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Examination of the surface and interfacial properties of an epoxide-urethane resin for surface coatings

By

Phillip Carpenter

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

December 1997

Institute of Polymer Technology and Materials Engineering

Supervisors:
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Abstract

Electrodepositable paints are used in the auto industry to provide the majority of the protection against corrosion to mild steel car body shells. They are generally epoxy/blocked isocyanate resins systems which are applied by action of an electropotential between the car and an anode. Upon heating to 175°C the blocked isocyanate deblocks, and crosslinking occurs predominantly via the formation of urethane and urea linkages. The aim of the project was to gain a better understanding of the factors which may affect the adhesion of the electrocoat resin polymer to a steel surface, to investigate possible replacements for the tin catalyst currently used, and to develop a quantitative mechanical test for paint adhesion. This was achieved by employing various analytical techniques including Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and mechanical testing.

Investigations using variable temperature infrared and reflectance infrared showed that when the resin was cured, not all the isocyanate reacted to form urethane/urea linkages and that some isocyanate may react with the metal surface or with other groups present in the resin matrix. However, no specific interaction between the electrocoat resin polymer and the steel surface could be determined. Hence model polymers containing different functional groups found in the resin were coated onto a steel substrate and the interactions observed by reflectance infrared spectroscopy. It was found that poly(acrylic acid) and two different amines gave rise to salts and chelate structures, and that poly(vinyl alcohol) showed differences in crystallinity close to the metal surface. No differences were observed with 4,4' diphenyl methylene diisocyanate (MDI) and poly(vinyl methyl ether). However at elevated temperatures it was found that MDI reacted with water, probably from the steel surface to give an acid salt structure, the same as observed with poly(acrylic acid).

An investigation into the effect of dibutyl tin oxide (DBTO) catalyst upon the blocked isocyanate crosslinker by DSC, indicated that it was not possible to determine the onset of deblocking by this method. DSC and variable temperature infrared spectroscopy investigations of DBTO, Bicat A and Bicat Z catalysts upon the
Abstract
deblocking of two pure blocked isocyanates (MDI blocked with butyl carbitol and methanol) indicated that Bicat Z showed catalytic activity in both cases. DBTO and Bicat A showed catalytic activity in the blocked isocyanate blocked with methanol. An attempt to develop a quantitative mechanical test indicated that the resin is strongly bound to the steel surface and that only after environmental exposure did the paint delaminate. After salt spray exposure, XPS analysis of the failed steel surface indicated the presence of an acid group. A thermodynamic experiment indicated that there were probably covalent bonds present which may to some extent explain the high joint strength. Preliminary investigations were carried out to develop a shim test, which may be used to evaluate a conductance measurement for determining delamination of a coating.
Acknowledgements

I wish to thank Dr. Ian Sutherland and Dr. Richard Heath at Loughborough University, for supervision of this project.

I thank the EPSRC and ICI Paints Ltd., Slough for the funding of this work, and in particular Dr. Brian Pearson, now at IDAC, for the industrial supervision of the project.

Finally I thank all those who have fed me, and encouraged me to complete this work.
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1.0 Introduction

Over the last thirty years there has been an increase in the body warranties given with new cars, guaranteeing the vehicle body from corrosion. This is not only a function of improved steel and design, but is also a function of the surface coating covering the car body, and the pre-treatment applied to the steel before coating. The purpose of the paint used as the surface coating is twofold: to act as a barrier between the steel body and the environment, thus, increasing the life span of the steel body, and to provide an acceptable visual performance. For effective protection the paint must be able to act as a mechanical and physical barrier (e.g. abrasion resistance), and as an electrochemical barrier preventing access of oxygen, water and ions to the steel\textsuperscript{1}. For visual performance a smooth gloss finish is usually required. Hence, a steel body is typically painted according to the following schedule: a primer, a surfacer and the top gloss coat, this is shown in Figure 1.1.

Although the painting schedule consists of three distinct layers, it is the primer coat which provides the majority of the corrosion resistance and protection to the steel. It is this coating material that was investigated in the work described in this thesis.
Chapter 1: Introduction

The primer paint is applied to the steel by an electrodeposition process, and is known as an “electrocoat”. The objective of the research was to develop further understanding of the properties of the ICI Paints electrocoat primer paint, particularly in the following areas:

a) how does the paint adhere to a mild steel substrate? This is important to know since if is known how the resin interacts, for example by mechanical and/or chemical mechanisms, then it may be possible to enhance this mechanism, so as to increase the interaction, and therefore possibly increasing the adhesive strength.

b) can a less hazardous alternative to the tin catalyst, employed to aid the cure reactions in the electrocoat resin be used? This is required to satisfy current safety criteria. What are the criteria used to determine the effect of catalyst upon cure and how can they be determined?

c) can a quantitative mechanical test be developed, to determine the adhesive strength of electrocoat paint to a mild steel substrate? Tests currently used at ICI Paints Ltd. include solvent rub and a cathodic delamination test.

Although these areas are quite distinct, they are also related. The adhesion mechanisms affect the adhesive strength of the electrocoat resin, and the choice of catalyst may affect what cure reactions occur, again, perhaps affecting the overall adhesive strength. For example, what would happen if the crosslinking reaction occurred at a temperature 40°C lower than the current temperature? Hence in the case of replacing the tin catalyst, there is a requirement for the catalyst to act within the same temperature regime as the currently used compound. Although some of these investigations were outside the scope of this thesis, investigations in to the three main
areas were carried out using a number of different analytical techniques. Reflection absorption infrared spectroscopy was performed to observe resin interactions with a mild steel substrate. With this technique, it is possible to probe through thin polymer layers, and observe interactions occurring in the region of the metal surface/polymer interface. Differential scanning calorimetry and variable temperature infrared spectroscopy were used to monitor the reactions occurring during the crosslinking of the resin. A combination of these two techniques allows changes in the thermal nature and changes in actual structure as a function of temperature to be determined.

Finally, a tensile test was used to determine the mechanical properties of the paint resin. Experimental results were also obtained from other techniques such as X-ray photoelectron spectroscopy and atomic force microscopy, to provide a more complete picture of what was occurring.

The work was supported by ICI Paints in Slough, who produce the electrocoat resin based upon a PPG patent\textsuperscript{2}. 
2.0 Literature

In this chapter the properties and preparation of the electrocoat resin are described, and theories relating to adhesion and experimental observations of adhesion discussed. Finally there is a section detailing the main techniques used in this work, and the associated literature.

2.1 The electrocoat paint

The primer used on the body panels of most modern cars is based on a relatively complex epoxy resin system, which is coated onto steel from an aqueous dispersion, by a process known as “electrodeposition”. This involves the paint being transferred from the dispersion to the substrate, by the action of an electrical potential; hence, it is known as an “electrocoat”. Crosslinking is then carried out at 175°C for 20 minutes, in the so called “stoving process”.

Chapter 2: Literature

Such a coating process relies on the paint resin being a conducting emulsion in water, with deposition occurring from the emulsion by either anodic or cathodic mechanisms\(^3\). Cathodic electrodeposition (CED) is the most common method of paint application in the automotive industry, and has several advantages over anodic deposition\(^4\). Table 2.1 shows the comparison between the two processes.

<table>
<thead>
<tr>
<th>Cathodic electrodeposition</th>
<th>Anodic electrodeposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improved throwing power* and coating uniformity for thin films.</td>
<td>Inadequate protection of bare steel surfaces in areas such as internal box sections, leading to pitting and corrosion.</td>
</tr>
<tr>
<td>Better paint stability.</td>
<td>Poor saponification resistance leading to loss of adhesion.</td>
</tr>
<tr>
<td>Freedom from substrate disruption during electrodeposition</td>
<td>Disrupts the phosphate coating during deposition, giving poor adhesion.</td>
</tr>
<tr>
<td>More costly than anodic deposition</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison between cathodic and anodic electrodeposition

To enable the paint to be dispersed into water the resin component of the paint needs to contain polar groups. In the case of CED, pendant amine groups incorporated into either the epoxy backbone or the crosslinker are protonated with an organic acid, usually acetic or lactic acid, which allows the formation of an emulsion in water. The emulsified resin carries a charge, and this allows its movement and coagulation on the surface of the anode or cathode when a potential is passed through the dispersion. The movement of the charged species in CED is shown by Figure 2.1, where the steel car body is represented by the cathode (\(-\)). The anode is usually made of graphite or stainless steel. As an electrocoat is deposited and builds up on the substrate surface, the electropotential is inhibited, and the transfer of resin molecules to the substrate

---

* "Throwing power" is the ability of the coating to coat awkward shapes, e.g. the inside of box sections.
Chapter 2: Literature

tends to zero. Hence, the thickness of the paint layer on the surface of the substrate is self-limiting, being dependent upon the initial potential applied.

\[
\begin{array}{c}
- \\
R''\text{NH}^+ R'\text{COO}' \\
\text{Paint emulsion} \\
+ \\
R''\text{NH}^+ : \text{Charged resin} \\
R'\text{COO}' : \text{Acid}
\end{array}
\]

Figure 2.1: The cathodic electrodeposition process.

There has been a considerable amount of work reported in which different resin oligomers, catalysts, crosslinkers and the overall performance of the materials\(^5\)\(^-\)\(^7\) has been studied. The final appearance of the emulsion, deposition yield and the quality of the films has been found to be dependent upon pH, the emulsifying solvent and the concentration of the epoxy resin in the emulsion\(^6\)\(^9\). It has been reported\(^7\) that an electrodepositable paint consisting of two different epoxy resins can provide better storage properties than a one component coating. The composition of such a coating was studied by Fourier transform infrared spectroscopy (FTIR)\(^8\). It was found that the yield of each resin in the electrocoat was dependent upon the individual phoretic velocity, and hence, composition of the coating will change during the electrodeposition process. The electrocoat formulation used commercially is complex, but consists of three major components; i.e. an epoxy/isocyanate base resin, a complex epoxy based pigment dispersion resin and water. It may also contain other minor components such as anti-crater agents, and organic solvents. In this work only the base resin has been examined as it was considered that a pigment resin would further complicate an already complex system. A second simplification was the use of untreated steel rather than phosphated steel, as may be found on most modern car body shells. The phosphating process further protects the steel from oxidation, and is thought to possibly act as a "mechanical key" aiding the adhesion of the coating to the metal surface. It was hoped that these two simplifications would enable the interaction between the steel surface and the epoxy base resin to be determined.
2.1.1 Synthesis of the base resin

The system studied in this research was synthesised in the laboratory of ICI Paints, by reacting a bisphenol A epoxy oligomer (epoxy equivalent weight \( ^+ \) 190) with a bisphenol A/ethylene oxide adduct. This forms an extended epoxy oligomer (EEW 1100), shown diagrammatically in Figure 2.2, which is crash cooled with blocked 4,4' diphenylmethane diisocyanate (MDI). The ethylene oxide adduct is used to introduce flexibility to the final polymer.

![Diagrammatic representation of the extended epoxy oligomer](image)

Figure 2.2: Diagrammatic representation of the extended epoxy oligomer

The extended epoxy oligomer is then reacted with a mixture of three secondary amines, N-methyl-ethanolamine, diethanolamine and a diketimine (formed from the reaction between diethyl triamine and methyl isobutyl ketone), which produces an epoxy/amine adduct of the form shown in Figure 2.3.

![Reaction product of the secondary amines with the epoxy ring on the epoxy backbone](image)

Figure 2.3: Reaction product of the secondary amines with the epoxy ring on the epoxy backbone. \( R \) and \( R' \) refer to the aliphatic chains attached to the secondary amines used in the reaction.

---

\(^+\) Epoxy equivalent weight (EEW) is the molecular weight of the oligomer divided by the number of epoxy units on the oligomeric chain.
Chapter 2: Literature

1) Formation of a urethane group

\[
\begin{array}{c}
\text{OH} \quad O=C=\text{N} \quad \text{R} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{R}
\end{array}
\]

2) Formation of a urea

\[
\begin{array}{c}
\text{NH}_2 \quad O=C=\text{N} \quad \text{R} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{N} \quad \text{N} \quad \text{R}
\end{array}
\]

Figure 2.5: Possible curing reactions

Primary aliphatic amines have higher reactivity rates with isocyanate groups, than primary or secondary hydroxyl groups\(^9\), hence the formation of urea linkages are preferred to the formation of urethane linkages.

Since this study was only concerned with the base resin component of the electrocoat, the resin was not emulsified, so the hydrolysis of the diketimine could not occur producing free primary amine groups. Hence, the main curing reaction would be between hydroxyl and isocyanate groups (i.e. to form urethanes). In the commercial hydrolysed paint resin, there are approximately 22 hydroxyl and 2 primary amine groups per oligomer chain. In the research system studied there are 22 hydroxyl and no amine groups per oligomer chain.

It should be borne in mind that in the industrial coating system there is also a "pigment resin", which is based on a similar epoxy/isocyanate resin plus a solid pigment/filler mixture. Hence cure occurs in both the base and pigment resins.
2.2 General adhesion theory

Adhesion may be defined as:

The state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both\textsuperscript{10}.

The word adhesion is from the Latin \textit{adhaerere}: which literally means to stick to; \textit{ad} to, and \textit{haerere} to stick. The term first appeared in the seventeenth century, and one of the earliest examples of the term being used in scientific context was by Robert Boyle in 1661\textsuperscript{11}.

No single theory of adhesion can be employed to explain all observed interactions between adhesives and their substrates (i.e. adherends). Theories to explain adhesion mechanisms\textsuperscript{12,13} may be split into five categories, namely:

a) adsorptive bonding,
b) mechanical keying,
c) electrical double layer,
d) molecular diffusion,
e) weak boundary layers (WBL).

2.2.1 Adsorptive bonding

This is probably the most popular theory of adhesion and is concerned with interactions which may act across the substrate/adhesive interface. The theory proposes that, provided there is sufficient intimate molecular contact across the interface, adhesion will occur because of the interatomic and intermolecular forces in
Chapter 2: Literature

the surface layers of the adhesive and substrate. There are two categories of interactions:

1. **Primary (chemisorption) interactions:** include ionic, covalent and metal complexing interactions. These interactions are the stronger of the two subcategories.

2. **Secondary (adsorption) forces:** most commonly Van der Waals forces, but hydrogen bonding may also be included. Van der Waals forces can be dispersion forces, dipole/induced dipole or dipole/dipole. It has been proposed by Fowkes that secondary interactions may be grouped into two categories; dispersion forces and acid-base interactions. Hydrogen bonding is a form of acid-base interaction and the strength of the bond is dependent upon the acidity of the hydrogen donor and the basicity of the hydrogen acceptor.

Evidence of covalent bonds has been found between certain polyurethane adhesives and epoxy based primers, bonds of an ionic nature have been reported between polymers such as poly (acrylic acid) and metal oxides. Chemical bonds, in the form of FeOSi⁺ have been found between silane primers and mild steel surfaces. However, some authors have cast doubt upon this work and believe that the layers of silane are too thick for this reaction/interaction to have occurred. Bell has found no evidence for primary bonding occurring between an epoxy resin and an etched or unetched aluminium surface.

It has been reported that secondary forces provide the mechanism which predominates in many joints, and that hydrogen bonds established at the interface are stronger than dispersion forces. Secondary forces are likely to be the first interactions occurring between the substrate and polymer matrix, and depend upon the surface of the substrate and the nature of the polymer matrix. It can be shown that dispersion forces can account for high adhesive joint strengths. However, these values are rarely realised owing to air voids, cracks and other defects within the resin which act as stress raisers when a joint is loaded.
2.2.2 Mechanical keying

This theory requires that an adhesive fills the interstices (cracks, holes, pores etc.) in a substrate’s surface, hence providing a mechanical key preventing separation. This effect may be improved by substrate pre-treatment (e.g. mechanical abrasion, chemical etching), which increases the surface roughness of the substrate enabling the adhesive to come into intimate contact with a greater surface area. It should be noted that, because of high viscosity or surface energy, an adhesive may not be able to completely penetrate the interstices in a rough surface. This will result in voids or other discontinuities at interfaces which may weaken the joint.

There is much evidence to suggest that for certain systems, increasing surface roughness will improve the bond strength, e.g. Packham et. al.\textsuperscript{23}, showed the advantage of increased roughness in the adhesion of polyethylene to metal. However, Tabor\textsuperscript{24,25} demonstrated that good adhesion can be attained between two smooth mica surfaces.

2.2.3 Electrical double layer

Deryaguin et. al.\textsuperscript{26}, have proposed that adhesion may be due to the transfer of electrons from one material to another at an interface, producing an electrostatic attraction. Experiments using a peel test showed that some of the joints were charged, and he claimed that the accompanying high peel strengths could not be explained by van der Waals of chemical bonds alone. Doubt has been thrown on these claims by some authors\textsuperscript{12} who claim indicate that deformation of substrates in peel tests need to be considered. A review of the electrical double layer theory by Wake\textsuperscript{13}, concluded that when films of adhesive substances, adhere to substrates, the electrical phenomena observed when they are peeled or separated, does not contribute appreciably to the force required to complete the separation.
2.2.4 Diffusion

Voyutskii\textsuperscript{27} suggested that the adhesion of polymers to each other, or themselves, is due to mutual migration, or interdiffusion, across the interface. For this to occur the molecules must have sufficient mobility to migrate, and must be mutually soluble (i.e. the solubility parameters must be similar). These conditions are usually found in the auto-adhesion of elastomers; e.g. solvent or thermal welding of plastics. Voyutskii supports these views with evidence based upon contact time, temperature and pressure. Vasenin\textsuperscript{28} has developed a mathematical model for the diffusion theory of adhesion based upon Fick's laws, from which he predicted that with a diffusion coefficient of \(10^{-18} \text{ m}^2/\text{s}\), it takes approximately 100 hours for segments of polybutylene sheet to penetrate each other to the depth of 10\(\mu\text{m}\). In cases where the same materials are studied it has been shown to occur, but where the solubility parameters differ no interdiffusion has been detected.

It should be noted that Voyutskii does not claim that interdiffusion occurs in polymer to metal bonds, although it has been postulated that there is a need for the adhesive to penetrate into the oxide layers.

2.2.5 Weak boundary layers

The theory of weak boundary layers (WBL) was first proposed by Bikerman\textsuperscript{29} in 1967. He proposed that if a region of low cohesive strength existed between and adhesive and an adherend, then low bond strengths would result. This region he called a "weak boundary layer" and stated that it could arise from either the adhesive, adherend or from the surrounding environment.

Examples of environmentally induced WBL can be dust, silicones, water etc., while internal sources include mobile additives from the system e.g. stabilisers, anti static agent etc. or, perhaps low molecular weight fractions of the polymer, which have migrated towards the substrate surface. A review of work published on polyolefins and fluoropolymers has been given by Brewis\textsuperscript{30}. 

\[\text{13}\]
2.3 Interfacial interactions

Paint resins contain many different functional groups e.g., carbonyl, amine, alcohol etc. which act as possible sites for interaction between a substrate (in this work, mild steel) and the resin. Much work has been published which examines interactions of specific functional groups with metal and polymer surfaces, the groups may be organic (alcohol etc.) or inorganic (silanes, phosphates etc.), and the interactions have been studied using a variety of techniques. The review in this section discusses work associated with paints or adhesives, interacting with various forms of steel surfaces, aluminium surfaces and, finally, other substrates.

Watts et al.\textsuperscript{31-34} have published many papers relating to adhesion of coatings to steel, generally using XPS to examine the interfaces and surfaces. An XPS study of aromatic moisture cured urethanes (ArMCU)\textsuperscript{31}, interacting with a steel surface, showed that the isocyanate component of the resin probably reacted with iron hydroxyls on the steel surface to form an acid type species; they also proposed tentative arguments for the oxidation of iron, i.e. from iron (II) to iron (III). It was shown that, when failure occurred, it was contained within the interphase region between the ArMCU and the steel. They found it impossible to monitor the cure of the system by XPS. In another study on cathodic disbondment of an epoxy powder coating\textsuperscript{32}, a three step process for disbondment was proposed. An initial step where at a point of failure or weakness, reduction of the metal oxide occurs followed by a second step where the reduction spreads, causing failure at the metal/metal oxide interface. Finally there is a third step, where the failure shifts to the oxide/polymer interface, allowing ingress of hydroxyl ions and cathodic delamination to occur.

By using substrates with different degrees of surface roughness, Watts proposed that in the latter stages of failure, the rate is dependent upon the surface profile, although in the initial step it is not. A further paper\textsuperscript{33} on the subject considered the same data, and reviewed mechanisms of cathodic delamination from other sources. The three commonly cited mechanisms for cathodic delamination were discussed, namely i) coating degradation, ii) true adhesive failure and iii) dissolution of the substrate oxide.
It was concluded that, although there are proponents and detractors for each case, there is evidence for all three mechanisms occurring and as such there is no universal mechanism for cathodic delamination. However, the more durable the coating (i.e. resistance to hydrolysis) the more likely that interfacial separation will occur, rather than cohesive failure as a result of coating degradation. Further work by Watts\textsuperscript{34} on the cathodic disbondment of three different classes of resin; polybutadiene, epoxy co-polymers and fusion bonded epoxy resin, has again indicated that all three mechanisms occur, but that the physical parameters of the resin and the electrochemical conditions determine which one of the three dominates. Experiments on polybutadiene indicated that the observed blistering phenomenon was interfacial failure and that oxide reduction was irrelevant to the failure process, occurring after the polymer had separated from the substrate. The epoxy co-polymer showed failure occurring adjacent to the bisphenol-A chain, which remained on the substrate after failure. However, Watts commented that to attribute failure to a specific mechanism would be misleading, and that only after surface analysis can the correct failure mechanism be determined.

Thery et. al.\textsuperscript{35} have published a study of the interactions between succinic anhydride and 304 stainless steel, reporting the formation of carboxylate species. From this they have predicted a mechanism in which the anhydride reacts through an acid stage, followed by a reaction of the acid groups with the metallic oxide to form a carboxylate anion, see Figure 2.6. They observed that the intensity of the infrared antisymmetric carboxylate transition peak increased with time, which was assigned to a change in the orientation of the carboxylate group on the steel surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.6.png}
\caption{Reaction of acid groups with a stainless steel oxide/hydroxide surface}
\end{figure}

\[ R \text{--} H \quad O \quad M^{n+} \quad H \]
\[ R \text{--} H \quad O \quad M^{n+} \quad H \]
\[ R \quad O \quad \text{--} \quad + \quad M^{n+} \quad M^{n+} \quad H \text{--} H \]
Interactions between a zinc coated steel substrate and an epoxy/dicyandiamine (dicy) resin were investigated by Gaillard et. al.\textsuperscript{36}. After coating a thin layer of dicy onto a piece of zinc coated steel they observed differences in the nitrile bands (21-2300 cm\textsuperscript{-1}) which were assigned to a reaction between the zinc and the dicy. There were no differences in the amine bands, i.e. the reaction was only via the nitrile group of the dicy molecule and not the amine group. Gaillard comments that the change has not been observed with either aluminium or iron substrates. In a lap-shear test consisting of zinc coated steel/epoxy-dicy polymer, he observed that the failure region was greatly enriched by nitrile groups. He proposed that this is potentially a weak boundary layer which may lead to cohesive failure within the adhesive.

The adhesion of polyethylene to aluminium is generally low\textsuperscript{37}. Methods for increasing the adhesion are either to modify the surface of the aluminium or the polyethylene. Hjertberg\textsuperscript{37-40} has published several papers examining both possibilities. In a study of copolymers of ethylene-butyl acrylate he found that hydrolysis of the aluminium surface resulted in an increase in adhesive strength. The reasons he gave for this were twofold: a hydrolysed surface contains more hydroxyl groups which are available to form interactions with the polymer, and that the hydrated surface is rougher and hence the potential for more mechanical effects is increased. Hjertberg has also published papers reporting the adhesion of polyethylene co-polymers to the aluminium surface. Copolymers of ethylene-butyl acrylate (EBA) and ethylene-vinyl acetate (EVA) with differing co-monomer contents were derivatised to form different functional groups, e.g. acid groups, alcohol groups. The polymer aluminium interaction was studied using FTIR and the T-peel test. Typical mechanical results for the different functional groups are shown in Figure 2.7:
From this type of data, based upon the T-peel test, Hjertberg has proposed that adhesive strength increases with the following functional groups:

\[-H << \text{-CO-O-CH}_3 < \text{-CO-O-C}_9\text{H}_9 < \text{-COONa} = \text{-OH} < \text{-COOH}\]

He also proposed several mechanisms in which the functional groups may interact. In a similar study copolymers of ethylene-vinyltrimethoxysilane (EVS), ethylene-acrylic acid (EAA) and EBA were used. The infrared spectra of thin cast films on aluminium surfaces showed significant shifts in the carbonyl stretching frequencies, and as the coatings became thinner and the spectra came from closer to the aluminium surface/copolymer interphase, a new peak became evident. This data, in conjunction with contact angle measurements, led Hjertberg to conclude that the polar groups interact with the aluminium substrate via Lewis acid/base interactions, and that the strength of the interaction is dependent upon the relative acidity/basicity and concentration of the functional group. EVS showed a marked increase in peel strength compared to the other polymers. This was probably due to Si-O-Al linkages rather than Lewis acid/base interactions. Another study of hydrolysed aluminium surfaces showed that the increased hydroxyl content on the surface resulted in strong interactions via hydrogen bonds, with the carbonyl groups present in EVA and EBA. Although reference was made to the earlier paper on Lewis acid/base interactions,
no experimental data was given to indicate that the interaction observed was an acid/base interaction.

A slightly different approach to interfacial investigations was demonstrated by Villoutreix et.al.\textsuperscript{41} who studied the effect of substrate composition upon the cure of an epoxy/dicyandiamine resin. The substrates contained different amounts of aluminium and zinc, and two contained either silicon or lead. Differential scanning calorimetry (DSC) at different heating rates was used to characterise the catalytic effect of the surface composition upon the crosslinking reaction. They observed that at higher heating rates (70°C/min) the curing exotherm was lower across all of the substrates. It was also noted that the different substrates had different activation energies, which were all less than the activation energy of the adhesive alone. This implied that there was a catalytic effect promoted by the substrate. Mechanical data, and observation of the failure interfaces, indicated that aluminium promoted adhesion, whereas the zinc and lead containing substrates showed pin hole porosity and lower mechanical strengths.

A review of adhesion mechanisms at epoxy/aluminium interfaces has been given by Barthés-Labrousse\textsuperscript{42}. He discussed work which considered the failure of epoxy/amine resins on real surfaces, a model compound (monoethanolamine) on a real surface, and the model compound on a model surface; Al (100). He commented that there was general agreement between the interface chemistry of the first two examples, i.e. that the model compound does mimic the resin. In the case of the idealised surface, Auger and high resolution electron energy loss spectroscopy (HREELS) experiments indicated that with an oxide free surface bonding occurred via nitrogen lone-pairs coordinated to soft acidic aluminium atoms, and that bonding to an oxidised surface was via oxygen lone-pairs to hard aluminium ions. When there was a hydroxylated surface, bonding occurred via alcohol groups, but this time forming an alkoxy species. For the hydroxylated surfaces, he proposed that the oxygen atoms are coordinated differently to that in the oxidised surface. X-ray photoelectron spectroscopy (XPS) data indicated that there was an interaction between the nitrogen atoms and the aluminium. However, the nature of the interaction was uncertain i.e. whether it was coordination of the nitrogen to the aluminium or protonation of the amine group.
Taylor et al.\textsuperscript{43} have studied the adhesion of an aromatic methacrylate based photocured resin to an alumina substrate for applications in the electronics industry. They used XPS and time of flight - secondary ion mass spectrometry (ToF-SIMS) to view the failure surfaces after immersion in water at 50°C for up to two weeks, and studied the effect of aggregation of small molecules at the polymer/substrate interface. They concluded that ToF-SIMS and XPS can characterise a failed interphase, and that, using ToF-SIMS, the presence of small molecules on the inorganic surface can be detected. They postulated that the aggregates not only migrate to form an interphase, but may also form an interphase along which failure can occur, i.e. functioning as a weak boundary layer. Hence, an additive may change the locus of failure from the polymer/metal interface to a region within the bulk polymer. Frenier and Growcock\textsuperscript{44} have given a review of the durability of an adhesive/metal bond as a function of oxide stability. XPS was used to study oxide stability and bond durability on aluminium and it was found that failure occurred by conversion of the aluminium oxide to hydroxide, which readily delaminated from the metal surface. It was also found that treating the oxide with a hydration inhibitor would prevent the conversion of the aluminium oxide to hydroxide\textsuperscript{45}.

A review of the fractal nature of polymer/metal interfaces and fundamentals of the molecular bonding has been given by Lee\textsuperscript{46}. He has described theoretical studies relating to molecular modelling and commented that these studies are in the early stages of development and, at present, cannot be widely used to study polymer/metal interphases.

A study of the orientation of poly(4-vinyl pyridine) on nitric acid etched silver was undertaken\textsuperscript{47}. The study indicated that the polymer side groups were adsorbed onto the silver in a flat orientation at ambient temperature. Upon heating at 130°C for 6 hours the pyridine ring “stands up” and orientates to form an N-bonded orientation, via donation of the lone pair.
2.4 Thermodynamic work of adhesion

The thermodynamic work of adhesion ($W_A$) is the reversible work done per unit area in the separation of a coating and substrate, and is given by Equation 2.1.

$$W_A = \gamma_S + \gamma_C - \gamma_{SC} \quad \textit{Equation 2.1}$$

Where:
- $\gamma_S$ is the specific surface excess free energy of the substrate
- $\gamma_C$ is the specific surface excess free energy of the coating
- $\gamma_{SC}$ is the specific excess interfacial free energy of the substrate and coating

If a coated substrate is immersed in a liquid it is possible to predict whether there will be delamination of the coating from a knowledge of the specific excess free energies of the substrate, the coating and the liquid. This theory assumes that only secondary forces act in adhesion.

The energetics of delamination in a liquid medium may be considered to have two components, Figure 2.8:

a) work of adhesion in a vacuum, given by equation 2.1;

b) free energy change on immersion$^{48}$, which is given by the following equation

$$W_{im} = \gamma_{SL} - \gamma_S \quad \textit{Equation 2.2}$$

Where:
- $\gamma_{SL}$ is the specific excess free energy of the substrate and the liquid
Figure 2.8: To indicate the processes occurring during separation.

Where \( V, L, S \) and \( C \) refer to the vacuum, immersion liquid, the substrate and the coating respectively, and \( \gamma_{CL} \) is the specific excess free energy between the coating and the liquid.

Combining these equations gives an overall free energy change (\( \Delta G \)):

\[
\Delta G = \gamma_S + \gamma_C - \gamma_{SC} + \gamma_{SL} - \gamma_S + \gamma_{CL} - \gamma_C
\]

Equation 2.3

Which reduces to

\[
\Delta G = \gamma_{SL} + \gamma_{CL} - \gamma_{SC}
\]

Equation 2.4

This gives a relationship which may be easily determined experimentally through the use of contact angles$^{49}$. If we assume only Van der Waals forces act in adhesion, then if \( \Delta G \) is negative, spontaneous separation of the two phases will occur; when the free energy is positive no separation occurs.
2.4.1 Contact angle measurement

Following Equation 2.1, the thermodynamic work of adhesion for a solid liquid system may be written as shown in Equation 2.5. Where \( \gamma_L \) is the specific surface excess free energy of the liquid.

\[
W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \quad \text{Equation 2.5}
\]

\[
\gamma_S = \gamma_{SL} + \gamma_L \cos \theta + \pi_e \quad \text{Equation 2.6}
\]

Young's equation (Equation 2.6), relates contact angle to the specific surface excess free energy, where \( \pi_e \) is the spreading pressure and is the decrease in the surface free energy due to vapour adsorption, and \( \theta \) is the contact angle between the phases (Figure 2.9).

![Figure 2.9: Showing the contact angle formed between a substrate and a liquid drop](image)

Combining Equations 2.5 and 2.6 gives the Young-Dupré relationship, Equation 2.7. For low surface energy materials like polymers, \( \pi_e \) is small and is often neglected\(^5\).

\[
W_{SL} = \gamma_L (1 + \cos \theta) + \pi_e \quad \text{Equation 2.7}
\]

Fowkes\(^51,52,53\) proposed that \( \gamma \) was the sum of the individual interfacial energies (excluding primary interactions) Equation 2.8.

\[
\gamma = \gamma^d + \gamma^p + \gamma^h + ............ \quad \text{Equation 2.8}
\]

where the superscripts \( d, p \) and \( h \) refer to the dispersive, polar and hydrogen bonding contributions to the specific surface excess free energies respectively. He also
proposed an equation for the interaction of a liquid upon a solid, providing the interaction was solely due to dispersion forces, and assuming that interfacial interactions could be approximated by taking a geometric mean, Equation 2.9,

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_{S}^{d}\gamma_{L}^{d})^{\frac{1}{2}} \quad \text{Equation 2.9} \]

Owens and Wendt\textsuperscript{49,54} have included the polar contributions and expanded Equation 2.8 to give:

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_{S}^{d}\gamma_{L}^{d})^{\frac{1}{2}} - 2(\gamma_{S}^{p}\gamma_{L}^{p})^{\frac{1}{2}} \quad \text{Equation 2.10} \]

Hence from Equations 2.5, 2.7 and 2.10 (ignoring the \( \pi_e \) term) the following equation for the work of adhesion between two phases \( S \) and \( L \), \( (W_{SL}) \), in terms of the individual components and the contact angle can be written as:

\[ W_{SL} = \gamma_L(1 + \cos \theta) = 2(\gamma_{S}^{d}\gamma_{L}^{d})^{\frac{1}{2}} + 2(\gamma_{S}^{p}\gamma_{L}^{p})^{\frac{1}{2}} \quad \text{Equation 2.11} \]

From literature, values for \( \gamma_S \), \( \gamma_L^{d} \) and \( \gamma_L^{p} \) can be obtained, and values of contact angle \( (\theta) \) are measured. Hence, values for \( \gamma_S \) can be calculated, allowing a value for \( \gamma_{SL} \) to be determined.

It has been suggested by Wu\textsuperscript{131,132,133} that the geometric mean is not the most appropriate equation, and that the individual surface excess free energies can be expressed better using a harmonic mean equation (Equation 2.12).

\[ \gamma_{SL} = \gamma_S + \gamma_L - \frac{4 \gamma_{S}^{d}\gamma_{L}^{d}}{\gamma_{S}^{d} + \gamma_{L}^{d}} + \frac{4 \gamma_{S}^{p}\gamma_{L}^{p}}{\gamma_{S}^{p} + \gamma_{L}^{p}} \quad \text{Equation 2.12} \]

However this approach has been little used by others who generally use the geometric mean based equation. It has been found by Sheng\textsuperscript{134}, that this method gave higher \( \gamma_S^{d} \) values and significantly higher \( \gamma_S^{p} \) for all surfaces tested.
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2.5 Infrared spectroscopy

Infrared (IR) spectroscopy is one of the oldest spectroscopic techniques. It has become one of the most widely used techniques for routine analysis of organic compounds and as an important research tool. There are many different forms of IR spectroscopy\(^5\) e.g. transmission, photo-acoustic, diffuse reflection infrared (DRIFT), reflection absorption spectroscopy, etc. This research programme has made extensive use of reflection absorption infrared, to investigate interactions occurring between polymers and metal surfaces, and transmission infrared, to determine the reaction mechanisms of the resin.

2.5.1 Instrumentation

Infrared instrumentation can be divided into two methods; dispersive and non-dispersive. Dispersive instruments use a prism or grating to separate the frequencies, whereas non-dispersive instruments tend to use an interferometer and a Fourier transform to produce the spectra. Fourier transform infrared\(^6\) (FTIR) is now the most commonly used form of infrared, and has several distinct advantages over a dispersive instrument, which are listed below:

- the helium-neon laser used as a reference results in a frequency accuracy of 0.01 cm\(^{-1}\) over the 4800 to 400 cm\(^{-1}\) range;
- since all frequencies are detected simultaneously, the spectrum can be collected very quickly whilst achieving the same signal to noise ratio as a dispersive instrument, (i.e. Felgett’s advantage);
- the interferometer has a large circular aperture rather than a small slit, hence there is an increased energy throughput. i.e. the so-called Jaquinot’s advantage;
- modern machines have a signal to noise of about \(10^5 : 1\), which allows detection of monolayers.
2.5.2 Reflection absorption spectroscopy (RAS)

This technique was developed by Greenler\textsuperscript{57,58} and is known by various names, including grazing angle incidence infrared; specular reflectance infrared or infrared absorption spectroscopy. It is used in the work described in this thesis to observe a layer of polymer coated onto a metal (mild steel) surface. A typical reflectance mirror arrangement is shown in Figure 2.10.

![Aluminium mirror](image)

**Figure 2.10**: A typical reflectance mirror arrangement

If an IR beam strikes the surface of a substrate at a non-normal angle of incidence the phase of the reflected ray will depend upon both the polarisation of the incident ray and the angle of incidence.
Figure 2.11: Phase shifts for light reflected from a metal surface.

Figure 2.11 indicates that for radiation polarised perpendicular to the surface, the phase change of the reflected radiation is nearly always 180° out of phase. This is also shown in Figure 2.12a, where the electronic vectors will very nearly cancel, and hence little absorbance will be observed from a layer on the surface. For radiation polarised parallel to the plane of incidence, Figure 2.11 indicates that the phase change varies rapidly at high angles of incidence (75 to 90°). Figure 2.12b shows electronic vectors where the phase shift upon reflection is 90°. Vector addition of the parallel polarised light gives rise to an elliptical standing wave with a sizeable component parallel to the metal surface. Hence in this case absorbance will occur with a layer on the metal surface. Note, that at grazing angle the electronic vectors will be 180° out of phase with each other, i.e. they will cancel and no absorption can occur. Hence the maximum angle possible for collecting information about the surface is in the region of 86 to 88°.

(a) perpendicular to plane of incidence,  
180° out of phase  
(b) parallel to plane of incidence,  
90° out of phase

Figure 2.12: Polarised infrared beams.
A reflection spectrum obtained from a coated steel sample will contain a large component associated with changes in the refractive index of the coating, which needs to be removed from the spectrum so that quantitative comparison of different spectra can be carried out. It also contains components from four different types of reflection, namely surface scattering, back surface specular, top surface specular and diffuse, shown in Figure 2.13.

Figure 2.13: Reflected light from a coating on a metal substrate. a) surface scattering, b) top surface scattering, c) back surface specular, d) diffuse

It is probable that only specular and back surface reflection are present in the coated steel samples used in this research. Top surface specular reflection comes from the top surface of the coating and gives rise to an asymmetry in the peaks of the spectra. This is a function of the refractive index and the extinction coefficient of the coating, which vary in the region of an absorption band as shown in Figure 2.14. The sum of these two bands gives rise to the asymmetry, which can be corrected by the use of the Krammer-Kroenig transformation. This correction eliminates the refractive index component from the spectrum, giving the true spectrum. Back scattered spectra indicate that there is essentially a double pass through the coating, generally giving a transmission like spectra. If the substrate was optically flat then interference fringes would exist giving an indication of the film thickness.
2.5.3 Transmission spectroscopy

This is probably the most common and simple to use of all IR techniques. As a solid, a sample may be dissolved in a suitable solvent and then coated onto a clean infra-red plate, typically sodium chloride. It may also be mixed with pure potassium bromide powder and pressed to form a disc. Both sodium chloride and potassium bromide are IR transparent, hence only a spectrum from the sample is obtained.

2.5.4 Applications of reflection absorption and transmission infrared spectroscopy

Reflection absorption spectroscopy has been used extensively in many diverse applications. Pilon et. al.\textsuperscript{59} have determined the cleanliness of cold rolled steel after
an annealing stage by identifying hydrocarbon stretching vibrations (2853 to 2954 cm\(^{-1}\)) and silicone/silicate groups (1080 and 799 cm\(^{-1}\)), from silicone oil contamination on the metal surface. Mertens\(^6\) has studied the nature of oxide films on different types of stainless steel. This has been achieved by producing spectra for pure samples of the constituent components (i.e. individual metal oxides) and identifying the relevant oxide peaks which were found on the steel surface. An investigation by Guillamet\(^6\) examined oxide films of \(\alpha\)-Cr\(_2\)O\(_3\) and \(\alpha\)-Fe\(_2\)O\(_3\) on iron. The peaks were initially calculated based upon the knowledge of the crystal form of the oxides and then compared to those obtained from the spectra. The author observed a peak at 660 cm\(^{-1}\), which moved to higher wavenumbers as the thickness of the oxide increased. Hence it was proposed that the position of this peak may be used as an indication of oxide thickness. There has been a large amount of work published which makes use of the reflection technique to understand the orientation of molecules on the surface of a metal. However, this work has largely been carried out on small molecules such as carbon dioxide, although cadmium arachidate (CdA) has also been investigated by Swalen\(^6\). Using 1 to 10 monolayers of CdA coated onto silver it was shown that as the film became thicker there was no difference in the position of any of the peaks. This was in contrast to the work described by Guillamet\(^6\), where film thicknesses were in microns instead of nanometers. Swalen also observed differences between the bulk transmission spectra and the spectra for one monolayer, which were probably due to surface orientation factors. Another investigation by the same author\(^6\) used polarised light on a Langmuir-Blodgett film (i.e. one monolayer) to identify the crystal packing and orientation of the molecules within the layer.

Molt\(^6\) has proposed that different surfaces give different absorption values at different angles and that for a specific surface there is an optimum angle. He supported this suggestion by examining phosphated surfaces, which were found to give the best absorption at an angle of 55 to 60°.

Fondeur and Koenig\(^6\) have published a series of infrared reflection studies on aluminium and treated aluminium. They have examined the effects on the oxide of chromic and sulphuric acid anodising, and a chemical treatment. With chromic acid anodising (CAA) they observed sites at which water had been adsorbed and an oxide
similar in structure to Gibbsite formed. They also observed the reaction of carbon dioxide with the surface to form carbonates. Sulphuric acid anodising (SAA) gave rise to peaks due to water and hydroxyl species, but peaks due to sulphates and oxyhydroxides also occurred. The chemically treated surface showed peaks attributed to hydroxyl and water, and to metal cyano linkages. Hence they proposed that chemical treatment produced a water and hydroxyl spectra very similar to the anodising spectra. On heating the samples to remove the water, it was observed that CAA had more water and hydroxyl sites than SAA. A study of the interactions between a epoxy/dicyandiamine and aluminium or anodised aluminium was also carried out. It was found that when aluminium was anodised there was a reduction in curing agent near the metal surface. However, when the aluminium was untreated it was found that the concentration of the curing agent near the surface was greatly increased. By observation of the carbonyl stretching frequency and the epoxy ring mode in the cured systems, they observed a high degree of cure in untreated aluminium near the interface and a considerably lower one for treated aluminium. Another study looked at the effects of moisture exposure on an epoxy coated aluminium substrate. A comparison of CAA and untreated aluminium using infrared reflection microscopy to produce a two dimensional map of a surface was carried out. On the CAA surface they observed the formation of “new” boehmite and an associated loss of Al-O-Al. The untreated aluminium showed oxide and oxyhydroxide being formed simultaneously. The moisture damage to the epoxy was confined to formation of carboxylate at the epoxy/air interface. Possart et. al. have used reflection infrared to investigate the interactions between different thicknesses of dicyanato bisphenol A and its cyclotrimer, with silicon and aluminium substrates. They suggested, by reference to calculated spectra, that the cyanate groups were not involved with intermolecular interactions and were not preferentially orientated. However, the cyclotrimer groups were orientated and involved with interactions.

Transmission infrared spectroscopy is a routine technique, but since the technique requires the infrared radiation to pass through the sample, it is not often used in adhesion studies. However, in the specific application of variable temperature
transmission infrared there is some literature applicable to the work described in this thesis.

It has been shown that data from variable temperature infrared spectroscopy can be used to describe basic kinetics of the thermal deblocking of isocyanates. Provd er et. al. have studied the effects of catalysts upon trimerised isophorone diisocyanate blocked with methyl ethylketoximine. They have shown that without catalyst, the deblocking reaction will start at around 110°C, and finish at around 200°C. They indicate that the effect of 1,4-diaza-[2,2,2]bicyclooctane (DABCO also known as triethylene diamine) catalyst was to reduce the temperature at which deblocking begins, and to catalyse side reactions reducing the amount of isocyanate available for crosslinking. The catalysts tetrabutyl ammonium chloride and dibutyl tin dilaurate (DBTDL) were also studied but showed no effects on the rate of deblocking. At temperatures greater than 170°C, DBTDL showed a reduced amount of free isocyanate compared to the uncatalysed system, which the authors explained by formation of allophanate structures in the resin, i.e. DBTDL affects the NCO/OH reaction as opposed to the deblocking reaction. The addition of a stoichiometric amount of a hydroxyl group to the system reduced the onset temperature of deblocking by 20°C, although they do not state whether the hydroxyl group is primary, secondary or tertiary. They claimed that the rate of cure is a function of both the deblocking and the crosslinking reactions.

Kothandaraman and Nasar have used variable temperature infrared to support data obtained from thermal analysis experiments for the deblocking of toluene diisocyanate blocked with phenol derivatives. These references are discussed further in Section 2.6.3.
2.6 Thermal Analysis

In this research thermal analysis was used to study of the effects of catalyst on the deblocking of blocked isocyanates found in the paint resin system.

Thermal analysis methods give information about how a sample varies as a function of temperature; most commonly changes in enthalpy and weight. Differences in enthalpy are monitored by either differential scanning calorimetry (DSC) or differential thermal analysis (DTA); the techniques give essentially the same results hence only DSC is considered here.

2.6.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) gives a direct calorimetric measurement e.g. temperature and enthalpy of reaction. The sample and reference are located in two independent cells, each with a temperature sensor and heater, and the difference in heat flow to a sample and to the reference is monitored against time or temperature. A typical DSC cell is shown schematically in Figure 2.15.
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A thermal transition can be either endothermic or exothermic, and may relate to one of the following phenomena, see Table 2.2:

<table>
<thead>
<tr>
<th>Possible phenomena</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase changes</td>
<td>Melting points, glass transition temperatures in polymers, changes in crystal structure. Deviation from a known melting point can give an indication of the degree purity of the sample.</td>
</tr>
<tr>
<td>Thermal decomposition</td>
<td>Loss of water in aluminium trihydrate, depolymerisation, deblocking of an isocyanate.</td>
</tr>
<tr>
<td>Chemical reactions</td>
<td>Reaction kinetics, $aA + bB = cC + \Delta H$</td>
</tr>
</tbody>
</table>

Table 2.2: Possible phenomena that may be studied by DSC

Typical endothermic processes are associated with phase changes, loss of water, reduction and some decomposition reactions, whereas typical exothermic processes are associated with crystallisation, oxidation and some decomposition reactions.

2.6.2 Thermal analysis and the deblocking of blocked isocyanates

Although there is extensive literature associated with DSC measurements, there is little published which deals with deblocking of 4,4' diphenyl methylene diisocyanate, which was used in this research; the only reference found in this area was by Anagnostou and Jaul\textsuperscript{74}. They compared data from variable temperature infrared measurements, which are known to indicate deblocking [see Section 2.5.4], to data recorded from DSC measurements. They found that the DSC endotherms correlated to the deblocking temperatures as indicated by infrared, and concluded that DSC is an appropriate technique for the analysis of the deblocking reaction of alcohol blocked isocyanates. They also evaluated the effect of adding a primary alcohol (i.e.
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Table 2.3: Categories of paint adhesion test methods

<table>
<thead>
<tr>
<th></th>
<th>Mechanical</th>
<th>Electrochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Qualitative</strong></td>
<td>scribing</td>
<td>AC methods</td>
</tr>
<tr>
<td></td>
<td>mechanical deformation</td>
<td>DC methods</td>
</tr>
<tr>
<td></td>
<td>other e.g. solvent rub, tape adhesion,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pencil hardness</td>
<td></td>
</tr>
<tr>
<td><strong>Quantitative</strong></td>
<td>tensile, shear, peel measurements</td>
<td></td>
</tr>
</tbody>
</table>

There are also many other chemical based tests e.g. salt spray, humidity testing etc. which are used to determine the resistance of coated samples to various environments. These may be used as tests in their own right or to artificially accelerate ageing of samples prior to testing by some other technique.

2.7.1 Types of mechanical tests

2.7.1.1 Qualitative methods

a) In the scribing tests, including mechanical scribing, a coating on the surface of a specimen is either hatched or cross cut, with a standard blade. The amount of delamination of the coating is determined both before and after application of a piece of adhesive tape (e.g. a particular grade of 3M’s Scotch Tape, usually defined in the test method) applied over the cut, and then pulled off. The amount of delamination of the coating from the substrate is compared against reference photographs to give a value for the adhesion. Questions arise as to the reproducibility of this method e.g. blade sharpness and variability in operator, etc..

b) In deformation methods, a specimen is mechanically deformed. This may be due to bending around a standard shaped mandrel, or by pressing a ball (of specific radius and hardness) into the uncoated side of the specimen. In either case the degree of delamination may again be estimated by the use of an adhesive tape “pull” and/or visual inspection.
Carbowax 400), and the effect of different pigments upon the deblocking temperature of the alcoholblocked isocyanate mixture. The effect of the primary alcohol was to decrease the temperature at which the onset of deblocking occurred, although no definite explanation is given as to why this should occur. Addition of a pigment to the blocked isocyanate raised, lowered or did not effect the onset temperature. Each pigment produced the same change in the onset temperature of a particular blocked isocyanate, however, each blocked isocyanate responded differently to the pigment. Kothandaram and Nasar\textsuperscript{71,72} have published several papers concerning the deblocking of blocked toluene diisocyanate (TDI). In these papers they report the use of several techniques including variable temperature infrared and DSC. A series of phenol derivatives were reacted with TDI to produce the blocked isocyanate, and the effect of the substituents on the phenol group were investigated in terms of the thermal stability of the compound. They found that the deblocking temperature was reduced by electron withdrawing substituents and increased by electron donating substituents on the phenol group. Mühlebach\textsuperscript{75} has used DSC in conjunction with gas chromatography-mass spectrometry to determine the onset temperature and dissociation products of various pyrazole (i.e. amine) blocked isocyanates in alcohol and amine crosslinker formulations. The structure of pyrazole is shown in Figure 2.16.

![Figure 2.16: The structure of pyrazole.](image)

Different derivatives of pyrazole; mono-, di- and tri-substituted variations were reacted with MDI, TDI, hexamethylene diisocyanate, isophorone diisocyanate and 1,3,5 tris (6-isocyanatohexyl) biuret. He commented that when the blocked isocyanate was mixed with the crosslinker, the deblocking temperature decreased, and suggested a mechanism for this process. He also stated that upon curing with either an alcohol or primary amine, that the blocking group may act as an adhesion promoter for various substrates.
Wicks\textsuperscript{76.77} has written two reviews concerning blocked isocyanates, blocked with different compounds. However, for alcohol blocked diisocyanates these generally only relate to TDI and aliphatic isocyanates. He commented, similarly to Mühlebach, that when a blocked isocyanate was mixed with either hydroxyls or primary amines, that the deblocking onset temperature was decreased.

Other papers by Kothandaram et. al.\textsuperscript{78.79} have used thermogravimetric analysis and a carbon dioxide evolution technique to determine the onset point of the deblocking reaction. They stated that dissolving the blocked isocyanates in different glycols reduced the onset temperature, as determined by the carbon dioxide evolution technique.

### 2.7 Mechanical testing of the paint resin

Paint coatings are subjected to mechanical stresses, e.g. when the substrate expands or contracts (especially if there is a large difference in the coefficient of thermal expansion between an organic coating and a metal substrate), when the paint is forced away from the substrate by the formation of rust at the interface or by mechanical impact. In attempts to both qualify and quantify adhesive strength, there have been many mechanical and electrochemical tests developed. However, many of the tests do not usually reflect the failure modes to be found in real life, e.g. the standard quantitative lap shear test involves complex forces that the paint would not normally be exposed to, and therefore such data should only be used to compare adhesion of different paint systems.

Tests to determine the properties of paint films fall into two main categories, which may be arbitrarily sub-divided again, see Table 2.3:
c) The final qualitative group consists of the tests which do not fall into the above categories, for instance tape pull off test or solvent wipe methods\textsuperscript{84}, without the initial cross hatching.

2.7.1.2 Quantitative methods
Quantitative mechanical tests can determine a physical value at which failure occurs. Generally these may be a force or an extension measurement at failure of the joint of assembly, although failure does not need to occur. The tests are generally based on four different types of loading; tensile, shear, peel or flexure or a combination of these modes of loading. Ideally a test which reflects the likely failure in service should be employed, however, this is not always possible. Only tensile type tests are considered below. Many tests have been developed to determine the strength of an adhesive/substrate bond and therefore, to determine the strength of a coating to a substrate the test may have to be modified.

a) Tensile methods commonly used are either butt pull-off or lap shear tests, see Figure 2.17.

![Figure 2.17: To show (a) butt joint and (b) lap shear joint construction](image)

If the tests were to be applied to an adhesive, say in the case of the lap shear joint, (Figure 2.17 (b)) then a known thickness of adhesive would be applied to the substrate and cured under pressure before testing. In the case of a paint resin, this
method of construction may not be possible, because of solvent entrapment or the
viscosity of the system etc. and the paint resin would be applied to the substrate,
cured and another adhesive used to bond the assembly together. This in itself may
give rise to problems; that of poor adhesion of the adhesive to the paint coating or
the metal jig, and diffusion of the adhesive into the paint film affecting the paint
film/metal surface bond properties.

2.7.2 Electrochemical tests

In an electrochemical test a potential is place on the sample, which results in either
oxidation or reduction type reactions occurring at the metal surface. Hence the
adhesion performance of the coating can be monitored in extreme environments. The
test methods are divided into two categories, AC and DC test methods.

a) There have been numerous reports of work carried out into the effects of cathodic
delamination in different hostile environments. It has been stated that the
rate of cathodic delamination is a function of the oxygen reduction rate at the
polymer/metal interface. The test is extensively used to measure wet adhesion in
the automotive industry, where a coated steel panel is scratched through to the
substrate to provide a point of failure in the coating before immersion in an
aqueous conducting medium. A potential is applied between the panel and an inert
electrode for a specific period of time. The amount of delamination is monitored
by visual inspection.

As discussed previously, coatings on metals are commonly delaminated in the
presence of hydroxyl ions, which have diffused through the coating or have come
in contact with the metal at the point of failure in the coating. Cathodic
polarisation increases the rate of formation of the hydroxyl ions in close proximity
to the coated substrate, which may then attack the coating/metal interface at the
region of the failure.

AC testing also includes electrochemical impedance spectroscopy (EIS).
Chapter 3: Experimental

3.0 Experimental

This chapter consists of four sections. The first two sections contain a description of the materials and chemical reagents used in the research programme. It should be noted that a chemical is differentiated from a material, as a common laboratory reagent such as sodium hydroxide or triple distilled water. The first section also describes the synthesis of two blocked isocyanates used to determine the effect of a catalyst upon the deblocking reaction. The third section describes the analytical techniques, i.e. experimental equipment and conditions used. The final section contains details with respect to procedures which have been developed or used extensively in this research.

As indicated in the introduction many different techniques were used in this research. Infrared spectroscopy was used in reflection mode to study the interactions between the paint resin and a steel substrate, and also between the functional groups and the steel substrate. Using this technique, as indicated in the literature survey, it should be possible to determine many interactions that occur between a polymers functional groups and the metal surface, at or near the interphase region. In order to determine if
the current tin catalyst could be replace by something deemed less hazardous, differential scanning calorimetry (DSC) was used along with variable temperature infrared. DSC was chosen, since catalysts can operate by lowering activation energies etc. and it was thought most probable that differences in the reaction thermograms should be observed with different catalysts. It was though that changes in the structure of the sample could be monitored by variable temperature infrared, and that the onset of any changes would be the appearance or disappearance of certain functional groups. It was also thought that it may give further detail of what happens after deblocking reaction had occurred. Other techniques which are described here were used to try and give a complete picture of what was happening, for example in the case of the mechanical testing experiments, X-ray photoelectron spectroscopy and Auger electron spectroscopy, were used to determine the actual region of failure in the butt joint. It was not possible to determine the loci of failure without using these sort of high energy techniques, which give information concerning the species present in the surface layers.

3.1 Materials

3.1.1 Substrates

Two types of mild steel substrate were used in these studies:
a) Cold rolled mild steel (Gold seal 8074), supplied by Pyrene, as sheets approximately 150 x 100 mm and 1 mm thick. Samples were cut to an appropriate size using a guillotine and used for infrared analysis of the functional groups and adhesion testing.
b) Mild steel shim was supplied by Knight Strip Steel, in a roll 25 mm wide by 0.1 mm thick. This was used for the shim test (Section 3.3.7.2)
3.1.2 Coatings and adhesives

The coatings and adhesives used in the research are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Coating/adhesive</th>
<th>Comments</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrocoat</td>
<td>Epoxy/isocyanate system synthesised as per Section 2.1.1, solids content 74%</td>
<td>ICI Paints Ltd.</td>
</tr>
<tr>
<td>Araldite Rapid</td>
<td>An epoxy/amine system</td>
<td>Evode</td>
</tr>
<tr>
<td>Superglue 3</td>
<td>A cyanoacrylate adhesive</td>
<td>Loctite</td>
</tr>
</tbody>
</table>

Table 3.1: Coatings and adhesives used in the research

The electrocoat resin has been studied throughout this thesis, and Araldite Rapid and Superglue 3 were used in the assembly of the butt joints.

3.1.3 Catalysts used in the deblocking experiments

The catalysts used in the deblocking experiments are shown in Table 3.2. Dibutyl tin dilaurate (DBTDL) catalyst was briefly studied, but owing to stability problems, gave inconsistent results. Hence its use is not further reported in this thesis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Major Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibutyl tin oxide</td>
<td>ICI*</td>
<td>Tin</td>
</tr>
<tr>
<td>Bicat A</td>
<td>Twinstar Chemicals</td>
<td>Zirconium/Bismuth complex</td>
</tr>
<tr>
<td>Bicat Z</td>
<td>Twinstar Chemicals</td>
<td>Zirconium/Bismuth complex</td>
</tr>
</tbody>
</table>

Table 3.2: The catalysts used in the deblocking experiments

* Supplied by ICI Paints from bulk supplies held at the site in Slough.
3.1.4 Blocked isocyanates

Investigations into the effects of the different catalysts were carried out on the industrial resin system, the industrial crosslinker and upon two pure blocked isocyanates. The two pure blocked isocyanates were synthesised in the programme from materials listed in Table 3.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’ diphenyl methylene diisocyanate</td>
<td>Kemira</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)ethanol</td>
<td>Aldrich</td>
</tr>
<tr>
<td>10:1 ether : petrol mixture</td>
<td>Aldrich</td>
</tr>
<tr>
<td>methanol</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

Table 3.3 : Materials used in the preparation of the blocked isocyanates

The preparation of the blocked isocyanates are described below, and spectral data to support the proposed structures is given in Appendix 1.

3.1.4.1 Blocked isocyanate 1 (BI1)

Pure 4,4’ diphenyl methylene diisocyanate (MDI) (5g), was reacted in excess 2-(2-butoxyethoxy)ethanol (10ml) at 65°C for 11 hours. Figure 3.1 shows the proposed reaction scheme. The product was separated from the starting materials using flash chromatography (10:1, ether : petrol)
3.1.5 Functional group compounds

Experiments using reflection infrared were carried out to gain an understanding of how functional groups may interact with a mild steel surface. The following compounds were chosen as examples of specific groups which were present in the resin system, Table 3.4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbrev.</th>
<th>Functional group</th>
<th>Molecular weight</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(acrylic acid)</td>
<td>PAA</td>
<td>acid</td>
<td>25,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>PVOH</td>
<td>alcohol</td>
<td>124-186,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>DETA</td>
<td>primary amine</td>
<td>103</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(ethylenimine)</td>
<td>PEI</td>
<td>secondary amine</td>
<td>25,000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Poly(vinyl methyl ether)</td>
<td>PVME</td>
<td>ether</td>
<td>unknown</td>
<td>Aldrich</td>
</tr>
<tr>
<td>4,4' Diphenyl methylene diisocyanate</td>
<td>MDI</td>
<td>isocyanate</td>
<td>250</td>
<td>Kemira</td>
</tr>
</tbody>
</table>

Table 3.4: The materials used in the functional group analysis experiments
3.2 Chemicals

In Table 3.5 the chemicals used throughout the project and their purpose is presented:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Use</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium hydroxide</td>
<td>5% solution in distilled water, used for cleaning mild steel tokens</td>
<td>Aldrich</td>
</tr>
<tr>
<td>sodium sulphate</td>
<td>0.1M solution in distilled water, used as an electrolyte in electrochemical testing</td>
<td>Aldrich</td>
</tr>
<tr>
<td>potassium bromide</td>
<td>mixed with samples to use in IR transmission spectroscopy</td>
<td>Aldrich</td>
</tr>
<tr>
<td>powder (99% purity)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diiodomethane (99%)</td>
<td>used for contact angle work</td>
<td>Aldrich</td>
</tr>
<tr>
<td>triple distilled water</td>
<td>used for contact angle work</td>
<td>laboratory produced</td>
</tr>
</tbody>
</table>

Table 3.5: Chemicals used in the research

3.3 Standard methods of analysis

3.3.1 Atomic force microscopy

Atomic force microscopy was used to determine the roughness of the steel surface. The images were collected using a Burleigh Personal SPM; in continuous topographic mode, with 256 steps in X and Y directions. The analysis was carried out by Mr K Sime at the Institute of Surface Science and Technology (Loughborough University). Roughness average (Ra) measurements were used to define surface roughness, Equation 3.1.
Chapter 3: Experimental

\[ R_a = \frac{1}{L} \int_0^L |y(x)| \, dx \quad \text{Equation 3.1} \]

where, \( l \) 1...5 were consecutive and equal sampling lengths, \( L \) was the length of the profile, and \( x \) and \( y \) the deviation from the profile mean line, see Figure 3.3.

![Figure 3.3](image)

Figure 3.3: To define the terms used in the calculation of \( R_a \)

3.3.2 Auger electron spectroscopy

Auger electron spectroscopy (AES) was used along with X-ray photoelectron spectroscopy to analyse the failed butt joint interfaces after environmental exposure. The spectra were collected using a Varian (10keV) spectrometer, with a primary beam energy of 3000 eV, and a current of approximately 1μA. Compositions were based upon a Fe₂O₃ reference material, and depth scale calibrations were based upon an experimentally derived etch rate taken from an iron thin film on glass. Analysis was carried out by Mr GW Critchlow at the Institute of Surface Science and Technology, (Loughborough University).
3.3.3 Contact angle measurement

Contact angle measurements were made, in order to perform the theoretical calculations for an adhesive thermodynamic experiment. As indicated in the literature section, it is possible to predict if a polymer may delaminate from a surface from a knowledge of thermodynamics, which can in turn be calculated from a knowledge of contact angles. The measurements were made using a Krüss contact angle system G40 (version 1.0 1987). Two liquids were used, diiodomethane and water (Section 3.2) and advancing measurements were made. The paint resin samples were bonded to a microscope slide, using double sided sticky tape to ensure sample flatness during the experiment.

A syringe was used to place a drop of liquid upon the sample, and the drop was allowed to equilibrate for two minutes, with the tip of the syringe still present. After which the experiment was carried out. For the advancing angle, liquid was added to the drop expanding it until the point of three phase contact moved along the surface, immediately this came to rest the angle was noted.

For each liquid the error in measured contact angle was less than $\pm 2^{\circ}$.

3.3.4 Differential scanning calorimeter

A Differential Scanning Calorimeter (DSC) was used both to monitor the thermal events associated with deblocking of a blocked isocyanate, and to observe the effects of different catalysts upon them.

The DSC used was a DuPont Instruments 910, and the results were analysed using a DuPont series 2000 Thermal Analyser. The DSC was operated at $5^{\circ}$C/minute between -25 and 350$^{\circ}$C, and calibrated using an indium standard. The sample size used was between 1 and 1.5 mg, and all experiments were carried out in a nitrogen atmosphere.
3.3.5 Electrochemical testing

Electrochemical testing was used to determine an acceptable paint thickness to provide protection in a cathodic environment. This paint thickness was used for other mechanical tests reported in this thesis. Mild steel plaques (150 x 100 mm) were electrocoated with standard electrocoat resin (Section 3.4.2.3) and were subsequently scratched from corner to corner diagonally, Figure 3.4. The plaques were immersed into an electrolyte (0.1 mol/dm$^3$ sodium sulphate), and a potential applied across the panel and a platinum electrode using a potentiostat. The voltage was set to maximum and the current varied with respect to the exposed area (scratch area - determined by Talysurf measurements, Section 3.3.8), to produce a current density of 4mA/cm$^2$. The duration of the exposure was 50 hours. An idealised set up is shown in Figure 3.4. After 50 hours that panel was washed with distilled water and the region of the scratch rubbed with a flat ended spatula (cross sectional area = 16 x 1 mm$^2$). The area of delamination was determined using a planimeter (ex. WF Stanley & Co. Ltd.), at least 10 measurements per specimen were made to determine the area.

![Diagram of electrochemical testing setup](image)

Figure 3.4 : Idealised set up for electrochemical testing

At least three panels of each coating thickness were tested.
3.3.6 Infrared spectroscopy

Infrared spectroscopy was used in reflection mode to study the interactions occurring between the paint resin and the steel substrate and the functional group polymers and the steel substrate. It was used in variable temperature mode to study any structural changes which may occur during cure, and to monitor the deblocking reaction of the blocked isocyanates.

A Nicolet 20 DXC spectrometer equipped with a mercury cadmium telluride (MCT) detector was used. All data was collected using 300 scans at 4 cm\(^{-1}\) resolution unless otherwise stated. Specific details of transmission spectroscopy and reflection absorption spectroscopy are given in the following sections.

A background spectra was collected for the purged spectrometer and any sample holder, then a reference consisting of an unpurged spectrometer and sample holder. The background spectra was automatically ratioed to any reference or sample spectra, hence the reference will be a spectra of water vapour and carbon dioxide. Sample spectra were collected after purging of the spectrometer. The reference spectra was subtracted from the sample spectra to remove water vapour and carbon dioxide from the spectra. All peak assignments were taken from Bellamy\(^{91}\), and Williams and Flemming\(^{92}\), unless otherwise indicated. The key to the symbols used to describe the vibrations and peaks is given in Appendix 2.

3.3.6.1 Transmission spectroscopy

Standard transmission spectra were taken using a sodium chloride plate coated with the sample solution in an appropriate concentration. All plates were stored in a desiccator and polished prior to use, using an infrared polishing kit (ex. Aldrich). Compounds which were insoluble in common organic solvents (e.g. salts) were mixed with potassium bromide powder and pressed into a disc. The transmission spectra of the uncured resin and cured resin were obtained by coating a thin layer of the resin on a cleaned sodium chloride plate, collecting a spectra and then curing the resin prior to collecting the cured spectra.
The variable temperature infrared measurements were performed using a Research Industrial Instruments Co. VLT2 heated cell, controlled by a Stanton Redcroft ramp generator. The temperature was monitored via a silver thermocouple attached to the cell, and recorded using a plotter. The rate of heating was 5°C/minute, unless otherwise stated. A programme was written using the Nicolet software which enabled spectra to be collected approximately every 12°C, which was run until the desired temperature was reached. A spectra consisted of 20 scans, (collected over a 5°C temperature range) from room temperature to 300°C. Considerable problems were encountered in developing this technique with elevated sample noise levels apparent in the final spectra. It was not thought possible to increase the number of acquisitions, as this would increase the temperature range over which the data was collected.

3.3.6.2 Reflection absorption spectroscopy (RAS)
A Spectra Tech model 500 reflection apparatus was used for measurements made on metal surfaces, set at an angle of 85° to the normal. The background and reference were collected using an aluminium mirror. The mirrors were cleaned when necessary using 3M Invisible Tape to remove the dust particles, and/or a methanol wash to remove any other contaminants, as per the instructions provided by Spectra Tech.

3.3.7 Mechanical Testing

3.3.7.1 The butt test
A butt style test was used to develop a quantitative mechanical test, since it should, in theory, subject the paint resin to only tensile forces. All tests were performed using a Lloyd 10,000 tensiometer in tensile mode, with a 50, 10 or 5 kN load cell. The butts were milled to provide a flat surface for bonding, and were then abraded with 250 grade wet and dry paper. They were cleaned in sodium hydroxide in an identical fashion to the plaques. No further treatment was applied. The butt joint assembly was stored in a dessicator for 24 hours prior to testing, with
the exception of the environmental exposure experiments, where testing was carried out immediately the exposure had finished. All tests were carried out at room temperature using a crosshead speed of 2 mm/min, unless otherwise stated. Data analysis was performed using the associated computer.

3.3.7.2 The shim test

The aim here was to develop a test whereby a capacitance measurement could be taken from a coated steel shim as it was loaded in tension. As a sample stretched, it was hoped the coating would delaminate from the shim before the shim failed, and the change in the capacitance measurement could be related to adhesion of the coating to the shim.

Mild steel shims were prepared by ICI Paints Ltd. into the shape of a dumbbell, see Figure 3.5, and were tested using a Lloyd 10,000 tensionmeter with a 5 kN load cell, at crosshead speeds indicated in Section 4.4.3.

A cell was constructed which allowed a shim to be surrounded by an electrolyte (0.1 mol/dm$^3$ sodium sulphate) enabling capacitance measurements to be taken across a platinum electrode and the shim.

The experimental set-up of the cell and the shim are shown in Figure 3.6.
Chapter 3: Experimental

Figure 3.6: The cell and shim test apparatus

3.3.8 Statistical calculations

The arithmetic mean ($\bar{x}$) and standard deviation were used to define the results. The standard deviation was calculated as follows.

$$\text{standard deviation} = \left( \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1} \right)^{\frac{1}{2}}$$

where, $x$ is the sample value, $n$ is the number of items, $\bar{x}$ the arithmetic mean.
3.3.9 Talysurf analysis

Talysurf measurements were made to determine the surface profile of a substrate. The technique was used to determine the approximate region of failure in butt joints; and the depth of the scratch of the scratched panels in the electrochemical test. In the case of a failed butt test a theoretical Talysurf profile is indicated in Figure 3.7.

```
Figure 3.7: Idealised Talysurf sample
```

Since the thickness of the resin layer applied to the token was known, any value over that of the resin thickness would be expected to be due to the Araldite adhesive left on the surface. Similarly, values less than the resin thickness were thought to be associated with a resin failure. From this it was possible to determine an approximate region of failure, i.e. whether it is an Araldite/resin or resin/steel failure.

3.3.10 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to analyse the steel substrate and failed butt joint interfaces. The spectra were collected using a VG Escalab MkI spectrometer employing a non-monochromised Al-Kα X-ray source (1486.6 eV) at a pressure of ca. $10^{-7}$ mbar. All spectra were recorded with an X-ray source power of 200 W (10Kv, 20mA) and in the constant analyser energy mode. Survey spectra were obtained at a pass energy of 100 eV with a 10 mm slit, whereas high resolution spectra were obtained at a pass energy of 20 eV with a 5 mm aperture. All spectra were obtained at a take-off angle of 90° with respect to the sample surface and charge referenced to the C1s peak at a binding energy of 284.6eV. Deconvolution of high
energy spectra was achieved using a modified van Cittert deconvolution algorithm to remove line shape and broadening effects of the Al-Kα line. The analysis was carried out by Dr. I Mathieson at the Institute of Surface Science and Technology, Loughborough University.

### 3.4 Procedures

This section contains information concerning experimental procedures that were used in this research.

#### 3.4.1 Steel cleaning

Mild steel (Section 3.1.1), was cut to the desired size using a guillotine. Since the samples were covered in oils from the rolling processes and for rust prevention, they required cleaning. Reflection absorption infrared spectroscopy was used to monitor the intensity of the hydrocarbon stretching peaks in the 3000 cm⁻¹ region. When these peaks were no longer present it was decided that the oils had been removed. It was found that washing the sample in an aqueous sodium hydroxide (5% weight/volume solution) at 60°C, and then washing the sample with several aliquots of distilled water at 60°C removed the oily contaminants. The samples were shaken to remove excess water and allowed to dry in air. A diagram of the cleaning schedule is shown in Figure 3.8.

All cleaning was carried out in an ultrasonic bath (i.e. Sonomatic T80D ex. Semat Technical UK Ltd):
3.4.2 Sample coating

Three different types of coating procedure were used in the research. The first two were performed at Loughborough University and the other was performed by ICI Paints Ltd.

3.4.2.1 The butt test
Cleaned metal tokens approximately 30 x 30 mm, were coated with the resin using a 25μ K-bar (ex. RK Print Coat Instruments Ltd.) to ensure wet film uniformity. The resin was cured at 175° C for 20 minutes. Specimen construction for the butt test is described in Section 4.4.

3.4.2.2 Functional group interactions
A polymer solution was dropped via a glass pipette onto a cleaned metal token (25 x 12 mm). The token was then left in an oven at approximately 40°C under reduced pressure, until all the solvent had evaporated. The concentration of the polymer solution varied between 1 and 0.001% weight/volume. Tokens coated with different concentrations of the same polymer were exposed to the evaporation process simultaneously. Approximately 0.17 g/cm² of polymer solution was deposited on
each token. When a comparison was made between the transmission and reflection infrared spectra, the same thickness of polymer was typically applied.

3.4.2.3 Electrodeposition
This technique was performed at ICI Paints Ltd. A cleaned steel substrate was immersed in a tank of emulsified electrocoat resin and connected up as the cathode. A current was applied between the cathode and anode, the magnitude of which was used to determine the film thickness of resin deposited onto the cathode. After removal from the tank, the resin was cured for 20 minutes at 175°C.

3.4.3 Environmental exposure

Environmental testing in this work comprised of immersion testing and salt spray exposure. The immersion testing utilised a 5% w/v sodium hydroxide solution as the exposure environment. This was later deemed to be too harsh and salt spray exposure was used, based upon ASTM's G85-94 and B117-95 which govern the running conditions of the salt spray chamber. The conditions used in this work were a 5% salt solution and a temperature of 35°C.
This chapter starts (Section 4.1) describing the results of characterisation of the metal substrate and the resin system. The effects of cure upon the resin system as both a free film and on a steel substrate were investigated using transmission and reflection infrared spectroscopy respectively. The effects of different amounts of catalyst upon the cure reactions were studied using DSC.

The resin also contains tin compounds, which were involved in catalysis of the deblocking and subsequent reactions. In order to comply with ICI Paints internal directives on toxicity, these tin compounds need to be removed and replaced by other less hazardous components. Section 4.2 discusses the results of predominately DSC investigations into the way in which different catalysts effect the deblocking reaction of a blocked isocyanate.

The electrocoat resin described previously (Section 2.1) is a complex mixture of reactive functional groups, all of which may effect the overall adhesion of the coating to a substrate. The investigations in Section 4.3 aim to give an appreciation of how different organic functional groups may interact with a steel surface.
An investigation into the strength of the bond formed between the resin and a steel substrate was carried out and is discussed in Section 4.4. This involved developing a quantitative mechanical test based upon a one inch butt test format, and preliminary investigations into an electromechanical test, which it was hoped would determine the point of failure of a coating from conductance measurements. By the nature of this process this section contains a large number of experimental procedures. A thermodynamic investigation of adhesion, based upon the work of Owens\textsuperscript{54}, was also performed.

4.1 Characterisation

4.1.1 The metal substrate

A knowledge of what was present on the surface would allow specific interactions between the resin and the steel to be determined, hence surface analysis of the metal substrate was undertaken to determine what compounds were present. Analysis was performed using X-ray photoelectron spectroscopy (XPS) and grazing angle FTIR. Atomic force microscopy (AFM) was used to give an indication of the surface roughness of the steel.

4.1.1.1 X-ray photoelectron spectroscopy

The XPS low resolution scan of the steel surface gave the following spectra, see Figure 4.1, high resolution results of specific areas are given in Table 4.1.
Assignment of the peaks associated with the iron atom were made using work published by Langevoort\textsuperscript{93}.  

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (ev)</th>
<th>Error</th>
<th>Assignment</th>
<th>Total percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe\ 2p_{1/2}$</td>
<td>710.6</td>
<td>$\pm &lt; 0.1$</td>
<td>$Fe_3O_4$</td>
<td>10.2</td>
</tr>
<tr>
<td>$2p_{3/2}$</td>
<td>724.3</td>
<td>$\pm &lt; 0.1$</td>
<td>$Fe_3O_4$</td>
<td></td>
</tr>
<tr>
<td>$Cls$</td>
<td>284.7</td>
<td>$\pm &lt; 0.1$</td>
<td>C-H, C-C</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
<td>286.7</td>
<td>$\pm 0.1$</td>
<td>C-O, C-O-C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>288.3</td>
<td>$\pm 0.1$</td>
<td>C=O</td>
<td></td>
</tr>
<tr>
<td>$Ols$</td>
<td>529.6</td>
<td>$\pm &lt; 0.1$</td>
<td>$Fe_3O_4$</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>532.2</td>
<td>$\pm 0.1$</td>
<td>organic oxygen</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: XPS binding energies and assignments for the clean steel surface

The XPS results showed the presence of iron $2p_{1/2}$ and $2p_{3/2}$ peaks, and iron II and iron III shake up satellites in the 714 ev and 720 ev regions respectively. This provides
evidence for the formation of iron II and iron III, which is commonly present as FeO\(_2\).Fe\(_2\)O\(_3\), i.e. Fe\(_3\)O\(_4\). An amount of organic matter was also detected on the surface. The O1s peak was subjected to a peak fitting program which gave the following binding energies for a 4 peak fit, see Table 4.2 and Figure 4.2.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>529.3</td>
<td>FeO(_{24})</td>
</tr>
<tr>
<td>2</td>
<td>530.2</td>
<td>Fe(_2)O(<em>3)(</em>{24})</td>
</tr>
<tr>
<td>3</td>
<td>531.6</td>
<td>organic(_{25})</td>
</tr>
<tr>
<td>4</td>
<td>533.1</td>
<td>OH/water(_{26})</td>
</tr>
</tbody>
</table>

Table 4.2: Binding energies for the fitted O1s peak for the steel substrate

Figure 4.2: The fitted O1s peak for the steel substrate
4.1.1.2 Infrared spectroscopy

The Kramers-Kroenig corrected reflection infrared spectrum of the metal substrate is shown in Figure 4.3. This spectrum indicated the presence of the following peaks, see Table 4.3:

![Infrared Spectroscopy](image)

**Figure 4.3: Reflection infrared spectra of a clean steel surface**

<table>
<thead>
<tr>
<th>Peak /cm$^{-1}$</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments (lit. value /cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3220</td>
<td>w</td>
<td>OH</td>
<td>related to water/OH on surface</td>
</tr>
<tr>
<td>1272</td>
<td>w</td>
<td>FeO.OH</td>
<td>$\beta$ FeO.OH (1300)$^{97}$</td>
</tr>
<tr>
<td>1064</td>
<td>m sh</td>
<td>?</td>
<td>/</td>
</tr>
<tr>
<td>1045</td>
<td>m</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$ (1050)$^{98}$</td>
</tr>
<tr>
<td>1021</td>
<td>m sh</td>
<td>FeO.OH</td>
<td>$\gamma$ FeO.OH (1010)$^{97}$</td>
</tr>
<tr>
<td>885</td>
<td>w</td>
<td>Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$ (890)$^{98}$</td>
</tr>
<tr>
<td>740</td>
<td>w</td>
<td>FeO.OH</td>
<td>$\gamma$ FeO.OH (737)$^{99}$</td>
</tr>
</tbody>
</table>

**Table 4.3: Peaks present in the reflection IR of the metal substrate**

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Literature\textsuperscript{97,99,100} indicated that the majority of absorptions from metal surfaces occur in the far infrared region, and only a few in the mid/far infrared interface region. Peaks were assigned according to literature, although some of them may be a little tentative. The peak at 1064 remains unassigned. Peaks associated with CH stretching (2800 to 3000 cm\textsuperscript{-1}) were not observed, which indicated that there was no organic matter (detectable by infrared) present on the metal surface.

The peaks observed associated with the steel substrate implied that there were two forms of iron oxide/hydroxide present; Fe\textsubscript{2}O\textsubscript{3} and hydrated FeO.

4.1.1.3 Roughness

The roughness average (R\textsubscript{a}) of a cleaned steel substrate was 610 nm (standard deviation = 52 nm). This data was collected from three different regions on a steel surface and was measured by atomic force microscopy (Section 3.3.1); the image is shown in Figure 4.4.

![Atomic force microscopy image of a cleaned steel surface](image-url)
4.1.1.4 Summary
There was evidence for the formation of Fe$_2$O$_3$ and FeO from both XPS, (in the form of Fe$_3$O$_4$) and infrared spectroscopy, and evidence from infrared spectroscopy which indicated that hydroxylated FeO was present. This was supported by the evidence from the peak fitted O1s XPS spectra, which indicated that water, probably in the form of hydroxyl was present (Table 4.2).
However, there was differing results for the amount of organic matter present on the steel surface. XPS indicated that there was a considerable amount, whereas infrared spectroscopy detected none. This observation can be easily explained since, XPS has a shallower sampling depth than infrared spectroscopy, and hence more signal can be obtained from the top few layers on the surface. There is also an inherent problem with reflection infrared on rough surfaces, which can be seen by considering the surface roughness. A real (i.e. rough) surface, has less specular reflectance than an optically flat one, therefore there are lower detection limits on a real surface using grazing angle infrared techniques.

4.1.2 The resin system
The resin system was characterised by transmission infrared spectroscopy, to determine bulk structural differences between an uncured and a cured resin sample. In order to determine differences that may occur at or near a metal surface, reflection infrared spectroscopy was used. Thermal analysis was used to monitor changes in enthalpy that may occur upon curing, and the effect that catalyst concentration had upon the thermal events.

4.1.2.1 Transmission infrared analysis of the ICI resin
Infrared transmission spectra for the uncured and cured resin are shown in Figure 4.5 and 4.6 respectively. The main peaks observed in the uncured resin are identified in Table 4.4.
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Figure 4.5: Transmission infrared spectra of the uncured resin

Figure 4.6: Transmission infrared spectrum of the cured resin
## Chapter 4: Results/Discussion

<table>
<thead>
<tr>
<th>Peak /cm$^{-1}$</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3391</td>
<td>m</td>
<td>OH ν</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3328</td>
<td>m</td>
<td>OH ν</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3068</td>
<td>w</td>
<td>CH ν</td>
<td>aromatic stretching</td>
<td>(3030)</td>
</tr>
<tr>
<td>3035</td>
<td>w</td>
<td>CH ν</td>
<td>aromatic stretching</td>
<td>(3030)</td>
</tr>
<tr>
<td>2963</td>
<td>m</td>
<td>CH ν$_{as}$</td>
<td>CH$_3$</td>
<td>(2962 ± 10)</td>
</tr>
<tr>
<td>2929</td>
<td>m</td>
<td>CH ν$_{β}$</td>
<td>CH$_2$</td>
<td>(2926 ± 10)</td>
</tr>
<tr>
<td>2871</td>
<td>m</td>
<td>CH ν$_{s}$</td>
<td>CH$_3$</td>
<td>(2872 ± 10)</td>
</tr>
<tr>
<td>1729</td>
<td>m</td>
<td>C=O ν</td>
<td>amide I in urethane linkage</td>
<td></td>
</tr>
<tr>
<td>1712</td>
<td>m</td>
<td>C=O ν</td>
<td>amide I in urethane linkage</td>
<td></td>
</tr>
<tr>
<td>1606</td>
<td>m</td>
<td>C=C ν$_{β}$</td>
<td>aromatic stretch</td>
<td>(1600)</td>
</tr>
<tr>
<td>1534</td>
<td>m - sh</td>
<td>NH δ'</td>
<td>amide II in urethane linkage</td>
<td></td>
</tr>
<tr>
<td>1510</td>
<td>s</td>
<td>C=C ν$_{β}$</td>
<td>aromatic stretch</td>
<td>(1500)</td>
</tr>
<tr>
<td>1459</td>
<td>m</td>
<td>CH δ'</td>
<td>C-CH$<em>3$ δ'$</em>{as}$ and CH$_2$ δ'</td>
<td>(1456 &amp; 1468)</td>
</tr>
<tr>
<td>1413</td>
<td>m/w</td>
<td>CN</td>
<td>amide III, associated with crosslinker</td>
<td></td>
</tr>
<tr>
<td>1361</td>
<td>m/w</td>
<td>CH δ</td>
<td>C-CH$<em>3$ δ'$</em>{as}$ and C(CH$_3$)$_2$</td>
<td></td>
</tr>
<tr>
<td>1297</td>
<td>m</td>
<td>OH δ</td>
<td>secondary hydroxyl</td>
<td>(1350 to 1260)</td>
</tr>
<tr>
<td>1244</td>
<td>s</td>
<td>CO ν</td>
<td>aryl ether in Ph-O-C</td>
<td>(near 1250)</td>
</tr>
<tr>
<td>1234</td>
<td>s</td>
<td>CO ν</td>
<td>ether in O=C-O-C</td>
<td>(1235)</td>
</tr>
<tr>
<td>1182</td>
<td>m/s</td>
<td>skeletal vibrat$^n$</td>
<td>(CH$_3$)$_2$-C$^{101}$</td>
<td>(1170 ± 10)</td>
</tr>
<tr>
<td>1117</td>
<td>m</td>
<td>OH ν + CO δ</td>
<td>secondary hydroxyl</td>
<td>(1100)</td>
</tr>
<tr>
<td>1067</td>
<td>m</td>
<td>R-O-R'</td>
<td>alkyl ether in O=C-O-C$^{102}$</td>
<td></td>
</tr>
<tr>
<td>1041</td>
<td>m</td>
<td>R-O-R'</td>
<td>alkyl in Ph-O-C</td>
<td></td>
</tr>
<tr>
<td>1012</td>
<td>m/w</td>
<td>CH δ$_{β}$</td>
<td>para disub aromatic$^{103}$</td>
<td></td>
</tr>
<tr>
<td>888</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>829</td>
<td>m</td>
<td>CH δ'γ</td>
<td>aromatic out of plane deformation$^{103}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Peak assignments for the uncured resin
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There were no significant differences in any of the peak positions in the infrared spectra of the cured and uncured resin samples. However, after scaling and subtracting the cured from the uncured spectra, differences in peak intensity were observed.

a) The peak at 1712 cm\(^{-1}\) (C=O, amide I) has decreased in intensity with reference to the peak at 1729 cm\(^{-1}\) (C=O, amide I).

From the urethane structure, shown in Figure 4.7, it can be seen that the carbonyl group is adjacent to nitrogen and oxygen atoms, where R relates to the blocking agent.

\[
\text{Figure 4.7: To show the position of the carbonyl group in a urethane linkage}
\]

Upon curing, formation of the crosslink occurs by dissociation of the blocking agent (a primary alcohol) and the subsequent reaction with a secondary alcohol on the polymer backbone, to form another urethane; R would then relate to the polymer backbone. Hence, there was no significant change in the environment or electronegativity of the carbonyl carbon atom, and correspondingly no change in the peak position was observed in the cured spectra\(^*\).

The decrease of the 1712 cm\(^{-1}\) peak with respect to the 1729 cm\(^{-1}\) peak and the overall intensity decrease of the two bands with respect to the CH skeletal band at 1182 cm\(^{-1}\), may indicate that not all the isocyanate is involved in the crosslinking reactions, and that some may be used to form dimers and trimers etc.

b) The peak at 1361 cm\(^{-1}\) (CH \(\delta\), in branched hydrocarbons) has increased with respect to peak at 1413 cm\(^{-1}\) (amide III, in crosslinker).

---

\(^*\) Although electronegativity of the \(\alpha\) carbon will greatly effect the carbonyl vibration it is not the only factor, although it is probably the most significant.
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The peak at 1361 cm\(^{-1}\) is probably a combination of two vibrations associated with C-CH\(_3\): 

\[ \text{C-(CH\(_3\))}_2 \text{ and C-CH}_3 \delta' \]

Upon curing the intensity of these hydrocarbon vibrations would be expected to remain the same, however there is an increase in the value of the peak at 1361 cm\(^{-1}\). This may be due to the formation of primary hydroxyls from the de-blocking of the crosslinker during cure, which also absorb in the 1350 cm\(^{-1}\) region.

c) The peak (shoulder) at 1534 cm\(^{-1}\) decreases upon cure.

This peak is associated with the crosslinker and is probably the amide II vibration in urethanes. It would be expected that upon cure this vibration would not shift in peak position since the changes occurring in atom order upon curing, are too distant to affect the vibration. This peak is a mixture of 40% OCN and 60% NH vibrations, and hydrogen bonding will shift the peak to higher wavenumbers. Hence, the reduction in intensity is probably due to a reduction in the urethane content of the resin upon curing.

d) There is a decrease in the intensity of peaks in the 1240 cm\(^{-1}\) region upon curing, after normalisation to a skeletal vibration at 1182 cm\(^{-1}\). In this region there are two peaks at 1234 and 1244 cm\(^{-1}\) assigned to CO stretching in ethers. The individual intensities for each component have not been determined because there is insufficient resolution between the two to give an accurate enough result. It is known that the peak at 1234 cm\(^{-1}\) is associated with the ester type linkage, Figure 4.8a, which in the electrocoat is formed from the reaction between an isocyanate and an alcohol, and therefore is associated with the blocked isocyanate crosslinker and the cured resin. This assignment is supported by analysis of the blocked isocyanates used in Section 4.2. The peak at 1245 cm\(^{-1}\) is typically that of a phenolic ether\textsuperscript{104}, Figure 4.8b, which is found only in the epoxy part of the resin system. However, examination of the resin crosslinker indicated the presence of a peak at 1250 cm\(^{-1}\), hence this peak at 1244 cm\(^{-1}\) is probably a combination of the resin and the crosslinker.

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![Figure 4.8](image.png)

Figure 4.8: To show differences in the C-O structure. a) ester type, b) phenolic type

There is less absorption of both peaks in the cured system compared to that of the uncured. This may imply that not all the isocyanate recombines with free alcohol to form urethane, and that some may dimerise, decompose or be used up in another way. There is an associated decrease in the peak at 1072 cm\(^{-1}\), a peak, assigned to the urethane ether linkage.

e) The alkyl ether peak at 1067 cm\(^{-1}\) has decreased upon curing.

Figure 4.9 indicates the differences in intensity of peaks in the 1000 to 1200 cm\(^{-1}\) region, normalised to a hydrocarbon peak at 1182 cm\(^{-1}\), that occurred upon curing.

![Figure 4.9](image.png)

Figure 4.9: To indicate peak area variation in the 1000 to 1200 cm\(^{-1}\) region normalised to a peak at 1182 cm\(^{-1}\).

It is apparent that the peak at 1041 cm\(^{-1}\) remains constant and that there is a decrease in the peak at 1067 cm\(^{-1}\). The peak at 1041 cm\(^{-1}\) is associated with alkyl
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CO stretch found in aryl/alkyl ethers a form of ether associated with the epoxy backbone, and as such no change would be expected upon curing. The peak at 1076 cm$^{-1}$ is an ester style linkage associated with the crosslinker. Upon curing there is a reduction in the amount of this component present which may imply that not all the isocyanate has recombined to form urethane.

The peak at 1117 cm$^{-1}$ associated with secondary hydroxyls decreases upon curing, which may be expected if the hydroxyl group is involved in the cure reaction.

The peak at 1012 cm$^{-1}$ associated with aromatic rings remains constant.

4.1.2.2 Reflection infrared analysis of the ICI resin

Since the interactions of resin with a steel substrate were to be studied, a series of reflection spectra were collected. Based upon a simple gel time experiment, spectra were collected after 3, 5, 7, 11, 16 and 21 minutes. Spectra from time 0 and 21 minutes i.e. uncured and cured, are shown in Figure 4.10 and 4.11.

![Figure 4.10: Reflection infrared spectra of the uncured epoxy resin on a steel surface](image)

Figure 4.10: Reflection infrared spectra of the uncured epoxy resin on a steel surface.
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The cured and uncured reflection spectra showed 5 regions of difference, which are detailed below.

a) Differences in the carbonyl stretches in the 1700 to 1730 cm\(^{-1}\)
b) Disappearance of a peak at 1536 cm\(^{-1}\)
c) Differences in the 1340 to 1460 cm\(^{-1}\) region
d) Differences in the 1249 to 1226 cm\(^{-1}\) region
e) Differences in the 1108 to 1017 cm\(^{-1}\) region

Differences "b, c and d" were the same as observed between the cured and uncured transmission spectra in Section 4.1.2.1, and hence can be assigned to the bulk resin. However, there were differences in regions "a" and "e" that were not observed in the transmission spectra.

a) Differences in the carbonyl stretch in the 1700 to 1730 cm\(^{-1}\) (amide I, in urethane):
In the uncured spectra, the main peak was observed at 1732 cm\(^{-1}\), with peaks at 1722 and 1714 cm\(^{-1}\) also apparent. Upon curing the main peak reduced and the

Figure 4.11: Reflection infrared spectra of the cured epoxy resin on a steel surface
other two peaks became predominant. A new weak peak at 1689 cm$^{-1}$ was observed. This peak is within the region for urethane carbonyls, but it is also close to the region assigned to carbonyls in -NHCONH- structures, which may be indicative of an allophanate structure.

Normalisation to a hydrocarbon peak at 1182 cm$^{-1}$ indicated a decrease in the overall intensity of the carbonyl groups upon curing.

e) Differences in the 1108 to 1017 cm$^{-1}$ region.

The peaks were normalised to a hydrocarbon peak at 1182 cm$^{-1}$ and the results are shown in Figure 4.12.

![Figure 4.12: To indicate peak area variation in the 1000 to 1200 cm$^{-1}$ region normalised to a peak at 1182 cm$^{-1}$](image)

Upon curing there was a decrease in the peaks at 1117 and 1067 cm$^{-1}$, a secondary hydroxyl and an ether respectively. Reduction in the intensity of the secondary hydroxyl signal would be expected if a reaction had occurred between the secondary alcohol, i.e. the polymer backbone, and the free isocyanate, which is a possible cure reaction. The ether linkage is associated with O=C-O-C', where the C' refers to the blocking agent or the polymer backbone, which would be either a primary or secondary carbon atom respectively. Upon curing differences in the environment of
the ether would be expected from a primary to a secondary carbon, and hence a
decrease in the intensity of the peak would be expected. A decrease was observed
which may imply that there is some primary nature of the carbon atom involved with
the ether linkage.

From the spectra collected at 3, 5, 7, 11 and 16 minutes during the cure cycle the
following differences were observed:

a) The 888 cm\textsuperscript{-1} region.

The peak at 888 cm\textsuperscript{-1} was observed to alter in intensity as cure progressed. The
peak area was normalised to the peak at 831 cm\textsuperscript{-1} which is assigned to an out of
plane C-H deformation in p-disubstituted aromatics. This peak is found in both the
epoxy and the crosslinker, and since no reaction of the aromatic is expected this
peak can be considered to be constant.

The normalised peak areas are indicated in Figure 4.13

![Figure 4.13: To show the change in the ratio of peak area of 888/831 cm\textsuperscript{-1} with
respect to cure time]
Figure 4.13 shows a trend where there is a maximum in the normalised peak area at 5 minutes, which decreases to below the initial value after 14 minutes, and further decreases to about 50% of the initial value after 21 minutes. This implies that the component present in the uncured state, becomes more available around 5 minutes and then decreases, possibly as a result of the cure reaction. No satisfactory assignment for the peak can be made at present, although it has been reported that it is associated with an ether peak in the vapour phase infrared spectra\textsuperscript{105}.

4.1.2.3 DSC analysis of the resin
As shown in Section 4.1.2, thermal analysis can be used to monitor the thermal events which occur during curing of the resin system. Since both the deblocking and crosslinking reactions involve changes in enthalpy, it was thought possible to observe the reactions, and the effects of catalyst upon the reactions, using DSC. If this theory is correct, then it was also thought possible to determine the effect of different catalysts upon the cure reactions, which may in turn could give an indication of a suitable replacement for the current tin based catalyst. To test the theory different concentrations of dibutyl tin oxide (DBTO) catalyst were tried using two different thermal schedules, i.e.

a) the standard experimental conditions (5°C/min),
b) in an attempt to simulate the environment the resin would normally be subjected to in an automotive stoving:
   
   ramp at 50°C/min. until 175 °C,\textsuperscript{†}
   
   isothermal for 20 minutes at 175°C.

The catalyst concentrations for both types of experiments were 0.5, 1.0, 1.5 and 2.0 percent weight/weight.

Linear heating of the resin indicated an endotherm around 40°C, followed by a gradual exotherm, see Figure 4.14. Addition of catalyst appeared to have no effect on the shape of the thermograms. This applied for all concentrations of catalyst. This implies that the onset of deblocking is not detectable by this method and that the cure

\textsuperscript{†} 50°C/min. is the fastest heating rate possible with the equipment.
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reaction is exothermic. Since no changes in the shape of the thermogram were observed for different catalyst concentrations, this suggests that the catalyst has no detectable effect upon curing for these conditions.

![Typical DSC thermogram for linear heating of the resin.](image)

Figure 4.14: Typical DSC thermogram for linear heating of the resin.

In the case of the simulated stoving oven, there is a difference in shape between the catalysed and uncatalysed samples. However, all samples showed an endotherm at approximately 175°C after 220 seconds, see Figure 4.15.

![Indicating the effect of different catalyst loadings upon the shape of the DSC thermograms](image)

Figure 4.15: Indicating the effect of different catalyst loadings upon the shape of the DSC thermograms
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The uncatalysed sample showed a endothermic reaction, whereas the two catalysed reactions showed an exotherm at the start of the experiment, with the common endotherm starting after approximately 170 seconds (153°C). After 300 seconds the thermogram traces remained linear.

4.1.2.4 Summary

Transmission and reflectance infrared studies of cured and uncured resin samples provided evidence, indicating a decrease in the urethane content of the resin system, i.e. after the degrading reaction not all the isocyanate combined to form urethane with the epoxy backbone. This implies that there may be some free isocyanate, dimer/trimer or other structure present. Although, no direct evidence for free isocyanate has been found.

The infrared reflectance spectra did not detect any chemical interactions occurring between the resin and the surface of the steel. This was not altogether surprising, although literature has indicated that interactions have been observed with commercial systems, e.g. Watts\(^{31}\) who tentatively proposed that an interaction between the isocyanate group and the steel surface was occurring. However in this experiment we may be observing an interphase region, i.e. not bulk and not the actual interface, but a region in between. This would explain why there are such similarities between the reflection and transmission experiments. The reflectance spectra also indicated that a carbonyl peak occurred at 1689 cm\(^{-1}\) which may be indicative of an allophanate/isocyanurate structure, and that there was more reaction of the secondary hydroxyl function. Since these results were obtained from vibrations towards the metal surface this may imply that different cure reactions occur in this region i.e. an interphase region. The increase in normalised peak at 888 cm\(^{-1}\), in the reflectance spectra, indicates that there is more of this group available. However, since an experiment monitoring cure as a function of time was not carried out for the transmission spectra, it cannot be determined whether this is a normal curing phenomenon or one related directly to the effect of the substrate.

The linear heating DSC experiments showed a gradual exotherm, the shape of which remained constant at different concentrations of DBTO, implying that the catalyst had no detectable effect upon cure, under these conditions. The simulated stoving
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Experiments showed small changes occurring during the heating part of the cycle. The DBTO catalyst delayed the onset of the endotherm, which was an abrupt transition as opposed to the gradual transition as observed for the uncatalysed sample.

4.2 Effects of catalyst upon the deblocking reaction of alcohol blocked isocyanates

From the resin characterisation discussed in Section 4.1, it would appear that the cure reaction was exothermic, and that the effect of catalyst upon the cure thermogram of the resin system was not detectable by DSC. The role of the catalyst is not greatly understood, and it is unclear whether it catalyses the deblocking reaction, the crosslinking reaction or both. Whilst no experiments were performed to answer this question, a study of the effect of different catalysts, and catalyst concentrations upon the deblocking reaction was carried out. It was thought that by investigating the crosslinker in isolation, that the effect of the catalyst could be determined and an alternative to the tin system proposed. An alternative catalyst should produce similar thermal characteristics, to DBTO, i.e. the thermograms should be similar.

The bismuth based catalysts, Bicat A and Bicat Z, were suggested by ICI Paints as potential replacements to dibutyl tin oxide (DBTO), the currently used tin based compound; although in the case of the studies on the industrial crosslinker, only DBTO was examined.
4.2.1 Analysis techniques

DSC and variable temperature infrared spectroscopy were used in this investigation to determine the deblocking onset temperature and subsequent reactions of the blocked isocyanate.

4.2.1.1 Differential scanning calorimetry

It is known that the deblocking reaction is exothermic, and hence the onset of this reaction should be the onset point of an exothermic peak in the thermogram\textsuperscript{65}. The effect of the catalyst was evaluated by observation of the following characteristics:

- melting point,
- onset temperature of the first minimum after the melting point, i.e. the onset of deblocking,
- first minimum peak (FMP).

The addition of a catalyst should reduce the onset temperature and, perhaps, the first minimum peak.

Little change was expected in the melting point since the blocked isocyanate would be solid and it is possible the catalyst would only be active on the surface of a blocked isocyanate crystal. Melting point, therefore, was used as a marker to ensure that the sample was not contaminated. If the sample were contaminated then the peak would change position and broaden. Upon melting the catalyst should be able to diffuse into the bulk of the blocked isocyanate more readily and effect the deblocking onset temperature. The onset point was taken as deviation from the base line, indicated by an exothermic peak on the thermogram. The minimum of the exothermic peak is the first minimum peak, at which temperature it is believed the majority of the deblocking has occurred. A typical thermogram is shown in Figure 4.16.
4.2.1.2 Infrared analysis
Variable temperature infrared was used to monitor the onset of deblocking by observing the temperature at which there was either a decrease in intensity of the urethane peaks, in the 1730 to 1700 cm\(^{-1}\) region, or an appearance of the isocyanate peak at 2250 cm\(^{-1}\). The same sample was used throughout each experiment, which enabled the spectra to be overlaid, and any differences observed.

4.2.2 Effects of catalyst upon the industrial crosslinker

The effects of DBTO catalyst on the industrial blocked isocyanate crosslinker was studied using DSC. The crosslinker with and without catalyst gave very similar thermograms, i.e. a small endotherm at the start of the thermogram, and then a gradual exotherm, Figure 4.17. No enthalpy change was observed that would indicate that deblocking was occurring.
Figure 4.17: DSC thermogram of the crosslinker, catalysed (—) and uncatalysed (---)

This may be due to the mixed nature of the crosslinker, comprising of monomers, dimers and trimers of 4,4’ diphenyl methylene diisocyanate (MDI), reacted with 3 different alcohols. It may be postulated that recombination or reaction between the free isocyanates may occur, absorbing the heat produced by the reaction. It should be noted that in all the published results found, pure blocked isocyanates were used rather than a mixture of compounds as in the industrial crosslinker. Hence the effects of catalyst upon two different alcohol blocked 4,4’ MDIs was investigated.
4.2.3 Effects of catalyst upon alcohol blocked 4,4’ diphenyl methylene diisocyanate

The blocked isocyanates were: 4,4’ MDI blocked with butylcarbitol (BII) and 4,4’ MDI blocked with methanol (BI2). Both of these monofunctional alcohols were used as blocking agents in the industrial crosslinker. Table 4.5 indicates the experiments performed using different levels of catalyst.

<table>
<thead>
<tr>
<th>Technique</th>
<th>BI</th>
<th>DBTO</th>
<th>Bicat A</th>
<th>Bicat Z</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>1</td>
<td>1%, 5%, 10%</td>
<td>1%, 10%</td>
<td>1%, 5%, 10%</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1%, 5%, 10%</td>
<td>1%, 5%, 10%</td>
<td>1%, 5%, 10%</td>
<td>✓</td>
</tr>
<tr>
<td>IR</td>
<td>1</td>
<td>1%, 5%, 10%</td>
<td>10%</td>
<td>1%, 10%</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1%, 5%, 10%</td>
<td>1%, 5%, 10%</td>
<td>1%, 5%</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 4.5: The experiments performed on the blocked isocyanates

All DSC results are taken from a minimum of three experiments, and the conditions used were those indicated in Experimental Section 3.3.2. The infrared data was from a single non-isothermal experiment.
4.2.3.1 Blocked isocyanate 1 (BII)

a) DSC

Figures 4.18 and 4.19 show the effect of different concentrations of catalyst upon the onset and first minimum peak features of the DSC exotherm.

Addition of Bicat A and DBTO caused changes in the onset conditions, although these changes show no significant deviation from the uncatalysed values. However, addition of Bicat Z caused a reduction in the onset temperature. A 1% loading reduced the onset to 166°C, while at 10% this value increased slightly to 170°C.
Addition of Bicat A gave no significant differences in the temperature for the first minimum peak with respect to the uncatalysed value. At 1% catalyst loading, both Bicat Z and DBTO reduced the temperature of the minimum peak: Bicat Z at 217°C was some 12°C lower than DBTO. However, at 10% catalyst loading, the first minimum peak for DBTO was 7°C lower than observed for Bicat Z. Both of these values were considerably lower than for the catalyst free condition.
Figure 4.20: The difference between the onset temperature and FMP verses catalyst concentration for BI1

The difference between the onset and FMP is shown in Figure 4.20. For Bicat A (1% loading) the difference was approximately 70°C and increased slightly at 10% catalyst loading. This implied that Bicat A had little effect upon the thermal events. For DBTO and Bicat Z catalysts, the difference between the onset and first minimum temperature decreased upon addition of 1% catalyst, while higher loadings had no further significant effect.

Summary
- With respect to onset temperature Bicat A gave similar results to DBTO. Bicat Z showed a marked improvement upon the onset of deblocking.
- With respect to the difference between the onset and FMP, DBTO shows a smaller temperature difference, than both Bicat A and Z.
- There is no obvious match for DBTO. Bicat A shows similar onset conditions, but dissimilar first minimum peak conditions to DBTO, and Bicat Z shows similar first minimum peak conditions but different onset conditions to DBTO.
b) Infrared

No isocyanate peaks were observed in the spectra, and determination of the onset of deblocking was assigned to the first observed decrease in the intensity of the urethane peak at 1730 cm\(^{-1}\). The peak at 1710 cm\(^{-1}\), signed to hydrogen bonded carbonyl groups, decreased in intensity as the temperature was increased and at 180\(^\circ\)C only the peak at 1730 cm\(^{-1}\) remained. This would be expected to occur, since at higher temperatures there is a decrease in hydrogen bonding. Figure 4.21 shows the temperature at which there was an initial decrease in the 1730 cm\(^{-1}\) urethane peak versus catalyst concentration for DBTO, Bicat A and Bicat Z.

![Graph showing temperature at which there was an initial decrease in the intensity of the urethane peak for BII versus concentration of catalyst.]

Figure 4.21: The temperature at which there was an initial decrease in the intensity of the urethane peak for BII

The infrared onset for uncatalysed BII occurred at 207\(^\circ\)C. One percent DBTO lowered the onset temperature to 202\(^\circ\)C, while a 5% loading lowered it further to 193\(^\circ\)C, although a 10% loading made little further difference. Ten percent Bicat A lowered the onset temperature to 198\(^\circ\)C. One percent Bicat Z lowered the onset
temperature to 174°C, although again, 10% catalyst loading made little further difference.

After deblocking had occurred there was a loss of peaks in all regions of the infrared spectra. It was thought that after this process had occurred that the alcohol evaporated leaving the free MDI, which would then melt, since its melting point is at 44°C. The MDI may then volatilise, polymerise or decompose. However, the last suggestion was thought more likely, since it is known that MDI will start to decompose about 210°C.

c) Summary
The DSC onset temperature correlated to the temperature of the initial reduction in the infrared urethane very well, and as such support the fact that deblocking was occurring at this point. This agrees to the results of Anagnostou and Jaul.

No infrared data could be collected to prove if the first minimum peak was the temperature at which deblocking was complete, since there was a loss of peaks in the spectra after deblocking had occurred.

4.2.3.2 Blocked isocyanate 2 (BI2)

a) DSC
Figures 4.22 and 4.23 show the effect of different concentrations of catalyst upon the onset and first minimum peak features of the DSC exotherm.
4.0 : Results/Discussion

Figure 4.22 : Onset temperatures for BI2 with different catalysts loadings

BI2 without catalyst showed an onset at 245°C and a first minimum peak at 261°C. The addition of 1% DBTO lowered the onset peak to 221°C, although higher levels of catalyst did not significantly alter the onset temperature. Bicat A (1%) lowered the onset temperature to 238°C, while a 10% loading reduced the onset temperature to 200°C. A 1% loading of Bicat Z, lowered the onset temperature to 209°C, but higher levels of catalyst had no further effect upon the onset temperature.
4.0 : Results/Discussion

The addition of 1% or 5% DBTO reduced the first minimum peak to 242°C, it then dropped to 233°C at 10% catalyst loading. One percent Bicat A caused a reduction in the first minimum peak to 234°C, while 10% catalyst loading caused a further reduction to 214°C. Bicat Z showed an initial decrease at 1% loading to 231°C, while 10% catalyst concentration gave a first minimum peak at 220°C.

Summary
• Neither Bicat A nor Z showed similar effects to DBTO for the onset and first minimum peak temperatures.
• Both Bicat A and Z show approximately the same temperature for the first minimum peak.
• The difference between the onset and FMP for the different catalyst concentrations show considerable errors, and hence no meaningful conclusions could be drawn as to the effect of catalyst upon rate of deblocking.
c) Summary

In the case of BI2 there is good correlation between the onset temperatures obtained by DSC and initial decrease in the urethane peak observed in the infrared spectra. From this data it can be seen that neither Bicat A or Bicat A, appear to mimic DBTO, for either the onset or FMP conditions.

4.2.4 Summary

The onset of deblocking for the industrial crosslinker could not be determined by DSC. The thermogram (Figure 4.17) obtained for the crosslinker was similar to the one obtained for the resin system in Section 4.1.2.3 (Figure 4.14). The industrial crosslinker is a complex system, and this may explain why the onset point could not be detected.

The deblocking temperature for two pure blocked isocyanates was determined using DSC and variable temperature infrared. In the case of BI2 the effect of the catalysts was to reduce the onset temperature at 1%w/v concentration and below (Section 4.2.3.2). However in BII, Bicat Z was the only catalyst to cause a significant change in onset temperature, DBTO and Bicat A caused no significant effects in the onset temperature. There was no infrared evidence to support the theory that the majority of the deblocking reaction had occurred by the FMP (Section 4.2.3.1).

Although in some cases Bicat A and Z show similar effects to DBTO, neither of them display the same trends in the two blocked isocyanates. At some concentrations one or other may be closer to the effect of DBTO, hence further investigation into other effects (e.g. mechanical strengths) should be carried out to determine which one of the two would be best to replace DBTO.
4.3 Functional group interactions

Adhesive and paint resins interact with metal surfaces via different mechanisms, predominantly mechanical or chemical in nature. However, in a complex resin system, as described in Section 4.1, identification of the surface specific interactions may be difficult. In the previous section model systems were studied providing an understanding of the effects of catalysts. In this section simple compounds containing the functional groups, present in the electrocoat, were studied to determine how they may react with a steel surface. Although this type of study has been carried out for aluminium, it is believed this is the first detailed study of functional group interactions on a steel substrate, using grazing angle reflection absorption infrared spectroscopy.

The compounds used in terms of functional groups are shown in Table 4.6.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Poly (acrylic acid)</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Poly (vinyl alcohol)</td>
</tr>
<tr>
<td>Amine</td>
<td>Diethylenetriamine</td>
</tr>
<tr>
<td>Amine</td>
<td>Poly (ethylenimine)</td>
</tr>
<tr>
<td>Ether</td>
<td>Poly (vinyl methyl ether)</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>4,4' Diphenyl methylene diisocyanate</td>
</tr>
</tbody>
</table>

Table 4.6: The compounds used in the functional group analysis

4.3.1 Acid : Poly (acrylic acid)

Although not present on the actual polymer backbone, an acid group is present to enable the resin to be dispersed in water, and may also be formed by the reaction of an isocyanate group and water from the metal surface. The transmission spectrum of poly (acrylic acid) (PAA), cast from a methanol solution is shown in Figure 4.25, and the significant peaks in the 4000 to 650 cm$^{-1}$ region are assigned in Table 4.7.
Chapter 4: Results/Discussion

Figure 4.25: The transmission infrared spectrum of poly (acrylic acid)

<table>
<thead>
<tr>
<th>Peak /cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3046</td>
<td>m</td>
<td>OH ν</td>
<td>in acid dimers</td>
<td></td>
</tr>
<tr>
<td>2956</td>
<td>m</td>
<td>CH ν</td>
<td>in CH₂ (2925)</td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>w</td>
<td>OH ν</td>
<td>hydrogen bonded (1700 to 2500)</td>
<td></td>
</tr>
<tr>
<td>1718</td>
<td>s</td>
<td>C=O</td>
<td>in acids (1725 to 1700)</td>
<td></td>
</tr>
<tr>
<td>1710</td>
<td>s</td>
<td>C=O</td>
<td>in acids (1725 to 1700)</td>
<td></td>
</tr>
<tr>
<td>1452</td>
<td>m/w</td>
<td>CH ν,</td>
<td>in CH₂ (1465 ± 20)</td>
<td></td>
</tr>
<tr>
<td>1410</td>
<td>m/w</td>
<td>CO ν + OH δ</td>
<td>(1440 to 1395)</td>
<td></td>
</tr>
<tr>
<td>1242</td>
<td>m</td>
<td>CO ν + OH δ</td>
<td>(1320 to 1211)</td>
<td></td>
</tr>
<tr>
<td>1171</td>
<td>m</td>
<td>CH₂ r</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>1115</td>
<td>w</td>
<td>CH</td>
<td>possibly</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>m/w</td>
<td>/</td>
<td>May be an isopropyl vibration (803)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Assignment for the peaks observed in the transmission infrared spectrum of poly (acrylic acid)
Chapter 4: Results/Discussion

The 1% coated tokens shows peaks at 1752 and 1674 cm\(^{-1}\) which were assigned to non-hydrogen bonded and hydrogen bonded carboxyl groups, respectively. Small peaks were detected at 1585 and 1543 cm\(^{-1}\). As the film becomes thinner, i.e. 0.1% PAA and more dilute solutions, the peaks at 1752 and 1675 cm\(^{-1}\) reduced in amplitude and the peak at 1585 cm\(^{-1}\) increased in intensity. This peak was assigned to CO\(_2^+\) asymmetric stretching \(35, 107\), and suggests the presence of an iron salt structure; see Figure 4.28.

\[
\text{Fe}^{3+} - \backslash - \text{O} - \text{O}
\]

Figure 4.28: Proposed chemical structure of the peak at 1585 cm\(^{-1}\).

The peak at 1543 cm\(^{-1}\) increased in intensity for the 0.01% coated tokens. This peak was not present in the transmission spectra of PAA, in either literature\(^{108}\) or in the coated series. However, the peak appeared in a transmission spectra collected using KBr disc preparation technique, and was seen in a literature spectra of the sodium salt of stearic acid\(^{109}\).

The 1% PAA coated tokens showed a shift of the peaks associated with CO\(_\nu\) and OH \(\delta\)' from 1410 and 1242 cm\(^{-1}\) to 1420 and 1285 cm\(^{-1}\) respectively. This would be expected if an interaction with the acid group had occurred. Peaks at 1171 and 1115 cm\(^{-1}\) remained constant implying that the associated groups took no part in the metal interaction. This would be consistent with a CH vibration assignment, since no change in the peak positions would be expected. The 1420 cm\(^{-1}\) peak was present in the 0.001% and 0.0001% PAA coated tokens, while the 1285 cm\(^{-1}\) peak was absent. This may be masked by the broad peak at 1300 cm\(^{-1}\) which was present on the cleaned tokens before coating, and as such is probably due to the metal.

Thus there is strong evidence for chemical bonding occurring between iron atoms of the metal and the carboxylate groups. The minimum possible thickness of a uniform coating, would be approximately 20 nm. Under these conditions the dominant IR
peaks were due to a carboxylic acid salt, suggesting that there was probably some diffusion of iron atoms into the adsorbed polymer producing an interphase region of appreciable thickness.

**4.3.2 Alcohol : Poly (vinyl alcohol)**

The IR transmission spectrum for poly (vinyl alcohol) (PVA) cast from hot dimethyl sulphoxide onto a sodium chloride plate is shown in Figure 4.28. The peaks associated with the functional groups present are assigned in Table 4.9:

![Figure 4.28: The transmission infrared spectrum of poly (vinyl alcohol)](image)
The peak (1144 cm\(^{-1}\)) was present in the transmission spectra and was observed for the 1\% coated tokens. For weaker PVA concentrations it reduced in intensity. This peak can be attributed to crystallinity within PVA, and as the polymer thickness decreased less crystallinity was observed. Therefore, towards the metal surface the polymer layer would have different mechanical properties in comparison to the bulk polymer. This may produce a weak layer near the polymer metal interface, which in turn may produce weak layers within the structure.

The peaks associated with CH \(\nu + \text{OH} \, \delta\) at approximately 1332 cm\(^{-1}\) remained constant for the different concentrations examined. The peak at approximately 1451 cm\(^{-1}\) showed a variation in the 0.1\% series, where it was found at 1436 cm\(^{-1}\). Since there is a low OH stretch value, this may imply that there is a reduced contribution to the peak than in the other cases, causing a slight shift in the peak position. The CO stretching vibration showed no difference in peak position.
4.3.3 Amine: Diethylenetriamine

Amines are present on the polymer backbone, from a reaction of the epoxy groups with a secondary amine (Section 2.1.1). Hence, it was thought useful to investigate whether any interaction occurred between a primary amine and a metal surface. It was also hoped to observe any interaction occurring between a secondary amine and the metal surface.

The diethylenetriamine molecule (Figure 4.30), was thought to be an ideal compound to study interaction of amines, since it contains both primary and secondary groups.

![Figure 4.30: The diethylenetriamine molecule](image)

To aid the assignment of the primary and secondary amine peaks observed in the infrared spectrum of diethylenetriamine, infrared analysis of dipropylamine and ethylenediamine was made. The spectrum of dipropylamine (neat solution on a sodium chloride plate) is shown in Figure 4.31. Tables 4.11 and 4.12 indicate the peak assignments for the dipropylamine and ethylenediamine. The peak assignments of diethylenetriamine are given in Table 4.13, and the infrared transmission spectrum (neat solution on a sodium chloride plate) is shown in Figure 4.32.
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Figure 4.31 : Transmission infrared spectrum of dipropylamine

<table>
<thead>
<tr>
<th>Peak /cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3296</td>
<td>w</td>
<td>NH ν</td>
<td></td>
<td>(3200 to 3500)</td>
</tr>
<tr>
<td>2970</td>
<td>s</td>
<td>CH ν₂</td>
<td>in CH₃</td>
<td>(2962 ± 10)</td>
</tr>
<tr>
<td>2940</td>
<td>s</td>
<td>CH ν₃</td>
<td>in CH₂</td>
<td>(2926 ± 10)</td>
</tr>
<tr>
<td>2886</td>
<td>m</td>
<td>CH ν₄</td>
<td>in CH₃</td>
<td>(2872 ± 10)</td>
</tr>
<tr>
<td>2815</td>
<td>m</td>
<td>CH ν₅</td>
<td>RCH₂NHR¹¹²</td>
<td></td>
</tr>
<tr>
<td>1463</td>
<td>m</td>
<td>CH δ'</td>
<td>in CH₂</td>
<td>(1465 ± 20)</td>
</tr>
<tr>
<td>1382</td>
<td>m/w</td>
<td>CH δ₂</td>
<td>in C-CH₂</td>
<td>(1375 ± 5)</td>
</tr>
<tr>
<td>1345</td>
<td>w</td>
<td>CH</td>
<td>CH₂ twist</td>
<td></td>
</tr>
<tr>
<td>1301</td>
<td>w</td>
<td>CH ω</td>
<td>CH₂ wag/twist</td>
<td>(1305)</td>
</tr>
<tr>
<td>1137</td>
<td>m</td>
<td>CN ν₆</td>
<td>secondary amine, CH₂NHR¹¹³</td>
<td></td>
</tr>
<tr>
<td>1091</td>
<td>w</td>
<td>CN</td>
<td></td>
<td>/</td>
</tr>
<tr>
<td>1012</td>
<td>w</td>
<td>CC</td>
<td>skeletal</td>
<td></td>
</tr>
<tr>
<td>894</td>
<td>w</td>
<td>CH r</td>
<td></td>
<td>/</td>
</tr>
<tr>
<td>723</td>
<td>m</td>
<td>CH₂ / NH / NH δ₆</td>
<td></td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.11 : Assignment for the peaks observed in the transmission infrared spectrum of dipropylamine

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The peak at 3296 cm\(^{-1}\) is very weak and is barely detectable. The peak at 2815 cm\(^{-1}\) is lower than the usual CH\(_2\) \(\nu\gamma\) due to its proximity to a NHR group. The secondary amine deformation frequency should occur in the 1550 to 1650 cm\(^{-1}\) region, however, it is a weak vibration and as such is not observed in the spectrum. It is probably too weak to be used for identification purposes.

The analysis of ethylenediamine was taken from a spectrum found in literature\(^{114}\).

<table>
<thead>
<tr>
<th>Peak /cm(^{-1})</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments (lit. value /cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3350</td>
<td>s</td>
<td>NH (\nu)as</td>
<td>Lower than expected (3500 to 300) probably due to hydrogen bonding. Typically shows 3 groups [61-2]</td>
</tr>
<tr>
<td>3280</td>
<td>s</td>
<td>NH (\nu)s</td>
<td></td>
</tr>
<tr>
<td>3180</td>
<td>s sh</td>
<td>NH (\nu)</td>
<td></td>
</tr>
<tr>
<td>2925</td>
<td>s</td>
<td>CH (\nu)β</td>
<td>in CH(_2) ((2926 \pm 10))</td>
</tr>
<tr>
<td>2840</td>
<td>s</td>
<td>CH (\nu)γ</td>
<td>in CH(_2) ((2853 \pm 10))</td>
</tr>
<tr>
<td>1596</td>
<td>s</td>
<td>NH (\delta)</td>
<td></td>
</tr>
<tr>
<td>1460</td>
<td>m</td>
<td>CH (\delta')</td>
<td>in CH(_2) ((1465 \pm 20))</td>
</tr>
<tr>
<td>1354</td>
<td>m</td>
<td>CH</td>
<td>CH(_2) twist</td>
</tr>
<tr>
<td>1300</td>
<td>m</td>
<td>CH (\omega)</td>
<td>CH(_2) wag/twist ((1305))</td>
</tr>
<tr>
<td>1130</td>
<td>w</td>
<td>NH</td>
<td>NH(_2) twist [61-2]</td>
</tr>
<tr>
<td>1094</td>
<td>m</td>
<td>CN</td>
<td>/ 61-2</td>
</tr>
<tr>
<td>1053</td>
<td>m</td>
<td>CN</td>
<td>NH(_2)-CH(_2)-CH(_2)-NH(_2)</td>
</tr>
<tr>
<td>896</td>
<td>s</td>
<td>CH (r)</td>
<td>/ Irscot</td>
</tr>
<tr>
<td>825</td>
<td>s</td>
<td>CN / CC</td>
<td>/ 61-2</td>
</tr>
</tbody>
</table>

Table 4.12: Assignment for the peaks observed in the transmission infrared spectrum of ethylenediamine
The peaks associated with the primary amine symmetric and asymmetric stretching vibrations occurred at lower wavenumbers than generally expected, however there can be no doubt as to the correct assignment of peaks, since they correlate to the equation proposed by Bellamy and Williams\textsuperscript{115}, where:

\[
v_\text{s} = 345.53 + 0.876 v_\text{as} \quad (\pm 5 \text{ cm}^{-1})
\]

No medium intensity peak at 2815 cm\textsuperscript{-1}, associated with RCH\textsubscript{2}NHR, was observed. The CH\textsubscript{2} peak at 2853 cm\textsuperscript{-1} is rather broad, and as such is probably masking this peak. The vibrations associated with the primary amine are far more intense than the vibrations associated with the secondary amine, and since they occur in the same general region the secondary amine vibrations were not observed. The peak at 1123 cm\textsuperscript{-1} was thought to be combination of NH twisting and CN stretching in secondary amines.

Results were taken from samples coated with 1\% and 0.1\% w/v diethylenetriamine solutions. The 1\% results showed features attributed to reflectance from the top surface and were corrected using the Krammer-Kroenig transformation. Peak positions of the new vibrations and those associated with the nitrogen atom are shown in Table 4.14.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>1% w/v concentration</th>
<th>0.1% w/v concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak</td>
<td>±</td>
</tr>
<tr>
<td>NH \textupsilon\textsubscript{s}</td>
<td>3287</td>
<td>15.1</td>
</tr>
<tr>
<td>new</td>
<td>1636</td>
<td>4.2</td>
</tr>
<tr>
<td>NH \delta</td>
<td>1583</td>
<td>8.4</td>
</tr>
<tr>
<td>new</td>
<td>1150</td>
<td>3.7</td>
</tr>
<tr>
<td>new</td>
<td>1117</td>
<td>0.8</td>
</tr>
<tr>
<td>CN</td>
<td>1057</td>
<td>1.4</td>
</tr>
<tr>
<td>new</td>
<td>1030</td>
<td>0.7</td>
</tr>
<tr>
<td>new</td>
<td>971</td>
<td>3.8</td>
</tr>
<tr>
<td>CN/CC</td>
<td>820</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 4.14: Infrared peak positions of the vibrations associated with the nitrogen atom in the coated series of diethylenetriamine (cm\textsuperscript{-1})
Several changes between the transmission spectrum and the coated samples were observed:

a) The peaks associated with NH stretching in the $3300 \text{ cm}^{-1}$ region appear as one broad peak centred on approximately $3280 \text{ cm}^{-1}$ in the coated series.

b) A new peak at approximately $1636 \text{ cm}^{-1}$ was observed.

c) Additional peaks in the CN stretching region were found at $1117$ and $1030 \text{ cm}^{-1}$.

d) A new peak at $971 \text{ cm}^{-1}$ was observed.

To try to determine if these new peaks were due to the formation of a diethylenetriamine salt near the surface, the chloride salt of diethylenetriamine was prepared. The chloride salt of dipropylamine was also prepared to aid the assignments of the salt peaks. This is shown in Figure 4.33.

![Infrared transmission spectrum of dipropylamine hydrochloride](image)

Figure 4.33: Infrared transmission spectrum of dipropylamine hydrochloride

Dipropylamine hydrochloride shows new peaks at $3392$, $2527$, $2420$, $1591$, $1047$ and $761 \text{ cm}^{-1}$, associated with secondary amine salts.

The infrared spectrum of diethylenetriamine hydrochloride is shown in Figure 4.34, and the peak assignments are presented in Table 4.15.
Chapter 4 : Results/Discussion

Figure 4.34: Transmission infrared spectrum of diethylenetriamine hydrochloride

<table>
<thead>
<tr>
<th>Peak / cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2994</td>
<td>s</td>
<td>NH ν</td>
<td></td>
</tr>
<tr>
<td>1585</td>
<td>m</td>
<td>NH₃ δₛ</td>
<td>in RNH₃⁺</td>
</tr>
<tr>
<td>1562</td>
<td>m</td>
<td>NH₃ δₛ</td>
<td>in RNH₃⁺</td>
</tr>
<tr>
<td>1433</td>
<td>m</td>
<td>NH₃ δ</td>
<td>in RNH₃⁺</td>
</tr>
<tr>
<td>1392</td>
<td>m/w</td>
<td>CN ν</td>
<td>/</td>
</tr>
<tr>
<td>1334</td>
<td>m/w</td>
<td>CN ν</td>
<td>/</td>
</tr>
<tr>
<td>1170</td>
<td>m/w</td>
<td>NH₂ ω</td>
<td>/</td>
</tr>
<tr>
<td>1110</td>
<td>m/w</td>
<td>NH₂ twist</td>
<td>/</td>
</tr>
<tr>
<td>1070</td>
<td>m/w</td>
<td>CN</td>
<td>/</td>
</tr>
<tr>
<td>1023</td>
<td>m</td>
<td>NH₃ r</td>
<td>in RNH₃⁺</td>
</tr>
<tr>
<td>981</td>
<td>m</td>
<td>NH₃ r</td>
<td>in RNH₃⁺</td>
</tr>
<tr>
<td>950</td>
<td>m/w</td>
<td>?</td>
<td>rocking vibration</td>
</tr>
<tr>
<td>753</td>
<td>s</td>
<td>NH</td>
<td>related to a secondary amine salt</td>
</tr>
</tbody>
</table>

Table 4.15: Assignments of the amine related peaks in the transmission infrared spectrum of diethylenetriamine hydrochloride
Chapter 4: Results/Discussion

Diethylenetriamine hydrochloride showed peaks at 1585, 1562 cm\(^{-1}\) (Table 4.15) and a weak shoulder at 1608 cm\(^{-1}\). These were assigned to the anti-symmetric and symmetric bending modes of the primary amine, each one being able to give two peaks due to force field distortion of the \(\text{RNH}_3^+\) group\(^{115}\). Literature\(^{117}\) of the infrared spectrum of ethylenediamine dihydrochloride, showed a peak at 1599 cm\(^{-1}\) and a weak shoulder at 1605 cm\(^{-1}\), assigned to \(\text{NH}_3^+\) asymmetric bend, which probably correspond to the peaks at 1608 and 1585 cm\(^{-1}\) observed here. The peak at 1562 cm\(^{-1}\) probably corresponds to the symmetric bend. The peak for a secondary amine hydrochloride should be observed in the 1591 cm\(^{-1}\) region. However, this would be much less intense than the peak due to the primary amine and as such would be masked. Although the chloride salt showed peaks in the same regions as the new peaks observed in the coated series, it was found that the infrared spectra of metal ethylenediamine complexes also showed these peaks\(^{118,119}\). Hence there appear two possibilities, salt formation between the diethylenetriamine and an appropriate anion, or a chelation between the iron at the surface and the primary amine groups. No evidence was found for any interaction of the secondary amine groups due to the low of intensity of the vibrations.

In diethylenetriamine, the peaks at 1150 and 1117 cm\(^{-1}\) (Table 4.14) are thought to be associated with the peak at 1123 cm\(^{-1}\) (Table 4.13), with the higher one being due to \(\text{NH}_2\) and the lower one associated with skeletal CN. The peaks at 1030 and 971 cm\(^{-1}\) (Table 4.14) were assigned to \(\text{NH}_3^+\) rocking and \(\text{NH}_2\) twisting respectively. The relative intensity of these peaks decreased dramatically from 1 to 0.1% w/v concentration solutions.
4.3.4 Amine: Poly (ethylenimine)

By using poly (ethylenimine) (PEI), see Figure 4.35, it was hoped to demonstrate the interactions between a nitrogen atom within a polymer chain and a steel surface.

\[
-(\text{CH}_2-\text{CH}_2-\text{NH})-
\]

Figure 4.35: The poly (ethylenimine) repeat unit.

The transmission infrared spectrum is shown in Figure 4.36, and assignment of the peaks are given in Table 4.16.
Chapter 4 : Results/Discussion

Table 4.16 : Assignment for peaks observed in the transmission infrared spectrum of poly (ethylenimine)

<table>
<thead>
<tr>
<th>Peak /cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3246</td>
<td>s</td>
<td>NH ν</td>
<td>(3500 to 3300)</td>
</tr>
<tr>
<td>2945</td>
<td>m</td>
<td>CH ν₂</td>
<td>in CH₂ (2926 ± 10)</td>
</tr>
<tr>
<td>2898</td>
<td>m</td>
<td>CH ν</td>
<td>in CH (2853 ± 10)</td>
</tr>
<tr>
<td>2861</td>
<td>s</td>
<td>CH ν₂</td>
<td>in CH₂ (2853 ± 10)</td>
</tr>
<tr>
<td>1644</td>
<td>m</td>
<td>NH δ</td>
<td>(1650 to 1550)¹</td>
</tr>
<tr>
<td>1563</td>
<td>s</td>
<td>NH δ</td>
<td>(1650 to 1550)¹</td>
</tr>
<tr>
<td>1468</td>
<td>s</td>
<td>CH δ'</td>
<td>in CH₂ (1465 ± 20)</td>
</tr>
<tr>
<td>1305</td>
<td>m/s</td>
<td>CH₂ ω</td>
<td>CH₂ wag/twist (1305)</td>
</tr>
<tr>
<td>1102</td>
<td>w/m</td>
<td>CN</td>
<td>CN νas</td>
</tr>
<tr>
<td>1056</td>
<td>w/m</td>
<td>CN</td>
<td>skeletal²⁰</td>
</tr>
</tbody>
</table>

It should be noted that the ethyleneimine monomer showed NH stretching peaks at 3341 cm⁻¹, while poly (ethylenimine) showed these peaks at 3241 cm⁻¹; it was thought that this was due to intramolecular hydrogen bonding in the polymer. The coated series of PEI on steel showed the following new peaks and peaks associated with the nitrogen atom, see Table 4.17.

Table 4.17 : Peak positions of the vibrations associated with the nitrogen atoms and new peaks, in the transmission and reflectance infrared of the PEI coated series

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Peaks /cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH ν</td>
</tr>
<tr>
<td>transmission</td>
<td>3246</td>
</tr>
<tr>
<td>1% w/v</td>
<td>3356</td>
</tr>
<tr>
<td>0.01% w/v</td>
<td>3203</td>
</tr>
<tr>
<td>0.001% w/v</td>
<td>3205</td>
</tr>
</tbody>
</table>

nd : not detected
The transmission spectrum showed peaks at 1644 and 1563 cm$^{-1}$ which were assigned to NH deformation (Figure 4.36, Table 4.16). In the 1% coated series the peaks at 1644 1563 cm$^{-1}$ were shifted to 1657 and 1566 cm$^{-1}$ respectively (Table 4.17) although the peak at 1563 cm$^{-1}$ was reduced to an insignificant weak shoulder, see Figure 4.37.

![Graph showing absorbance vs. wavenumber/cm$^{-1}$ for transmission, 1%, and 0.01% series.](image)

Figure 4.37 : Peaks observed in the transmission infrared spectrum of PEI, and reflection infrared spectra for different concentrations of PEI coated tokens in the 1700 to 1500 cm$^{-1}$ region

A new peak was observed at 1612 cm$^{-1}$ (Table 4.17), which may be assigned to a secondary amine salt. This assignment was supported by the spectrum of dipropylamine hydrochloride shown in Figure 4.34, which has a peak associated with a secondary amine salt at 1591 cm$^{-1}$. This spectrum also shows peaks at 2527 and 2420 cm$^{-1}$ which are combination bands in secondary amine salts. These unfortunately were not observed at any concentration of the coated series or in the literature spectrum of poly (ethylenimine) hydrochloride$^{121}$, as they would provide further evidence for the formation of a salt. The literature spectrum of PEI hydrochloride is shown in Figure 4.38.
In this case no evidence could be found in literature of metal complexes with amines from a polymer backbone. However, it may be postulated that it is also be occurring here since, the chelation effect was probably observed in the case of diethylenetriamine.

![Graph](image)

Figure 4.38: The transmission infrared spectrum of poly(ethylenimine) hydrochloride\(^{121}\).

The transmission infrared spectra of PEI and 1% coated tokens showed two peaks at 1102 and 1056 cm\(^{-1}\), and at 1135 and 1061 cm\(^{-1}\) respectively (see Figure 4.39), which are not detected in the more dilute concentrations. These peaks were assigned to CN stretching.

![Graph](image)

Figure 4.39: Peaks in the 1000 to 1200 cm\(^{-1}\) region from reflectance infrared for the coated series of PEI, with the transmission infrared of PEI included for comparison.
These bands are typically of weak intensity, as would be expected, since less PEI was deposited upon the surface.

The peak at approximately 1060 cm\(^{-1}\), assigned to a CN stretch, is observed for PEI (Figure 4.36), PEI hydrochloride (Figure 4.38) and 1% coated series spectra (Figure 4.39). If it was purely due to vibrations associated with CN stretching then it may be expected to change position if any interactions were to occur with the nitrogen atom. Since it changes very little, this may imply that the vibration was not purely a CN vibration, but may also have some CC characteristics associated with it. The CC vibration in this region would not be expected to greatly change upon an interaction with the amine group.

4.3.5 Ether : Poly (vinyl methyl ether)

Poly (vinyl methyl ether) (Figure 4.40) was used to observe the interactions between an ether group and the steel surface. Figure 4.41 shows the transmission infrared spectra for poly (vinyl methyl ether) (PVME), which agrees to those indicated in literature\(^{122}\). Peak assignments for the transmission spectra are given in Table 4.18.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\vdash_{n} & \\
\text{OCH}_3 & 
\end{align*}
\]

Figure 4.40 : The poly (vinyl methyl ether) repeat unit
Chapter 4: Results/Discussion

Figure 4.41: The transmission infrared spectrum of poly (vinyl methyl ether)

<table>
<thead>
<tr>
<th>Peak /cm$^{-1}$</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2971</td>
<td>s</td>
<td>CH $\nu_a$</td>
<td>in CH$_3$</td>
<td>(2962 ± 10)$^{123}$</td>
</tr>
<tr>
<td>2931</td>
<td>s</td>
<td>CH $\nu_\beta$</td>
<td>in CH$_2$</td>
<td>(2926 ± 10)</td>
</tr>
<tr>
<td>2880</td>
<td>s</td>
<td>CH $\nu_s$</td>
<td>in CH$_3$</td>
<td>(2872 ± 10)</td>
</tr>
<tr>
<td>2819</td>
<td>s</td>
<td>CH $\nu$</td>
<td>in CH$_3$-O</td>
<td>(2815-30)</td>
</tr>
<tr>
<td>1460</td>
<td>m</td>
<td>CH $\delta'$</td>
<td>in CH$_2$</td>
<td>(1465 ± 20)$^{124}$</td>
</tr>
<tr>
<td>1452</td>
<td>m</td>
<td>CH $\delta'$</td>
<td>in CH$_2$</td>
<td>(1465 ± 20)</td>
</tr>
<tr>
<td>1365</td>
<td>m</td>
<td>CO</td>
<td>in COCH$_3$</td>
<td>(1355-60)</td>
</tr>
<tr>
<td>1182</td>
<td>m/s</td>
<td>CH $\gamma$</td>
<td>in CH$_3$</td>
<td>$^{125}$</td>
</tr>
<tr>
<td>1117</td>
<td>m/s</td>
<td>COC</td>
<td>Associated with C-O-C in ethers $^{126}$</td>
<td></td>
</tr>
<tr>
<td>1099</td>
<td>s</td>
<td>COC</td>
<td>Associated with C-O-C in ethers</td>
<td></td>
</tr>
<tr>
<td>1087</td>
<td>s</td>
<td>COC</td>
<td>Associated with C-O-C in ethers</td>
<td></td>
</tr>
<tr>
<td>1010</td>
<td>m</td>
<td>CO</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>790</td>
<td>m/w</td>
<td>CO</td>
<td>in CH$_3$-O</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.18: Assignment for peaks observed in the transmission infrared spectrum of poly (vinyl methyl ether)
Chapter 4: Results/Discussion

Figure 4.42 shows the transmission infrared of PVME and the reflectance infrared of the 1% and 0.1% w/v PVME coated tokens in the 1600 to 700 cm\(^{-1}\) range, and a comparison of the peak positions associated with the ether linkage, is given in Table 4.19.

![Graph showing the transmission infrared spectrum of PVME, and reflectance infrared spectra of 1% and 0.1% w/v PVME coated tokens in the 1600 to 700 cm\(^{-1}\) range.](image)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Peaks /cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(w/v)</td>
<td>CO</td>
</tr>
<tr>
<td>trans.</td>
<td>1365</td>
</tr>
<tr>
<td>1%</td>
<td>1377</td>
</tr>
<tr>
<td>0.1%</td>
<td>1372</td>
</tr>
</tbody>
</table>

Table 4.19: Assignment of peaks associated with the ether linkage, in the transmission and reflection infrared spectra of PVME

Comparing these results for each coating concentration, negligible differences in the spectra were observed (Table 4.19) No differences were observed for the hydrocarbon
4.3.6 Isocyanate: 4,4' diphenyl methylene diisocyanate

4,4' diphenyl methylene diisocyanate (MDI) was chosen to investigate the interactions that may occur between an isocyanate group and a steel surface. The molecules also contain aromatic groups which it was thought could also possibly interact with the steel surface. MDI is also present in the resin system. The structure of the compound is shown in Figure 4.43.

![Structure of 4,4’ diphenyl methylene diisocyanate](image)

Figure 4.43 : Structure of 4,4’ diphenyl methylene diisocyanate

The transmission spectra of MDI (cast from THF) is shown in Figure 4.44. The peaks are assigned in Table 4.20.
Figure 4.44: The transmission infrared spectrum of MDI

Table 4.20: Assignment for the peaks observed in the transmission infrared spectrum of 4,4' diphenyl methylene diisocyanate

<table>
<thead>
<tr>
<th>Peak /cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments (lit. value /cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3035</td>
<td>w</td>
<td>CH ν</td>
<td>aromatic hydrocarbon (3030)</td>
</tr>
<tr>
<td>3018</td>
<td>w</td>
<td>CH ν</td>
<td>aromatic hydrocarbon (3030)</td>
</tr>
<tr>
<td>2295</td>
<td>s /sh</td>
<td>N=C=O</td>
<td>isocyanate stretch</td>
</tr>
<tr>
<td>2273</td>
<td>s</td>
<td>N=C=O</td>
<td>isocyanate stretch (2296 ± 6)</td>
</tr>
<tr>
<td>1608</td>
<td>w</td>
<td>C=C</td>
<td>aromatic stretch (nr 1600)</td>
</tr>
<tr>
<td>1572</td>
<td>w</td>
<td>C=C</td>
<td>aromatic stretch (nr 1580)</td>
</tr>
<tr>
<td>1520</td>
<td>m</td>
<td>C=C</td>
<td>aromatic stretch (nr 1500)</td>
</tr>
<tr>
<td>1104</td>
<td>w</td>
<td>CC</td>
<td>aromatic skeletal</td>
</tr>
<tr>
<td>1016</td>
<td>w</td>
<td>CH δ'_p</td>
<td>aromatic in plane deformation</td>
</tr>
<tr>
<td>833</td>
<td>w</td>
<td>CH δ'_γ</td>
<td>aromatic out of plane deformation</td>
</tr>
</tbody>
</table>
There are two peaks which have been assigned to the isocyanate group at 2273 and 2295 cm\(^{-1}\) (Table 4.20), which is uncommon in isocyanates. The two peaks observed in these studies may be due to the fact that MDI used was a commercial system, and therefore, may contain traces of 2,4'-MDI. This trace component would not be expected to change the spectrum significantly in any other way, since it is very similar to the 4,4 MDI isomer. The weak peak which occurs at 1590 cm\(^{-1}\) is an indication of the presence of an isocyanate group in conjunction with an aromatic ring.

If an interaction were to occur with the steel substrate, it would be expected to occur via the aromatic ring or via the isocyanate group. Examination of the coated series in the region of the isocyanate peaks gave the following results, see Figure 4.45 and Table 4.21:

![Figure 4.45: The two peaks in the isocyanate region from the reflectance infrared spectra of the MDI coated steel tokens.](image-url)
Chapter 4: Results/Discussion

<table>
<thead>
<tr>
<th>Solution</th>
<th>NCO peaks/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>transmission</td>
<td>2277</td>
</tr>
<tr>
<td>1.0 % w/v</td>
<td>2257</td>
</tr>
<tr>
<td>0.1 % w/v</td>
<td>2271</td>
</tr>
<tr>
<td>0.01 % w/v</td>
<td>2273</td>
</tr>
<tr>
<td>0.003 % w/v</td>
<td>2276</td>
</tr>
</tbody>
</table>

Table 4.21: Transmission and reflection infrared spectra peak positions, for the isocyanate group at different concentrations of MDI

The peaks are very consistent and the only anomaly is the peak at 2257 cm⁻¹ for the 1% coated samples, which is 20 wavenumbers lower than the rest. No viable explanation can be given for this shift, since the peaks return to approximately 2271 cm⁻¹, at weaker concentration solutions. Hence it appears that no interaction occurs between the isocyanate groups and the steel surface that can be observed by infrared spectroscopy.

Analysis of the peaks associated with the aromatic ring indicated the following:

<table>
<thead>
<tr>
<th>Solution</th>
<th>C=C Peaks</th>
<th>C-H peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1608</td>
<td>1572</td>
</tr>
<tr>
<td>1.0 % w/v</td>
<td>1604</td>
<td>1574</td>
</tr>
<tr>
<td>0.1 % w/v</td>
<td>1608</td>
<td>1576</td>
</tr>
<tr>
<td>0.01 % w/v</td>
<td>1606</td>
<td>1575</td>
</tr>
<tr>
<td>0.003 % w/v</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

*nd*: not detected

Table 4.22: Transmission and reflection infrared spectra peak positions, for the aromatic group at different concentrations of MDI
Chapter 4: Results/Discussion

In the transmission spectra there are two peaks at 1572 and 1590 cm\(^{-1}\) (Figure 4.44, Table 4.20), in the coated series only one the peak at 1572 cm\(^{-1}\) was observed (Table 4.22). It was thought that the peak at 1590 cm\(^{-1}\) was too weak to be observed, rather than an indication that the isocyanate group was not present, since the isocyanate group was present in all the experiments, as shown in Figure 4.44. There are no other significant differences between the transmission spectrum and the spectra of the coated series, or differences within the coated series.

From this experiment it would appear that under these deposition conditions, no interactions can be detected between either the isocyanate, or the aromatic group and the metal surface. This is rather surprising since it is known that isocyanates are used as primers in the case of, for example, rubber/metal bonding, and hence some form of interaction would be expected. It was also suggested by Watts\(^{31}\) that an aromatic moisture cured urethane probably formed isocyanate-iron hydroxyl bonds with a steel surface. However, the isocyanate used by Watts was a liquid system, and designed to cure in the presence of moisture, whereas the pure 4,4' MDI used in the above experiment was a solid, and not expected to react or cure under the deposition conditions. Since the MDI in the experiment did not pass through a liquid phase i.e. by heating, solid crystalline MDI was probably observed on the steel surface.

It was thought that if the coated samples were heated, i.e. melted and allowed to flow on the steel surface, then an interaction may be observed. Hence, a 0.01% solution in THF was prepared and deposited onto clean tokens; and a clean sodium chloride plate, to produce transmission spectra to act as a comparison. The tokens and plates were heated to 50, 100 or 150°C for 10 minutes, causing the MDI to melt and flow, and hopefully react, in the case of the tokens, with the steel surface. The resulting reflectance and transmission spectra showed very similar features. No change was observed in the position of the peak assigned to the NCO vibration; in reflectance this peak appeared at 2285 cm\(^{-1}\) while in transmission it occurred at 2280 cm\(^{-1}\), Figure 4.46.
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Figure 4.46: The peaks in the isocyanate region from the reflectance infrared spectra of the MDI coated steel tokens exposed to different temperatures.

However, peaks associated with carbonyl stretching and NH deformation were found, and are indicated in Table 4.23.

<table>
<thead>
<tr>
<th>Peak position (cm⁻¹)</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1553</td>
<td>NH δ</td>
<td>amide II (1570 to 1515)</td>
<td></td>
</tr>
<tr>
<td>1597</td>
<td>CO₂⁻ vₚₛ</td>
<td>carboxylic acid salts</td>
<td></td>
</tr>
<tr>
<td>1695</td>
<td>C=O v</td>
<td>isocyanurates/allophanates (reflectance only)</td>
<td></td>
</tr>
<tr>
<td>1714</td>
<td>C=O v</td>
<td>carboxylic acid dimers</td>
<td></td>
</tr>
<tr>
<td>1728</td>
<td>C=O v</td>
<td>carboxylic acid dimers</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.23: Reflection infrared spectra peak positions for the carbonyl and amine groups observed in the MDI spectra
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A peak at 1597 cm\(^{-1}\) was observed, which was assigned to a carboxylic acid salt (Figure 4.47), and it was thought that this was the same peak as observed in the Section 4.3.1, which was assigned to a Fe COO\(^-\).

![Graph showing absorbance vs. wavenumber](image)

Figure 4.47: The peak observed at 1597 cm\(^{-1}\), assigned to a carboxylic acid salt

This peak and the others indicated in Table 4.23 indicate the formation of urethane like structures probably from a reaction of the isocyanate group and water from either the metal surface or the atmosphere. This would produce a compound of the form shown in Figure 4.48

![Proposed structure](image)

Figure 4.48: Proposed structure formed between MDI and either water on the steel surface or the atmosphere

This compound may ionise, resulting in the peak at 1597 cm\(^{-1}\), or dimerise to give the peaks at 1714 and 1728 cm\(^{-1}\). The reflectance spectra also give peaks assigned to isocyanaurates/allophonates which were not observed in the transmission spectra.

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This may imply that the dimerisation/trimerisation reaction is promoted by the presence of the iron or other species present on the surface.

4.3.7 Summary

As a result of studying the interactions between a model polymers or compounds containing a specific functional group, the following observations were made:

- Poly (acrylic acid) shows an interaction between the acid group and an iron from the surface of the steel.
- Poly (vinyl alcohol) becomes less crystalline towards the surface of the steel. This may contribute to a weak boundary layer within the PVA structure.
- In the case of diethylenetriamine there is evidence to suggest either salt formation with an appropriate anion present on the surface, or more likely chelation with an iron atom on the steel surface. For poly (ethylenimine) a new peak was observed, which again, was probably a chelation type reaction, although no evidence from literature could be found to support this.
- Poly (vinyl methyl ether) and 4,4' diphenyl methylene diisocyanate showed no interaction observable by infrared spectroscopy between the functional groups and the steel surface.
- At elevated temperatures, 4,4'-MDI indicated the presence of carboxylic acid salts, carboxylic acid dimers, implying that there has been an interaction between the isocyanate group and most probably the steel surface.
4.4 Adhesion testing

Paint tests are generally qualitative in nature, but the aim here was to try to produce a quantitative test for an electrocoat paint resin. In this section the results of two classes of test will be described and discussed, namely electrochemical methods and mechanical tests.

The electrochemical test employed was a cathodic polarisation method which is performed in industry to determine the resistance of the coating to hydroxyl ions. Panels of different coating thicknesses were scratched and subjected to a cathodic potential, while the amount of delamination after the period of exposure was monitored. Two types of mechanical test were carried out: the butt test and the shim test. The first mechanical test was a standard butt tensile test, which was initially carried out without environmental exposure. However, later environmental exposure was employed to aid failure at the paint resin/steel interface. The second mechanical test employed a coated piece of shim steel which was subjected to mechanical stress. This was a preliminary investigation for a test which would hopefully measure delamination via a capacitance measurement. The majority of electrocoat paint tests carried out at ICI Paints Ltd. utilised a 25 micron paint coat thickness, and as shown in Section 4.4.1 this thickness has been shown to be effective in cathodic polarisation experiments. Hence this was the resin thickness used in this research.

4.4.1 Electrochemical testing

Coatings can be delaminated by the presence of hydroxyl ions, and this phenomenon has been used to evaluate the effectiveness of new coatings. The aim of this experiment was to determine the effect of a set current density upon different thicknesses of coating on a steel panels.
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Several specimens, covering a range of coating thickness, were immersed in 0.1 M sodium sulphate and subjected to a 4mA/m² current density for 50 hours. The results are shown in Figure 4.49 and Table 4.24.

Figure 4.49: Area delaminated vs. coating thickness for exposure to 0.1M sodium sulphate at 4mA/m² for 50 hours

<table>
<thead>
<tr>
<th>Coating thickness (µm)</th>
<th>Area of delamination</th>
<th>Coating thickness (µm)</th>
<th>Area of delamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>132</td>
<td>11</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>45</td>
<td>16</td>
<td>36</td>
</tr>
<tr>
<td>16</td>
<td>36</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>22</td>
<td>23</td>
<td>31</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 4.24: Area of delamination for different thicknesses of coated panel

The 6µm thick coating showed total delamination. It was observed that for values between 20 and 30µm the amount of delamination was roughly consistent. However, below 20µm the amount of delamination increases significantly until total delamination
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occurred. This justifies the coating thickness of 25µm utilised by ICI Paints Ltd. in their experiments. Although based on this data, 20µm thickness is probably sufficient 25µm provides a margin for inconsistencies in a metal surface.

4.4.2 Mechanical - the butt test

A standard butt style test (Section 3.3.7.1) was used, as in theory this method subjects the sample to purely tensile forces. This style of test has been successfully used by E Sheng\textsuperscript{127} to test the adhesion of poly(propene) films where steel butts of 1 inch in diameter were used.

The butt construction shown in Figure 4.50 was initially used.

![Figure 4.50: Initial butt construction](image)

However, this failed to work, owing to the fact that the resin contained methyl isobutyl ketone (MIBK), which produced voids in the resin layer upon curing at 175°C, leading to irreproducible results. MIBK was added to decrease the viscosity of the resin, and proved impossible to remove satisfactorily. However, avoiding its use as a thinner in the resin would have given a coating which was too viscous for practical use. Therefore it was decided that the plaques would be coated and cured, and then another adhesive used to bond the butt assembly together. An epoxy adhesive was chosen as it provided a
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high mechanical strength relatively easily. The adhesive was Araldite Rapid (ex. Ciba-Geigy) and the new assembly is shown in Figure 4.51.

![Diagram](image)

Figure 4.51: Second butt assembly

However, this assembly produced new problems due to the introduction of two more interfaces where the adhesion may fail; i.e. the Araldite/steel interface and the Araldite/resin interface.

This butt construction also failed to produce the desired affects, even after the resin surface of the steel plaque had been thoroughly cleaned and abraded, prior to bonding to the steel butt. Results indicate failure at about 2200N. However, this failure was generally observed at the Araldite/resin and Araldite/steel interfaces, although a little occurred at the resin/steel interface. Failure also occurred at the interface between the non-coated side of the plaque and the butt.

The next sample assembly was based upon the previous experimental test sample, which indicated that there was slight failure regions at the resin/steel interface. It was hoped that failure could be observed between the paint resin and the steel, by using a token coated on both sides, see Figure 4.52.
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However, failure again occurred predominantly at the Araldite/steel and resin interface, although a number of failures were also observed at the resin/steel interface. It was noticed that the resin/steel failure was commonly on the face of the plaque, which had been coated first, i.e. the face which had undergone two cure cycles. Hence, it was concluded that the second cure cycle negatively affects the adhesion of the resin, possibly by some degradative mechanism. In an attempt to increase the strength of the Araldite adhesive, different cure cycles were investigated. The given strengths for different cure programs are shown in Figure 4.53\textsuperscript{128}.

![Figure 4.53: The third butt construction](image)

![Figure 4.53: Adhesive strength for Araldite under different cure cycles](image)
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The temperatures employed in the Araldite cure conditions (Figure 4.53) were all less than the paint resin cure temperature, therefore little damage may be expected to occur to the resin from being exposed to such conditions. Experiments using the different Araldite cure conditions employed a singly coated plaque construction, as shown in Figure 4.51. Since it was shown that a plaque coated on both sides (Figure 4.52) was ineffective. However, in all cases failure occurred at the Araldite/resin and Araldite/steel interfaces. Some failure at the resin/steel interface may have occurred in small isolated regions, however, this proved too irreproducible to be useful.

Under the conditions used in these experiments it was practically impossible to consistently produce failure at the resin/steel interface or cohesively within the resin. Hence a period of environmental exposure was employed where the coated tokens were exposed to an liquid at an elevated temperature. Since all the tests needed to be undertaken within a short period of time after exposure, this ruled out the use of Araldite to bond the assembly together. Therefore in all further tests the assembly was bonded with a Superglue 3 (ex. Loctite) cyanoacrylate adhesive after the cure cycle and environmental exposure.

In the first instance the plaques were exposed to boiling water for 5, 10 and 60 minutes. Similar problems were encountered in that all failed at the resin/cyanoacrylate interface, as opposed to the resin/steel interface. Hence the more corrosive environment of 5M boiling sodium hydroxide was tried. This gave results as indicated in Table 4.25.

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Locus of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 minutes</td>
<td>failure of the resin/cyanoacrylate interface</td>
</tr>
<tr>
<td>5 minutes</td>
<td>desired failure i.e. resin/steel interface</td>
</tr>
<tr>
<td>10 minutes</td>
<td>some resin/cyanoacrylate failure and some resin/steel failure.</td>
</tr>
</tbody>
</table>

Table 4.25: Locus of failure after exposure to boiling 5M sodium hydroxide solution

The experiment indicated that without exposure to sodium hydroxide solution failure occurred in the resin/cyanoacrylate interface around 7000 N, but 5 minutes exposure to sodium hydroxide solution was sufficient to cause failure of the resin/steel interface, at a
force of 350 N. Ten minutes exposure to sodium hydroxide gave a failure load of 310 N, apparently at the resin/cyanoacrylate interface. However, it was thought that the exposure may have affected the surface and top few atomic layers of the paint resin, resulting in low adhesion of the cyanoacrylate adhesive to the resin. This may occur by migration of low molecular weight components, present in the paint resin, forming a weak boundary layer. However, this was not investigated further due to lack of time. Exposure to sodium hydroxide solution was deemed to be too harsh, and a better test was thought to be exposure to a salt spray environment, similar to ASTM 117-95. Electrocoated panels were placed in a salt spray chamber for up to 14 days. After which time they were tested in a butt style test, assembled with superglue. The following table gives a description of the observations from the experiment, Table 4.26.

<table>
<thead>
<tr>
<th>No. of days exposure to salt spray</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Failure occurred at either the superglue/butt or resin/superglue interfaces or within the superglue. (Force = 4524 ± 32N).</td>
</tr>
<tr>
<td>1</td>
<td>Failure occurred at either the superglue/butt or resin/superglue interfaces or within the superglue. (Force = 4495 ± 50N).</td>
</tr>
<tr>
<td>7</td>
<td>Failure occurred at either the superglue/butt or resin/superglue interfaces or within the superglue. Although there are small areas of delamination occurring, about pin head size at blemish points on the coating. (Force = 4200 ± 48N).</td>
</tr>
<tr>
<td>14</td>
<td>Failure occurs between the electrocoat and the steel surface. (Force = 1348 ± 42N).</td>
</tr>
</tbody>
</table>

Table 4.26 : Observations of the failed butt joints after salt spray exposure

4.4.2.1 Surface analysis of the failed butts

The failure of the sample exposed to 5M sodium hydroxide solution for 5 minutes was determined visually, and it was apparent that a layer of polymer had been removed from the plaque. However, it could not be ascertained whether failure was adhesive, i.e. within the resin/steel interface, or cohesive, within the resin. The XPS spectra of
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The butt and plaque side of the assembly are shown in Figures 4.54 and 4.55 respectively, and a percentage composition of the plaque, butt and components used is shown in Table 4.27:

![Figure 4.54: XPS spectrum of the butt side of the failed assembly](image)

![Figure 4.55: XPS spectrum of the plaque side of the failed assembly](image)
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analysis (Atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>carbon</td>
</tr>
<tr>
<td>Butt side of assembly</td>
<td>70.4</td>
</tr>
<tr>
<td>Plaque side of assembly</td>
<td>65.1</td>
</tr>
<tr>
<td>Paint resin</td>
<td>76.3</td>
</tr>
<tr>
<td>Cyanoacrylate</td>
<td>73.1</td>
</tr>
</tbody>
</table>

(<0.2, <1: detection limit)

Table 4.27: XPS results for failed butt joint, resin and cyanoacrylate

These results imply that there is near interfacial failure, as it is apparent that there is some polymer still on the metal plaque side of the assembly. It is not failure due to a weak oxide layer on the steel surface, since there is no iron on the butt side of the assembly. This implies that there is an interfacial region in the resin, between the bulk and the metal surface which is strongly bonded to the steel. There were two other interesting features in these spectra:

1. Tin 3d_{5/2} and 3d_{3/2} peaks in the 485 eV region were observed on the butt side of the assembly and not on the plaque side. They were probably due to the dibutyl tin oxide catalyst, which was used to aid the cure reaction. This may imply that there has been migration of the tin catalyst to the interphase region, which may have formed a weak boundary layer. However, it should be noted that there was no tin observed in the XPS spectra of the resin.

2. The XPS background shape of the plaque side of the assembly showed a characteristic slope in the 700 to 950 eV region, which was indicative of an underlying metallic species.

To try to determine the thickness of this polymer layer, which would then indicate the region of failure, Auger electron spectroscopy (AES) was used too examine the failed interfaces, and the results are shown in Table 4.28.
<table>
<thead>
<tr>
<th>Depth</th>
<th>Elemental analysis (Atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulphur</td>
</tr>
<tr>
<td>0 nm</td>
<td>1.0</td>
</tr>
<tr>
<td>5 nm</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4.28: AES results from the failure surface of the plaque

These results showed that the plaque’s surface contained a higher amount of carbon, nitrogen and oxygen, than would be expected from normal atmospheric deposits. The amount of carbon was indicative of approximately 2 layers of atoms on the surface. The iron was indicative of iron oxide present on the surface in the form of Fe₂O₃. When this surface was etched to a depth of 5 nm, predominately iron oxide, in the form of Fe₂O₃, was observed. This led to the conclusion the failure was near interfacial at the resin/steel interface.

Failure of the butts exposed to a salt spray environment was expected to show a similar result; the XPS results are shown in Figures 4.56 and 4.57, and in Table 4.29.

![XPS spectrum](image)

Figure 4.56: XPS spectrum of the butt side of the failed assembly
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There are a few points to note:

1. The high resolution C1s spectrum of the plaque (Figure 4.58) shows the presence of the peaks nominally associated with CH and C bonded to O. The 4.2 eV gap would suggest the formation of an acid anion.

![](image)

Figure 4.58: High resolution C1s of the metal plaque surface

2. There is no tin on either the plaque or the butt side of the failure, as observed in the sodium hydroxide exposure.

4.4.2.2 Summary

- The resin was found to strongly adhere to a steel substrate, such that no failure could be induced in a standard butt test format without exposure to a corrosive environment. After exposure to boiling sodium hydroxide and a salt spray environment, near interfacial failure was observed at the electrocoat resin/steel interface. This was supported by results obtained using AES and XPS.
- The salt spray high resolution C1s spectrum indicated that there was probably an acid salt type structure present on the metal plaque surface. This may be formed from an isocyanate metal surface interaction, as described in Section 4.3.6.
XPS indicates that after sodium hydroxide exposure migration of the tin catalyst to the interface occurred, this was not observed after salt spray exposure, and as such is probably induced by the exposure to sodium hydroxide.

4.4.3 Mechanical - the shim test

The aim of the research was to develop a test whereby capacitance measurements of a stressed coated steel shim could be made, which could then be related to adhesion of the coating to the substrate. It was believed that the coating should fail before the shim, and that the capacitance should change as the coating delaminated. It was not possible within the scope of this project to fully develop and evaluate this method. However, as a first step, an evaluation of the experimental apparatus, (capable of recording any capacitance changes that may occur during the shim test) was undertaken. The test criteria examined were force to break and extension at break.

As indicated in Section 3.3.7.2, a cell was constructed which enabled the shim to be subjected to a mechanical stress and to be surrounded by an electrolyte to measure capacitance values. The steel shim test pieces were initially tested, annealed and unannealed, to prove that the annealed shim was more ductile, Tables 4.30 and 4.31 respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crosshead speed (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Force (N)</td>
<td>mean s.d.</td>
</tr>
<tr>
<td>annealed</td>
<td>297.0 17</td>
</tr>
<tr>
<td>unannealed</td>
<td>633.1 23.9</td>
</tr>
</tbody>
</table>

*na : data unavailable, s.d. : standard deviation*

Table 4.30 : Force to break of annealed and unannealed shims
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Table 4.31: Extension at break for annealed and unannealed shims.

The annealed steel gave a greater extension than the unannealed steel. Hence, using an annealed shim there should be more potential for the coating to fail before the shim fails. The annealed shims were electrocoated with paint resin, and tested in the cell with a conducting liquid present, although no conductance measurements were taken. The following results (see Table 4.32) were obtained with a crosshead speed of 1 mm/min.

Table 4.32: Affects of coating and the cell upon the force to break and extension of an annealed shim

The cell reduced the extension of an annealed shim, although the value of the force to break was similar to the value obtained without the cell. The cell increased the force to break of a coated shim by 47 N, while the extension was slightly reduced.

Coating the shim caused a reduction in the extension at break and an increase in the force to break. The increase in the force to break may be due to the coating providing
more resistance to the force applied by the tensiometer. However, it was found impossible to cast a thin film of the coating to determine its mechanical properties and to see if this affect could be observed.

There are many possible reasons why the extension at break should decrease. Two were investigated further: hydrogen embrittlement, which may occur during the coating process and the effect of the resin cure parameters, (i.e. 175°C for 20 minutes).

a) Hydrogen embrittlement

Hydrogen is formed during electrolysis, which may be absorbed by the steel and cause embrittlement. The shims were electrolysed at 4mA/m² for 50 hours and gave the following results, see Table 4.33.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Force to break (N)</th>
<th>Extension (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>std. dev.</td>
</tr>
<tr>
<td>shim</td>
<td>297.0</td>
<td>17.0</td>
</tr>
<tr>
<td>treated shim</td>
<td>310.8</td>
<td>18.2</td>
</tr>
</tbody>
</table>

Table 4.33: Force to break and extension of annealed shims with and without exposure to a hydrogen rich environment

The exposure had negligible affect upon the force to break, but the extension was reduced by 22% compared to an untreated shim. Hence, although a reduction in the mean extension of the shim was observed, it was not of the same extent as that observed after the coating procedure, which gave about a 50% reduction (see Table 4.32). It was thought that any hydrogen present in the shim may be driven off by heating, causing the mechanical properties to return almost to the original values. Electrolysis of the shim followed by exposure to heat (i.e. 40°C for 90 hours) gave the following results, shown in Table 4.34.
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<table>
<thead>
<tr>
<th>Sample</th>
<th>Force to break (N)</th>
<th>Extension (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>s.d.</td>
</tr>
<tr>
<td>shim</td>
<td>297.0</td>
<td>17.0</td>
</tr>
<tr>
<td>treated shim</td>
<td>253.8</td>
<td>28.7</td>
</tr>
</tbody>
</table>

Table 4.34: The effect upon force to break and extension of annealed shims after exposure to a hydrogen rich environment, followed by heat.

The mean force to break was lower than for the untreated shim, although the value still remained within the limits of error (11%). The value was lower than found in previous electrolysis experiment (see Table 4.33). The extension value was greatly reduced with respect to both the untreated shim (see Table 4.34) and the electrolysis experiment (see Table 4.33). This may imply that thermal exposure has more of an affect upon the physical properties of the shim than the electrolysis experiments.

b) Thermal exposure

Uncoated annealed shims were exposed to 175°C for 20 minutes, and then tested. The following force to break and extension values were obtained, see Table 4.35.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Force to break (N)</th>
<th>Extension (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>std. dev.</td>
</tr>
<tr>
<td>shim</td>
<td>297.0</td>
<td>17.0</td>
</tr>
<tr>
<td>treated shim</td>
<td>279.9</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Table 4.35: Force to break and extension of uncoated annealed shims with and without exposure to 175°C for 20 minutes.

The heat treatment appears to have negligible affect on the force to break compared to an untreated shim, reducing it by 17 N, which is within the error limits. However, the extension is reduced by approximately 50%, which was significantly lower than the untreated samples. The reduction in the extension is similar, although not as marked as observed in the electrolysis and then heat treatment (Table 4.34).
It does support the argument that the thermal treatment has more effect upon the ductile properties of the shim than any hydrogen embrittlement that may occur during the processing.

4.4.1.1 Summary

• Annealed shims are more ductile than unannealed shims.
• When the shim was coated with paint resin, the extension of the shim was reduced by about half. This was attributed to a thermal affect from the resin cure cycle rather than hydrogen embrittlement from the electrolysis of the painting procedure.
• The effect of the cell was to reduce the extension of both the coated and uncoated shims, which may be due to friction between the cell seals and the metal substrate. Even so no precise explanation for the magnitude of the decrease in the extension value can be given.
• An increase in the force to break of the coated shim may be explained as an additional force associated with the coating attached to the shim. Hence a greater force is required to cause failure of the assembly.

4.5 Thermodynamic work of adhesion

As indicated in Section 2.4 the value for an overall change in the free energy ($\Delta G$) per unit area between a coating and substrate immersed in a liquid, can be calculated from a knowledge of the independent surface excess free energy values ($\gamma$), Equation 2.4.

$$\Delta G = \gamma_{SL} + \gamma_{CL} - \gamma_{SC}$$

Equation 2.4
Where

\[ \gamma_{SL} \] is the specific surface excess free energy of the substrate and the liquid,
\[ \gamma_{CL} \] is the specific surface excess free energy of the coating and the liquid,
\[ \gamma_{SCe} \] is the specific surface excess free energy of the substrate and coating.

If the value for \( \Delta G \) is negative then, assuming that only secondary forces act in adhesion, it may be predicted that the coating will delaminate from the substrate surface.

### 4.5.1 Theoretical calculations of free energy change (\( \Delta G \))

Specific excess surface free energy values for the metal surface can be obtained from literature\textsuperscript{129}. The values used for the steel substrate were for Fe\textsubscript{2}O\textsubscript{3}, which it has been shown is present on the metal surface (Section 4.1.1), and it was thought that based upon the AES results in Section 4.4.2, that the paint resin would be in contact with Fe\textsubscript{2}O\textsubscript{3}. To determine the free energy values for the resin (equation 2.11), contact angle experiments were performed using diiodomethane (DIM) and triple distilled water.

The individual energy components for DIM, water and steel are shown in Table 4.33

<table>
<thead>
<tr>
<th></th>
<th>( \gamma ) (mJ/m\textsuperscript{2})</th>
<th>( \gamma' ) (mJ/m\textsuperscript{2})</th>
<th>( \gamma'' ) (mJ/m\textsuperscript{2})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.6</td>
<td>50.6</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>DIM</td>
<td>50.76</td>
<td>( \equiv 0 )</td>
<td>50.76</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1357</td>
<td>1250</td>
<td>107</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.36: Free energies for water, DIM and Fe\textsubscript{2}O\textsubscript{3}

The experimental contact angles formed with water and DIM on the resin surface are given in Table 4.37.
Table 4.37: Contact angle formed between water and DIM on the resin surface

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Mean (degrees)</th>
<th>Std.dev (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>82.8</td>
<td>1.9</td>
</tr>
<tr>
<td>DIM</td>
<td>35.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Equation 2.11 relates the contact angle to the individual component energies, hence two simultaneous equations can be formed in terms of water and DIM to calculate the energy components for the resin surface.

\[
\gamma_L (1 + \cos \theta) = 2(\gamma_s^d \gamma_L^d)\gamma_s + 2(\gamma_s^p \gamma_L^p)\gamma_s
\]

Equation 2.11

Solving these equations gives the individual component energies for the resin, which are shown in Table 4.38.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_s^p)</td>
<td>2.2</td>
</tr>
<tr>
<td>(\gamma_s^d)</td>
<td>41.6</td>
</tr>
<tr>
<td>(\gamma_s)</td>
<td>43.8</td>
</tr>
</tbody>
</table>

Table 4.38: Specific surface excess free energy values for the resin

The above values can be substituted into Equation 2.10, with the values from Table 4.34 to calculate the free energy between the different phases in the two liquids, i.e. \(\gamma_{SL}, \gamma_{SC}\), etc. (Table 4.39).

\[
\gamma_{SL} = \gamma_s + \gamma_L - 2(\gamma_s^d \gamma_L^d)\gamma_s - 2(\gamma_s^p \gamma_L^p)\gamma_s
\]

Equation 2.10
Table 4.39: The individual specific surface excess free energies of interaction between the resin, steel and liquid of contact, in mJ/m²

<table>
<thead>
<tr>
<th>Component</th>
<th>DIM (mJ/m²)</th>
<th>Water (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ_{CL}</td>
<td>2.7</td>
<td>829.6</td>
</tr>
<tr>
<td>γ_{SL}</td>
<td>1260.4</td>
<td>34.7</td>
</tr>
<tr>
<td>γ_{SC}</td>
<td>1162.5</td>
<td>1162.5</td>
</tr>
</tbody>
</table>

The values can then be substituted into Equation 2.4 to give the overall free energy change (ΔG) for a coated token immersed in the specific liquid. These values are given in Table 4.40.

Table 4.40: Free energy changes for a coated token in water and DIM

<table>
<thead>
<tr>
<th>Solution</th>
<th>ΔG (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>-298</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>100</td>
</tr>
</tbody>
</table>

Hence from this work, it can be concluded that if you immerse a coated token in water the coating should delaminate from the metal surface, however, in DIM the coating should remain on the surface.

4.5.2 Practical applications of theoretical calculations

Results for exposure of coated tokens to water and DIM at room temperature are given in Table 4.41. DIM exposure was carried out in a brown glass vessel in a sealed pot, to prevent the degradation of the DIM.
Chapter 4: Results/Discussion

<table>
<thead>
<tr>
<th>Days</th>
<th>Water/DIM</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>116</td>
<td>water</td>
<td>soft, able to peel off of the surface of the metal</td>
</tr>
<tr>
<td>460</td>
<td>water</td>
<td>soft, able to peel off of the surface of the metal</td>
</tr>
<tr>
<td>685</td>
<td>DIM</td>
<td>soft, can be scratched off</td>
</tr>
</tbody>
</table>

Table 4.41: Results for time exposure to water and DIM

In all cases the polymer remained on the surface of the steel token. The tokens that were exposed to water for 116 days could be peeled off, however, those exposed to DIM could only be removed by scratching using a spatula. According to Owens\(^{54}\), separation of the coating from the substrate will occur spontaneously, if any delamination occurs at all. XPS analysis of a token exposed to water for 460 days gave the following results, Table 4.42

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analysis (Atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>carbon</td>
</tr>
<tr>
<td>Polymer side</td>
<td>66</td>
</tr>
<tr>
<td>Metal side</td>
<td>25.3</td>
</tr>
</tbody>
</table>

/ = <1% : detection limit

Table 4.42: XPS results for the polymer and metal failure interfaces after 460 days in water

It was observed that there was iron on both sides of the failure, which implied that there was probably failure within the metal substrate as opposed to the polymer or at the interface. Hence, even after this period of time, it appears likely that the polymer metal bond is still intact. So, it can be concluded that in this case, no obvious separation had occurred, probably only swelling of the polymer.
4.5.3 Further Contact angle experiments.

Further contact angle measurements were carried out in order to determine the errors associated with the work of adhesion calculation. The liquids used were water, ethylene glycol, dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF). The experiments were carried out using the resin which had been electrocoated onto a piece of mild steel. Contact angle measurements gave the following results, as shown in Table 4.43.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Mean (degrees)</th>
<th>Std.dev. (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>81.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>47.5</td>
<td>1.7</td>
</tr>
<tr>
<td>DMSO</td>
<td>21.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 4.43: Contact angle formed between water, ethylene glycol and DMSO and the electrocoat resin surface

DMF was also used, but reacted upon contact with the electrocoat producing invalid results. The results for water, ethylene glycol and DMSO were entered into a computer programme supplied by Professor J. Comyn (Appendix 6), which was used to calculate the individual surface specific excess free energies for the electrocoat and the overall work of adhesion, including errors. The free energy values for the polymer calculated are given in Table 4.44.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mean value (mJ/m²)</th>
<th>Error (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γₚ</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>γₙ</td>
<td>37.2</td>
<td>0.5</td>
</tr>
<tr>
<td>γₛ</td>
<td>40.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4.44: Specific surface excess free energy values for the resin
Chapter 4: Results/Discussion

An Owens-Wendt plot is also shown with the errors in the measurements included, Figure 4.58.

\[
\frac{1 + \cos \theta}{2} \left( \frac{\gamma_L}{\sqrt{2 \gamma_c}} \right)
\]

\[
\text{Work of adhesion} = -283 \pm 3.4 \text{ mJ/m}^2
\]

This value is similar to that obtained originally as shown in Table 4.40, and again the error is small.

4.5.4 Summary

Theoretical calculations predict, that assuming only secondary forces act in adhesion, if you immerse a coated token in water the coating should delaminate spontaneously
from the metal surface. Experimental evidence indicates that this is not the case. Hence, there must be some other form of interaction occurring, e.g. a primary interaction, mechanical action between the coating and the substrate. It was proposed that the lack of failure of the coating may be because of kinetic parameters as opposed to thermodynamic ones. Kinetically, if water is present at the interface it is possible to displace the polymer molecules, and after a period of time, total saturation will occur and the polymer should be displaced the coating will delaminate. However, a quick examination of Fickian sorption and an attempt to calculate the concentration of the water migration through the coating (based upon a diffusion coefficient of $1.3 \times 10^{-12}$), implied that after 2 years of exposure to water that the interface should be totally saturated. In fact the interface should be saturated after about 30 minutes. Although the interface is saturated no delamination occurred and as such it is unlikely that kinetic factors are affecting the adhesion.

The possible of primary interactions occurring between the resin and the steel surface has been demonstrated using infrared reflectance spectroscopy experiments (Section 4.3). There may also be other interactions occurring due to the elevated temperatures used in the cure process, however because of surface roughness and the complexity of the chemistry involved, no researchers have yet reported that they have been able to directly observe chemical reactions.

4.6 General discussion of results

At the beginning of this thesis (Section 1), three basic questions were posed:

a) How does the electrocoat paint adhere to a clean mild steel substrate?

b) Can a less hazardous alternative to the tin catalyst, employed to aid the cure reactions in the electrocoat resin be used? In particular, what are the criteria used
to determine the effect of catalyst upon the deblocking of a blocked isocyanate and
the subsequent crosslinking reactions?

c) Can a quantitative mechanical test be developed to determine the adhesive strength
of electrocoat paint to a mild steel substrate?

Results presented in Sections 4.0 to 4.5 of this thesis, which seek to answer these
individual questions, are now discussed.

4.6.1 Paint adhesion

To investigate the various adhesion mechanisms by which the electrocoat resin may
bond to a mild steel surface, reflection infrared spectroscopy was used. In order to
identify the interactions attributable to the bulk material, and those which may result
from the electrocoat resin/steel interaction, transmission spectra of uncured and cured
resin were collected. Investigations were carried out upon the uncoated steel surface.
XPS and reflection infrared studies of the steel surface, showed the presence of $\text{Fe}_2\text{O}_3$
and hydroxylated FeO. Transmission infrared analysis of the electrocoat resin showed
that a decrease in the urethane content of the resin occurred after curing. This implied
that there may be some free isocyanate, dimer/trimer or other structure present,
however no evidence for free isocyanate was found. The infrared reflectance spectra
of the electrocoat resin showed the same changes as observed in the transmission
experiments, plus two further differences. A carbonyl peak at 1689 cm$^{-1}$ was
observed, which may be indicative of an allophanate/isocyanurate structure, and a
greater degree of reaction of the secondary hydroxyl function was also observed.
Since these results were obtained from vibrations towards the steel surface this may
imply that different cure reactions occur in this region. It was thought that this was
probably an interphase region, as opposed to an interface, since the spectra had many
similarities to the transmission spectra, which are presumed to representative of the
bulk. Since the resin was very complex, the low levels of surface reaction may be
obscured by the bulk chemistry, and hence model systems containing similar
functional groups as in the electrocoat resin were studied, in order to observe any interaction that may occur between the functional groups and the steel surface. Table 4.45 indicates which model compounds were investigated and gives a summary of the results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Summary of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (acrylic aid)</td>
<td>Poly (acrylic acid) showed an interaction between the acid group and an iron group present in the steel.</td>
</tr>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>Poly (vinyl alcohol) became less crystalline as the spectra approached the surface region. This region may enhance the formation of a weak boundary layer.</td>
</tr>
<tr>
<td>Amines</td>
<td>Diethylenetriamine provided evidence for the formation of either a salt, in the presence of an appropriate anion at the surface, or, more likely chelation with an iron atom from the steel substrate. The spectra for poly (ethylenimine) also implied a chelation type reaction, although no evidence from literature could be found to support this.</td>
</tr>
<tr>
<td>Poly (vinyl methyl ether)</td>
<td>There was no interaction observable by infrared spectroscopy between the functional group and the steel surface.</td>
</tr>
<tr>
<td>4,4' diphenyl methylene diisocyanate</td>
<td>No interaction was observed between the isocyanate or the aromatic groups and the steel surface by infrared spectroscopy, for any concentration of MDI solution. At elevated temperatures there was no change in the position of the isocyanate group. However, new peaks were observed, which were assigned to isocyanurate links, carboxylic acid dimers and carboxylic acid salt peaks as observed with poly (acrylic acid).</td>
</tr>
</tbody>
</table>

Table 4.45 : Model compounds investigated and a summary of the interactions observed for the functional group analysis experiments
The interaction of an acid group with a steel surface is well known and has been reported several times (Section 2.3). Although a change in the intensity of the crystalline peak of poly (vinyl alcohol) has been observed, this has not been previously reported with respect to a steel surface. Iron containing organometallic amine compounds have been reported, however the formation of such compounds in the context of adhesion has not been reported previously. For 4,4' MDI the absence of any evidence of interactions occurring between the isocyanate (NCO) group and the steel surface, even at elevated temperatures was somewhat surprising. However, the formation of carbonyl groups was observed in the elevated temperature experiments, the formation of carbonyl groups; in particular, the formation of a peak at 1597 cm\(^{-1}\), which was assigned to an iron-carboxylic acid salt as shown in figure 4.59. This is the same structure as that observed in the poly (acrylic acid) experiments.

\[
\text{Fe}^{3+} \quad O \quad O
\]

Figure 4.59 : The proposed structure between the steel surface and an acid linkage, formed from an isocyanate

This is possibly the first direct evidence of a chemical reaction in this system. It is similar to the structure tentatively proposed by Watts\(^{31}\) (Figure 4.60) from changes in the iron satellite peaks and C1s, during XPS studies of an isocyanate resin system and a mirrored steel surface.

\[
\text{R,} \quad \text{N} \quad \text{O} \quad \text{Fe} \quad (\text{OH})_x
\]

Figure 4.60 : The structure proposed by Watts, for interactions between an aromatic moisture cured urethane and a steel surface\(^{31}\)
In both cases there has been a reaction between an isocyanate group and either the hydroxylated surface or water vapour in the atmosphere, forming an acid salt. The C1s XPS data Watts reports, appears similar to that indicated in Figure 4.58, and although he assigns the shift to the above structure (Figure 4.60) it could equally be assigned to a CO₂ peak. However in this work, there was infrared evidence to support the structure given in Figure 4.61, which was unavailable to Watts.

Results from thermodynamic experiments (Section 4.5) indicated that some form of chemical interaction was probably occurring between the electrocoat resin and the steel surface which maintained adhesion. The calculated results predicted that immersion of a coated token in water should cause spontaneous delamination of the coating from the steel surface. However, in this case spontaneous delamination was not observed, and in fact, no delamination was observed after 460 days immersion in water, implying that a primary interaction had probably occurred.

It was suggested that kinetics may play a significant part in the adhesion process, as opposed to a primary interaction. Although water is likely to diffuse through the coating to the interface region, it is thought that there is insufficient activation energy to allow the water molecules to displace the polymer molecules and cause failure. This was demonstrated by the fact that after 460 days exposure to water, the coating was still bonded to the steel, i.e. it is probably not limited kinetically.

Therefore, although no chemical interaction between the commercial electrocoat resin and the steel surface was directly observed by infrared spectroscopy, most likely because of the complicated nature of the system, the results of the specific group interactions and thermodynamic experiments implied that such an interaction was probably occurring. These interactions were most likely occurring between acid groups (formed from the reaction of an isocyanate group and water) or amine groups (if they become available at elevated temperatures), since it has been demonstrated that these groups are capable of forming interactions. Taken together these findings provide evidence for chemical interaction in these systems.
4.6.2 Deblocking experiments

The criteria used to determine the effect of catalyst upon the deblocking reactions, were easily observed in differential scanning calorimetry (DSC) thermograms, and in variable temperature infrared results, Section 4.2. They were:

a) The melting point: this was present only in the pure blocked isocyanates, which were solids. The analysis of its position and sharpness gave an indication of the purity of the sample, i.e. had the sample absorbed any contaminants since it was last used? If there was a shift in the position or a dramatic broadening, then the sample was rejected and a new one prepared.

b) The onset temperature: this was taken as the first major exothermic deviation from the baseline. From variable temperature infrared data changes associated with deblocking were observed in the region of the temperature at which an exothermic deviation from the baseline in the DSC thermogram occurred.

c) The first minimum peak: this was the minimum peak after the onset of deblocking had occurred, and was thought to be the temperature at which the majority of the deblocking reaction has occurred. This remains unproven, since in the case of the pure blocked isocyanates, the MDI probably degraded soon after deblocking had occurred.

Based upon the above criteria, DSC experiments carried out using the industrial resin and crosslinker gave no information about the effect of the catalyst upon any deblocking reaction that may have been occurring, and indicated only a gradual exotherm which is probably indicative of overall cure. Literature indicated that in all previously known cases, investigations had been carried out using pure blocked isocyanates. Hence, in this case two pure alcohol blocked isocyanates were tested. Two recommended bismuth based catalysts, Bicat A and Bicat Z, were compared to dibutyl tin oxide (DBTO) catalyst which is currently in use. However, although Bicat A and Bicat Z showed similar effects to DBTO at specific catalyst concentrations, neither of them displayed the same overall trends with both blocked isocyanates. Bicat Z gave a reduced onset temperature in both blocked isocyanates, however, this
is not necessarily desirable, since the reduced onset temperature may affect other mechanical properties and the overall adhesion to the steel.

### 4.6.3 Quantitative testing

Two main experiments were carried out in order to provide the basis for the development of a quantitative test for the electrocoat resin adhesion: a butt style test (Section 4.4.2) and preliminary investigations into a shim experiment (Section 4.4.3).

Cathodic polarisation experiments indicated that a coating thickness of 25 μm was satisfactory to maintain the integrity of the paint coating under cathodic conditions, and hence this thickness was used in all subsequent adhesions tests. This coating thickness is the same as used by ICI Paints Ltd. Various butt style assembly types were used to test the electrocoat resin. However, in all cases it was found that the resin strongly adhered to the steel substrate, and no failure at the electrocoat resin/steel interface was observed. Never the less, after exposure to a corrosive environment near interfacial failure was observed in the vicinity of the electrocoat resin/steel interface, which was confirmed using XPS and AES. XPS also indicated that the metal surface contained an acid salt group, which was probably formed from a reaction between an isocyanate group and the steel substrate (Section 4.6.1). Hence, the XPS data provides further evidence that there is a reaction between the iron and the isocyanate at the interface. Since after salt spray exposure, the steel plaques surface showed no nitrogen, it can be proposed that failure in this region occurs between the nitrogen and the acid carbonyl

In the preliminary investigations into the development of a shim testing method to evaluate electrocoat resin adhesion, it was found that annealed shims were more ductile than unannealed shims, and when the shim was coated with electrocoat resin, the extension of the shim was reduced by approximately half. This was attributed to a thermal effect from the resin cure cycle, rather than hydrogen embrittlement produced during electrolysis of the coating procedure. The effect of the conductance test assembly (the cell) was to reduce the extension of both the coated and uncoated shims.

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Chapter 4 : Results/Discussion

This effect may be due to friction between the cell seals and the steel substrate. Even so, to provide a definite explanation for the magnitude of the decrease in the extension further investigation needs to be carried out. The observed increase in the force to break of the coated shim in the cell, may be due to an additional force, associated with the coating attached to the shim, resulting in a greater force being required to cause failure of the assembly.

In this experiment no real conclusion could be drawn, with respect to adhesion of the electrocoat resin to the steel substrate and further work needs to be completed, including some conductance measurements upon the system. These values may indicate whether it is plausible to continue using a dynamic test, i.e. one where there is a dynamic load applied to the shim, or whether it is better to use a static load.
5.0 Conclusions

This thesis shows the benefits of using a combination of methods including FTIR, DSC, surface energy calculations, XPS etc. and model compounds, to try and reconstruct and identify key factors affecting the behaviour of a complex commercial resin system. In this case, model compounds have been used to show interactions which may occur between different functional groups and the steel surface, and model crosslinkers (blocked isocyanates) to show the effect of catalyst upon the deblocking reaction, before the subsequent crosslinking reaction.

Also from the results presented in this thesis several more specific conclusions can be made:

There is evidence for the formation of an iron carboxylic acid salt structure between the electrocoat resin and the steel surface. It was found that this type of structure may be formed from a reaction of 4,4' diphenyl methylene diisocyanate (upon heating) or
poly (acrylic acid), and the steel surface. Infrared analysis of the resin indicated that there was probably a reduction in the urethane groups in the electrocoat resin/metal interphase region, at it was thought that some of the urethanes have reacted to form free isocyanate, which has then reacted with the metal surface. Infrared spectra of the interphase region provided evidence for the formation of allophanate/isocyanurate and probably greater reaction of the secondary hydroxyl group with a free isocyanate group. Thermodynamic experiments indicate that a primary interactions were probably formed between the electrocoat resin and steel surface during the cure process.

Further investigations into other specific functional groups and a real (i.e. rough) steel surface indicated that there was probably a chelation type of interaction between an amine group and an iron atom present on a steel surface, and that poly (vinyl alcohol) changes in crystallinity as the steel surfaces approaches. No interaction was observed between poly (vinyl methyl ether) and the steel surface. It is believed that the interactions between the amines and the steel substrate and the interaction between poly (vinyl alcohol) and the steel substrate have not been previously reported.

A quantitative value for interfacial adhesive failure between the electrocoat resin and a steel surface can be obtained after five minutes exposure to boiling aqueous sodium hydroxide solution (5 molar), or 14 days salt spray. XPS data indicated that near interfacial failure had occurred, and that there was a thin layer of polymer left on the metal surface. This layer was characteristic of an acid containing species.

Differential scanning calorimetry and variable temperature infrared spectroscopy, can be used to monitor the deblocking of the pure, alcohol blocked isocyanate compounds synthesised in this programme. However, the techniques were unable to monitor the deblocking reaction in the industrial crosslinker system. It was found that the first exothermic deviation from the baseline was a good indication of the onset temperature, and that there was no infrared evidence to support the theory that the majority of the deblocking reaction had occurred by the first minimum point.

Neither of the bismuth organo-metallic catalysts, Bicat A and Bicat Z were able to mimic the effects of DBTO, in the deblocking of two pure blocked isocyanates, although Bicat A and Bicat Z gave similar effects to dibutyl tin oxide catalyst for
specific catalyst concentrations. Bicat Z gave a reduced onset temperature in both blocked isocyanates, which is not necessarily desirable, since the reduced onset temperature may affect other mechanical properties and overall adhesion to the steel.
Further work

The following areas for further study have been identified by this work.

a) To find a catalyst which will mimic DBTO with blocked isocyanates, and then hopefully cure the electrocoat resin system satisfactorily. Perhaps this testing should be expanded to include some mechanical testing, to determine the effect of the catalyst upon the final mechanical properties of the coating.

b) To study different functional groups on different metal surfaces, e.g. aluminium, galvanised steel etc. and surfaces with different degrees of surface roughness. If a smooth surface was studied then it should be possible to coat the surface with a monolayer of the polymer in question. It would also be interesting to study the effect of applying these groups at a raised temperature, since this may mimic the conditions of a curing/cured resin more precisely.

c) To further develop the shim test. Specifically to determine if failure of the coating can be detected by capacitance measurements, and to see if it produces any reproducible results at different loadings and/or for different periods of time.
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Appendix 1.0 gives the spectral data to support the proposed structures of the blocked isocyanates, that were synthesised according to procedures indicated in Section 3.1.3. The blocked isocyanates were used for studies into the effect of catalyst upon the deblocking temperatures.
NMR spectroscopy

Figure A1.2: The hydrogen NMR spectra for B11
### Table A1.2: Assignments of the peaks in the hydrogen NMR spectra of BII

<table>
<thead>
<tr>
<th>ppm</th>
<th>multiplicity</th>
<th>integral</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>2</td>
<td>4</td>
<td>aromatic H</td>
</tr>
<tr>
<td>7.1</td>
<td>1</td>
<td>4</td>
<td>aromatic H</td>
</tr>
<tr>
<td>7.0</td>
<td>2</td>
<td>2</td>
<td>NH</td>
</tr>
<tr>
<td>4.3</td>
<td>4</td>
<td>2</td>
<td>?</td>
</tr>
<tr>
<td>3.9</td>
<td>1</td>
<td>2</td>
<td>Ar-CH₂</td>
</tr>
<tr>
<td>3.8</td>
<td>?</td>
<td>4</td>
<td>?</td>
</tr>
<tr>
<td>3.7</td>
<td>4</td>
<td>4</td>
<td>CH₂-CH₂</td>
</tr>
<tr>
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<td>5</td>
<td>4</td>
<td>?</td>
</tr>
<tr>
<td>1.5</td>
<td>?</td>
<td>4</td>
<td>CH₂-C₃H₇</td>
</tr>
<tr>
<td>1.3</td>
<td>?</td>
<td>4</td>
<td>CH₂-C₂H₅</td>
</tr>
<tr>
<td>1.1</td>
<td>?</td>
<td>4</td>
<td>CH₂</td>
</tr>
<tr>
<td>0.9</td>
<td>?</td>
<td>6</td>
<td>CH₃</td>
</tr>
</tbody>
</table>

Figure A1.3: Mass spectrum of BII
Summary

The infrared spectra shows peaks which are assigned to urethane functionalities at 1730, 1710 and 1535 cm\(^{-1}\). The spectra also indicates a NH stretch at 3311 cm\(^{-1}\), these peaks were not present in the spectra of the starting materials. There is no indication of either a NCO peak at 2250 cm\(^{-1}\) or peaks associated with alcohols.

The NMR indicates a NH peak at 7.0 ppm which was not present in the starting materials.

The mass spectrum shows peaks at 250 and 163 m/z. These are indicative of the starting materials, and it was thought that the compound spontaneously broke into its starting materials at the beginning of the experiment, since the same sample gave a peak associated with NH in the NMR spectra.

Hence it is thought that the structure is that indicated in Figure A1.4.

A1.4 : The proposed structure of BII
Appendix 1.0

Blocked isocyanate 2 (BI2)

Infrared analysis

Figure A1.5: Infrared transmission spectra for BI2

<table>
<thead>
<tr>
<th>Peak /cm$^{-1}$</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Comments</th>
<th>(lit. value /cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3331</td>
<td>m</td>
<td>NH ν</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1705</td>
<td>s</td>
<td>C=O ν</td>
<td>urethane amide I</td>
<td></td>
</tr>
<tr>
<td>1599</td>
<td>m</td>
<td>C=C ν</td>
<td>aromatic skeletal</td>
<td></td>
</tr>
<tr>
<td>1531</td>
<td>s</td>
<td>NH δ'</td>
<td>amide II</td>
<td></td>
</tr>
<tr>
<td>1433</td>
<td>m</td>
<td>CH δ</td>
<td>in CH$_3$-O</td>
<td></td>
</tr>
<tr>
<td>1411</td>
<td>m</td>
<td>C=C ν</td>
<td>aromatic skeletal</td>
<td></td>
</tr>
<tr>
<td>1313</td>
<td>m</td>
<td>NH δ'</td>
<td>amide II</td>
<td></td>
</tr>
<tr>
<td>1236</td>
<td>s</td>
<td>CO ν</td>
<td>in O=C-O</td>
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<td>819</td>
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<td>aliphatic ether</td>
<td></td>
</tr>
<tr>
<td>785</td>
<td>w</td>
<td>COC</td>
<td>aliphatic ether</td>
<td></td>
</tr>
</tbody>
</table>

Table A1.3: Assignment of the peaks observed in the infrared spectra of BI2
Figure A1.6: The hydrogen NMR spectra of Bi2
Table A1.4: Assignments of the peaks in the hydrogen NMR spectra of BI2

<table>
<thead>
<tr>
<th>ppm</th>
<th>multiplicity</th>
<th>integral</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.7</td>
<td>1</td>
<td>1</td>
<td>aromatic H</td>
</tr>
<tr>
<td>6.8</td>
<td>2</td>
<td>2</td>
<td>aromatic H</td>
</tr>
<tr>
<td>6.5</td>
<td>2</td>
<td>2</td>
<td>NH</td>
</tr>
<tr>
<td>3.25</td>
<td>1</td>
<td>3</td>
<td>either CH₂ or CH₃</td>
</tr>
<tr>
<td>2.4</td>
<td>1</td>
<td>2</td>
<td>either CH₂ or CH₃</td>
</tr>
</tbody>
</table>

Summary

Infrared spectra shows peaks assigned to NH stretching and amide I and II deformations, which are found in urethane linkages. No evidence of the starting material was found.

NMR indicates a peak at 8.7 ppm which can be assigned to NH.

The mass spectrum shows a peak at 314 m/z which is the mass of the proposed structure. It also indicates a peak at 282 m/z which would be due to the loss of one methanol group and a peak at 250 m/z which is MDI, i.e. loss of two methanol groups.
Hence it is thought that the structure is that indicated in Figure A1.8.

A1.8: The proposed structure of BI2.
Appendix 2.0 gives the nomenclature used in the infrared analysis experiments and tables.
Symbols for intensity

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>strong</td>
</tr>
<tr>
<td>m</td>
<td>medium</td>
</tr>
<tr>
<td>w</td>
<td>weak</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
</tbody>
</table>

A combination may be used e.g. m/w to indicate a medium weak peak.

Symbols for vibrations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν</td>
<td>stretch</td>
</tr>
<tr>
<td>δ'</td>
<td>deformation (bend, twist or rock)</td>
</tr>
<tr>
<td>δ</td>
<td>bend</td>
</tr>
<tr>
<td>ω</td>
<td>wag</td>
</tr>
<tr>
<td>γ</td>
<td>out of plane</td>
</tr>
<tr>
<td>β</td>
<td>in plane</td>
</tr>
<tr>
<td>as</td>
<td>asymmetric</td>
</tr>
<tr>
<td>s</td>
<td>symmetric</td>
</tr>
</tbody>
</table>
Appendix 3.0 gives the results of the cleaning experiments conducted in sodium hydroxide, Section 3.4.1.
Introduction

The metal substrate used in this work, was supplied covered in preservatives and cutting oils. Hence, in order to produce clean steel substrates for use, a cleaning procedure was required. It was decided that a commercial cleaner may leave traces of various agents on the substrate surface, and therefore, pure sodium hydroxide was used.

Infrared spectroscopy was used to investigate that amount of hydrocarbon on the surface after different periods of cleaning.

Method

Tokens (1 x ½ inches) were cleaned in sodium hydroxide (5% w/v) at 25, 40 and 60°C for between 30 and 300 seconds, and then washed according to the following sequence:

1 minute distilled water
2 minutes distilled water
2 minutes distilled water

The samples were then analysed using infrared spectroscopy to determine the amount of hydrocarbon present, and the results are shown in Table A3.1. A peak associated with hydrocarbon asymmetric stretch at 2952-72 cm$^{-1}$ (assigned to the oily contaminates on the substrate surface) was ratioed to a peak associated with Fe$_2$O$_3$ at 885 cm$^{-1}$. This gave an indication of the amount of hydrocarbon left on the steel surface after each cleaning period.

After exposure to the washing procedure, SEM images and EDAX analysis failed to detect any sodium hydroxide on the surface of the steel token.

All cleaning and washing was carried out in an ultrasonic bath.
Results

The ratioed amount of hydrocarbon is shown in Table A3.1, and Figure A3.1

<table>
<thead>
<tr>
<th>Cleaning time</th>
<th>Cleaning temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>0s</td>
<td>7.26</td>
</tr>
<tr>
<td>30s</td>
<td>2.53</td>
</tr>
<tr>
<td>60s</td>
<td>2.15</td>
</tr>
<tr>
<td>180s</td>
<td>1.65</td>
</tr>
<tr>
<td>300s</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Table A3.1: Ratioed hydrocarbon results of the cleaning experiments

Figure A3.1: Graph to indicate normalised hydrocarbon results
Conclusions
The 60 °C cleaning temperature showed the best results, and it was decided that a 60 second clean would be adequate for our purposes, as further cleaning time only altered the hydrocarbon level slightly.
Appendix 4.0 gives tables of experimental data collected during the deblocking experiments of BI1.

The parameters indicated in the tables are:

- **mpt**: melting point
- **onset**: the onset of the deviation from the baseline, taken as the onset of deblocking.
- **peak**: The first minimum peak after the onset point.
### Differential Scanning Calorimetry data

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>39.96</td>
<td>204</td>
<td>279.02</td>
</tr>
<tr>
<td>11</td>
<td>39.17</td>
<td>197</td>
<td>259</td>
</tr>
<tr>
<td>15</td>
<td>38.50</td>
<td>192</td>
<td>270</td>
</tr>
<tr>
<td>19</td>
<td>39.46</td>
<td>201</td>
<td>264</td>
</tr>
<tr>
<td>20</td>
<td>39.42</td>
<td>209</td>
<td>271.92</td>
</tr>
<tr>
<td>mean</td>
<td>39.30</td>
<td>200</td>
<td>268</td>
</tr>
<tr>
<td>±</td>
<td>0.48</td>
<td>5.8</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Table A4.1: Uncatalysed results

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>41.29</td>
<td>204.11</td>
<td>221.03</td>
</tr>
<tr>
<td>47</td>
<td>42.49</td>
<td>201.34</td>
<td>225.89</td>
</tr>
<tr>
<td>48</td>
<td>41.46</td>
<td>197.99</td>
<td>229.71 (x)</td>
</tr>
<tr>
<td>90</td>
<td>38.39</td>
<td>219.69</td>
<td>240.98</td>
</tr>
<tr>
<td>mean</td>
<td>41.07</td>
<td>205.78</td>
<td>229.3</td>
</tr>
<tr>
<td>±</td>
<td>1.58</td>
<td>8.3</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table A4.2: 1% DBTO catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>41.84</td>
<td>199.82</td>
<td>224.65</td>
</tr>
<tr>
<td>50</td>
<td>41.85</td>
<td>193.12</td>
<td>216.72</td>
</tr>
<tr>
<td>51</td>
<td>40.61</td>
<td>207.01</td>
<td>228.61</td>
</tr>
<tr>
<td>mean</td>
<td>41.28</td>
<td>199.98</td>
<td>223.00</td>
</tr>
<tr>
<td>±</td>
<td>7.61</td>
<td>5.67</td>
<td>5.39</td>
</tr>
</tbody>
</table>

Table A4.3: 5% DBTO catalyst
### Table A4.4: 10% DBTO catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>41.80</td>
<td>144.6</td>
<td>157.4</td>
</tr>
<tr>
<td>53</td>
<td>42.33</td>
<td>152.3</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>42.07</td>
<td>140.4</td>
<td>166.3</td>
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<td>59</td>
<td>41.88</td>
<td>132</td>
<td>169.6</td>
</tr>
<tr>
<td>82</td>
<td>41.59</td>
<td>132</td>
<td>172</td>
</tr>
<tr>
<td>104</td>
<td>42.24</td>
<td>135</td>
<td>162</td>
</tr>
<tr>
<td>mean</td>
<td>42.07</td>
<td>136</td>
<td>163.3</td>
</tr>
<tr>
<td>±</td>
<td>0.31</td>
<td>4.9</td>
<td>6.8</td>
</tr>
</tbody>
</table>

### Table A4.5: 1% Bicat A catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>36.54</td>
<td>212.72</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>35.91</td>
<td>194</td>
<td>260.84</td>
</tr>
<tr>
<td>102</td>
<td>36.50</td>
<td>209</td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>36.40</td>
<td>207.6</td>
<td>286.5</td>
</tr>
<tr>
<td>110</td>
<td>36.40</td>
<td>213.4</td>
<td>272.10</td>
</tr>
<tr>
<td>111</td>
<td>36.20</td>
<td>204</td>
<td>266.88</td>
</tr>
<tr>
<td>mean</td>
<td>36.34</td>
<td>206.79</td>
<td>271.57</td>
</tr>
<tr>
<td>±</td>
<td>0.25</td>
<td>6.53</td>
<td>9.49</td>
</tr>
</tbody>
</table>

### Table A4.6: 10% Bicat A catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>38.84</td>
<td>189</td>
<td>280.94</td>
</tr>
<tr>
<td>97</td>
<td>38.38</td>
<td>199</td>
<td>273</td>
</tr>
<tr>
<td>98</td>
<td>38.61</td>
<td>194</td>
<td>265</td>
</tr>
<tr>
<td>mean</td>
<td>38.61</td>
<td>194</td>
<td>272.9</td>
</tr>
<tr>
<td>±</td>
<td>0.19</td>
<td>4.10</td>
<td>6.5</td>
</tr>
</tbody>
</table>

183
### Table A4.7: 1% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>37.81</td>
<td>173.57</td>
<td>217.30</td>
</tr>
<tr>
<td>131</td>
<td>37.34</td>
<td>165.49</td>
<td>214.96</td>
</tr>
<tr>
<td>133</td>
<td>37.95</td>
<td>160</td>
<td>219.21</td>
</tr>
<tr>
<td>mean</td>
<td>37.70</td>
<td>166.35</td>
<td>217.16</td>
</tr>
<tr>
<td>±</td>
<td>0.26</td>
<td>5.57</td>
<td>1.74</td>
</tr>
</tbody>
</table>

### Table A4.8: 5% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>123</td>
<td>39.22</td>
<td>171</td>
<td>232.07</td>
</tr>
<tr>
<td>124</td>
<td>38.40</td>
<td>163</td>
<td>211.33</td>
</tr>
<tr>
<td>127</td>
<td></td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>129</td>
<td>39.33</td>
<td>176.4</td>
<td>222.23</td>
</tr>
<tr>
<td>mean</td>
<td>38.98</td>
<td>171.35</td>
<td>221.87</td>
</tr>
<tr>
<td>±</td>
<td>0.41</td>
<td>5.21</td>
<td>8.47</td>
</tr>
</tbody>
</table>

### Table A4.9: 10% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>38.02</td>
<td>167</td>
<td>212</td>
</tr>
<tr>
<td>122</td>
<td>38.46</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>36.91</td>
<td>154.6</td>
<td>215.32</td>
</tr>
<tr>
<td>126</td>
<td>37.92</td>
<td>168</td>
<td>213</td>
</tr>
<tr>
<td>128</td>
<td>38.43</td>
<td>170.4</td>
<td>221.32</td>
</tr>
<tr>
<td>mean</td>
<td>37.95</td>
<td>170.4</td>
<td>215.6</td>
</tr>
<tr>
<td>±</td>
<td>.56</td>
<td>12.12</td>
<td>3.62</td>
</tr>
</tbody>
</table>
Variable temperature infrared

The temperatures at which there was an initial decrease in the urethane intensity are shown in Table A4.10.

<table>
<thead>
<tr>
<th>Catalyst concentration (%w/w)</th>
<th>DBTO catalyst</th>
<th>Bicat A catalyst</th>
<th>Bicat Z catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>207</td>
<td>207</td>
<td>207</td>
</tr>
<tr>
<td>1</td>
<td>201</td>
<td>/</td>
<td>174</td>
</tr>
<tr>
<td>5</td>
<td>193</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>10</td>
<td>192</td>
<td>198</td>
<td>175</td>
</tr>
</tbody>
</table>

Table A4.10: Temperature at which there was an initial decrease in urethane intensity (°C).
Appendix 5.0 gives tables of experimental data collected during the deblocking experiments of BI2.

The parameters indicated in the tables are:

- **mpt** melting point
- **onset** the onset of the deviation from the baseline, taken as the onset of deblocking.
- **peak** The first minimum peak after the onset point.
### Appendix 5.0

**Differential Scanning Calorimetry data**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>185.96</td>
<td>244.8237</td>
<td>262.39+</td>
</tr>
<tr>
<td>13</td>
<td>187.06</td>
<td>229.73</td>
<td>270.63</td>
</tr>
<tr>
<td>14</td>
<td>186.64</td>
<td>237</td>
<td>249.35</td>
</tr>
<tr>
<td>16</td>
<td>187.12</td>
<td>243</td>
<td>256</td>
</tr>
<tr>
<td>32</td>
<td>187.04</td>
<td>258</td>
<td>264</td>
</tr>
<tr>
<td>33</td>
<td>187.04</td>
<td>259</td>
<td>266</td>
</tr>
<tr>
<td>mean</td>
<td>186.7</td>
<td>245.3</td>
<td>261.3</td>
</tr>
<tr>
<td>±</td>
<td>0.61</td>
<td>10.53</td>
<td>6.79</td>
</tr>
</tbody>
</table>

Table A5.1: Uncatalysed results

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>183.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>183.53</td>
<td>231.79</td>
<td>247.98</td>
</tr>
<tr>
<td>41</td>
<td>183.67</td>
<td>220.36</td>
<td>241.07</td>
</tr>
<tr>
<td>42</td>
<td>184.31</td>
<td>226.43</td>
<td>242.46</td>
</tr>
<tr>
<td>mean</td>
<td>183.67</td>
<td>226.19</td>
<td>241.74</td>
</tr>
<tr>
<td>±</td>
<td>0.47</td>
<td>4.6</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Table A5.2: 1% DBTO catalyst
### Appendix 5.0

#### Table A5.3: 5% DBTO catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>180.80</td>
<td>218.13</td>
<td>249.37</td>
</tr>
<tr>
<td>44</td>
<td>182.75</td>
<td>221.79</td>
<td>236.07</td>
</tr>
<tr>
<td>45</td>
<td>182.29</td>
<td>218.75</td>
<td>241.68</td>
</tr>
<tr>
<td><strong>mean</strong></td>
<td>181.95</td>
<td><strong>219.56</strong></td>
<td>242.37</td>
</tr>
<tr>
<td><strong>±</strong></td>
<td>0.83</td>
<td><strong>1.60</strong></td>
<td><strong>5.45</strong></td>
</tr>
</tbody>
</table>

#### Table A5.4: 10% DBTO catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>182.2</td>
<td>225.2</td>
<td>235.6</td>
</tr>
<tr>
<td>35</td>
<td>180.9</td>
<td>222.4</td>
<td>242.71</td>
</tr>
<tr>
<td>36</td>
<td>181.64</td>
<td>222.6</td>
<td>227.4</td>
</tr>
<tr>
<td>37</td>
<td>182.48</td>
<td>213.62</td>
<td>227.88</td>
</tr>
<tr>
<td><strong>mean</strong></td>
<td>181.08</td>
<td><strong>220.9</strong></td>
<td><strong>233.4</strong></td>
</tr>
<tr>
<td><strong>±</strong></td>
<td>0.6</td>
<td><strong>4.37</strong></td>
<td><strong>6.3</strong></td>
</tr>
</tbody>
</table>

#### Table A5.5: 1% Bicat A catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>183.89</td>
<td>232.20</td>
<td>234.13</td>
</tr>
<tr>
<td>65</td>
<td>184.37</td>
<td>218.91</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>182.94</td>
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<td></td>
</tr>
<tr>
<td>85</td>
<td>183.63</td>
<td>239.6</td>
<td></td>
</tr>
<tr>
<td><strong>mean</strong></td>
<td>183.73</td>
<td><strong>230.7</strong></td>
<td>234.13</td>
</tr>
<tr>
<td><strong>±</strong></td>
<td>0.52</td>
<td><strong>7.33</strong></td>
<td></td>
</tr>
</tbody>
</table>
### Table A5.6: 5% Bicat A catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>183.99</td>
<td>195.8</td>
<td>224.78</td>
</tr>
<tr>
<td>61</td>
<td>182.42</td>
<td>230.67</td>
<td>211.52</td>
</tr>
<tr>
<td>62</td>
<td>182.47</td>
<td>236</td>
<td>211.74</td>
</tr>
<tr>
<td>63</td>
<td>183.12</td>
<td>196</td>
<td>222.95</td>
</tr>
<tr>
<td>86</td>
<td>184.36</td>
<td>234.53</td>
<td>/</td>
</tr>
<tr>
<td>mean</td>
<td>183.00</td>
<td>214.62</td>
<td>217.75</td>
</tr>
<tr>
<td>±</td>
<td>0.63</td>
<td>18.81</td>
<td>6.15</td>
</tr>
</tbody>
</table>

### Table A5.7: 10% Bicat A catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>181.75</td>
<td>213</td>
<td>222.99</td>
</tr>
<tr>
<td>57</td>
<td>181.15</td>
<td>195</td>
<td>202</td>
</tr>
<tr>
<td>92</td>
<td>181.64</td>
<td>199</td>
<td>210.94</td>
</tr>
<tr>
<td>93</td>
<td>182.85</td>
<td>196</td>
<td>223.21</td>
</tr>
<tr>
<td>mean</td>
<td>181.85</td>
<td>200.75</td>
<td>214.75</td>
</tr>
<tr>
<td>±</td>
<td>0.65</td>
<td>7.22</td>
<td>8.90</td>
</tr>
</tbody>
</table>

### Table A5.8: 1% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>185.80</td>
<td>207.86</td>
<td>231.83</td>
</tr>
<tr>
<td>88</td>
<td>185.67</td>
<td>208.53</td>
<td>229.55</td>
</tr>
<tr>
<td>91</td>
<td>185.69</td>
<td>209.70</td>
<td>234.42</td>
</tr>
<tr>
<td>mean</td>
<td>188.48</td>
<td>208.81</td>
<td>231.93</td>
</tr>
<tr>
<td>±</td>
<td>0.06</td>
<td>0.76</td>
<td>1.99</td>
</tr>
</tbody>
</table>
### Table A5.9: 5% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>185.70</td>
<td>209</td>
<td>221.65</td>
</tr>
<tr>
<td>77</td>
<td>186.53</td>
<td>212</td>
<td>229.50</td>
</tr>
<tr>
<td>78</td>
<td>186.32</td>
<td>204</td>
<td>227.77</td>
</tr>
<tr>
<td>mean</td>
<td>186.09</td>
<td>208.33</td>
<td>226.31</td>
</tr>
<tr>
<td>±</td>
<td>0.28</td>
<td>3.30</td>
<td>3.37</td>
</tr>
</tbody>
</table>

### Table A5.10: 10% Bicat Z catalyst

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>mpt</th>
<th>onset</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>185.37</td>
<td>204</td>
<td>217.4</td>
</tr>
<tr>
<td>68</td>
<td>186.33</td>
<td>205</td>
<td>222.97</td>
</tr>
<tr>
<td>69</td>
<td>185.49</td>
<td>202</td>
<td>219.66</td>
</tr>
<tr>
<td>72</td>
<td>185.33</td>
<td>198</td>
<td>221.43</td>
</tr>
<tr>
<td>73</td>
<td>185.78</td>
<td>199</td>
<td>218.94</td>
</tr>
<tr>
<td>mean</td>
<td>185.63</td>
<td>201.6</td>
<td>220.09</td>
</tr>
<tr>
<td>±</td>
<td>0.34</td>
<td>2.73</td>
<td>4.94</td>
</tr>
</tbody>
</table>
Variable temperature infrared

<table>
<thead>
<tr>
<th>Catalyst concentration (% w/w)</th>
<th>DBTO catalyst</th>
<th>Bicat A catalyst</th>
<th>Bicat Z catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>238</td>
<td>238</td>
<td>238</td>
</tr>
<tr>
<td>1</td>
<td>215</td>
<td>220</td>
<td>207</td>
</tr>
<tr>
<td>5</td>
<td>209</td>
<td>204</td>
<td>202</td>
</tr>
<tr>
<td>10</td>
<td>209</td>
<td>196</td>
<td>/</td>
</tr>
</tbody>
</table>

Table A5.11: Temperature at which there was an initial decrease in urethane intensity (°C).
Appendix 6.0 gives copies of the computer programme supplied by Professor J Comyn used to calculate the surface specific excess free energies and the work of adhesion for the electrocoat/steel system.
Programme to determine the surface energy parameters with error, from contact angles with water, ethylene diol, and DMSO.

REM "name of file theta3a"
REM "calculates surface energy parameter with errors, from contact angles with water, ed, dmso. with print"
INPUT "Contact angle DMSO"; C2
INPUT "Contact angle ED"; C3
INPUT "contact angle water"; C4
Y2 = 3.68 * (1 + COS(.01745 * C2))
Y3 = 4.461 * (1 + COS(.01745 * C3))
Y4 = 7.796 * (1 + COS(.01745 * C4))
SYX = .499 * Y2 + .805 * Y3 + 1.529 * Y4
SY = Y2 + Y3 + Y4
A = (3 * SYX - 2.833 * SY) / 1.678
B = (3.234 * SY - 2.833 * SYX) / 1.678
GP = A * A
GD = B * B
D2 = A * .499 + B - Y2
D3 = A * .805 + B - Y3
D4 = A * 1.529 + B - Y4
W = (D2 * D3 + D3 * D3 + D4 * D4) / 2
DA = SQR(1.264 * W)
DB = SQR(1.069 * W)
DGD = 2 * B * DB
DGP = 2 * A * DA
G = GP + GD
DG = SQR(DGP * DGP + DGD * DGD)
PRINT "SLOPE A="; A
PRINT "INTERCEPT B="; B
PRINT "POLAR COMPONENT GP ="; GP
PRINT "DISPERISVE COMPONENT = ", GD
PRINT "DA ="; DA
PRINT "DB ="; DB
PRINT "ERROR IN POLAR COMPONENT ="; DGP
PRINT "ERROR IN DISPERSIVE COMPONENT ="; DGD
PRINT "Y2 ="; Y2
PRINT "Y3 ="; Y3
PRINT "Y4 ="; Y4
PRINT "SURFACE ENERGY ="; G
PRINT "ERROR IN SURFACE ENERGY"; DG

Programme to calculate the "Work of Adhesion" in the dry and wet environments, with errors.

REM "file name WORKAD, calculates work of adhesion, dry and in water, with errors.
INPUT "Dispersive component of adhesive"; DA
INPUT "Polar component of adhesive"; PA
INPUT "Error in DA"; DDA
INPUT "Error in PA"; DPA
INPUT "Dispersive component of substrate"; DS
INPUT "Polar component of substrate"; PS
INPUT "Error in DS"; DDS
INPUT "Error in PS"; DPS
DW = 21.8
PW = 51
WD = 2 * SQR(DS * DA) + 2 * SQR(PS * PA)
J = DS / DA * DDA ^ 2
K = DA / DS * DDS ^ 2
L = PS / PA * DPA ^ 2
M = PA / PS * DPS ^ 2
DWD = SQR(J + K + L + M)
N = DW / DA * DDA^2
P = PW / PA * DPA^2
Q = DW / DS * DDS^2
R = PW / PS * DPS^2
DWW = SQR(J + K + L + M + N + P + Q + R)
WW = 2 * (DW + PW - SQR(DA * DW) - SQR(PA * PW) - SQR(DS * DW) - SQR(PS * PW) + SQR(DA * DS) + SQR(PA * PS))
PRINT "Work of adhesion in dry = "; WD; "\+/-\"; DWD
PRINT "Work of adhesion in wet = "; WW; "\+/-\"; DWW