]  
(67)

where \(\phi\) is the heating rate, \(a\) is the radius of cylindrical specimens, \(f(q/dt)\) is a function of the heating rate, \(dq/dt\) is the rate of heat absorption per unit volume, \(k\) is constant, \(t\) is time and \(T_0\) is the initial temperature.

The differential temperature is given by:

\[
\theta = T_s - T_r = f\left(\frac{dq}{dt}\right) - \phi \frac{p c a^2}{4k}
\]  
(68)

and

\[
\frac{d\theta}{dt} = f'\left(\frac{dq}{dt}\right) d^2q/dt^2
\]  
(69)

From this last equation he concluded that when \(d^2q/dt^2 = 0\), \(d\theta/dt\) was also zero. So when \(d^2q/dt^2 = 0\) the optimum rate of reaction occurs and a
maximum temperature difference, i.e. the peak in DTA/DSC deflection, must occur at the maximum rate of reaction (i.e. the reaction occurs equally in all parts of the specimen and that there are unchanging thermal characteristics). This conclusion is only an approximation of the behaviour of the material in the vicinity of the thermocouple but only so far as the small region can be considered to react homogenously. Since this is not the case, the Kissinger method is necessarily an approximation 163.

The preceding sections have shown that description of a chemical reaction by a mathematical model of rate law is often useful. However, it must be remembered that predictions made are only applicable within often very narrow limits of the data being evaluated. The physical and chemical use of such rate laws may give a good description over a certain range of reaction because the rate reacts very sensitively to those parameters which do not appear explicitly, namely stoichiometry of the reaction; the presence of solvents and catalysts; packing efficiency for heterogeneous samples; flow, rate and; type of purge gas 176. Although there are benefits in using gross rate laws as a first step in finding the reaction mechanism, the inherent risk with this is that it may hinder identification of the true mechanism 167. Furthermore, with particular reference to single heating rate data it must be remembered that analysis of such data can lead to the validation of preconceived ideas for a reaction mechanism which actually only applies over a particular range of the degree of reaction, thus rendering such analysis virtually useless 176.

A main advantage of isoconverisonal methods has been identified as being the calculation of consistent activation energies which are in good agreement with values from isothermal experiments. Variations of E with α are usually an indication of a complex reaction mechanism with at least two elemental steps. The relative contributions of these reactions to the overall reaction rate vary with temperature and the effective activation energy varies with the extent of conversion. A disadvantage of the approach is that the value of A cannot be determined without knowledge of the model f(α) 164.
At the end of all this analysis it must not be forgotten that the mechanistic clues are not yet the reaction mechanism, but rather a path leading to it that can further be followed only by using "species-specific" experimental techniques\textsuperscript{176}.

1.6.5.11 Summary

In summary, classification of methods of kinetic analysis as either differential or integral methods is not of great practical use because data can be transformed readily from one to the other by use of numerical methods of differentiation and integration. The isoconversional approach eliminates the need to identify the rate equation, or kinetic model, during the initial stages of a kinetic analysis\textsuperscript{164}. The values of the Arrhenius parameters for many reactions are relatively insensitive to the rate equation applicable, but for a complete analysis the values of A and E obtained in this first stage may then be used in identifying the conversion function\textsuperscript{168}. Irrespective of the method of analysis chosen, i.e. isoconversional or isothermal, it has been illustrated that the information obtained can often only be applied within very narrow limits of the evaluated data. Furthermore, these methods do not actually give the reaction mechanism, which can only be found by further investigation using chemical analytical techniques.

In our study, DSC was used to conduct kinetic investigations, specifically to ascertain any differences in the kinetic behaviour of the unmodified and modified cure reactions. Characterisation of the cure kinetics of the adhesive is intended to facilitate a better comprehension of the chemical and, subsequently, the physical properties of the material. This should in turn provide an explanation for the observed mechanical properties.
1.6.6 Solvent Swelling

Solvent swelling was used to investigate the bulk property of crosslink density and to ascertain the effect on it of stearic acid. This is directly linked to the effect of stearic acid on the adhesive cure reaction. If stearic acid inhibits the primary cure reaction as described in equation 13 in Section 1.5.1 then the crosslink density of the modified adhesive will be reduced. Conversely, if this reaction is accelerated then the crosslink density should increase in the modified adhesive in comparison to the unmodified material.

Flory\textsuperscript{184} states when a crosslinked polymer is placed in a solvent it does not dissolve completely. Instead the polymer absorbs some of the solvent, which causes it to swell. The swollen gel is in fact a solution, albeit an elastic rather than a viscous solution. The amount by which the polymer swells represents a competition between two forces. The free energy of mixing $\Delta H$, or entropy of dilution, will cause the solvent to penetrate and try to dilute the polymer solution. This is an entropic event and as such may be enhanced by increasing the temperature. As the polymer chains in the crosslinked polymer network begin to elongate under the swelling action of the solvent an elastic retractive force is generated in opposition to this deformation. As swelling proceeds, the opposing retractive force increases and the diluting force decreases. Ultimately, a state of equilibrium swelling or steady state is reached in which the two forces are balanced.

Since the steady state swelling ratio is a direct function of extent of crosslinking in the sample, swelling experiments are a simple technique to characterise polymer networks. Swelling measurements can be used to index polymer systems with different levels of crosslinking, at a basic level. At a higher level of analysis, the crosslink density, molecular weight between crosslinks, and number of crosslinks per chain can be computed if the Flory interaction parameter for the polymer-solvent system is known\textsuperscript{184}. 
1.6.6.1 Theory

The free energy change of mixing when an isotropic polymer sample is placed in a pure solvent can be written in terms of the ordinary free energy of mixing $\Delta F_m$ and the free energy associated with expansion of the polymer network $\Delta F_{el}$ as

$$\Delta F = \Delta F_m + \Delta F_{el}$$  \hspace{1cm} (70)

The free energy of mixing is described in terms of the number of solvent molecules $n_1$, the volume fractions of solvent and polymer, $v_1$ and $v_2$, and the Flory interaction parameter $\chi_1$ as

$$\Delta F_m = kT \left[ n_1 \ln v_1 + \chi_1 n_1 v_2 \right]$$  \hspace{1cm} (71)

The elastic component of the free energy $\Delta F_{el}$ is associated with the change in the entropy as the network is deformed, and can therefore be written in terms of the linear deformation factor $\alpha_s$ as

$$\Delta F_{el} = \left[ kT \nu_e / 2 \right] 3 \alpha_s^3 - 3 - \ln \alpha_s^3$$  \hspace{1cm} (72)

where $\nu_e$ is the effective number of chains in the network. The chemical potential of the solvent in the gel is defined as

$$\mu_1 - \mu_1^0 = N \left( \partial \Delta F_m / \partial n_1 \right)_{T,p} + N \left( \partial \Delta F_{el} / \partial \alpha_s \right)_{T,p} \left( \partial \alpha_s / \partial n_1 \right)$$  \hspace{1cm} (73)

where $N$ is Avogadro's number. It is noted that $\alpha_s^3 = \frac{V}{V_0}$ where $V_0$ is the volume of the unswollen network and $V$ the volume of the swollen network.
Accordingly, \( \frac{V_0}{V} = \nu_2 \). Incorporating the molar volume of the solvent \( \varphi_1 \) to compute the solvent contribution to the volume yields the expression:

\[
\alpha_3^3 = \frac{1}{\nu_2} = (V_0 + n_1 \varphi_1 / N)V_0
\]  

(74)

Therefore, one can evaluate equation 73 with equations 72, 71, and 74 to yield:

\[
\mu_1 - \mu_1^0 = RT \left( \ln \left( 1 - \nu_2 \right) + \nu_2 + \chi_1 \nu_2^2 + \varphi_1 \left( \nu_2 / V_0 \right) \left( \nu_2^{13/3} - \nu_2 / 2 \right) \right) 
\]

(75)

At equilibrium, the chemical potential of the solvent in the polymer will equal the pure solvent, so that the left side of equation 75 will be equal to zero. Rearranging equation 75 yields:

\[
- \left[ \ln \left( 1 - \nu_2 \right) + \nu_2 + \chi_1 \nu_2^2 \right] = \varphi_1 \left( \nu_2 / V_0 \right) \left( \nu_2^{13/3} - \nu_2 / 2 \right) 
\]

(76)

Rewriting the number of chains/unit volume in terms of the specific volume of the polymer \( \bar{\nu}_x \) and the molecular weight between cross links \( M_c \) such that

\[
\frac{\nu_x}{V_0} = - \frac{1}{\bar{\nu}_x M_c}
\]

and further rearrangement gives the final expression for the crosslink density \( \nu_x \).

\[
\frac{1}{\bar{\nu}_x M_c} = \nu_x = \frac{\ln \left( 1 - \nu_2 \right) + \nu_2 + \chi_1 \nu_2^2}{\varphi_1 \left( \nu_2^{13/3} - \nu_2 / 2 \right)}
\]

(77)

Experimentally, one measures the swell ratio \( q = \frac{V}{V_0} = \frac{1}{\nu_2} \) and, knowing the Flory interaction parameter, computes the crosslink density and molecular weight between crosslinks \( M_c = \frac{1}{\bar{\nu}_x} \).
Chapter 1

1.7 General Summary

The aim of the present case study was to establish the mechanism by which stearic acid reduced the strength of an aluminium bonded joint. The roles of strength at the interface, cohesive phases and distribution of stresses within the joint were discussed in relation to their impact on joint strength. This led to a discourse of the effect of surface pre-treatment; the role of the adhesive with respect to surface chemistry and bulk properties; and factors that influence distribution of stresses.

The popular explanation given by researchers for premature material failure in the presence of stearic acid has been the formation of a weak boundary layer of the saturated fatty acid at the interface of the joint. Thus by using advanced surface analytic techniques, such as XPS and SSIMS, this reasoning will be tested. The influence of cohesive strength within the adhesive on overall joint strength was also discussed. As the adhesive used in this study, Sylgard 184, is dependent upon the formation of crosslinks for strength within this phase it was also proposed that stearic acid may inhibit this process thereby weakening the adhesive and causing an erosion adhesion via this mechanism. This theory was investigated using FTIR techniques in conjunction with DSC based kinetic analysis and solvent swelling experiments to provide a measure of the effect of stearic acid on crosslinking. Finally, it was considered that stearic acid may react to produce areas of stress concentration in the adhesive matrix so causing premature failure as a result of ensuing stress concentration. In relation to this, FEA combined with experimental joint strength assessment methods, such as T-peel and lap joints, to perform stress analysis of joints.

Chapter 2 produces a detailed description of all the experiments carried out within this study.
Chapter 2 Experimental Procedures

In this chapter, firstly a description is given of all the materials used, along with pretreatment conditions specified. The joint configurations and test conditions are detailed for the main mechanical tests. A description of the thermal analysis and FT-IR spectroscopy procedures used to investigate cure kinetics follows.

2.1 Materials

2.1.1 Adhesive

The adhesive used in this study was Sylgard 184, a PDMS-based adhesive that is manufactured by Dow Corning. As supplied it is a two-part adhesive consisting of an elastomer base and a curing agent. However, in this study an accelerator was added in order to reduce cure time from 48 hours at room temperature to 24 hours. Table 2.0 illustrates the typical properties of Sylgard 184 in its two part form, as supplied by Dow Corning.

<table>
<thead>
<tr>
<th>Colour</th>
<th>Clear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cps or mPa/sec)</td>
<td>3900</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.03</td>
</tr>
<tr>
<td>Heat cure time</td>
<td>45 minutes @ 100°C</td>
</tr>
<tr>
<td>Weight Averaged Mw (g/mol)</td>
<td>33000</td>
</tr>
</tbody>
</table>

Table 2.0 Typical Properties of Sylgard 184
2.1.1.1 Unmodified adhesive

The adhesive was made by mixing the individual components in a plastic cup in a 10:1:1 weight ratio of base to curing agent to accelerator. The components were stirred gently using a wooden spatula so as not to incorporate too much air. The mixture was then degassed using a vacuum pump for 15 to 20 minutes so that as much air as possible was removed.

2.1.1.2 Modified adhesive

The adhesive was made by mixing the individual components in a plastic cup in a 10:1:1 weight ratio of base to curing agent to accelerator. Stearic acid that had been ground in an agate mortar and pestle and sieved through a 212 micron mesh was then added to the adhesive in the required quantities. The components were stirred as described above.

2.2 Aluminium alloy substrates

The substrates chosen for investigation were 1xxx series aluminium foil, 60μm thick, and clad aluminium-copper alloy, 2024-T3. The code T3 designates that the material has been solution heat-treated, cold worked and naturally aged. The aluminium foil was used for the peel test and the 2024-T3 was used for single lap shear (SLS) tests. The composition of these alloys can be found in Table 2.1.
Chapter 2

Experimental Procedures

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>T024-T3, Clad</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 2.1  Alloy composition

The 1xxx series alloy is virtually pure (99.99%) aluminium with a small amount of copper and is also the cladding material for the 2024-T3 alloy.

2.3  Additives

2.3.1  Stearic Acid, Zinc Stearate and Calcium Stearate Modifiers

\[ C_{17}-H_{35}-C-O-(\text{metal or H}) \]

Figure 2.0  Stearates Chemical Formula.

Figure 2.0 illustrates the chemical formula for the stearates used in this study. Stearic acid was supplied by Fisher and zinc and calcium stearates were supplied by Avocado Research Chemicals. Each additive was prepared for use by grinding using an agate mortar and pestle. The powder was then sieved through a 212 μm mesh in order to control particle size. The properties of these materials are shown in the table below.
Table 2.2  Physical Properties of Stearates

<table>
<thead>
<tr>
<th>Fatty Acid/Salt</th>
<th>Appearance</th>
<th>Chemical Formula</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic Acid</td>
<td>White, flakes</td>
<td>CH₃(CH₂)₁₆COOH</td>
<td>284.47</td>
<td>67-69.6</td>
</tr>
<tr>
<td>Zn Stearate</td>
<td>Fine, white powder</td>
<td>Zn(C₁₈H₃₅O₂)₂</td>
<td>632.32</td>
<td>130</td>
</tr>
<tr>
<td>Ca Stearate</td>
<td>Fine white powder</td>
<td>Ca(C₁₈H₃₅O₂)₂</td>
<td>607.04</td>
<td>179-180</td>
</tr>
</tbody>
</table>

Stearic acid was added in the range 0.1 wt% to 1.0 wt% and its effect on adhesion, as measured by the T-peel test studied. 1.0 wt % Calcium and zinc stearate were used for comparative purposes to investigate the effect of these additives on measured adhesion.

2.3.2  Acetic Acid

![](image)

Figure 2.1  Molecular Structure of Acetic Acid (Ethanoic Acid)

Glacial (pure) acetic acid was used in order to investigate the effect of hydrocarbon chain length on adhesion. The physical properties of acetic acid are presented in Table 2.3.
Acetic acid was chosen in order to investigate the effect of carbon chain length on adhesion. 1.0 wt% glacial acetic acid was added.

### 2.4 Substrate Pretreatment

#### 2.4.1 Degrease only

The minimum pretreatment was a simple degrease operation and preceded the following pretreatment procedures. During degreasing the substrates were placed in a beaker of acetone in a Decon FS200b ultrasonic bath initially for 5 minutes, then the used acetone was changed and replaced with fresh acetone and ultrasonic treatment applied for another 5 minutes. Following completion of the degreasing procedure the substrates were left to dry completely under ambient conditions.
2.4.2 Grit-blast (GB)

Initially the substrates were degreased using the procedure described above. Following this the substrates were placed one at a time inside the blasting chamber of a Guyson Blast cleaner. The material was blasted with brown Alumina 30/40/SS at a pressure of $6.5 \times 10^5$ Pa.

2.4.3 Sulphuric Acid/Chromic Acid Etch (CAE)

The substrates were degreased using the procedure described in section 2.4.1 and then rinsed in cold deionised water for 2 minutes. Subsequently the substrate was placed in a 5L FPL etch solution ($H_2SO_4/Na_2CrO_4$) for 5 minutes at $70 \pm 1^\circ C$. On completion of the etch procedure, the substrate was rinsed in deionised water for 2 minutes and dried under ambient conditions, until completely dry before bonding.

2.4.4 Chromic Acid Anodise (CAA)

The substrates were primarily subjected to the degreasing process described in section 2.4.1 and then processed according to the CAE process described above. Immediately after removal from the etching bath, the substrates were anodised using 40/50 anodising treatment. The temperature of the anodising bath was maintained between $38^\circ C - 42^\circ C$. The CAA anodising procedures are listed below with the maintenance controls for users of this process:
Chapter 2

Experimental Procedures

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic acid</td>
<td>35-50g/l</td>
</tr>
<tr>
<td>Chlorides (NaCl)</td>
<td>0.20g/l</td>
</tr>
<tr>
<td>Sulphates (Na₂SO₄)</td>
<td>0.50g/l</td>
</tr>
<tr>
<td>Voltage</td>
<td>40-50±1V (DC)</td>
</tr>
<tr>
<td>Ramp rate</td>
<td>See Figure</td>
</tr>
<tr>
<td>Anodising time</td>
<td>35-45 minutes</td>
</tr>
</tbody>
</table>

After anodising the parts were rinsed in deionised water at ambient temperature for 5 minutes and then dried in ambient conditions until completely dry.

Figure 2.2 Operating Cycle for standard CAA 40/50V Process
Chapter 2

2.5 Mechanical Testing

2.5.1 Adhesion Tests

2.5.1.1 T-peel Test

The adhesive was prepared using the procedures detailed in sections 2.1.1 and 2.1.1.2. Immediately following degassing the adhesive was poured onto pretreated 1xxx series Al foil sheets sandwiched by 304.8 mm² glass plates separated by Al spacers, which were 0.06 mm thick. All joints were tested after curing for 24 hours at room temperature and ambient conditions. The dimensions for the assembled joints are shown below, in Figure 2.3. The spacers were used for bondline control purposes.

![Figure 2.3 T-peel Joint Configuration. (a) plan view, (b) side view](image-url)
A Lloyd Instruments 10000 Tensometer was used to carry out the peel test experiments. The load cell used was 500 N and the instrument was set in the peel mode. The rate of testing was 50 mm/min and all tests were carried out at room temperature. The dimensions for test joints were 100mm x 30mm. The width was chosen to coincide with that of the jaws. A 2.54 cm (1 inch) strip was left free. Nine samples of unmodified and modified joints were tested. Immediately after testing, the failed joints were wrapped in aluminium foil so that exposure of the surfaces to air was limited. This was done so that the failed surfaces could be subjected to further analysis.

2.5.1.2 Single Lap Shear (SLS) Joint Test

SLS testing was used to provide complementary information to the peel test to investigate the effect of joint geometry on the observed effect of stearic acid on adhesive strength. As peel tests induce interfacial failure it was necessary to establish whether the reductive effect of stearic acid was merely a consequence of joint geometry.

SLS joints were prepared using the various pre-treatments described in Section 2.4. To make the SLS joints the mixed and degassed adhesive was poured onto the overlap area of the coupon and both coupons were held together by bull-dog clips. SLS joints were prepared using 2024-T3 clad alloy coupons. The dimensions are shown below.
Experimental Procedures

Figure 2.4 Dimensions of SLS joints. (a) plan view, (b) side view

The joints were tested on Lloyd Instruments 10000 Tensometer with a 500 N load cell for the degreased coupons; 50 KN load cell for the anodised coupons; 10 KN load cell for the grit blasted and etched coupons. All tests were conducted at crosshead speed of 50 mm/min. The maximum mean load to failure was then recorded. Five replicates per treatment were tested and the average taken.
Chapter 2
Experimental Procedures

2.5.2 Tensile Test-Dumbbell Specimens

Tensile tests were carried out on dumbbell specimens of unmodified and modified adhesive. The samples were prepared by curing each type of adhesive in an aluminium mould 100 mm x 100 mm and 3 mm thick so that a sheet was formed. A cutter (Wallace) was then used to cut dumbbells with a gauge length of 30 mm and a diameter of 3 mm ± 0.01 mm. The test was carried out on a Lloyd Instruments 10000 Tensometer in the tensile test mode with a load cell of 500N. The test rate was 50mm/min. Five samples each of the unmodified and modified adhesive were tested.

2.6 FE MODELLING OF T-PEEL JOINTS

This section discusses the finite element model of the T-peel joint geometry. The finite element models were constructed with the commercial finite element program MSC Mentat and solved using the solver MSC Marc. The finite element models have been employed for the purpose of investigating the stress distribution of T-peel joint systems, both with aluminium as adherends and unmodified Sylgard 184 and modified Sylgard 184 adhesives. Particular consideration is given to the stress distribution in the adhesive and adherend near the fillet area.

2.6.1 Physical model

The physical situation being modelled is considered first. The T-peel joints comprising of aluminium as adherends and Sylgard 184 as adhesive is considered and the following factors are considered
Chapter 2

Experimental Procedures

- The T-peel joint dimensions
- The method of loading
- Nature of boundary condition
- Geometrical symmetry

Figure 2.5 is a simplified diagram of the T-peel joints showing its dimensions.

2.6.1.1 Material Properties

The material properties for the aluminium adherend were taken as standard handbook values and are shown in Table 2.4. The material properties for the adhesives were obtained experimentally using a tensile testing machine. Dumbbell samples of both adhesives were made and the dimensions of the narrow section were 3 mm × 3 mm. These were pulled at a constant rate of 50 mm/min until failure. Five samples of each adhesive were tested. The material properties of the adhesives are shown in Table 2.5. For all the analyses performed, linear material properties and geometrical non-linearities have been assumed. The material properties for the adhesives were determined using the experimental data fit function for elastomers in MSC. Mentat. The Mooney-Rivlin material model provided the best fit for the uniaxial data obtained from the uniaxial tests.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's Modulus [MPa]</th>
<th>Poisson's ratio</th>
<th>Yield Stress, $\sigma_y$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>69000</td>
<td>0.33</td>
<td>165</td>
</tr>
</tbody>
</table>

Table 2.4 Material properties for the aluminium adherend
Chapter 2 Experimental Procedures

<table>
<thead>
<tr>
<th></th>
<th>$C_{01}$ [MPa]</th>
<th>$C_{10}$ [MPa]</th>
<th>$C_{11}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sylgard 184 Unmodified</td>
<td>-0.2564</td>
<td>0.6170</td>
<td>0.2997</td>
</tr>
<tr>
<td>Sylgard 184 M (0.1 wt% Stearic Acid)</td>
<td>0.0186</td>
<td>0.1578</td>
<td>0.0531</td>
</tr>
<tr>
<td>Sylgard 184 M (0.3 wt% Stearic Acid)</td>
<td>-0.2862</td>
<td>0.6418</td>
<td>0.3012</td>
</tr>
<tr>
<td>Sylgard 184 M (0.4 wt% Stearic Acid)</td>
<td>-0.0509</td>
<td>0.5025</td>
<td>0.4283</td>
</tr>
<tr>
<td>Sylgard 184 M (1.0 wt% Stearic Acid)</td>
<td>-0.4138</td>
<td>0.7717</td>
<td>0.3658</td>
</tr>
</tbody>
</table>

Table 2.5 Material properties for the adhesives

2.6.1.2 Finite Element Model

The T-Joint was modelled using a 2-dimensional model. The 2D 8 node continuum plane strain reduced integration element was used to examine the stress distribution in the joint.

This element has genuine quadratic contact features and can capture stress concentration better than linear elements. The bond between the adhesive and adherend is assumed to be perfect and the interface and adhesive free of voids. This assumption of a perfect bond means that the finite element model takes no account of the adhesion properties of the interface.

Due to symmetry, only half of the joint is modelled and the constraints and loads were applied to mimic the tensile loading conditions on the specimen while it was secured in non-rotating clamps. The load was applied in the form of displacement along the $x$-axis applied to all the nodes at the free end so they all move by the same amount in the $x$-direction. These nodes were also constrained against movement perpendicular to the load and against rotation around the $z$-axis. Symmetrical conditions were imposed by constraining the nodes at the symmetry plane against movement along the $x$-axis. These boundary conditions are illustrated in Figure 2.5.
Figure 2.5  T-peel specimen (dimensions in mm)
2.6.1.3 Mesh Design and Element Performance

The large differences between the mechanical properties of adhesive and the adherend lead to an ill-conditioned numerical problem. A mesh convergence study was performed with models of different mesh densities and element types in order to minimize numerical errors. The mesh was refined at the regions of high stress gradients near the interface and fillet area. Figure 2.7 shows a typical mesh of the joint near the fillet area.
**Figure 2.7** FE Mesh showing fillet area mesh density
Chapter 2 Experimental Procedures

2.7 Surface Analytical Techniques

The surface analysis results described below were used to investigate the effect of additives, particularly stearic acid, on the mode of failure. SSIMS and XPS were used to complement one another. These were used primarily because of their surface sensitivity; as previously discussed.

2.7.1 SSIMS

A Cameca 3F SIMS instrument was used to analyse the surface of the failed peel samples. A positive ion spectrum was produced using a duoplasmatron ion gun using negative oxygen at 12.5 keV. The mass spectrometer was a magnetic sector type. The intensity of the beam was <1nA and conditions were such that less than 1% monolayer was removed during analysis. The sample area analysed was 150 μm, with a mass resolution ($m/\Delta m$) of >250.

2.7.2 XPS

XPS spectra were recorded on a VG Scientific Escalab MK 1 Vacuum generator with an unmonochromatised Al K$_\alpha$ X-ray source (1486.6 eV) and operated in constant analyser energy (CAE) mode. A source potential of 9 kV was used at 20 mA current. For later experiments this was reduced to 8.5 kV at 20 mA. The survey spectra were obtained at a pass energy and scan width of 1000 eV and the high resolution spectra using 25 eV pass energy with summation of multiple scans to reduce noise. XPS spectra were calibrated by assuming 285 eV binding energy for aromatic (C-C) and aliphatic carbon (C-H). Quantification was achieved by measurement of peak area following subtraction of a Shirley type background. Analysis was conducted on 10mm$^2$
samples of the polymer and metal side of failed joints generated from the peel test.

2.7.3 ATR

This technique was used to supplement SSIMS and XPS data. Spectra were collected using a Mattson 3000 FTIR Spectrometer with the ATR apparatus attached. The samples examined were failed peel test samples. Spectra were collected over the mid-infrared range using 200 scans at a resolution of 4 cm\(^{-1}\). All spectra were obtained by pressing the failure surfaces on an internal reflection element (IRE). At each internal reflection, the IR radiation actually penetrates a short distance (~1 \(\mu\)m) from the surface of the IRE into the sample. The background for these samples was air.

2.8 Kinetic Analysis by DSC

The aim of these experiments was to measure the kinetics of the crosslinking reaction in order to determine the activation energy (\(E_A\)) of the hydrosilylation reaction of Sylgard 184.

2.8.1 Sample preparation

The adhesive mixture was prepared according to the procedure outlined in Sections 2.1.1.1 and 2.1.1.2. After thorough mixing, the degassing stage was omitted. Approximately 25 mg of adhesive was inserted into aluminium pans (40\(\mu\)l). These pans and lids were weighed before and after the addition of the
adhesive mixture so that the mass of the adhesive could be calculated and noted. The following samples were studied:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sylgard 184</td>
<td>Base:crosslinker 10:1</td>
</tr>
<tr>
<td>Sylgard 184 + 0.3 wt%</td>
<td>Base:crosslinker:stearic acid 10:1:0.3 wt%</td>
</tr>
<tr>
<td>stearic acid</td>
<td></td>
</tr>
<tr>
<td>Unmodified adhesive</td>
<td>Base:crosslinker:accelerator 10:1:1</td>
</tr>
<tr>
<td>Modified adhesive</td>
<td>Base:crosslinker:accelerator:stearic acid</td>
</tr>
<tr>
<td></td>
<td>10:1:1:0.1, 0.3, 1.0 wt%</td>
</tr>
</tbody>
</table>

Table 2.6 Adhesive Preparations for DSC

2.8.1.1 Kissenger Method

Once the sample had been sealed in the Al pans, a hole was made in the lid of the pan in order to allow any gases evolved during the experiment to escape. Samples were placed in a low temperature Mettler DSC30 cell and studied at heating rates ($\phi$) of 20, 10, 5, 2 and 1 °C/min. The temperature range employed was from -100°C to 200°C. The cell was purged with Argon in order to create an inert atmosphere. The cure reaction, was analysed by a Mettler TA3000 system. As the progress of the reaction was followed a trace of heat flow versus temperature was produced. The areas under any peaks produced were calculated giving a value pertaining to the enthalpy of the reaction (mJ). The maximum peak temperature ($T_m$) was obtained from the plot. This data was used to plot a graph of $\ln(\phi/T_m^2)$ against $1/T_m$, the slope of which gave $E_A$ and the intercept $A$. Following the end of each analysis the
samples were processed once more at the same scan rate. This ensured that the reaction was complete.

2.8.1.2 Friedman Method

This experiment was carried out on a TA instruments Q1000 series instrument and samples were placed in hermetically sealed Al pans to control the pressure of the enclosed system. The heating rates chosen for this experiment were 1, 2, 4 and 8°C/min from 0°C to 200°C. At 1 and 2°C/min the temperature was modulated at ± 0.5°C every 60 sec. The temperature was not modulated at the higher heating rates as this technique is applied to low heating rates. The machine was programmed to run isothermally for 10 minutes at 0°C, and then to ramp the temperature up at the selected heating rate up to 200°C and remain at this temperature for 10 minutes. The chamber was purged with nitrogen at a rate of 30 mL/min. The results were analysed using the Friedman analysis. Plots of $\ln(\frac{d\alpha}{dt})_a$ vs $1/T_a$ were drawn the slope of which gave $E/R$ thus enabling calculation of the activation energy.

2.8.1.3 FTIR Spectroscopy

In the present study, FTIR was employed to investigate the effect of stearic acid on the hydrosilylation cure reaction. The technique described by Hertz et al.\textsuperscript{163} formed the foundation of this investigation. In the cited study the progress of the hydrosilylation reaction was followed by continuous recording of the infrared spectra. The requirements for quantitative analysis as stipulated by the Beer-Lambert law were met by creating a path between the NaCl cell windows of 0.05mm. The same procedure was used in the present study. Here, spectra were collected using a Mattson 3000 FTIR Spectrometer. The liquid samples of unmodified and modified adhesive were prepared by forming a film of between two NaCl discs separated by 0.05 mm
polyethylene spacers. 0.5 ml of liquid was injected into the apparatus using a syringe. The adhesive film was then allowed to cure at room temperature and the progress of the reaction followed by inserting the NaCl plates into the spectrometer. Spectra were collected over the range 300 to 4000 cm\(^{-1}\); 64 scans were accumulated at a resolution of 4 cm\(^{-1}\). The same number of scans was used to record the background, which was air. Spectra were collected initially every 10 minutes for the first hour, and then every 20 minutes for up to 8 hours. The last reading was taken after 72 hours had elapsed. The rate of the reaction was determined by measuring the areas of the peaks pertaining to SiH with respect to a reference peak that occurs at 1944 cm\(^{-1}\) which remains unchanged during the reaction. With this method, conversion rate can be described by \( \tau = A_0 - A_t / A_0 \).

2.9 Solvent Swelling

Solvent swelling is the traditional method of detecting and assessing crosslinking in polymers. In this experiment toluene was the chosen solvent as it is commonly employed in the literature for similar experiments with PDMS.

Vertical slices, approximately 17x3x3 mm, were cut from cast sheets of cured, unmodified and modified, adhesive using a steel ruler and scalpel. Casting was carried out according to the procedure outlined in Section 2.5.2. After weighing \( W_0 \) the strips were immersed in 20 cm\(^3\) of toluene at room temperature (20\(^{\circ}\)C) for 24 hours before being removed and twice blotted between paper tissues and then re-weighed \( W_t \). After removal from the solvent the strips were allowed to dry in air for 48 hours and reweighed \( W_d \).
Chapter 3. Results

3.1 Joint Assessment

In this section the results of the effects of joint configuration, additives, and substrate pretreatment on joint strength are displayed.

3.1.1 T-peel test

To assess bond strength peel testing was carried out on joints undoped, also known as unmodified, and doped or modified with up to 1wt% stearic acid, as detailed in Sections 2.5.1.1. The results of the following tests were obtained from 1xxx series Al foil samples that had been etched using the procedure outlined in Section 2.4.3. All tests were conducted after 24 hours. Mean peak loads were used in determining peel strengths, which were calculated using equation 17 in Section 1.6.1.1.2. The errors stated in Tables 3.0, 3.1 and 3.2 were calculated using $\Delta P = \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$ where $P$ is peel strength, $x$ is the average of the mean peak loads used in determining peel strengths (N) and $y$ is the average sample width (m). Peel strength is a function of the variables peel load and sample width, so this method calculates the propagation of errors for each variable for each measurement.

Figure 3.0 shows a selection of typical force (N)/extension (mm) curves for unmodified joints and joints modified by concentrations representing relatively small and large amounts of stearic acid additive.
Chapter 3 Results

Figure 3.0  Typical force/extension curves for stearic acid modified, FPL etched, T-peel joints

The area under the peel curves represents the energy absorbed by the joint. The critical parameter is the force per unit width required to peel the joints.

Figure 3.1 demonstrates the effect of stearic acid concentration on FPL etched joints, as measured by the T-peel test. The data points were fitted to a third order polynomial line of best fit. Errors in Table 3.0 are calculated as described above.
Figure 3.1  Effect of stearic acid on adhesive strength.

![Graph showing effect of stearic acid on adhesive strength.](image)

<table>
<thead>
<tr>
<th>wt% stearic acid</th>
<th>Peel strength (N m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>318 ± 35</td>
</tr>
<tr>
<td>0.1</td>
<td>249 ± 28</td>
</tr>
<tr>
<td>0.2</td>
<td>248 ± 28</td>
</tr>
<tr>
<td>0.3</td>
<td>190 ± 21</td>
</tr>
<tr>
<td>0.4</td>
<td>173 ± 19</td>
</tr>
<tr>
<td>0.8</td>
<td>136 ± 15</td>
</tr>
<tr>
<td>1.0</td>
<td>123 ± 14</td>
</tr>
</tbody>
</table>

Table 3.0  Peel strength values for unmodified and stearic acid modified T-peel joints.
Table 3.0 depicts the numerical values of data points in Figure 3.1. The table shows that there is a graduated reduction in peel strength as stearic acid content is increased. Overall, between 0 wt% and 1.0 wt% stearic acid there was a 61% reduction in peel strength. The reduction in peel strength between 0 wt%, 0.1 wt% and 0.2 wt% stearic acid was in the region of 22%. At 0.3 wt% the difference in peel strength was about 40%. This difference increased to around 45% when 0.5 wt% stearic acid was added. At 0.8 wt% there was, approximately, a 56% reduction in peel strength compared to the strength of unmodified joints. The largest fall-off in joint strength was obtained when 1.0 wt% stearic acid was incorporated into the adhesive. At this concentration joint strength was reduced by about 61%.

3.1.1.1 The effect of other additives on peel strength

Calcium and zinc stearate and glacial acetic acid were used in a parametric study into the effect of different additives on joint strength. Calcium and zinc stearate were chosen to investigate the effect of their metal substituents on adhesion as they are popular mould release agents along with stearic acid. They were also chosen to ascertain whether the effect on adhesion observed with stearic acid was due to the COOH group or due to the long chain hydrocarbon. Acetic acid has a short carbon chain length, so it was chosen to investigate the effect of carbon chain length on the observed reduction in the presence of saturated fatty acids. Each joint was modified with 1.0 wt% of each additive. All joints were pretreated using the FPL procedure described in Section 2.4.3 and prepared and tested according to instructions described in Section 2.5.1.1. Subsequent joint strength was assessed after curing for 24 hour at room temperature. Each test was repeated three times and average maximum peel force values used in determining peel strength. These results are shown in Figure 3.2.
Figure 3.2  Effect of alternative additives on adhesive strength.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Peel strength (N m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>318 ± 35</td>
</tr>
<tr>
<td>1.0 wt% Stearic acid</td>
<td>123 ± 14</td>
</tr>
<tr>
<td>1.0 wt% Acetic acid</td>
<td>427 ± 50</td>
</tr>
<tr>
<td>1.0 wt% Calcium stearate</td>
<td>250 ± 28</td>
</tr>
<tr>
<td>1.0 wt% Zinc stearate</td>
<td>185 ± 20</td>
</tr>
</tbody>
</table>

Table 3.1  Affect of additives on adhesive strength as measured by T-peel test at room temperature and after curing for 24 hours.
From Figure 3.2 the peel strength of acetic acid modified joints was higher than the peel strength for unmodified joints, 427 N m⁻¹ compared with 318 N m⁻¹ respectively. 1.0 wt% zinc stearate reduces joint strength to a greater extent than the same amount of calcium stearate. Adding zinc stearate reduces joint strength by approximately 40% compared with around 20% with calcium stearate. However, stearic acid has the most substantial decline in strength with a 60% reduction in comparison with joints made from unmodified adhesive.

3.1.1.2 SLS test

SLS joints were used to assess whether the effect observed with the T-peel configuration was peculiar to the peel geometry or whether it was due to a material response. The effects of joint configuration and surface pretreatment on joint strength were investigated. Clad 2024-T3 aluminium was used to produce the joints. Pretreatments were carried out according to Section 2.4. Joints were modified with 0.3 wt% stearic acid. The results of these studies are shown in Figure 3.3.
Figure 3.3 The effect of SLS joint configuration and surface pre-treatment on adhesive strength of unmodified and modified joints.

Firstly, Figure 3.3 shows that substrate pretreatment has an effect on the final joint strength. Furthermore, modification with 0.3wt% stearic acid appeared to enhance joint strength when SLS joint configuration was used to assess joint strength. This apparent enhancement in joint strength was more dramatic when the adherend was etched compared with the other pretreatments. The least reduction was given when the substrate was only degreased (DG).

The effect of surface pretreatment on adhesion measured by T-peel test was also investigated. Both unmodified and joints modified with 0.3wt% stearic acid were studied.
Figure 3.4 The effect of surface pre-treatment on T-peel strength.

As with the SLS joints, substrate pre-treatment affects joint strength in the T-peel test. In this instance the largest difference is seen after the substrate has been anodised. The smallest difference is again achieved after only degreasing the adherend.
Table 3.2 Comparison of the effect of joint configuration and surface pre-treatment on adhesive strength.

Table 3.2 shows that the presence of stearic acid improved joint strength of SLS joints but reduced it in T-peel joints, showing that joint strength is affected by configuration. Larger errors occurred where joints dismantled immediately upon application of the load. In such instances failure load was noted as zero.
3.2 Failure Analysis

The surfaces of joints failed during the T-peel test were characterised by SEM, SSIMS, XPS and ATR to determine mode of failure of unmodified and modified joints. Both polymer and metal surfaces of these joints were examined. Polymer surfaces were used as a reference to characterise the bulk adhesive. The metal surfaces were themselves used to determine mode of failure and also to establish whether stearic acid had migrated to the interface. In all cases the adherends were etched using the FPL procedure described in Section 2.4.3. These analyses were performed as soon as possible after the failure surfaces were generated. However, when this was not possible the samples were wrapped in aluminium foil and sealed in sample bags in order to prevent contamination.

3.2.1 SEM

Both surfaces exposed by peeling were examined by SEM, SSIMS, XPS and ATR as described in Section 2.7. SEM represents the first tier of failure analysis. The figures below show only SEM micrographs of the metal surface of failed joints. The polymer side of failure was also studied for references purposes. These surfaces were very similar with very little variation in features. A typical example is shown in Figure 3.5. These micrographs show that the texture of the substrate is visible through the adhesive.
Figure 3.5  SEM micrograph of features typical of the polymer surface of failed (a) unmodified and (b) modified (0.3wt%) joints

The following SEM studies show plan views of the scalloped nature of the surfaces which is a result of the shallow, hexagonal cell structure peculiar to the FPL etch process of aluminium\(^{11}\). This cell structure is said to have a concentration of protruding whiskers\(^{11}\). Also evident is presence of adhesive material in some of the pores. The area of penetration varies with stearic acid content, ranging from large area of pore penetration by the adhesive in the unmodified case to small area of penetration (0.1wt% and 0.2 wt%, respectively) to no penetration at all (0.3wt%, 0.4wt%, 0.5wt% and 0.8wt%, respectively).
Figure 3.5.1 Low (a) and high (b) magnification of SEM images of metal side of an unmodified joint

Figure 3.5.2 Low (a) and high (b) magnification of SEM images of metal side of 0.1 wt% stearic acid modified joint
Figure 3.5.2 Low (c) and high (d) magnification of SEM images of metal side of 0.2wt% stearic acid modified joint.

Figure 3.5.2 Low (e) and high (f) magnification of SEM images of metal side of 0.3wt% stearic acid modified joint.
Figure 3.5.2 Low (g) and high (h) magnification of SEM images of metal side of 0.4wt% stearic acid modified joint.

Figure 3.5.2 Low (i) and high (j) magnification of SEM images of metal side of 0.5wt% stearic acid modified joint.
Results

Figure 3.5.2 Low (k) and high (l) magnification of SEM images of metal side of 0.8wt% stearic acid modified joint.

Figure 3.5.2 Low (m) and high (n) magnification of SEM images of metal side of 1.0wt% stearic acid modified joint.

The majority of Figures 3.5.2 (a-l) all show apparent interfacial failure. Figure 3.5.2 (m) and (n) show evidence of cohesive failure at 1.0wt% stearic acid. The elemental analysis of the discrete particles on this surface revealed that they were mainly Cu in composition. AES of this substrate in another unrelated study revealed a small Cu content in the 1xxx series Al foil. It is
thought that Cu is present in the substrate in the form of inclusions and so could have been transferred from the metal to the polymer side during the peel test. In addition, most pictures show evidence of voids probably caused by air bubbles not completely removed during the degassing stage.

3.2.2 SSIMS

SSIMS fragmentation patterns for the failed surface generated during peel testing are shown below. The pattern for the polymer side of each joint appears to be similar in appearance in terms of the mass of the peaks presented in the spectra. The characteristic peaks for PDMS, at 28 (Si), 43 (CH$_3$Si$^+$), 73 ((CH$_3$)$_3$Si$^+$), 147 (C$_5$H$_{15}$OSi$_2^+$) 207, 221, 281 atomic mass units are all evident. Where the adhesive has been unmodified peaks pertaining to stearic acid are also of interest. The characteristic peaks reported for stearic acid occur at 267 and 285 atomic mass units. The peak at 267 atomic mass units is present in the spectra for the unmodified and 0.3wt% modified adhesives but not in the spectra for 0.4 and 1.0wt% modified adhesive. Since this peak is present in the unmodified adhesive which has no stearic acid its detection in the 0.3wt% modified adhesive cannot be confidently attributed to stearic acid. The other characteristic peak for stearic acid at 285 atomic mass units is not present in any of the spectra.
Chapter 3 Results

(a)

(b)
Figure 3.6.1 The SSIMS spectra of the polymer surfaces of an unmodified (a), 0.3wt% modified (b), 0.4wt% modified (c) and 1.0wt% modified (d) failed T-peel joint.
Figures 3.6.2(a)-(d) represent the spectra for the metal side of failed joints. The presence of both Si\(^+\) and Al\(^+\) (27 atomic mass units) indicates a mixed mode of failure as Si originates from the adhesive and Al from the substrate. Na\(^+\) is detected at 23 atomic mass units in some of the spectra and is derived from the etch solution as an impurity. Once again the characteristic peaks for PDMS are evident in all spectra as is the 267 mass peak for stearic acid. Once more the presence of the latter peak in the unmodified joint surface means that it must represent a positive ion not attributed to the stearic acid molecule.
Figure 3.6.2 SSIMS spectra of the metal surface of (a) an unmodified, (b) a 0.3wt%, (c) a 0.4wt% and (d) a 1.0wt% stearic acid modified T-peel joints.
The ratio of Al:Si peaks should give an indication of changes to the contribution to failure, whether interfacial or cohesive, with stearic acid addition. For instance, a higher proportion of Si on the metal side of failed joints would suggest that failure was more cohesive; conversely a lower proportion of Si would imply that failure was more interfacial. A comparison of this showed no conclusive increase or decrease in the cohesive component (see Table 3.3).

<table>
<thead>
<tr>
<th>Stearic acid content (wt%)</th>
<th>Al:Si ratio on metal side of failed T-peel joints (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmodified</td>
<td>1:5</td>
</tr>
<tr>
<td>0.3</td>
<td>1:1</td>
</tr>
<tr>
<td>0.4</td>
<td>1:50</td>
</tr>
<tr>
<td>1.0</td>
<td>1:0.5</td>
</tr>
</tbody>
</table>

Table 3.3 The effect of stearic acid on the ratio of Al to Si peak intensity on the metal side of SSIMS spectra of failed T-peel joints.
3.2.3 XPS

Subsequent chemical analysis of the failure surfaces was conducted with XPS. The polymer side of failure was used to characterise the bulk adhesive and also as a reference for any adhesive material that maybe found on the metal side of failed joints. Sylgard 184 is a PDMS-based adhesive so the main elements of interest on the polymer side are Si, O, and C, in a respective ratio of 1:1:2. To ensure accuracy of this method the constancy of this ratio is checked on both surfaces. Once again the metal side is used to identify mode of failure so Al will be an additional element of interest on this surface. On the metal surface Si will be an indication of cohesive failure and Al will represent interfacial failure as it originates from the substrate. Should both elements be present then any changes in the Al:Si ratio will be used as an indication of any changes in failure mode.

Figure 3.7 (a)-(f) represent spectra of the polymer and metal sides of failed joints generated by the T-peel test. Table 3.4(a) and (b) show the chemical composition of these surfaces.
Figure 3.7  (a) Polymer side of unmodified peel joint (b) Metal side of unmodified T-peel joint.

Figure 3.7  (c) Polymer side of 0.3 wt% modified joint (d) Metal side of 0.3 wt% modified T-peel joint
Table 3.4(a) The chemical composition of the polymer and metal side of failure for an unmodified joint and a joint modified with 0.3 wt% stearic acid.

<table>
<thead>
<tr>
<th>Stearic Acid Content (wt%)</th>
<th>Polymer Side</th>
<th>Metal Side</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Element (At %)</td>
<td>Element (At %)</td>
</tr>
<tr>
<td></td>
<td>Si  O  C  Al  S</td>
<td>Si  O  C  Al  S</td>
</tr>
<tr>
<td>Unmodified</td>
<td>25.6 26.2 48.3 0.0 0.0</td>
<td>21.7 32.0 40.4 3.8 2.2</td>
</tr>
<tr>
<td>0.3 wt%</td>
<td>24.9 26.5 48.7 0.0 0.0</td>
<td>16.4 35.0 37.0 9.7 1.9</td>
</tr>
</tbody>
</table>

Figure 3.7 (e) Polymer side of 0.4 wt% modified joint (f) metal side of 0.4 wt% modified T-peel joint
Figure 3.7  (g) Polymer side of 1.0 wt% modified joint (h) metal side of 1.0 wt% modified T-peel joint

<table>
<thead>
<tr>
<th>Stearic Acid Content (wt%)</th>
<th>Polymer Side</th>
<th>Metal Side</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>O</td>
</tr>
<tr>
<td>0.4 wt%</td>
<td>25.0</td>
<td>27.0</td>
</tr>
<tr>
<td>1.0 wt%</td>
<td>25.1</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 3.4(b) The chemical composition of the polymer and metal side of failure for joints modified with 0.4 wt% and 1.0 wt% stearic acid.
As expected the Si, O, C and Al are present from the adhesive (Si, O, C) and substrate (Al). Sulphur detected comes from the FPL etch solution, which is a combination of Cr(VI) and $\text{H}_2\text{SO}_4$. In most cases examination of surfaces shows that the Si:O:C:Al ratio is maintained, with allowances for error. However, with 1.0wt% stearic acid there is an excess of carbon so that the 1:1:2 ratio of Si:O:C for PDMS becomes 1:1:3 (refer to Table 3.4b). This excess cannot be fully explained by the presence of stearic acid. SSIMS showed no evidence for stearic acid on this surface.

With respect to failure analysis, a mixed mode of failure is indicated, as both Si and Al was detected. This applies whether the adhesive is unmodified or modified. Exploring the Al:Si ratio for evidence of increased interfacial behaviour (i.e. reduction in Si component) failed to establish a consistent pattern. Furthermore, narrow scans of the C1s peak of metal sides of these joints failed to reveal evidence of COOH functionality, which would indicate stearic acid presence at the joint surface. The source of S found on the metal surfaces was the FPL etch solution.
Figure 3.8, below, shows the ATR spectrum of the polymer surface of the unmodified joint. According to Table 3.5 the peaks present may be attributed to PDMS. This spectrum was used as a reference for the spectra of modified joint surfaces. As with SSIMS and XPS, the polymer side of failed joints was interpreted as representing the bulk adhesive. Therefore, it was thought that stearic acid in the modified adhesives would be identified since there was a higher concentration in the bulk adhesive. However, subsequent analysis of the modified surfaces revealed no differences between the unmodified surface and the modified. Thus only the spectra for 0.5 wt% stearic acid modified spectra is shown to represent modified surfaces as a whole, see Figure 3.9.
Figure 3.8  ATR Absorbance spectrum of the polymer side of a failed, unmodified joint surface.

Figure 3.9  ATR Absorbance spectrum of the polymer side of a failed, 0.5 wt% modified joint surface.
Based on the structure of the cured material on the left of this schematic, the peaks in the absorbance spectrum can be identified. The table below illustrates the peak assignments for Figures 3.8 and 3.9.
### Table 3.5 Wavenumber positions of characteristic peaks for silicones.

<table>
<thead>
<tr>
<th>Group</th>
<th>Vibration</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMe</td>
<td>CH$_3$ asymmetric</td>
<td>1440 to 1390</td>
</tr>
<tr>
<td></td>
<td>deformation</td>
<td>1280 to 1240</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ symmetric</td>
<td>870 to 750</td>
</tr>
<tr>
<td></td>
<td>deformation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rocking</td>
<td></td>
</tr>
<tr>
<td>Si-C</td>
<td>Stretch</td>
<td>870 to 750</td>
</tr>
<tr>
<td>SiMe</td>
<td>SiMe$_2$ stretch</td>
<td>885 to 805</td>
</tr>
<tr>
<td></td>
<td>SiMe stretch</td>
<td>775</td>
</tr>
<tr>
<td>SiMe</td>
<td>CH$_3$ asymmetric</td>
<td>1440 to 1390</td>
</tr>
<tr>
<td></td>
<td>deformation</td>
<td>1280 to 1240</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ symmetric</td>
<td>870 to 750</td>
</tr>
<tr>
<td></td>
<td>deformation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rocking</td>
<td></td>
</tr>
<tr>
<td>Si-C</td>
<td>Stretch</td>
<td>870 to 750</td>
</tr>
<tr>
<td>SiMe</td>
<td>SiMe$_2$ stretch</td>
<td>885 to 805</td>
</tr>
<tr>
<td></td>
<td>SiMe stretch</td>
<td>775</td>
</tr>
<tr>
<td>Si-Alkyl</td>
<td>Si-CH$_2$ wag</td>
<td>1250 to 1220</td>
</tr>
<tr>
<td></td>
<td>Si-ethyl</td>
<td>1190 to 1175</td>
</tr>
<tr>
<td></td>
<td>Si-higher alkys</td>
<td>1300 to 650</td>
</tr>
<tr>
<td></td>
<td>Short linear and branched</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alkyl groups on Si</td>
<td></td>
</tr>
<tr>
<td>SiCH$_2$Si</td>
<td>-CH$_2$- wag</td>
<td>1080 to 1040</td>
</tr>
<tr>
<td></td>
<td>-CH$_2$- scissors</td>
<td>1380 to 1340</td>
</tr>
<tr>
<td>SiOMe</td>
<td>Asymmetric C-H stretch</td>
<td>2945</td>
</tr>
<tr>
<td></td>
<td>Symmetric</td>
<td>2840</td>
</tr>
<tr>
<td></td>
<td>-CH$_3$ rock</td>
<td>1190</td>
</tr>
<tr>
<td></td>
<td>Asymmetric Si-O-C stretch</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>Symmetric Si-O-C stretch</td>
<td>850 to 800</td>
</tr>
<tr>
<td>Si-OH</td>
<td>Free SiOH stretch</td>
<td>3690</td>
</tr>
<tr>
<td></td>
<td>H bonded SiOH</td>
<td>3200 to 3400</td>
</tr>
<tr>
<td></td>
<td>Si-O stretch</td>
<td>950 to 830</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>Si-O-Si</td>
<td>1130 to 1000</td>
</tr>
<tr>
<td></td>
<td>Asymmetric stretch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>disiloxanes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkyl-substituted disiloxanes</td>
<td>1070 to 1040</td>
</tr>
<tr>
<td>(Me$_2$SiO)$_x$</td>
<td>Asymmetric stretch</td>
<td>Doublet with maxima at 1090 to 1015</td>
</tr>
</tbody>
</table>
As with SSIMS and XPS analyses, the metal side of failed joints were used to identify the locus of failure. Figure 3.10 shows ATR spectra of the metal side of unmodified and modified joints that have been incorporated into one figure in order to observe any difference in the chemistries of the surfaces.

![ATR spectra of the metal side of failed unmodified and modified joints.](image)

**Figure 3.10** ATR spectra of the metal side of failed unmodified and modified joints.

The blue curve represents the surface of the unmodified joint. Comparing this curve with the modified curves shows the similarities between the surfaces. From Table 3.5 these peaks can be confidently attributed to the presence of PDMS on the metal surfaces. All the curves show the presence of the CH\textsubscript{3} symmetric deformation of SiCH\textsubscript{3} at 1259 ±4 cm\textsuperscript{-1}; Si-O-Si asymmetric stretch at 1006 to 1064 ±4 cm\textsuperscript{-1}, this peak has the characteristic doublet. The peaks in the range 600 cm\textsuperscript{-1} to 1000 cm\textsuperscript{-1} ±4 cm\textsuperscript{-1} are not considered useful for identification as this region is prone to vibrations from many types of chemical bonding. The spectrum for the joint modified with 0.5 wt% stearic acid also
has a small amount of SiH, at 2156 ±4 cm⁻¹, from the crosslinker present on the surface of the joint. This group is not found on the surface of the unmodified nor the other modified joints. Also solely on this surface are peaks attributed to CH₃ asymmetric deformation of SiCH₃ at 1452 and 1413 ±4 cm⁻¹. Inspection of these spectra show no significant shifts in wavenumber that can be attributed to the formation of new bonds at the surface. Furthermore, the absence of the characteristic OH stretching vibration in the 3200 to 3400 cm⁻¹ region of the spectra means there are no hydrogen bonded silanols (SiOH), nor are there any hydrated oxides of aluminium present on these surfaces. Similarly, the absence of a peak at 3690 cm⁻¹ indicates that there are no free SiOH groups on these surfaces. The ATR spectra of the metal surfaces of failed stearic acid modified joints do not show peaks characteristic of saturated carboxylic acids, so stearic acid is not present on these surfaces.

In summary, all failure analysis shows a mixed interfacial/cohesive failure mechanism close to the metal surface, i.e. within the interphasial polymer both with unmodified and modified Sylgard 184.
3.2.5 Failure analysis of different substrate pretreatments on SLS and T-peel joints.

The chemical composition of failed surfaces of the joints prepared using the different substrate pretreatment processes were conducted using XPS. Since there were instances of joints failing at lower loads than others despite undergoing the same pre-treatment and joint preparation procedures, chemical analysis has been conducted on joints that failed at high loads and low loads so that the causes for these variations may be established. What follows is the chemical analysis of degreased (DG), grit blast (GB), etched, and chromic acid anodised (CAA) SLS (Table 3.6) and T-peel joints (Table 3.7).

3.2.5.1.1 Degreased SLS joints

The ratio of Si:O:C on unmodified side A of the stronger joint is approximately 1:1:3. Unmodified side B for this joint maintains the 1:1:2 ratio of these elements. Both Side A and B of the weakest joint has the correct ratio of Si:O:C.

For the modified adhesive where the joint failed at a higher load there is an excess of C on Side A and an excess of C and O on side B. Where failure occurred at a lower load there is an excess of C and O on Side B. These excesses are more substantial in the stronger joint.
3.2.5.1.2 Degreased T-peel joints

The ratio of Si:O:C on the polymer side is 1:1:2 (within errors) regardless of joint strength. On the metal side of the unmodified high strength joint there is an excess of O (1:2:1). This excess is even higher on the same side of the low strength joint (1:5:2). The extra oxygen detected is most probably due to metal oxides present.

3.2.5.2.1 Grit-blast SLS joint

For the unmodified adhesive, both sides of the high and low strength joints exhibit the correct amount of stoichiometric Si:O:C consistent with PDMS. Al is detected on both surfaces of the high strength joint, but only on Side A of the low strength joint and at a lower level.

For the modified adhesive Al is present more on Side A of the high strength joint than the low strength joint. However, the lower strength joint has more excess C and O on Side A and B respectively.

3.2.5.2.2 Grit-blast T-peel joint

There are no grit-blast results for T-peel joints as the adherend was too thin and therefore unsuitable for this pretreatment.
3.2.5.3.1 FPL etch SLS joint

Lower strength of the unmodified joint appears to be caused by inadequate rinsing of the substrate as exemplified by the presence of impurities from the etch solution. There is also an excess of C and O.

For the modified adhesive there is Al on both sides of the high strength joint in addition to an excess of carbon. Conversely, Al is only on side B of the low strength modified joint. Furthermore, the correct ratio of Si:O:C is maintained.

3.2.5.3.2 FPL Etch T-peel joint

1:1:2 ratio for Si:O:C is maintained irrespective of joint strength or modification on the polymer side of failed joints. The ratio is further maintained on the metal side of the high strength unmodified joint. The metal side of the low strength unmodified joint exhibits Al and an excess of O (1:2.5:2).

The metal side of both high and low strength modified joints also maintain this ratio but there is more Al on the surface of the high strength joint.

3.2.5.4.1 CAA SLS joint

For the unmodified adhesive lower strength appears to be caused by Al on the surface of this joint.

More Al on the surface of the low strength modified joint also appears to be the primary cause of variations in strength. However, excesses of C and O may also be responsible.
3.2.5.4.2 CAA T-peel joint

Polymer and metal side of high and low strength unmodified joints maintain 1:1:2 ratio, although the high strength joint does so more closely.

The polymer sides of the modified joints, both high and low strength, exhibit the correct ratio of Si:O:C within errors. This relationship also applies to the metal side these joints, and again is much closer in the higher strength joint. In addition there is more Al on the low strength joint.
### Table 3.6

<table>
<thead>
<tr>
<th></th>
<th>Side A</th>
<th>Side B</th>
<th>Side C</th>
<th>Side D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition At %</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>28.1</td>
<td>34.4</td>
<td>41.3</td>
<td>43.9</td>
</tr>
<tr>
<td>Si</td>
<td>47.4</td>
<td>34.5</td>
<td>41.4</td>
<td>43.9</td>
</tr>
<tr>
<td>Al</td>
<td>1.7</td>
<td>3.9</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Zn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Si</td>
<td>18.1</td>
<td>18.7</td>
<td>18.8</td>
<td>18.7</td>
</tr>
<tr>
<td>Al</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Zn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Surface Pre-treatment Strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>281.4</td>
<td>34.9</td>
<td>41.3</td>
<td>43.9</td>
</tr>
<tr>
<td>High</td>
<td>47.4</td>
<td>34.5</td>
<td>41.4</td>
<td>43.9</td>
</tr>
<tr>
<td>Modified</td>
<td>34.5</td>
<td>41.4</td>
<td>43.9</td>
<td>43.9</td>
</tr>
<tr>
<td>Unmodified</td>
<td>41.4</td>
<td>43.9</td>
<td>43.9</td>
<td>43.9</td>
</tr>
</tbody>
</table>
Table 3.7: XPS chemical analysis of T-peel joints subjected to a variety of substrate pre-treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Metal Side Composition at %</th>
<th>Polymer Side Composition at %</th>
<th>Surface Joint Composition at %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>32.7 39.1 13.4 14.7</td>
<td>48.5 26.9 24.6</td>
<td>Low</td>
</tr>
<tr>
<td>Modified</td>
<td>36.5 35.4 20.1 8.0</td>
<td>48.1 26.8 25.1</td>
<td>Modified</td>
</tr>
<tr>
<td>Unmodified</td>
<td>46.4 28.9 24.7</td>
<td>49.0 26.3 24.7</td>
<td>Unmodified</td>
</tr>
<tr>
<td></td>
<td>49.2 26.5 24.3</td>
<td>48.6 26.3 25.2</td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>45.3 31.7 20.3 2.8</td>
<td>48.0 27.8 24.2</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>37.0 35.0 16.4 9.7</td>
<td>48.7 26.5 24.9</td>
<td>Modified</td>
</tr>
<tr>
<td>Etch</td>
<td>28.0 48.1 15.6 5.6</td>
<td>47.3 27.6 25.1</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>48.3 26.8 24.9</td>
<td>48.3 26.2 25.6</td>
<td>Unmodified</td>
</tr>
<tr>
<td>DC</td>
<td>30.7 39.7 20.4 9.2</td>
<td>49.1 27.5 23.5</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>24.7 48.5 10.4 2.3</td>
<td>48.4 26.6 25.1</td>
<td>Modified</td>
</tr>
<tr>
<td></td>
<td>21.1 60.4 9.3 9.7</td>
<td>46.9 28.4 24.7</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>18.9 50.2 8.3 22.6</td>
<td>48.0 27.5 24.5</td>
<td>Unmodified</td>
</tr>
</tbody>
</table>

Results
3.2.6 Failure analysis of joints modified with alternative additives.

SEM, XPS and ATR analysis of joints modified with 1.0 wt% calcium stearate, zinc stearate and glacial acetic acid were conducted on failure surfaces generated by the T-peel test. The results of these tests are demonstrated in the following sections.

3.2.6.1 SEM characterisation

These surfaces are similar to those modified with stearic acid. At low magnification the etching lines are evident as well as some voids. At high magnification the characteristic scallops of an etched aluminium surface are evident.

Figure 3.11 SEM micrographs of the polymer side of a failed calcium stearate modified joint.
At low magnification the underlying etched metal oxide surface is visible. At high magnification the crater effect of etching is seen as well as the presence of voids. There appears to be no evidence of polymer on this surface suggesting that the joint failed interfacially, or close to the interface with the polymer not resolvable by FEGSEM.
Chapter 3

Results

Figure 3.13  SEM micrographs of the polymer side of a failed zinc stearate modified joint.

Both low and high magnification micrographs of zinc stearate modified joints, see Figure 3.13, are very similar to the polymer surfaces of calcium stearate modified joints in Figure 3.11.

Figure 3.14  SEM micrographs of the metal side of a failed zinc stearate modified joint.
The metal side of zinc stearate modified joints is also very similar to calcium stearate modified joints. The globules seen at low magnifications were identified by EDX analysis as Al/Cu composition. At high magnification there is some evidence of adhesive on this surface, as indicated by the marker.

Figure 3.15 Low magnification SEM micrograph of polymer side of a failed glacial acetic acid modified joint.

Only the low magnification micrograph is show in Figure 3.15 as there was no distinction between the surfaces at high magnification, i.e. it remained featureless. The adhesive appears not to take the form of the metal underneath, unlike in previous examples.
At low magnification features resembling sand dunes can be seen on the metal surface of the failed joint. Closer inspection, at high magnification, reveals cracks present in the polymer surface. Voids are also clearly seen in the high magnification micrograph. Figure 3.16 indicates a cohesive mode of failure with glacial acetic acid.

Figure 3.16  SEM micrograph of metal side of glacial acetic acid modified joint.
3.2.6.2 XPS Analysis

Figure 3.17 XPS spectrum of the polymer side of a calcium stearate modified joint.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.9</td>
<td>47.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>27.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.4</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Table 3.8 Chemical composition of polymer side of failed calcium stearate modified joint.
Figure 3.18 XPS spectrum of the metal side of a calcium stearate modified joint.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>41.4</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>533.2</td>
<td>32.6</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.7</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Table 3.9 Chemical composition of metal side of failed calcium stearate modified joint.

Table 3.8 shows that the polymer side of this joint has a 1:1:2 ratio of Si:O:C. The ratio of elements on the metal side also equates to approximately 1:1:2 with the remainder of the oxygen accounted for by the Al oxide, see Table 3.9.
Figure 3.19  XPS spectrum of the polymer side of a zinc stearate modified joint.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.0</td>
<td>47.6</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>27.3</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>25.1</td>
</tr>
</tbody>
</table>

Table 3.10  Chemical composition of polymer side of a failed zinc stearate modified joint.
Figure 3.20  XPS spectrum of the metal side of a zinc stearate modified joint.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>28.4</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>533.0</td>
<td>48.8</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>12.7</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Zn</td>
<td>2p3</td>
<td>1023.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3.11  Chemical composition of metal side of a failed zinc stearate modified joint.

The polymer side of the failed zinc stearate modified joint has similar amounts of Si:O:C as the joint modified with the same amount of calcium stearate and thus maintains the 1:1:2 ratio of these elements. On the metal side, this relationship is not preserved as there is an excess of O, that is after the required amount has been attributed to Al as Al$_2$O$_3$. However, the 1:2 ratio
between Si and C is basically preserved. Table 3.11 shows that the O and Al peaks have been moved to slightly higher energies on the metal side compared with the polymer side, see Table 3.10. Similarly the Al peak in the zinc stearate modified spectrum, see Table 3.11, has moved to a higher energy than the same peak when the joint has been modified with calcium stearate, refer to Table 3.9. Figure 3.20 indicates a mixed mode of failure due to the presence of Al and Si peaks from the adherend and adhesive respectively. Table 3.11 indicates that failure is more interfacial with zinc stearate than with calcium stearate. Furthermore zinc has been detected on the metal side of the failed joint but not the polymer side, whereas no calcium has been detected on either surface.

![Figure 3.21 XPS spectrum of the polymer side of a glacial acetic acid modified joint.](image-url)

Figure 3.21 XPS spectrum of the polymer side of a glacial acetic acid modified joint.
Chapter 3

Table 3.12 Chemical composition of polymer side of a failed glacial acetic modified joint.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>47.2</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>27.0</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>25.8</td>
</tr>
</tbody>
</table>

Once more, the 1:1:2 relationship between Si:O:C is maintained when glacial acetic acid is used to modify the adhesive. Furthermore, relatively the same amount of each element is present on the polymer side of calcium and zinc stearate modified joints as there is for glacial acetic acid modified joints.

Figure 3.22 XPS spectrum of the metal side of a failed glacial acetic acid modified joint.
<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.9</td>
<td>49.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.7</td>
<td>25.6</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.4</td>
<td>25.2</td>
</tr>
</tbody>
</table>

Table 3.13  Chemical composition of metal side of a failed glacial acetic acid modified joint.

The lack of Al on the metal failure surface suggests that failure is cohesive with glacial acetic acid. Furthermore, the amounts of these elements on both surfaces are relatively the same, as are their binding energies.
Chapter 3

3.3 Cure Kinetics

This section reviews the results of kinetic studies conducted by following the progress of the hydrosilylation cure reaction using FTIR, and by investigating the effect of stearic acid on the kinetic constants, apparent activation energy $E_A$ and pre-exponential constant $A$, using DSC.

3.3.1 FTIR

The cure reaction was followed using the method described in Section 2.8.1.3.

![Figure 3.23(a) The effect of stearic acid on degree of conversion after curing at room temperature for up to 72 hours](image)
The fastest rate of conversion was achieved with 0.3 wt% stearic acid and the slowest with 1.0 wt% stearic acid. None of the curves reach 100% conversion. The highest conversion over 72 hours was attained with 0.4 wt% stearic acid and the lowest with 1.0 wt% stearic acid.

**Figure 3.23(b)** The effect of stearic acid on conversion rate after curing at room temperature for 24 hours.

Figure 3.23(b) shows the effect of stearic acid over 24 hours. The main difference here is that the highest conversion is attained with 0.3 wt% stearic acid compared with 0.4 wt% over 72 hours (see Figure 3.23c).
Figure 3.23(c) shows that after 24 hours of curing at room temperature the hydrosilylation reaction is catalysed when 0.1-0.3 wt% stearic acid is added to the adhesive so that the final conversion is successively more than the unmodified reaction. The final conversion rose from 65% for the unmodified adhesive to 73% for the reaction modified with 0.3 wt% stearic acid. Above 0.3 wt%, the cure reaction begins to slow down until at 1.0 wt% stearic acid the final conversion falls to 50%.

Figures 3.23(a)-(c) show that stearic acid has a catalytic effect on the adhesive cure reaction.
(SH) groups with time in an unmodified cure reaction.

Figure 3.24 IR spectra showing depletion of vinyl (CH2=CH2 and SH)

Results
Reaction modified with 0.1 wt% stearic acid.

Figure 3.25 IR spectra showing depletion of vinyl (CH=CH) and silyl (SiH) groups with time in a cure.
Figure 3.26 IR spectra showing depletion of vinyl (CH2-CH2) and silyl (SiH) groups with time in a cure reaction modified with 0.3 wt% stearic acid.
Results

Figure 3.27  IR Spectra showing depletion of (CH$_2$=CH$_2$) and Si(1) groups with time in a cure reaction modified with 0.4 wt% stearic acid.
Chapter 3

Figure 3.28 IR Spectra showing depletion of vinyl (CH=CH) and silyl (SiH) groups with time in a cure reaction modified with 0.5 wt% stearic acid.
Figures 3.24 to 3.28 show the progress of the cure reaction over time. The depletion of the silyl peak is accompanied by an associated reduction in the vinyl peak which confirms the proposed cure reaction illustrated in Section 1.5.1, which depicts the formation of a crosslinked network of SiCH₂CH₂Si linkages. The peak at 1944 ± 4cm⁻¹ does not change over time and was used for ratio purposes.
Chapter 3

3.3.2 DSC

3.3.2.1 Kissenger Method

DSC was used to investigate the effect of stearic acid on $E_A$ and $A$ using the technique described in section 2.8.1.1. $E_A$ and $A$ were calculated from the slope and intercept (respectively) of the curves in Figure 3.29, using $\ln(\phi/T_m^2)$ vs $1/T_m$, equation 62 in section 1.6.5.9. The equation for each fitted line is positioned along side framed in corresponding coloured boxes.

![Figure 3.29](image)

**Figure 3.29** The Kissenger analysis of the effect of stearic acid on the kinetics of the cure reaction.
Chapter 3 Results

The curves in Figure 3.29 are virtually all parallel to one another but the curves for the unmodified and modified (0.1, 0.3 and 1.0 wt%) reactions are translated along the x-axis towards the right hand side of the graph. The shift is just due to the differing ratios of $E_A$ and $A$, due to different values of the constant $c$ in the fitted equation $y=mx+c$. The kinetic constants for each reaction system are displayed in Table 3.14.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$E_A$ (kJ mol$^{-1}$)</th>
<th>$A$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sylgard 184</td>
<td>70.25 ± 0.44</td>
<td>5.3 (± 1.21) x10$^7$</td>
</tr>
<tr>
<td>Unmodified</td>
<td>57.43 ± 0.5</td>
<td>3.4 (± 1.6) x10$^6$</td>
</tr>
<tr>
<td>0.1 wt% stearic acid</td>
<td>56.10 ± 1.9</td>
<td>4.5 (± 6.0) x10$^6$</td>
</tr>
<tr>
<td>0.3 wt% stearic acid</td>
<td>75.86 ± 1.3</td>
<td>3.9 (± 4.0) x10$^9$</td>
</tr>
<tr>
<td>1.0 wt% stearic acid</td>
<td>61.73 ± 0.3</td>
<td>1.8 (±0.9) x10$^7$</td>
</tr>
<tr>
<td>Sylgard 184 + 0.3 wt% stearic Acid</td>
<td>64.27 ± 2.5</td>
<td>6.8 (± 0.1) x10$^6$</td>
</tr>
</tbody>
</table>

Table 3.14 Kinetic constants determined using the Kissenger method of analysing thermal data for a variety of adhesive formulations.

3.3.2.2 Friedman Analysis

The Friedman analysis is $\ln(\frac{d\alpha}{dt})_a$ versus $1/T_a$, which is given in equation 55 in section 1.6.5.9. Figure 3.30 was constructed using this equation. The start of the reaction is measured from 10% and the end from 90% to avoid the ambiguities inherent in discerning when a reaction begins and ends.
Figure 3.30  Variation of Activation Energy with Extent of Reaction in Sylgard 184.

The Friedman method of kinetic analysis uncovers the variation in $E_A$ with $\alpha$ (extent of reaction) that takes place in the reaction for Sylgard 184. From the start of the reaction there is a 40 kJmol$^{-1}$ reduction in the activation energy for the reaction.
Chapter 3

Results

The figures below depict untreated data for the unmodified and a modified adhesive mixture, Figures 3.31 and 3.32 respectively. As the non-linearity of these curves was conferred to plots of $\ln(d\alpha/dt)_a$ versus $1/T_a$ at 1, 2, 4 and 8 °C min$^{-1}$ it was not possible to perform further kinetic analyses of these results. Consequently, $E_A$ and $A$ were unable to be determined for these reactions.

![Figure 3.31 Kinetic Analysis of an unmodified cure reaction](image-url)

Figure 3.31 Kinetic Analysis of an unmodified cure reaction
Although it has not been possible to determine $E_A$ and $A$ values for the unmodified or modified cure reactions using the Friedman method, this analysis has made known the complexities of this reaction.
3.4 Bulk Properties

3.4.1 Solvent Swelling

The effect of stearic acid content on crosslink density was investigated using the method described in Section 2.9. This effect was studied by modifying the adhesive with 0.1, 0.3 and 1.0 wt% stearic acid. The crosslink density was calculated using equation 77 in section 1.6.6.1.

![Figure 3.33](image)

Figure 3.33 shows that stearic acid increases the molecular weight between crosslinks $M_c$, which means that the crosslink density is reduced in the modified adhesive. However, 0.3 wt% stearic acid gave the smallest
Chapter 3 Results

reduction in crosslink density compared with 0.1 and 1.0 wt% stearic acid. The values plotted are the average of four for samples for each composition and the errors represent the standard deviation.

3.4.2 Tensile Test

Dumbbells were prepared and tested as described in section 2.5.2. Five specimens of each sample were tested and the average maximum strength was plotted. Figure 3.34 illustrates the effect of stearic acid on tensile properties.

Unmodified (a)
0.1 wt% Stearic Acid
(b)

0.3 wt% Stearic Acid
(c)
Results

Figure 3.34 Effect of stearic acid on tensile properties.
Figure 3.35(a-b) The effect of stearic acid on stress distribution

Figure 3.35 illustrates the results of applying a constant 5N load on the stress distribution through the centre of the adhesives. On the graph, the x-axis refers to the distance in the Y direction, at x=0.03 mm, along the centre of the
modelled joint, (refer to Figure 2.6). In order to generate these curves a best fit of the stress/strain data was performed so that Mooney coefficients could be determined. These coefficients are used to model neo-Hookean materials, which are considered isotropic and incompressible. The Mooney coefficients were used as input parameters or material properties for the subsequent peel stress analysis. They were determined from the uniaxial tensile tests. Figure 3.35a validates the peel joint model as it shows that the peel stresses are the driving the deformation. This is exemplified by the fact that Figure 3.35a closely resembles Figure 3.35b. With the exception of the result for 0.4 wt% stearic acid, the stresses acting in this region were the same irrespective of modification. From this analysis, initially the peel stress is concentrated at the edge of the adhesive. Then as the distance from the edge increases the peel stress lessens, and goes into compression before eventually evening out further into the bulk of the adhesive. The adhesive containing 0.4 wt% stearic acid is essentially in a higher stress state than the other materials.
### 3.6 Summary

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-peel</td>
<td>Assessment of joint strength as a function of stearic acid concentration, saturated fatty acid derivative, surface pretreatment</td>
</tr>
<tr>
<td>SLS</td>
<td>Alternative assessment of joint strength as a function of stearic acid modification and surface pretreatment</td>
</tr>
<tr>
<td>SEM, SSIMS, XPS and ATR</td>
<td>Failure surface analysis for identification of mode of failure,</td>
</tr>
<tr>
<td>FTIR</td>
<td>Determining the effect of stearic acid on silyl conversion</td>
</tr>
<tr>
<td>DSC</td>
<td>Determination of the effect of stearic acid on cure reaction in terms of kinetic constants $E_A$ and $A$</td>
</tr>
<tr>
<td>Solvent Swelling</td>
<td>Determination of the effect of stearic acid on crosslink density</td>
</tr>
<tr>
<td>Tensile test</td>
<td>To determine the effect of stearic acid concentration on tensile properties.</td>
</tr>
<tr>
<td>FEA</td>
<td>Stress analysis as a function of stearic acid content.</td>
</tr>
</tbody>
</table>

**Table 3.15** Summary of experiments performed and their aims.

The results of these studies will now be discussed in greater detail.
A reduction of adhesion with increasing levels of stearic acid incorporated into a PDMS-based adhesive has been clearly demonstrated. This confirms earlier work undertaken in the literature$^{80-83}$ (see Appendix 1); in the literature two possible mechanisms for this process were proposed, as discussed in Chapter 1. Firstly, it was suggested that stearic acid migrated to the surface of the joint causing interfacial failure in a weak boundary layer. An alternative explanation was that stearic acid inhibited the hydrosilylation cure reaction of Sylgard 184 so that the formation of crosslinks was retarded. This mechanism was thought to affect the joint by reducing the cohesive strength of the adhesive. A number of investigations into the two proposals were performed. What follows is a discussion of the results gathered.

4.1 The effect of stearic acid on joint strength

Joint strength was primarily measured using the T-peel test. Figure 3.1 demonstrates the dramatic effect on adhesion exerted by stearic acid and validates the results of earlier studies undertaken at AWE as well as those conducted by various authors in the literature$^{80-83}$. The latter observed that increasing amounts of stearic acid reduced levels of mould sticking in rubber compounding.

Figure 3.1 showed that adding 0.1 wt% and 0.2 wt% stearic acid to the adhesive reduced joint strength by 22% for both concentrations. However, the difference in strength between unmodified Sylgard 184 and modification with 0.3 wt% stearic acid was 40%, from 318 N/m to 190 N/m. At 0.4 wt% and 0.5 wt% the difference in peel strength with respect to the unmodified adhesive was 46%, a difference which grew to 57% when 0.8 wt% stearic acid was added. Finally the overall decline in adhesive strength at 1.0 wt% was close
Chapter 4 Discussion

Thus below a concentration of 0.3 wt% stearic acid the measured effect maybe considered a pseudo reduction in strength so that 0.3wt% becomes a critical concentration for the measured effect of stearic acid on peel strength. The influence of additive concentration was also detected by Schneberger and Nakanishi81. When a sample is pulled apart at a constant rate, the measured force should ideally be constant. In practice, however, this is not so as shown by the curves in Figure 3.0. Thus when the results are reported, the mean values of such curves are used to determine peel strength. The curves in Figure 3.0 show the variation of the steady state force when failure is initiated continuously and its rate of propagation is the same as the testing rate. These variations have been shown to be due to sample imperfections22.

4.2 Failure analysis

Failure surfaces generated by T-peel test were examined and compared with respect to the effect of modification, with stearic acid, on failure mode. Initial characterisation using SEM showed apparent interfacial failure in unmodified joints and in those modified with up to 0.8wt% stearic acid (refer to Figures 3.5.1 and 3.5.2a-I). These micrographs showed that increasing modification resulted in reduced penetration of the oxide pores by the adhesive, in addition to poorer overall coverage of the substrate surface. Thereby, suggesting that the wettability of the substrate by the modified adhesive was possibly reduced. Degree of wetting is determined by surface chemistry of the adhesive and the substrate, which in turn governs their surface energies. The energy of an unmodified adhesive surface was found to be higher than the energy of modified surface (22.10 mN m⁻¹ versus 19.55 mN m⁻¹), so in principle the modified adhesive should spread more easily across the substrate surface. Although this finding contradicted SEM evidence it was not considered significant as the difference was slight. Consequently, wettability was not considered an issue as it was accepted that this small reduction in
surface energy did not contribute significantly to the overall energy difference between the substrate and the adhesive.

Further surface analysis by SSIMS and XPS indicated that failure took place via a mixed interfacial/cohesive mode. These analyses also showed that this failure mode remained consistent even after modification. Namely, there was no consistent transition from cohesive to interfacial failure that could be associated with a weak boundary layer. Further to this, there was no evidence of characteristic positive ions for stearic acid at 267 amu (C17H35-C≡O+) or at 285 amu (C18H37O2+) in the SSIMs spectra of modified metal surfaces. Similarly high energy XPS scans of the C 1s peak failed to show shifts in binding energy connected with carboxylic acids.

ATR was also used in collaboration with SSIMS and XPS to characterise failure surfaces (refer to Figure 3.10). These figures showed that there was a residual layer of PDMS on unmodified and modified failed metal surfaces. As a result, it was decided that failure took place in a cohesive layer very close to the interface with possibly some limited interfacial failure. The degree of interfacial failure was not dependent upon the levels of stearic acid added. Aluminium detected by both SSIMS and XPS demonstrated the surface sensitivity of these techniques. SSIMS conditions in this study were such that less than 1% monolayer was removed during analysis and calculated sampling depth for XPS was 9nm.

The ATR spectra also failed to show the characteristic broad intense O-H stretching band typically found from 3500 to 2500 cm⁻¹ and often centred around 3000 cm⁻¹. Since no other functional group has such a broad intense band at high wavenumber, this band by itself can be used as evidence that a sample contains a carboxylic acid. Thus ATR analysis also failed to provide evidence of stearic acid at the interface. Therefore, the result of failure analyses using a combination of techniques was found to contradict commonplace literature reports of a weak boundary layer of stearic acid. An investigation by Fletcher⁸⁴ also disputed the validity of the migration theory. In this report migration of zinc stearate was studied by examining cross-sections
of polyester resin matrixes with SEM and an EDX analyser. The author found that zinc stearate was present throughout the moulded polyester matrixes in an approximately homogenous manner. Therefore, it was concluded that there did not appear to be any significant migration of zinc stearate to the surface and so the study concluded that migration theory could not adequately explain the mechanism of mould release with zinc stearate. In summary, the two most widely used theories to explain the release properties of stearic acid modified polymers were proven not to be applicable to the present bonding system.

4.3 The effect of stearic acid on cure kinetics

An alternative proposition for the cause of the erosion of adhesive strength in the presence of stearic acid was that cohesive strength was reduced as a result of the inhibition of the hydrosilylation cure reaction. However, as mentioned above, this was shown by a number of methods not to be the case. Instead it was found that stearic acid actually accelerated the cure reaction.

4.3.1 FTIR

Firstly FTIR was used to follow the progress of the hydrosilylation reaction for periods up to 72 hours. Results for conversion for 24 hours were interpolated from Figure 3.23a and displayed in Figure 3.23b. The latter clearly showed that initially the rate of the cure reaction of the unmodified adhesive was similar when 0.1 wt%, 0.2 wt% and 0.4 wt% stearic acid were added. When 0.5 wt% and 1.0 wt% stearic acid were incorporated in the unmodified adhesive, the rate of hydrosilylation was slower. The fastest cure rate was achieved with 0.3 wt% stearic acid. In Section 4.1 it was suggested that 0.3 wt% stearic acid was a critical concentration for the function of stearic acid
whereby below this concentration there was only 'pseudo' effect on measured adhesion. Although it is considered that this concentration remains critical for curing at room temperature for 24 hours, Figure 3.23c casts some doubt on the suggested 'pseudo' effect of lower concentrations. Here, it was shown that the overall effect of stearic acid on final conversion was incremental, but real. Furthermore, despite the relative fall-off in final conversion in modified adhesive formulations comprising 0.4 wt% and 0.5 wt% stearic acid the final conversions for these reactions were 71% and 69% respectively, compared with 65% for the unmodified adhesive. However, 1.0 wt% was considered an inhibitive concentration due to slower conversion rate and the lower degree of final conversion.

Figure 2.23b also showed that for all the studied systems the bulk of the cure reaction took place within the first 325 minutes, or so, of initiation so that beyond this time period conversion remained fairly constant for 24 hours. However Figures 3.23a and 3.23c showed that after 72 hours the final conversion increased and the latter showed that maximum conversion shifted to 0.4 wt% stearic acid. In addition, at 0.5 wt% and 1.0 wt%, final conversion remained unchanged. Some studies have documented the side reactions associated with hydrosilylation\textsuperscript{113,114}, which have been described in Section 1.5.1. It is postulated that completion of the main cure reaction, described by equation 13 and shown below, was proceeded by reactions such as the hydrolysis of remaining SiH groups to form SiOH or perhaps condensation of two SiOH groups formed as a result of hydrolysis so that crosslinking, in both cases, would take place via Si-O-Si linkage. The latter reactions represent the post cur reactions described by equations 14 and 16, respectively.:

$$(\text{Crosslinker}) \quad \rightarrow \quad \text{Si-O-Si}$$

Figures 3.24 to 3.28 show the simultaneous consumption of silyl and vinyl groups, thus confirming the formation of primary crosslinks via equation 13. They also show that after 72 hours virtually all the vinyl groups have completely reacted so that there is an excess of silyl groups remaining.
4.3.2 Kinetic analysis by thermal methods

4.3.2.1 Kissenger analysis

The Kissenger method of kinetic analysis was used, in the first instance, to determine the effect of stearic acid on the apparent activation energy $E_A$ and pre-exponential constant $A$ for the studied hydrosilylation reaction from the slope and intercept of the curves displayed in Figure 3.29. Table 3.14 lists the resultant calculated values for both $E_A$ and $A$, respectively, for a number of formulations. In terms of the reaction process and what each kinetic constant describes, firstly the activation energy refers to the energy barrier that exists for all chemical reactions and which must be overcome by the reactant species in order for the reaction to proceed. The pre-exponential constant is a measure of the number of times per second that the reactant molecules are in the correct configuration for the reaction to occur. From this definition, $A$ was affiliated to the rate of reaction. Determination of $k$ from equation 35 in Section 1.6.5.3 actually yielded values similar to those for $A$.

Initially, the catalytic effect of the accelerator was confirmed. Table 3.14 shows how the activation energy of the 2-part, ‘as-received’ product from Dow Corning, termed Sylgard 184 specifically to distinguish between the unmodified 3-part product used as a control formulation in this study that is also essentially Sylgard 184, was considerably reduced from 70.25 kJ mol$^{-1}$ to 57.43 kJ mol$^{-1}$. Values for $A$ showed the unmodified reaction was approximately 15 times slower than Sylgard 184. However, the slower rate for the unmodified reaction was offset by the significantly lower initial energy barrier that the reactants had to overcome. Hence, the reduction of cure time from 48 hours to 24 hours at room temperature with the aid of the accelerator.

When a small amount of stearic acid, represented by 0.1 wt% concentration, was added there was a relatively small reduction in $E_A$ compared with the
unmodified reaction. Similarly, there was a small rise in the rate of this modified reaction with respect to the unmodified reaction, $4.5 \times 10^6$ s$^{-1}$ compared to $3.4 \times 10^6$ s$^{-1}$ respectively.

Increasing the level of modification with 0.3 wt% stearic acid increased $E_A$ from 57.43 kJ mol$^{-1}$ to 75.86 kJ mol$^{-1}$ so that for this particular formulation the activation energy exceeded that for the 2-part Sylgard 184 product. However, this steep rise in $E_A$ was compensated for by an equally sharp increase in $A$. Compared with the unmodified reaction, this formulation was over 1000 times faster. So, here in contrast to the previous situation where a slower rate was offset by a reduced $E_A$, the significant rise in activation energy was counteracted by an extremely fast rate of reaction. Furthermore, it was observed that when mixing these formulations, degassing time had to be shortened for this formulation in order to accommodate a faster onset of cure.

In comparison, although the reaction with 1.0 wt% stearic acid ($1.8 \times 10^7$ s$^{-1}$) was around 200 times slower than with 0.3 wt% stearic acid ($3.9 \times 10^9$ s$^{-1}$), it was, however, just over 5 times faster than the unmodified reaction ($3.4 \times 10^6$ s$^{-1}$). The energy for 1.0 wt% despite being lower than with 0.3 wt%, was still above $E_A$ for the unmodified reaction which was 57.43 kJ mol$^{-1}$. Again this effect was cancelled out by the faster rate of reaction with 1.0 wt% stearic acid. Once more, during adhesive preparation the degassing stage was shortened to reflect this but to a significantly lesser extent than with 0.3 wt% stearic acid content.

Finally the Kissenger method was used to study the effect of stearic acid on 2-part Sylgard 184. Table 3.14 shows that stearic acid behaved in the same way as the accelerator by reducing $E_A$ from 70.25 kJ mol$^{-1}$ to 64.27 kJ mol$^{-1}$. As with the accelerator, the rate of reaction compared with Sylgard 184 was reduced so that with stearic acid the reaction was 8 times slower. This was compared with 15 times with the accelerator. However, cure rate of Sylgard 184 with stearic acid was found to be twice as fast as when the accelerator was used. The parallel effect of stearic acid and accelerator was confirmed in
a separate study conducted by researchers at AWE whereby cure time for Sylgard 184 was also reduced from 48 hours to 24 hours.

4.3.2.2 **Friedman analysis**

The Kissenger method of analysing kinetic information from thermal analysis data assumes that the reaction occurs equally in all parts of the specimen and that there is unchanging thermal characterisation. As these assumptions are only valid in the material in the vicinity of the thermocouple, but only so far as the small region can be considered to react homogenously, by its very nature the Kissenger analysis is an approximation of the behaviour of the material. Consequently, the Friedman analysis was used in order to perform a more robust analysis of cure as this method analyses the reaction at each extent of reaction or degree of conversion.

The Friedman method revealed that $E_A$ varied with extent of reaction (refer to Figure 3.30). This meant that $E_A$ was not a constant. In the literature this was indicative of complex, multi-step reactions which can involve several processes with different activation energies and mechanisms. In such situations the reaction rate can only be described by complex equations where the activation term is no longer constant but dependent on the progress of the reaction.

Further to this the Friedman analysis was performed on unmodified and modified (0.3 wt% stearic acid) reactions. The results of these analyses are illustrated in Figures 3.31 and 3.32 respectively. The non-linearity of these prevented $E_A$ and $A$ being calculated by the slope and intercept, respectively. The various methods of deriving kinetic constants described in Section 1.6.5.1 are all based on the Arrhenius equation (equation 34 in Section 1.6.5.3). Thus with reference to the Friedman analysis a linear dependence of $\ln(d\alpha/dt)_{\alpha}$ over $1/T_{\alpha}$ with the slope $-E/R$ is assumed. Since this was not the
case and a non linear relationship was instead exposed it was concluded that both unmodified and modified reactions were not based on Arrhenius kinetics.

From the literature, the initial assumptions of kinetic analysis of thermal data were that a single conversion function \( f(\alpha) \) and a single set of Arrhenius parameters \( (E_A \text{ and } A) \) may be applied over a full range of extent of reaction \( (\alpha) \) was not applicable in this case. As a result, the kinetic triplet of \( f(\alpha), E_A \) and \( A^{168} \) were not able to be determined as they were used to define a single step reaction which was at variance with the multi-step nature of this reaction. On the other hand, although the Kissenger analysis is an approximation, it was found to closely mimic laboratory based observations as well as spectroscopic measurements discussed in the previous section. Therefore, the results of this analysis were considered sufficient validation of the catalytic effect of stearic acid.

### 4.4 Crosslink Density

The catalytic behaviour of stearic acid on hydrosilylation modelled by the Kissenger analysis, coupled with increased final conversion from FTIR spectroscopy intimated an associated increase in crosslink density of the adhesive network. However, swelling experiments showed that crosslink density was in fact reduced when stearic acid was added. This was indicated by an increase in the molecular weight between crosslinks in the modified adhesive. This effect was not as marked when 0.3 wt% stearic acid was added. The swelling data not only disagrees with FTIR spectroscopy conversion measurements, but it also contradicts observations made with regards to the reduced tacticity of the adhesive when stearic acid was added. Moreover the rise in modulus (as indicated by the slop of the stress strain curves could also be interpreted as an indication of increasing crosslink density with stearic acid. Figures 3.24-3.28 confirm the conversion measurements are applicable to the primary crosslinking reaction between
pendant SiH and terminal vinyl groups. The marked difference between swelling data and conversion data derived from spectroscopic measurements was attributed to dissimilar rates of reaction in the bulk (swelling data) and in a thin film (FTIR). Simpson et al.\textsuperscript{13,114} cite a number of reasons for this with specific reference to a two-part PDMS-based Dow Corning silicone rubber product with the same functional groups as the material in the present research. The authors name the following as possible explanations for differences in bulk and interfacial reaction rates: (1) surface segregation of reactive components leading to a depletion in the bulk and excess of these components at the interface; (2) the enhancement of diffusivity of reactive components and short range mobility of polymers in thin films, which would effect the rate of crosslinking at the interface and within the bulk material; (3) shorter average diffusion distance for oxygen and water in thin films and/or near the interface of the atmosphere/substrate as a result of large surface area to volume ratio. Consequently the rate of the hydrosilylation reaction can be catalysed by oxygen, or perhaps hydrolysis may occur as a result of the permeability of silicones to water vapour. Either reaction would interfere with the crosslinking chemistry; (4) the presence of an interface with a substrate may instigate reactions that compete with the crosslinking reaction. Simpson et al. state that reactive groups in silicones such as SiOH chain ends will bond to surface hydroxyl groups on the substrate surface.

Although the study by Simpson et al. has furnished the author with a variety of theories for the differences between the rate of reaction at the interface and in the bulk, at the present time this author is unable to explain this particular discrepancy. Perhaps it would be fruitful to collect swelling data from sections of the cured adhesive. This would enable direct comparison of crosslink density of the surface with the bulk. Alternatively, nanoindentation measurements have been previously used to show a positive correlation between increased hardness and modulus and crosslink density. So similarly measurements can be taken along a gradient of the adhesive in order to distinguish between surface and bulk properties.
4.5 Mechanical properties

The incomplete conversion displayed in Figures 3.23a to 3.23c signified that Sylgard 184 (here referring to the control formulation of base, crosslinking agent and accelerator) is a pressure sensitive adhesive (PSA). This was further corroborated by the tacticity of the cured adhesive which reduced with stearic acid addition. The degree of crosslinking in PSAs is a fundamental parameter in their mechanical performance as increased crosslinking tends to produce a stiffer more brittle material. Consequently, the effect of stearic acid on mechanical properties was investigated.

Cast sheets of unmodified and modified Sylgard 184 were prepared and a uniaxial tensile test performed on dumbbell specimens punched from the sheets. The tests represented the effect of stearic acid on mechanical properties of these specimens after curing for up to 24 hours. Five specimens were produced from each sheet. Figures 3.34(a) to 3.34(e) were derived from the load/displacement curves displayed in Appendix 2.0. They show the variability within each set of tests. Inspection using optical microscopy revealed that the edges of each specimen was subject to flaws which were most likely caused by the bluntness of the blade of the punching tool used to produce the dumbbell specimens. These flaws were considered to be the source of this variability.

Despite this inconsistency, a trend of increasing modulus, or stiffness, and toughness emerged with increasing additions of stearic acid. Although the increase in modulus had been anticipated, as a result of measured increase crosslink density and the observed reduction in tacticity, toughening of the material was surprising since an increase in modulus in PSAs is usually accompanied by lower strain to failure. Not only that but electron microscopy of stearic acid used throughout this study showed it was characterised by short, needle-like with jagged edges, similar to shards of broken glass (ref. Appendix 3.0) Hence failure had been expected to take place in a more brittle
manner with the tips of stearic acid particles acting as stress concentrations. Optical analysis of failed tensile specimens disclosed that stearic acid was evenly distributed within the bulk of the adhesive, but at the higher concentration (0.8 wt% and 1.0 wt%) these particles had a tendency to agglomerate in the bulk. Furthermore, optical analysis also revealed the presence of spherical structures that resembled cured rubber often situated in close proximity to the stearic acid particles. It was concluded that stearic acid, acting as a sort of nucleating agent, accelerated the cure process in its immediate surroundings, hence the appearance of these discrete rubber-like particulates. The homogenous distribution of these rubber particles alleviated the local stress concentrations. It is thought that the propagation of cracks initially arising from these local areas of stress concentration, i.e. the aforementioned flaws or the sharp edges of the stearic acid particles, was retarded by the rubber particles which enhanced bulk energy dissipation during fracture. Rubber particles are routinely incorporated into the matrix of brittle adhesives, such as epoxies, to achieve a similar effect.

4.5.1 Finite Element Analysis of Stresses

The peel test is essentially a measure of peel energy, the fracture energy per unit area or width. So referring back to Chapter 1 where adhesion was considered a sum of energy processes containing a surface work term and an energy dissipative term the peel energy also comprises a surface work of adhesion or cohesion term and (according to circumstances) terms for plastic, viscoelastic and other losses which occur during fracture. Since the area under the peel curve is an indication of toughness, it was reasoned that successive reduction of this area with stearic acid addition meant that modification reduced the toughness of the adhesive, therefore the modified material would be unable to dissipate stresses as robustly as the tougher unmodified material. Thus finite element analysis was used to assess the stress state of unmodified Sylgard 184 and modified Sylgard 184.
The Mooney-Rivlin coefficients used as input parameters for the finite element simulations of deformation were obtained by curve fitting experimental uniaxial tensile data. Mooney-Rivlin was selected to model deformation in the T-peel joint as it simulates materials that undergo large strains and small volume changes. The constants obtained from the stress/strain curves are shown in Table 2.5 and constituted the material properties of the adhesive. The resultant peel stress simulation, see Figure 3.35b, showed that adding 0.4 wt% stearic acid caused the adhesive to be in a higher stress state than the unmodified adhesive. The other modified curves experienced similar levels of stress for the same region of analysis as the unmodified adhesive. This finding was deemed to be suspect on two fronts. In the first instance the Mooney-Rivlin coefficients were based on experimental tensile stress/strain curves and the fact that the analysis was conducted on elements running through the centre of the bondline meant that the analysis should have detected the toughening effect of stearic acid described earlier in Section 4.4. However, this was not possible, mainly due to software problems when attempts were made to use higher order elements to model the strain, which would have allowed the increase in modulus to be detected. As a result of time constraints it was not possible to solve these issues. Secondly, failure of the subsequent peel stress simulation to model the confirmed effect of stearic acid on adhesion was attributed to the fact that insufficient material data was available. Initially, it was presumed that uniaxial data would suffice as there was stress in one direction, namely the peel stress. However, upon completion of the analysis it was found that biaxial data was also required as there were stresses operating in three directions which were almost equal to each other, with the peel stress as the driver (refer to Figure 3.35(a) and Figure 3.35(b). Failure analysis has already confirmed that both the unmodified and modified joints failed cohesively in a region very close to the interface. Therefore it is suggested that the analysis be repeated with material properties obtained from a micromechanical test, such as depth sensing nanoindentation, in the region where failure occurs as opposed to using bulk material properties to model what is essentially a surface effect.
Despite the set back with FEA, further consideration of the problem of the mechanism by which stearic acid reduces joint strength led to the conclusion that premature failure was a result of the increase in modulus observed from tensile tests. This increase in modulus means that the modified adhesive is able to carry higher stresses. However, since the toughening effect precipitated by stearic acid was confined to the bulk, recall that earlier surface characterisation using a combination of techniques failed to detect stearic acid at the surface, a mechanism for transmitting these stresses into the bulk material was not available, hence premature failure at low levels of joint load.

4.6 Parametric studies

The effects of parameters such as additives, surface pretreatment and joint configuration on adhesion were also investigated in the present study. The results of these studies are discussed in the following sections.

4.6.1 The effect of substrate pretreatment

The effect of surface pretreatment was investigated in order to ascertain whether the effect of reduced joint strength with stearic acid could be repeated with other mould release agents and saturated fatty acids. Figure 3.4 shows irrespective of pretreatment, modification of the adhesive, in this instance with 0.3 wt% stearic acid, consistently reduced joint strengths. As expected the smallest difference in adhesive strength was observed for degreased surfaces. Appendix 4.0 shows that these surfaces were not textured in any way. Since there were no contributions to joint strength, such as roughness effects or chemical interactions, other than ubiquitous secondary forces, to facilitate wetting of the adhesive this effectively meant that the adhesive just sat on the substrate surface. Consequently not only
were the lowest strengths recorded but also the effect of modifying the adhesive was imperceptible.

The peel strength of the FPL etched surface was significantly increased because of the micro-roughness of the substrate and the chemical stability conferred by the treatment. This resulted in an enhancement of the wettability of the adhesive to the substrate so that it was able to penetrate the oxide pores. Consequently when the peel force was applied fracture energy increased as a result of the additional energy required to stretch the adhesive and also because the chemical pretreatment had increased the thermodynamic work of adhesion and so produced a stronger interface. However, etching only produces thin barrier layers (approximately 20nm according to literature) so the strength of the etched joint reflects adhesive fibre pull out.

This result should have been augmented in the anodised substrates, but was not due to the preferential anodisation of the Ti alloy screws used to hold the specimens in place during this pretreatment. These screws were unintentionally placed in contact with the anodising bath. Appendix 4.0 shows the cross-section of a substrate that has been etched using the FPL solution and subsequently anodised using the 40/50V process. This SEM micrograph shows the characteristic morphology of substrates processed. The barrier layer at the bottom of the honeycomb morphology associated with anodised surfaces represents a greater surface area for wetting, and adhesive penetration, than the morphology of etched surfaces. Therefore upon infiltration of this morphology by the adhesive extra work would be required to break these strands of adhesive as opposed to pulling them out. Furthermore, the alteration of the surface chemistry by the anodising regime would also have enhanced \( W_A \). Ultimately, it was considered that significantly greater peel force would have been measured after applying the anodisation had preferential pretreatment of the jigs Ti alloy screws not taken place.

The lower joint strengths measured when stearic acid was added to the adhesive (0.3 wt%) substantiated the claim that premature failure was caused
by an increase in modulus. Fracture energy of etched and anodised surfaces possess both the energy components $W_A$ and $\psi$ since chemical pretreatments enhance the work of adhesion term by modifying the chemistry of the surface and the energy dissipative term as a result of the penetration of the micro-rough morphology. Modulus becomes important as its value determines the amount of elastically stored energy at a given strain which is reduced providing fracture energy $G$ when fracture occurs. The shallower peel curves given by the modified adhesive indicate that this material does not have a large amount of elastically stored energy to release during fracture. Therefore, when failure was initiated in the above examples the modified adhesive became highly stressed and at a lower strain.

4.6.2 The effect of joint configuration

It was established in earlier in this report that joint geometry influences the distribution of stresses within a joint. For example peel joints, by their very nature, concentrate stresses at the interface of the joint whilst the stresses in single lap joints are concentrated at the edges of the overlap. Consequently, the influence of joint configuration on the effect of stearic acid was studied using the single lap (SLS) joint. Appendix 5.0 shows the chemical composition derived from XPS analysis for SLS (5A) and T-peel (5B) joints subjected to a variety of pretreatments.

As expected there was relatively no difference in adhesive strength between degreased surfaces for the reasons explained earlier, namely a planar surface with nothing other than weak intermolecular forces to hold the surfaces together, hence weak joints were formed. Grit-blasting the surface raised joint strength 3 to 4 times compared with degreasing. This was the result of the macro-roughened surface conferred by mechanical pretreatments. Although there are no pictures available of this surface, there are sources to be found in the literature. The improvement in joint strength was attributed to an in
increase in energy dissipation $\psi$ during fracture which has been cited to provide an increase in adhesion\textsuperscript{188}. Therefore, there should be a consecutive increase in energy dissipation with FPL etched and CAA specimens as a result of their microporous morphology. This was found to be the case for anodised specimens but not so for etched specimens as they failed at lower load than grit-blasted joints. Surface analysis of the etched specimen showed copious amounts of impurities probably as a result of rising by previous users of the etch solution prior to immersion of their substrates.

This study also provided support for the proposed mechanism of reduced joint strength with stearic acid since joint strength was boosted in the SLS configuration. This was ascribed to the fact that stresses concentrated at the edges of the overlap propagated through the bulk adhesive. Consequently, the toughened adhesive was able to employ energy dissipative mechanisms to improve fracture energy. This study confirmed that if failure takes place within the modified adhesive layer, then adhesion was ameliorated.

4.6.3 The effect of alternative additives

The effect of alternative additives on adhesion was studied using calcium and zinc stearate, which as also widely used as mould release agents in rubber processing. Acetic acid was used to investigate the effect of carbon chain length on adhesion. Figure 3.2 demonstrates the results of this study. It was found that none of these alternatives lowered adhesion to the same extent as the same quantity of stearic acid. The lowest level of adhesion was achieved with zinc stearate. Furthermore, a comparison of the amount of Si, O, and C on both metal and polymer surfaces revealed that the stoichiometric ratio of these elements was identical for both surfaces (1:1:1.8 for the polymer side, 1:1:1.9 for the metal side with respect to Si:O:C) when modified with calcium stearate and acetic acid. However, modification of the adhesive with zinc stearate resulted in different stoichiometry for each surface (1:1:1.9 for the
polymer surface, 1:2.7:2.2 for the metal surface with respect to Si:O:C). From this it is evident that zinc stearate does exert an effect on the chemistry of the adhesive. In addition zinc is present on the metal side of failed joints but not on the polymer side. Contrastingly, calcium is not present on either side of the failed joints. Therefore it is possible to assume that the zinc stearate has migrated in its entirety to the surface of the polymer/metal interface. Surface characterisation with SEM indicated interfacial failure with both calcium stearate and zinc stearate. ATR of these surfaces corroborated this, whereas both SSIMS and XPS suggested a mixed failure mode with a greater percentage of the cohesive component. Due to the surface specivity SSIMS and XPS failure was deemed to occur cohesively. As XPS also betrayed almost 3 times the stoichiometric amount of oxygen in zinc stearate modified joints, failure was qualified as having taken place cohesively in a an oxygen-rich interphasial region. This region was thought posses poor mechanical properties, thereby causing failure at lower loads with zinc stearate than compared with acetic acid and calcium stearate.

There was an improvement on the original strength of the unmodified adhesive with acetic acid. The peel strength of the unmodified adhesive increased from 318 N m\textsuperscript{-1} to 427 N m\textsuperscript{-1}. Analyses of this surface using a combination of SEM, SSIMS, XPS and ATR spectroscopy all showed that joints modified with acetic acid failed in a cohesive manner (refer to Appendix 6). As literature studies had noted that release properties were not evident in saturated fatty acids with less than 12 Cs in their hydrocarbon chain acetic acid was not considered to have modified the adhesive. Therefore the phenomenon of adhesion enhance was thought to be explained by etching of the substrate by the acid. Aluminium substrates are often pretreated by etching them in strong acids such as nitric acid. Any subsequent enhancement in topography of the substrate surface could account for the augmentation of adhesive strength. Attempts were made to remove the residual cohesive layer of adhesive in order to substantiate this postulation, however these efforts were unsuccessful.
Chapter 5 Conclusions

- From the Literature Review, the only established mechanism for premature joint failure is the weak boundary layer theory. This also happens to the most routinely proposed mechanism for poor adhesion or increased mould sticking in the presence of stearic acid.

- At the start of this investigation a number of hypotheses were proposed to explain this phenomenon; (1) in accordance with popular and cited theories, it was suggested that stearic acid formed a cohesively weak layer at the interface. It was thought that this would be characterised by a transition from cohesive failure to interfacial failure as a result; (2) it was also put forward that stearic acid may work by inhibiting the cure reaction to reduce the degree of crosslinking which would adversely impact cohesive strength within the adhesive and affect adhesion through this route.

- In the first instance the degradation of joint strength when small amounts of stearic acid were added was reproduced using the T-peel test. Analysis of the failure surfaces ensued to determine the mode of failure and to ascertain the location of stearic acid. ATR was used to confirm cohesive failure whilst SSIMS and XPS indicated the proximity of this cohesive layer to the interface. ATR analysis also established that the cohesive layer was a PDMS-type possibly interphasial material. Surface analysis also disputed the validity of the migration theory so readily espoused in the literature. Neither SSIMS nor XPS analysis were able to detect stearic acid at the interface. This was especially so when high resolution scans of the C 1s peak in XPS were performed in order to establish the presence of shifts in the binding energy associated with COOH group at the end of the saturated fatty acid chain of stearic acid.
FTIR demonstrated that stearic acid had a catalytic effect of cure as did kinetic analysis of thermal data using the Kissenger method. As this was an approximation based on 'frugal' assumptions the Friedman Analysis was performed on kinetic data. This analysis revealed that the hydrosilylation cure reaction was a complex, multi-stage process not based on Arrhenius kinetics. FTIR also showed that Sylgard 184 is a pressure sensitive adhesive as maximum degree of conversion after 24 hours was 73%. The hydrosilylation reaction was also confirmed as a result of simultaneous consumption of silyl and vinyl groups tracked by FTIR spectroscopy. The advent of post-cure reactions was also intimated.

Uniaxial tensile tests at various concentrations of stearic acid were performed and showed a surprising increase in modulus and toughness with modification. This was attributed to the presence of discrete particles of cured rubber dispersed homogeneously throughout the adhesive matrix. It was suggested that stearic acid acted as a nucleating agent, initiating curing in the matrix immediately surrounding the particle.

Finite element analysis of the stress distribution in the unmodified and modified adhesive was unsuccessFully carried out. The FE model did not fit experimental data. This was attributed to incorrectly attempting to model surface effects with data derived from bulk mechanical properties. The limitation of the FE method in modelling toughening mechanisms was also highlighted.

Parametric studies revealed that stearic acid out performed its metallic derivatives, calcium and zinc stearate. It was also suggested that concentrated acids, such as glacial acetic acid, produce an etching effect on the substrate surface acting as an additional pretreatment whereby joint strength was augmented. Of the three alternative additives zinc stearate reduced joint strength by the largest degree and
this was attributed to cohesive failure in an oxygen rich interphasial region. XPS analysis also demonstrated that zinc stearate was present only on the metal surface of failed joints suggesting complete migration of this additive to the surface. In contrast to calcium stearate and stearic acid where there was no evidence of calcium or stearic acid on either surface of their respective joints. When joint geometry was altered so that failure propagated within the adhesive layer, as in SLS tests, it was found that adhesion was enhanced. This was attributed to the toughening mechanism of the dispersed cured rubber particulates.

- As the initial suppositions about WBLs and cure inhibition were found to be invalid an alternative proposal for the mechanism of action of stearic acid was put forward instead. It was postulated that stearic reduces joint strength as measured by T-peel test by increasing the crosslink density of a near surface interphasial region causing a concurrent rise in modulus. It has been asserted that modulus defines the amount of elastically stored energy at a given strain that can be released providing fracture energy G when fracture occurs. The shallower peel curves given by the modified adhesive indicated that this material does not have a large amount of elastically stored energy to release during fracture, so giving rise to brittle failure of the modified adhesive. Failure analysis limited this effect to a cohesive layer near the interface, since the toughening effect described earlier was found to be a bulk material property. Consequently, the modified adhesive does not to posses the mechanism to facilitate energy dissipative modes of failure. Therefore, when failure is initiated the modified material becomes highly stressed and fails at a lower energy to strain.
The limitation of the finite element method when trying to model macroscopic events caused by surface, submicron effects, especially when bulk material properties are assigned to what may well be an interphasial region has been highlighted in the current research. As a result it is felt that accurate determination of the mechanical properties of the region of failure would yield better results. It is also accepted that both uniaxial and biaxial data would be beneficial in order to develop a more robust FE model. both of these sets of data would probably help to perform analysis up to larger strains which would enable a better fit to the stress/strain curves.

The notion of the polymer/metal oxide/metal interface as a three-dimensional interphase is widely accepted. These interphases form for many reasons and it in order to fully understand them and their contribution to joint performance characterisation of this region is essential. A thorough analysis of polymer/metal (oxide) interphases according to Boerio et al.\textsuperscript{191} comprises characterisation of both the substrate surface and the overlayer, identification of the mechanisms by which the polymer interacts with the substrate and the changes induced by these interactions, determination of the rates at which these reactions occur, determination of how processing affects the structure and properties of the interphase. These aspects of the interphase can be studied using spectroscopy, advanced surface analysis methods such as ion scattering spectroscopy (ISS) and SSIMS and XPS and the mechanical properties of these regions may be measured with the use of nanoindentation and nanoscratch instruments. Nanoindentation enables the material properties of thin films and coatings on a multilayer structure with reasonable accuracy.

Nanoindentation or depth sensing indentation (DSI), is a testing technique which measures the mechanical properties of a material via continuously recording the forces applied and the corresponding displacement during an
indentation. It has been used to show the significant differences in mechanical properties of the interphase and the bulk matrix\textsuperscript{92}. In another study the DSI technique was used to investigate the distribution of mechanical properties through the bondline for several adhesive joints for comparison with the mechanical properties measured from bulk adhesive samples used for conventional uniaxial testing. This study found that elastic modulus derived from of DSI was approximately 5-20\% higher than that derived from uniaxial tests\textsuperscript{94}. Limitations to this test do exist in so far as at times the bounds of the study maybe outside the spatial resolution of the DSI test so that interphase material may be missed and incorrectly presumed to be absent as was the case in a study conducted by Zheng and Ashcroft\textsuperscript{94}.

Further studies could also include the use of TOF-SSIMS to help determine adhesion mechanisms and the possible formation of Al-O-Si bonds at the interface. The spectrometer used for this investigation does not have sufficient mass resolution to achieve this.
References


References


22 Ch. 8 Gardon J. L. 1967. Variables and Interpretation of Some Destructive Cohesion and Adhesion tests. (In:) Patrick R L (ed.) *Treatise on adhesion and adhesives vol. 1: Theory*,.


References


References


52 Iwamoto, N. E., 1995, Comparisons of Experimental Data to Indices of Adhesion Derived from Dielectric Models, Polymer Engineering and Science, vol. 35(12): 1811-1817


References


References


77 Miyagi Z et al., 1994. Study of Peeling properties of pressure-sensitive adhesives using a newly developed image processing system


References


References


References


References


References


XPS handbook


Briggs, D 1998 Surface Analysis of Polymers by XPS and Static SIMS. Cambridge: Cambridge University Press


References


References


166 Borchardt H J and Daniels F 1957, The Application of Differential Thermal Analysis to the Study of Reaction Kinetics


References


188 Packham D E, The mechanical theory of adhesion-A seventy year perspective and its current status.

189 Critchlow G W and Brewis D M Influence of surface macroroughness on the durability of epoxide-aluminium joints


Appendices

Appendix 1.0

Earlier work conducted at AWE shows a dramatic reduction in adhesive strength with minute amounts of stearic acid. Control values equate to the unmodified adhesive in the present study.

Effect of Stearic Acid on Adhesion

![Graph showing the effect of stearic acid on adhesive strength.](image-url)

- Typical Control Values
- Percentage stearic acid by weight
- Peel strength N/m
Appendix 2.0

What follows are load v displacement curves of uniaxial tensile test carried out on unmodified and modified Sylgard 184. The curves below show variation within each set off 5 tests carried out at each concentration of stearic acid.

![Tensile Properties of Unmodified Sylgard 184](image-url)
Appendices

Appendix 2.0

Tensile Properties of Sylgard 184 Modified with 0.1wt% Stearic Acid

Tensile Properties of Sylgard 184 Modified with 0.3wt% Stearic Acid
Appendices

Appendix 2.0

Tensile Properties of Sylgard 184 Modified with 0.4wt% Stearic Acid

Tensile Properties of Sylgard 184 Modified with 0.5wt% Stearic Acid
Appendices

Appendix 2.0

Tensile Properties of Sylgard 184 Modified with 0.8wt% Stearic Acid

![Graph showing the tensile properties of Sylgard 184 modified with 0.8wt% Stearic Acid. The x-axis represents the extension in millimeters, ranging from 0 to 45. The y-axis represents the load in Newtons, ranging from 0 to 14. Several lines are plotted, each representing a different condition or sample.](image-url)
Appendix 3.0

In this section are displayed scanning electron micrographs of stearic acid and the metal stearates of calcium and zinc used in this study. All of these images were taken by a Cambridge stereoscan 360 instrument operating with primary beam energy of $10 \times 10^3\text{V}$ and a current of approximately $250\times 10^{-12}\text{A}$. In all examples, samples were gold sputter coated prior to analysis.
Appendices

Appendix 4.0

In this section are contained electron microscope pictures of degreased, FPL etched and CAA surfaces used in this study. All images were taken using a LEO 1530VP field emission gun scanning electron microscopy (FEGSEM) instrument operating with primary beam energies of $20 \times 10^3$V. There was no requirement for gold coating of these samples.

![High magnification plan view of acetone degreased 1xxx series Al surface.](image)

This surface is not textured in any way. The primary function of degreasing is to remove organic debris from the surface of the adherend prior to bonding.
High magnification plan view of FPL etched 1xxx series Al surface

Present is the scalloped effect of the surface oxide that is characteristic of this process. There is no cross section of this surface as the oxide is too thin, with a typical layer thickness of 20nm.
High magnification of plan view of aluminium surface initially FPL etched then anodised using 40/50 CAA process.

Cross-section of 1xxx series Al surface etched (FPL) and anodised (40/50 CAA)

Pictured are a plan and cross-section view of an adherend that has been etched and subsequently anodised. The cross-section shows the oxide, barrier layer and the metal surface, respectively.
Appendix 5.0

The following pages contain XPS survey scan spectra of SLS joints pretreated by degreasing (DG), grit-blasting (GB), etching (FPL Etch) and anodising (CAA). Examples of joints that failed at high loads and low loads for each set of pretreatments are included.
Appendix 5A

Side A-Unmodified-DG-High Joint Strength

![Graph showing binding energy distribution for Side A](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.0</td>
<td>30.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.0</td>
<td>41.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>101.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.55</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Side B-Unmodified-DG-High Joint Strength

![Graph showing binding energy distribution for Side B](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>48.2</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>29.3</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>22.5</td>
</tr>
</tbody>
</table>
Side A-Unmodified-DG-Low Joint Strength

Element | Peak | B.E. | % At
---|---|---|---
C | 1s | 285.1 | 48.6
O | 1s | 532.8 | 28.0
Si | 2p | 102.6 | 23.4

Side B-Unmodified-DG-Low Joint Strength

Element | Peak | B.E. | % At
---|---|---|---
C | 1s | 285 | 47.6
O | 1s | 533 | 28.2
Si | 2p | 102.6 | 24.2
Appendices

Appendix 5A

Side A-Modified-DG-High Strength Joint

![Graph showing binding energy vs intensity for Side A-Modified-DG-High Strength Joint]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>45.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.5</td>
<td>32.0</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.8</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Side B-Modified-DG-High Joint Strength

![Graph showing binding energy vs intensity for Side B-Modified-DG-High Joint Strength]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>48.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>531.9</td>
<td>33.0</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>101.9</td>
<td>5.5</td>
</tr>
<tr>
<td>Ca</td>
<td>2p</td>
<td>347.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.42</td>
<td>12.7</td>
</tr>
</tbody>
</table>
Side A-Modified-DG-Low Joint Strength

Element | Peak | B.E.  | % At |
---------|------|------|------|
C        | 1s   | 284.8| 48.8 |
O        | 1s   | 532.9| 27.9 |
Si       | 2p   | 102.5| 23.3 |

Side B-Modified-DG-Low Joint

Element | Peak | B.E.  | % At |
---------|------|------|------|
C        | 1s   | 285  | 38.4 |
O        | 1s   | 531.9| 37.0 |
Si       | 2p   | 101.9| 7.9  |
Na       | 1s   | 1073 | 0.3  |
Al       | 2p   | 74.42| 16.4 |
Appendices

Appendix 5A

Side A-Unmodified-GB-High Joint Strength

![Graph showing the binding energy spectrum for Side A-Unmodified-GB-High Joint Strength]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>43.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.4</td>
<td>31.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>19.8</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.23</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Side B-Unmodified-GB-High Joint Strength

![Graph showing the binding energy spectrum for Side B-Unmodified-GB-High Joint Strength]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>37.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>36.6</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75</td>
<td>10.7</td>
</tr>
</tbody>
</table>
Appendices

Appendix 5A

Side A-Unmodified GB-Low Joint Strength

![Graph showing binding energy distribution for Side A.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>45.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>29.5</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>21.6</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.06</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Side B-Unmodified GB-Low Joint Strength

![Graph showing binding energy distribution for Side B.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.9</td>
<td>48.4</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>27.4</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.2</td>
</tr>
</tbody>
</table>
### Side A-Modified-GB-High Joint Strength

![Graph showing elemental peaks for Side A](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>41.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.2</td>
<td>33.4</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.3</td>
<td>10.9</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.93</td>
<td>14.6</td>
</tr>
</tbody>
</table>

### Side B-Modified-GB-High Joint Strength

![Graph showing elemental peaks for Side B](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>51.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>26.2</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>22.3</td>
</tr>
</tbody>
</table>
### Side A-Modified-GB-Low Joint Strength

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>46.6</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.55</td>
<td>10.5</td>
</tr>
</tbody>
</table>

### Side B-Modified-GB-Low Joint Strength

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>49</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.7</td>
<td>27.2</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.1</td>
<td>23.8</td>
</tr>
</tbody>
</table>
**Side A-Unmodified-FPL Etch-High Joint Strength**

![Graph showing binding energy vs intensity for Side A-Unmodified-FPL Etch-High Joint Strength](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>47.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>28.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.0</td>
</tr>
</tbody>
</table>

**Side B-Unmodified-FPL Etch-High Joint Strength**

![Graph showing binding energy vs intensity for Side B-Unmodified-FPL Etch-High Joint Strength](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>40.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>36.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>17.8</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.4</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Appendices

Side A-Unmodified-FPL Etch-Low Joint Strength

![Graph of binding energy and intensity for Side A](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.2</td>
<td>23.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>51.9</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>6.8</td>
</tr>
<tr>
<td>Fe</td>
<td>2p3</td>
<td>712.5</td>
<td>1</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Zn</td>
<td>2p3</td>
<td>1023.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Na</td>
<td>1s</td>
<td>1073.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>2ps</td>
<td>579</td>
<td>2.3</td>
</tr>
<tr>
<td>S</td>
<td>2p</td>
<td>170</td>
<td>6.8</td>
</tr>
<tr>
<td>N</td>
<td>1s</td>
<td>402.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Side B-Unmodified-FPL Etch-Low Joint Strength

![Graph of binding energy and intensity for Side B](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>48.0</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>533</td>
<td>27.6</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.4</td>
</tr>
</tbody>
</table>
Side A-Modified FPL Etch-High Joint Strength

Element | Peak | B.E. | % At  
--- | --- | --- | ---  
C | 1s | 285 | 43.1  
O | 1s | 532.8 | 33.3  
Si | 2p | 102.7 | 18.2  
Al | 2p | 75.83 | 5.4

Side A-Modified FPL Etch-High Joint Strength

Element | Peak | B.E. | % At  
--- | --- | --- | ---  
C | 1s | 285.1 | 52.6  
O | 1s | 532.4 | 27.7  
Si | 2p | 102.2 | 12.2  
Al | 2p | 74.93 | 5.4  
P | 2s | 191.3 | 1.3  
Ca | 2p | 348.3 | 0.8
Appendices

Appendix 5A

Side A-Modified FPL Etch-Low Joint Strength

![Graph showing intensity vs. binding energy for Side A-Modified FPL Etch-Low Joint Strength.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>48.0</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>533.1</td>
<td>27.8</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Side B-Modified FPL Etch-Low Joint Strength

![Graph showing intensity vs. binding energy for Side B-Modified FPL Etch-Low Joint Strength.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>45.2</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>31.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>20.3</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.44</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Side A-Unmodified-CAA-High Joint Strength

Element | Peak | B.E. | % At  
---|---|---|---
C | 1s | 285 | 48.7 
O | 1s | 532.8 | 26.4 
Si | 2p | 102.6 | 24.9 

Side A-Unmodified-CAA-High Joint Strength

Element | Peak | B.E. | % At  
---|---|---|---
C | 1s | 284.9 | 49.2 
O | 1s | 532.8 | 26.3 
Si | 2p | 102.5 | 24.4 
Na | 1s | 1074 | 0.1
### Side A-Unmodified-CAA-Low Joint Strength

![Graph showing binding energy vs. intensity with peaks for different elements]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>47.3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.7</td>
<td>28.2</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.4</td>
<td>24.5</td>
</tr>
</tbody>
</table>

### Side B-Unmodified-CAA-Low Joint Strength

![Graph showing binding energy vs. intensity with peaks for different elements]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>40.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>36.0</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>18.7</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.32</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Appendices

Appendix 5A

Side A-Modified-CAA-High Joint Strength

![Graph showing binding energy vs. intensity for Side A.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>47.4</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>28.3</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>23.9</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.87</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Side B-Modified-CAA-High Joint Strength

![Graph showing binding energy vs. intensity for Side B.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>44.7</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>29.9</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>22.0</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.83</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Appendices

Side A-Modified-CAA-Low Joint Strength

![Graph of Side A-Modified-CAA-Low Joint Strength](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>28.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.5</td>
<td>43.4</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>101.7</td>
<td>10.3</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75</td>
<td>18.1</td>
</tr>
<tr>
<td>Ca</td>
<td>2p</td>
<td>346.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Side B-Modified-CAA-Low Joint Strength

![Graph of Side B-Modified-CAA-Low Joint Strength](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>40.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>33.5</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>18.7</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>71.19</td>
<td>7.5</td>
</tr>
<tr>
<td>Ca</td>
<td>2p</td>
<td>348.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Appendices

Appendix 5B

The following pages contain XPS survey scan spectra of peel joints pretreated by degreasing (DG) and anodising (CAA). Examples of joints that failed at high loads and low loads for each set of pretreatments are included. As the FPL pretreatment was the predominant treatment in the study there are numerous examples of related XPS spectra within the body of the text.
### Polymer side-Unmodified-DG-High Joint Strength

![Graph showing binding energy and intensity for polymer side](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>48</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>27.5</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

### Metal side-Unmodified-DG-High Joint Strength

![Graph showing binding energy and intensity for metal side](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>18.9</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>50.2</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>22.5</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.8</td>
<td>8.3</td>
</tr>
<tr>
<td>N</td>
<td>1s</td>
<td>397.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>
### Polymer side-DG-Unmodified - Low Joint Strength

![Graph of polymer side-DG-Unmodified](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>46.9</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>28.4</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.7</td>
</tr>
</tbody>
</table>

### Metal side-DG-Unmodified - Low Joint Strength

![Graph of metal side-DG-Unmodified](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285.1</td>
<td>21.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.1</td>
<td>60.4</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>101.9</td>
<td>9.3</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.55</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Polymer side-Modified-DG-High Joint Strength

Element | Peak | B.E. | % At  
--- | --- | --- | ---  
C | 1s | 285 | 48.4  
O | 1s | 532.8 | 26.6  
Si | 2p | 102.6 | 25.1  

Metal side-Modified-DG-High Joint Strength

Element | Peak | B.E. | % At  
--- | --- | --- | ---  
C | 1s | 285 | 24.7  
O | 1s | 532.8 | 44.5  
Si | 2p | 102.6 | 10.4  
Al | 2p | 74.87 | 20.3
Appendices

Appendix 5B

Polymer side-Modified-DG-Low Joint Strength

![Graph showing intensity vs. binding energy for polymer side.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>49.1</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>27.5</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>23.5</td>
</tr>
</tbody>
</table>

Metal side-Modified-DG-Low Joint Strength

![Graph showing intensity vs. binding energy for metal side.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>30.7</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>39.7</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>20.4</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>74.61</td>
<td>9.1</td>
</tr>
</tbody>
</table>
Polymer side-Unmodified-CAA-High Joint Strength

Element | Peak | B.E. | % At
---|---|---|---
C | 1s | 285 | 48.6
O | 1s | 433.2 | 26.3
Si | 2p | 102.6 | 25.2

Polymer side-Unmodified-CAA-High Joint Strength

Element | Peak | B.E. | % At
---|---|---|---
C | 1s | 285.1 | 49.2
O | 1s | 532.8 | 26.5
Si | 2p | 102.6 | 24.3
Appendices

Polymer side-Unmodified-CAA-Low Joint Strength

![Graph showing binding energy (eV) vs. intensity for polymer side.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>284.9</td>
<td>49</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.8</td>
<td>26.3</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>24.7</td>
</tr>
</tbody>
</table>

Metal side-Unmodified-CAA-Low Joint Strength

![Graph showing binding energy (eV) vs. intensity for metal side.]

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E.</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>46.4</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.9</td>
<td>28.9</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>24.7</td>
</tr>
</tbody>
</table>
Polymer side-Modified-CAA-High Joint Strength

Element | Peak | B.E. | % At  
---|---|---|---
C | 1s | 285 | 48.1  
O | 1s | 532.7 | 26.8  
Si | 2p | 102.5 | 25.1  

Metal side-Modified-CAA-High Joint Strength

Element | Peak | B.E. | % At  
---|---|---|---
C | 1s | 285 | 36.5  
O | 1s | 532.8 | 35.4  
Si | 2p | 102.5 | 20.1  
Al | 2p | 8 | 8
Polymer side-Modified-CAA-Low Strength Joint

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E. (eV)</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>48.5</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>532.6</td>
<td>26.9</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.5</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Metal side-Modified-CAA-Low Strength Joint

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E. (eV)</th>
<th>% At</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s</td>
<td>285</td>
<td>32.7</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>433.2</td>
<td>39.1</td>
</tr>
<tr>
<td>Si</td>
<td>2p</td>
<td>102.6</td>
<td>13.4</td>
</tr>
<tr>
<td>Al</td>
<td>2p</td>
<td>75.06</td>
<td>14.7</td>
</tr>
</tbody>
</table>
Appendix 6.0

Failure analysis of peel joints modified with alternative additives.

Acetic Acid

Characterisation of the metal surface confirms cohesive failure. SSIMS shows PDMS peaks at 28, 43, 73 and 147 amu. XPS shows cohesive failure with Si, O and C present in ratio 1:1:2. AATR shows PDMS film on surface of metal.

Calcium Stearate

SSIMS indicates mixed mode of failure, XPS indicates mixed mode of failure but only small amount of Al was detected. Ratio of Si to O to C remains 1:1:2. ATR indicated interfacial failure as there was no adhesive residue on the metal.

Zinc Stearate

SSIMS indicates mixed mode of failure, as did XPS. XPS also revealed excess of O, almost 3 times the amount. In contrast, ATR indicated interfacial failure
SSIMS and ATR characterisation of the metal side of joints modified with 1.0wt% glacial acetic acid.
SSIMS and ATR characterisation of the metal side of joints modified with 1.0wt% calcium stearate.
SSIMS and ATR characterisation of the metal side of failed joints modified with 1.0 wt% zinc stearate