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Fundamental Studies of Polyurethane – Aluminum Adhesion: Phenyl Isocyanate Interaction with Prepared Aluminum Oxide Surfaces

by

Lisa A. Pokrajac

A thesis submitted in conformity with the requirements for the degree of Master of Science Graduate Department of Chemistry University of Toronto

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ABSTRACT

Carbamate bond formation has been postulated as one of the key mechanisms in polyurethane – aluminum adhesion. Reactions between phenyl isocyanate (PIC) and aluminum foils after three different surface treatments (room temperature air exposure, boiling water, and boiling water followed by drying) were studied as a model system for polyurethane – aluminum interactions. These oxides were analysed for surface hydroxyl concentration using XPS and SEM. PIC vapour was dosed on the surfaces, at a constant pressure, with varying exposure times. The adlayers were analysed using XPS, ER FTIR and TPD MS.

The Boiled sample had the highest surface hydroxyl and water content, and adsorbed the most organic material upon PIC dosing. The MS, ER FTIR and XPS analyses showed the surface adsorbate in all cases was 1,3-diphenyl urea. The bonding of the adlayer was sufficiently strong to promote adhesion.
to my family,

the Poker-jacks of all trades
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1.0 INTRODUCTION

Adhesion n. maintenance of contact; unnatural union of surfaces

This dictionary definition of *adhesion* describes a very simple concept: the joining of two materials that otherwise would not be found together, over an explicit period of time. This joining may be deliberate and beneficial: a rubber sole is glued to the bottom of a shoe. But often adhesion is accidental and unwanted: chewing gum previously on the floor is now stuck to the bottom of the same shoe. In either case, the adhesive properties of a material are of great interest to scientists, engineers, and anybody who wants, or who does not want, two things joined together.

In order to research, design or engineer a better adhesive, or conversely to discourage adhesive properties, it is necessary to have a fundamental understanding of how adhesives work. Many theories exist attempting to explain adhesion, but to date there still remains no one universally accepted mechanism. Each adhesive has specific sticking properties, whereas each adherend, the material to which a second is adhered, has surface features and chemistry that are unique to it.

There are a multitude adhesive-adherend systems, and it is quite probable that each has its own characteristic adhesion mechanism. One such system of great interest is the polyurethane foam - aluminum metal system.
1.1 Objectives

The polyurethane - aluminum system is an interesting area of study, yet the adhesion mechanism is not currently known.\(^{23}\) It may be a result of mechanical interactions, electrostatic interactions, covalent bond formation, or a combination of the three.\(^{24}\) Given the reactivity of isocyanate and the high hydroxyl concentration on an aluminum surface, it is possible that a carbamate bond is formed.

The objective of this thesis will be to use phenyl isocyanate (PIC) as a model compound to study the possibility of carbamate bond formation. Three aluminum oxide samples were prepared \textit{ex-situ} with varied surface hydroxyl concentrations. They included a surface with a saturation coverage of hydroxyls and water, a surface with a high coverage of hydroxyls with surface water removed, and a surface with an adventitious oxide layer. Once prepared, these surfaces were dosed \textit{ex-situ} with a controlled amount of PIC vapour. Analysis for carbamate bond formation was then carried out using three complimentary analytical techniques: External Reflectance Fourier Transform Infra Red Spectrometry (ER FTIR) for carbamate functional group detection; X-ray Photoelectron Spectroscopy for chemical shifts and elemental composition analysis; and Temperature Programmed Desorption – Mass Spectrometry (TPD MS) for desorption bond-energy analysis and quantification of carbamate molecules formed.

1.2 Practical Importance of Polyurethane - Aluminum Adhesion

There are many varieties of polyurethanes, including thermoplastic elastomers and durable coatings, yet the most common and well-known polyurethanes take the form of flexible and rigid foams. With an optimised combination of starting materials, these foams can be tailor made for specific solvent resilience, low temperature flexibility, and high load bearing capacity. As such, flexible foams have found various uses as cushioning, bedding and carpet underpads, while rigid foams are often used as appliance insulation.\(^{56}\)
All polyurethanes, whether they are foams, thermoplastic elastomers or durable coatings, are produced in a similar manner. However, foams differ from the other forms as a result of a gas-forming reaction that allows the polymer to expand to many times its original volume with the formation of open cells. This gives the foam its characteristic texture. Foams take their shape via two processes. The first method involves the formation of slabstock foams, where the foam “buns” are cured in air, which can then be cut into a variety of shapes with the desired dimensions. The second method exploits the foam’s ability to expand and fill a container to yield a pre-formed product ready for commercial use. In this case, the starting materials are injected into aluminium moulds where the polymerisation and curing takes place. The moulds are then opened and the foam products are (easily) removed.

In practice, however, polyurethane foam manufacturers have encountered problems with the foam adhering to the aluminium mouldings. This adhesion proves very costly to the manufacturer since time must be spent removing the foam debris and cleaning the moulds with solvent (creating specific environmental concerns), and the cost of the materials spent for unusable foam is not recoverable. Although certain surface pretreatments such as waxy anti-adhesion sprays are currently being used to prevent this occurrence, the moulds must be constantly cleaned, the coating must be periodically re-applied, and the procedure is still time consuming. Clearly, there is a need for more effective adhesion prevention.

In theory, the most efficient method of polyurethane adhesion prevention must focus at the molecular level, where the actual adhesion occurs. However, the mechanism of polyurethane adhesion to aluminum is not known, and the key to a better understanding lies with the fundamental chemistry of polyurethane-aluminum interactions. It is thus necessary to investigate the reaction of the polyurethane at the aluminum surface.
1.3 Types of Adhesion

As mentioned earlier, there is no single mechanism that governs all adhesive systems, including one that involves polymer-metal interactions. However, considerable studies have been conducted since the 1930's to explain this phenomenon, and numerous theories have been postulated. Of these theories, three have been accepted as reasonable adhesion mechanisms: mechanical interlocking, electrostatic interactions, and chemical bonding.24

1.3.1 Mechanical Interlocking

This is the oldest adhesion theory, and it has been formulated predominately through empirical and observational methods.3 One observation was that gluing was more successful on rough rather than smooth surfaces.24 Through more recent analyses it was found that glue’s adhesion was a result of a liquid polymer flowing into the pores, wetting the surface and other superficial features on the surface. Wetting is a term that describes the polymer’s ability to cover the surface and irregularities of the topography, and the success depends largely on the viscosity of the polymer. The lower its viscosity, the better its ability to flow into the nooks and crannies of the surface. Low molecular weight polymers and oligomers usually have lower viscosity and are known to have the best wettability. Once the liquid is applied to the adherend, it penetrates the pores, and after curing, the polymer is well locked into place.

The adhesion of polymers on anodised aluminum has been studied by Fourche et al.3 They found that the oxide formed by anodic oxidation is composed of a network of hexagonal cells, each having one pore located directly in the centre. When a liquid adhesive is placed on this oxide, the pores are quickly filled by means of capillarity, thus securing the polymer:

![Diagram of adhesive liquid filling pores](image-url)
This mechanism is virtually physical by nature, and can be simply described as the adsorption of the adhesive to a substrate.

1.3.2 Chemical Bonding

This encompasses all of the chemical bonding forces acting within any chemical system. (This type of adhesion occurs when the adhesive reacts with the substrate in such a way that electrons are shared, or a new chemical bond is formed.) Adhesion in this case is described in terms of van der Waals forces, London (dipole-dipole interactions) forces, hydrogen bonding, and covalent bonding.\(^4\)

Table 1.3.1: Comparative Bond Energies

<table>
<thead>
<tr>
<th>Type of Bond</th>
<th>Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>70-700</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10-50</td>
</tr>
<tr>
<td>London</td>
<td>10-20</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>0-10</td>
</tr>
</tbody>
</table>

Adhesion by chemical bonding is found to take place rather frequently in the case of polymer-metal interfaces. For instance, the deposition of polyimide on an aluminum surface results in an organometallic complex: C-O-Al.\(^3\) The chemical bonds are formed at this interface as a result of a charge transfer from the aluminum to the polyimide:

![Chemical bond diagram](image-url)
Of these forces, the covalent bond has the largest bond energy, ranging from 70 to 700 kJ mol\(^{-1}\). It is difficult however, to observe these bonds in their indigenous state, since only a very small fraction of the molecules at the interface take part in the chemical interaction.\(^3\) The strength of the adhesion may be increased by other forms of chemical bonding acting on the cured polymer at the interface. The polymer may have many polar functional groups at the surface that can participate in hydrogen, London and van der Waals bonding to various active points on the metal surface. From this, it is reasoned that the adhesion due to the formation of a covalent bond at the interface will be very strong.

1.3.3 Electrostatic Attraction

This mechanism was theorised with the observation of static electricity. In dry conditions, two substances that were joined often emitted light after their separation. This suggested the presence of electrical forces between the two materials.

In this theory, it is proposed that a double layer develops when two materials of differing nature are brought in contact with each other. As soon as the bi-layer is formed, the opposing electrical charges keep the two materials joined. For polymers and metals, the adhesive-substrate system is analogous to that of a capacitor whose plates consist of an electrical bi-layer. For this adhesion mechanism, both surfaces play an active role in the formation of the electrical interface and thus the adhesive process, which is unlike the mechanical interaction theory.

The mechanics for this form of adhesion are not easily identified. For instance, the electrostatic double layer must be broken in order to be analysed. In addition to this, the electrostatic forces may be confused for electron acceptor-donor interactions, such as the case with chemical systems. For the most part, this theory is seldomly used to explain adhesion.
Although no one knows how adhesion truly works, it is agreed that adhesion is an interfacial phenomenon. This is the one aspect that is similar to all three theories. It is apparent that the adhesion process is a complex one.

1.4 Polyurethane Chemistry

Polyurethanes are a class of materials that contain the urethane linkage

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{C} \\
\text{O}
\end{array}
\]

whose formation is an important step in urethane polymerisation. Since the urethane linkage is usually formed with the reaction of an isocyanate and a compound containing an active hydroxyl group, the chemistry of polyurethanes is often spoken in terms of isocyanate chemistry. Isocyanates are compounds with one or more isocyanate groups

\[
-N=\text{C}=O
\]

Its reactivity can be seen by the resonance structures:

\[
\begin{array}{c}
R-\stackrel{\ominus}{\text{N}}-\text{C}=\text{O} \\
\end{array} \quad \begin{array}{c}
R-N=\text{C}=O \\
\end{array} \quad \begin{array}{c}
R-\stackrel{\oplus}{\text{N}}-\text{C}=O
\end{array}
\]

as it has the highest electron density at the oxygen atom giving it the largest net negative charge. With the nitrogen having an intermediate charge, and the carbon a positive charge, an electrophilic centre about the carbon-nitrogen double bond is formed. This group will react with hydrogen atoms that are attached to atoms more electronegative than carbon, such as the hydroxyl from an alcohol. In this case a nucleophilic attack from the hydroxyl is possible:

\[
R-N=\text{C}=O + R'-\text{CH}_2-\text{OH} \rightarrow R-\stackrel{\ominus}{\text{N}}-\text{C}=\underset{\ominus}{\text{O}}-\text{CH}_2-R
\]
Here, the urethane is made by an addition reaction: the N-C double bond breaks, the active hydrogen adds to the nitrogen, and the negative alkoxide adds to the positive C=O. The isocyanate reactivity is increased with certain electron-withdrawing groups adjacent to it. Hence, aromatic isocyanates such as TDI and MDI are much more reactive than the aliphatic counterparts.

1.4.1 Isocyanate Reactions

The isocyanate can also react with water to give carbamic acid, which is thermally unstable, and decomposes to give an amine and carbon dioxide:

\[
\text{isocyanate} + \text{water} \rightarrow \text{carbamic acid} \\
R-N=C=O + H-O-H \rightarrow R-N-C=O \text{ (carbamic acid)} \\
\text{heat} \\
R'\text{-NH}_2 + \text{CO}_2 \\
\text{amine} \quad \text{carbon dioxide}
\]

Free isocyanate and an amine can yield a disubstituted urea:

\[
\text{isocyanate} + \text{amine} \rightarrow \text{disubstituted urea} \\
R-N=C=O + R'\text{-NH}_2 \rightarrow R-N-C-N-R \\
\text{disubstituted urea}
\]

A disubstituted urea and a free isocyanate can form a biuret:

\[
\text{isocyanate} + \text{disubstituted urea} \rightarrow \text{biuret} \\
R-N=C=O + R'\text{-N-C-N-R}'' \rightarrow R-N-C-N-R' \\
\text{biuret}
\]
1.4.2 Polymerisation and Foaming

To form a polymer, the reaction must include poly-functional starting materials. To form polyurethane, a di- or polyisocyanate must react with an alcohol or a polyol. To form a foam, the bubbles must be introduced through the polyurethane and expanded. This is often done simultaneously as the isocyanate and water, already present in solution, form aniline and carbon dioxide during a competing reaction. The CO₂ diffuses through the medium, and the polymer then expands to form a foam. If water is inherent in the reaction, so too are aniline, urea and biuret, all of which are present in the final polyurethane product. This is the case for many commercially prepared foams.⁵⁶

To manufacture moulded foams, a mixture of polyol, catalysts and other ingredients is added to one container while the isocyanate is carefully measured in a separate one. The two solutions are added to a third container and vigorously mixed for the desired cream time.

Table 1.4.1: Constituents of Polyurethane Foams

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>100</td>
</tr>
<tr>
<td>Inorganic Filler</td>
<td>0 – 150</td>
</tr>
<tr>
<td>Water</td>
<td>1.5 – 5.5</td>
</tr>
<tr>
<td>Si Surfactant</td>
<td>0.5 – 2.5</td>
</tr>
<tr>
<td>Anime Catalyst</td>
<td>0.1 – 1.0</td>
</tr>
<tr>
<td>Tin Catalyst</td>
<td>0 – 0.5</td>
</tr>
<tr>
<td>Additives</td>
<td>Variable</td>
</tr>
<tr>
<td>Auxiliary Blowing Agent</td>
<td>0 – 35</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>25 – 27</td>
</tr>
</tbody>
</table>

The mixture is either allowed to form in air as slabstock foam, or poured into a mould, often aluminum. As mentioned earlier, polyurethane foam adheres readily to the Al moulds, and a pre-applied mould release reagent is necessary to enable removal of the finished product.
1.5 Aluminum Metal and Its Oxides

Aluminum is a very lightweight and abundant metal, that enjoys a wide range of applications. Its appearance is a dullish, silver-white, which is due to the oxide that is formed immediately when the clean surface is exposed to air. This oxide is thought to be responsible for aluminum resistance to corrosion to external agents, increasing its popularity even further.

Aluminum oxides in powder form are very popular industrial materials as they can have high surface areas, excellent thermal resistance, and strong chemical reactivities which make them popular for many catalytic applications. There are many forms of aluminum oxide, or alumina, in which the form of the alumina depends on the level of hydration. This ranges from the hydroxides known as gibbsite, bayerite and nordstrandite, to the oxy-hydroxides such as boehmite and pseudoboehmite, to the oxide known as corundum. These oxides are known as transitional oxides since the hydroxides and the oxy-hydroxides can change with heat and pressure to other forms of alumina.

Generally speaking, the surface of any alumina is a complex mixture of Al, O, and OH ions that can combine to give both Bronsted and Lewis acid-base activity. As a Bronsted acid, a vacant \( \text{Al}^{3+} \) site can abstract a water molecule to give \( \text{AlOH} \), then lose a proton to yield a negatively charge \( \text{O}^- \) site:

\[
\text{Al}^{3+} + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{AlOH} \quad \rightarrow \quad \text{AlO}^- + \quad \text{H}^+
\]

As a Bronsted base, a negative \( \text{AlO}^- \) site can accept a proton to give \( \text{AlOH} \):

\[
\text{AlO}^- + \quad \text{H}^+ \quad \rightarrow \quad \text{AlOH}
\]
As a Lewis acid, the $\text{Al}^{3+}$ site abstracts electrons from one of the lone electron pairs from the oxygen contained in the water molecule:

$$\text{AlOH} \rightarrow \text{OH} \rightarrow \text{Al}^+$$

Thus, it can be clearly seen that the alumina surface is very active in acid-base chemistry. The abundance of Bronsted acid sites, Lewis base sites, and surface hydroxyl groups, renders the alumina surface very hydrophilic.$^9$-$^{13}$

1.5.1 Reaction of Aluminum and Water

Bulk oxide powders are easily characterised by X-ray Diffraction (XRD), Infra Red (IR) and Nuclear Magnetic Resonance (NMR) techniques.$^{14}$ However, these techniques cannot easily characterise the metal-oxide surface explicitly as bayerite, boehmite or corundum, due to the relatively low surface area and thickness of only 14 to 20 Å.$^{15,16}$ Surface analytical techniques, such a valence electron spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy (AES) have been used to find the elemental composition of the polycrystalline oxides. Here, asymmetric peak shapes and careful fitting of the O1s peaks have been used to distinguish between Al-O and the OH surface groups.$^7,8,14,17,18-21$

Placing aluminum metal in boiling water creates a new surface. During this time, there is an induction period, or a certain amount of time is necessary for water to diffuse through the primary oxide. As the outer surface begins to hydrolyse, it can either dissolve in solution or precipitate back onto the surface as a porous oxide. The structure and composition of the oxide films formed depends on the reaction temperature. Between 20 and 90C a layer of pseudoboehmite is adjacent to the metal, and bayerite is in contact with the water; from 90 to 100C the adherent layer of pseudoboehmite is saturated with physically adsorbed water; and from 100 to 375C, the entire surface becomes covered with pure boehmite. Evidence for the dissociation of water and incorporation of oxygen atoms on the surface occurs with the evolution of hydrogen gas bubbling through the solution.$^{22}$ IR stretching frequencies of 3280 - 3090 cm$^{-1}$ documents what is actually formed on the surface as a metastable
aluminum hydroxide.\textsuperscript{23} Also, the AlOH nucleates and grows easily in sheets at single (010) layers much like that of the boehmite structure. At the hydroxide - water interface, the layer looks much like a random pile of loosely connected platelets of varying thickness and pore dimensions.\textsuperscript{24} Thus, the aluminum metal submersed in boiling water reaction topographically changes the surface to become porous, while the chemical structure becomes an oxy-hydroxide – hydroxide mix. The hydroxyl concentration on the surface is clearly related to the amount of water adsorbed to the surface and relative humidity of the atmosphere. These hydroxyl groups are stable to an annealing temperature above 700 K.\textsuperscript{25}

1.6 Polyurethane - Metal Adhesion Studies

The study of polymer adhesion is by no means a new area. Numerous investigations have been conducted on a macro-scale level to find adhesive joint failure and relative peel strengths on different substrates,\textsuperscript{26} the effects of time and weathering,\textsuperscript{27} and the durability of bonding after vigorous physical-mechanical endurance tests.\textsuperscript{28,29}

1.6.1 Surface Analytical Techniques

On the molecular level, several surface techniques have been employed to analyse the adhesion process at the polymer-metal interface. XPS and IR have been of great utility for providing information for thin film characterisation,\textsuperscript{30-32,45} whereas SEM has been advantageous in providing visual images of surface and bulk morphology.\textsuperscript{27,30,33,45}

1.6.1.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy can determine the elemental composition of the outermost atomic layers of a sample. A sample is bombarded with soft X-rays, most commonly MgK\(\alpha\) (1253.6 eV) and AlK\(\alpha\) (1486.6 eV), which then emits photoelectrons that can be analysed in terms of their binding energies. The kinetic energy (KE) of emitted photoelectrons is given by
\[ KE = h\nu - BE - \phi \]

where \( h\nu \) = energy of the irradiating photon

\( BE \) = binding energy of the electron to the atomic nucleus, and

\( \phi \) = spectrometer work function.

Analysis of the binding energies not only provides elemental information and compositions, but the chemical state of the element can also be determined by means of the changes in chemical shifts.\textsuperscript{34}

XPS has been extensively applied to both Al hydration studies\textsuperscript{14,17,18,23,24} and polyurethane surface analysis.\textsuperscript{34-40} For Al surfaces, XPS is beneficial in the determination of the chemical binding states: the Al\textsuperscript{0} valence state appears as a peak at approximately 72.5 eV, and the Al\textsuperscript{3+} state appears at around 75 eV; and the O 1s peak can be deconvoluted to OH at 532 eV, whereas the corresponding O\textsuperscript{2-} valence state occurs at 530 eV.\textsuperscript{14,17-19} The major constituents of polyurethane foams are oxygen, nitrogen, and carbon. The chemical environments for oxygen and nitrogen are easily identified in these foams, as C=O at 532 eV and N-C at 400 eV. The C 1s peak can be deconvolved as C-C and C-H at 284.5 eV, C-N at 286.5 eV, C-O at 287.9 eV, and C=O at 289.4 eV.\textsuperscript{35-40}

Many studies have used XPS to study the metal-polymer interface to develop improved adhesion technology. To identify the chemical bonds prevailing at the polyurethane-aluminum interface, XPS has been useful in characterising carbide-like species.\textsuperscript{41} In a study where Al was vapour deposited onto polyimide, the chemical shifts in the O 1s and Al 2p photoelectrons were used to determine Al-O-C formation; the chemical bond formation between the polyimide and aluminum surface.\textsuperscript{42} In this study, Al 2p peaks were monitored at different Al coverages. At low coverages, the Al peak exhibited a binding energy at 75.5 eV, whereas at high Al coverages, the peak appeared at 72.5 eV. The 3 eV chemical shift to higher binding energy tells that the Al electrons are bound more tightly due to the Al-O-C formation. The O 1s, C 1s and N 1s spectra do not exhibit such profound chemical shifts with the change in coverage. Other studies, such as polyethylene, polypropylene, and polyacrylic acid coated with aluminum, have shown similar results.\textsuperscript{43,44}
1.6.1.2 External Reflectance Fourier Transform Infrared Spectroscopy (ER FTIR)

Infrared spectroscopy (IR) is a well-established means of molecular identification. Through the vibrational frequencies, functional groups can be characterised, and the variations in the IR frequencies can be used to discriminate between the same functional groups found in different chemical environments.\textsuperscript{46,47}

IR has been used to quantify and detect interactions between adsorbents and adsorbates. Adsorbent and surface reactions on various oxides that have been monitored by IR include benzaldehyde, benzoic acid, formic acid, and acetic acid on Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{48,49} In these cases, the technique was used to identify the adsorbed species.

1.6.2 Temperature Programmed Desorption Mass Spectrometry (TPD MS)

TPD MS is a popular analytical technique in the field of surface chemistry.\textsuperscript{50-56} A vapour is adsorbed on to a surface, and the reaction products are monitored as the sample is heated. TPD has been extensively used to characterise the energetics and surface stoichiometry for adsorbates on clean metal surfaces. The technique can reveal bond energies, and the reaction order may be deduced from desorption kinetics. Desorption trace-analysis of different initial coverages can tell if the desorption is disassociative or associative. In addition to this, provided the vacuum system volume and pumping speed have been measured, TPD can provide a quantitative measure of the amount of adsorbate present on the surface.\textsuperscript{55}

In a typical experiment, the dosed sample is contained in an ultra-high vacuum (UHV) chamber and linearly heated. The desorbed material can be detected with mass spectrometry while the change in temperature is monitored simultaneously with a small thermocouple mounted on the sample holder.\textsuperscript{56} As the temperature increases, the surface material can desorb and often decompose. As the temperature ramp continues, the rate of material desorption increases, and it eventually reaches a maximum, then drops to zero once all the surface material is desorbed. The resulting data is a plot of gas concentration as a function of temperature:
The data from an experiment often takes this form.

\[ \text{\textbf{1.6.2.1 Adsorption of Gases on Solids}} \]

When a vapour is exposed to a solid surface, two forms of adsorption can occur. If the vapour simply condenses on the surface and is held by weak van der Waals forces, it is considered to be \textit{physisorbed} on the surface. However, if the gaseous material and the surface undergo a chemical reaction, intermediate chemical bonds are formed and the material is said to be \textit{chemisorbed}. Although a chemisorbed bond is weaker than the bulk chemical bonds, the bond energies of chemisorption are considerably higher than that of physisorption. Generally, chemisorption bonds range from 100 - 700 kJ mol\(^{-1}\) compared to 4 - 40 kJ mol\(^{-1}\) for that of physisorption bonds.\textsuperscript{57}
1.6.2.2 Surface Coverage

Once an adsorbed material occupies all of the available sorption sites on the catalyst surface, one monolayer (ML) is formed. At this point, few further gas-surface reactions can occur, and most material that accumulates above this occurs as a result of condensation, or the vapour reacting with the already-adsorbed material. Integration of the TPD peak gives the surface coverage ($\theta$). The probability of adsorption can be expressed as the sticking coefficient of the system, denoted as $S$. This value is defined as the number molecules that absorb to the surface ($\theta$) relative to the number of times gaseous molecules hit the surface, or collision frequency.\textsuperscript{56}

$$S = \frac{\theta}{\Gamma}$$

where $\Gamma$ is in terms of molecules cm$^{-2}$ s$^{-1}$. The derivation of collision frequency can be found in the Data Analysis Section, Chapter 10. The sticking coefficient can also be considered a quantitative measure of the vapour's "reactiveness" with the surface.

1.6.2.3 Reaction Rates

The desorption of adsorbed gas molecules on the surface can easily be viewed as a kinetic process, where the rate expression takes the form:

$$-\frac{d\theta}{dt} = k \theta^x$$

(equation 1.6.1)

where $\theta$ is the surface concentration of the adsorbed gas species, $k$ is the rate constant for the reaction, and $x$ is the reaction order of the desorption. As with all reaction kinetics, the rate constant $k$ is dependent on temperature, as illustrated in the Arrhenius equation,

$$k = k_o e^{\frac{-E_a}{RT}} \theta^x$$

(equation 1.6.2)
where \( k_o \) is the pre-exponential factor, \( E_o \) is the activation energy of the reaction, \( T \) is the temperature, and \( R \) is the gas constant. With this expression, \( k_o \) can be substituted into the aforementioned rate equation to give:

\[
\frac{-d\theta}{dt} = k_o e^{\frac{-E_o}{RT}} \theta^x
\]

(equation 1.6.3)

Now, \( k_o \) is the pre-exponential factor that tells about the degrees of freedom that the adsorbed species has on the surface, and the number of precursor states that exist. \( k_o \) is often denoted \( \nu \), and for molecules or species having masses ranging from 5 to 2000 amu, \( 10^{13} < \nu < 2 \times 10^{14} \). The resulting expression give the rate equation for a first order desorption process:

\[
\frac{-d\theta}{dt} = \nu e^{\frac{-E_o}{RT}} \theta^x
\]

(equation 1.6.4)

This form of the rate equation is known as the Polanyi-Wigner equation. The rate of desorption can be determined at any point during the desorption process using the surface coverage and the corresponding temperature.\(^{55-58}\)

1.6.2.5 Activation Energy of Desorption

The bond dissociation energies can be found from the temperature at which the desorption occurs. With a linear temperature ramp,

\[
T = T_o + \beta t
\]

(equation 1.6.5)

with \( T_o \) as the initial temperature, \( \beta \) as the temperature ramp in units of \(^\circ\)C s\(^{-1}\), and \( t \) as the length of time for the ramp in seconds. Upon substituting the functional form for temperature (equation 1.6.5) into the Polanyi-Wigner rate expression (equation 1.6.4) and differentiating with respect to temperature, the activation energy for a first order desorption process takes the form:
\[ E_{des} = R \frac{T_{\text{max}}}{\beta} \left( \ln \frac{v}{T_{\text{max}}} - 3.64 \right) \]

(equation 1.6.6)

This form is known as Redhead's Equation for activation energy determination, where \( E_a \) is a function of the temperature at which the rate of desorption reaches a maximum (\( T_{\text{max}} \)), and of the temperature gradient.\(^5\)

1.7 Introduction to Current Work

1.7.1 Model Compounds

In order to form polyurethane foam, an isocyanate must react with a hydroxyl. Since there can be a large concentration of hydroxyl groups on an aluminum mould surface, it is feasible to suggest that some isocyanate in the polyurethane reaction mixture may react with some of the aluminum surface hydroxyls and result in a covalent bond. That would mean a di- or poly-functional isocyanate could have one NCO functional group reacted with a polyol from the polyurethane mix. Then, another NCO from the same isocyanate molecule reacting with an hydroxyl from the aluminum surface could form a carbamate bond. Thus, the bulk of the polyurethane foam could anchor itself to the Al mould:

```
H N R
O=C
O--O
Al
```
1.7.2 Isocyanate and Surface Hydroxyl Reactions

Model compounds that have functional groups analogous to that of the polyurethane foam’s starting materials can be investigated. The obvious choice for a model compound for the isocyanate is phenyl-isocyanate,

\[
\text{N} = \text{C} = \text{O}
\]

as it has only one NCO group and an aromatic ring, much like the starting materials for commercial foam productions. With the understanding of isocyanate chemistry, it is postulated that the isocyanate should react with the surface hydroxyls in much the same way it reacts with a polyol hydroxyl. In this case, an isocyanate-hydroxyl reaction would yield a carbamate bond. The existence of this bond would provide many answers to the nature of aluminum-polyurethane adhesion.

To study the presence of this bonding, three distinct experimental steps were necessary. First, the preparation and analysis of three aluminum oxide surfaces were conducted: XPS and SEM compared a “boiled” oxide, a “boiled-then-dried” oxide, and the “natural” oxide, for their surface hydroxyl and water concentration. Secondly, these samples were then dosed with PIC vapour and analysed for distinct carbamate functionalities by ER FTIR, and for Al-O-C chemical shifts by XPS. Finally, these surfaces were compared with the boiled sample that was annealed to 500°C to study the effects of surface water on carbamate bond formation. TPD MS was used to compare the changes in concentration, sticking coefficient, and desorption kinetics after PIC dosing.
2.0 MATERIALS AND METHODS

2.1 Preparation of Oxides on Aluminum Foil

2.1.1 Oxide Preparation

Ultra-high purity polycrystalline aluminum foil was purchased from the Aldrich Chemical Company, Inc. (Milwaukee, WI) with a thickness of 0.13 mm, and at 99.99% purity. The aluminum foils were treated in three different ways that result in oxide layers with very different surface characteristics and hydroxyl content.

2.1.1.1 Natural Oxide

The aluminum foil was cut into 2 x 2 cm pieces, and used as-is to study the nature of the oxide on the aluminum formed in air at room temperature. This sample will be referred to as the Natural sample for the rest of the thesis.

2.1.1.2 Boiled Oxide

The 2 x 2 cm foil pieces were refluxed using 150 mL distilled-deionized water at 100°C for one hour. The reflux apparatus consisted of a 250 mL round-bottomed flask equipped with a reflux condenser, a heating mantle, and a Variac controller. These samples were used immediately after preparation. This will be referenced as the Boiled sample for the rest of the thesis.

2.1.1.3 Boiled-then-Dried Oxide

The foil was prepared as described in Section 2.1.1.2 and was annealed to 500°C for 1 hour inside the UHV chamber, on a custom-made sample holder. The sample holder is
illustrated in Figure 2.1.1 and the UHV system is described in Section 2.2. These samples here and after will be referenced as Dried.

2.1.1.4 Sample Holder for XPS and TPD Experiments

The sample holder was equipped with a heating stage and a thermocouple. Here, 2 Macor® supports were fastened to a copper stage plate to provide electrical insulation, and a gold-coated Si wafer (2 x 0.6 x 0.1 cm) was mounted on the Macor® supports and held in place by 2 Mo foil strips. The thermocouple consisted of alumel and chromel wires attached to a 1.5 x 1.5 cm ceramic plate that sat directly on the Si wafer. The sample was placed on the ceramic and held in place by a stainless steel face-plate fastened by 4 screws to the Macor® support.

The heater is powered by a Power Ten Series 3300 power supply, Model 2050 (Sunnyvale, CA) and interfaced to a computer. The temperature is controlled by means of the Labview VI in-house programmed software.

2.2 XPS Analysis

The XPS analyses were performed on a Leybold-Heraeus system, comprising of dual UHV chambers, is equipped with an EA-11 Leybold-Heraeus Energy Analyser in the XPS chamber, and an Extrel quadropole mass analyser in the MS chamber, as shown in Figure 2.1.2.1. Samples were introduced into the UHV system via an atmospheric load-lock, and the UHV system was allowed to equilibrate to a background pressure of 10⁻⁸ to 10⁻⁹ Torr prior to XPS analysis. Unmonochromatised Al Kα (hv = 1486.6 eV) radiation was used as the excitation source which was run at 150 W power (10 kV and 15 mA.) The X-ray source is situated at 90° to the energy analyser on this system. The emitted photoelectrons were sampled from a 1.44 cm² surface area, at 30° take-off-angle (TOA) to the electron analyser. High-resolution spectra of C 1s, O 1s, N 1s, and Al 2p photoelectrons were recorded at 50 eV pass energy. The sensitivity factors used were empirically obtained through correlation of the surface composition of the
Figure 2.1.1: Custom Sample Holder, Equipped with Heater and Thermocouple

Top view

Side view
same samples run on a Leybold MAX 200 with known sensitivity factors. The Leybold-Heraeus system sensitivity factors for C 1s, O 1s, N 1s and Al 2p are 0.296, 0.711, 0.477, and 0.193 respectively.

Curve fitting was conducted with Matlab ESCA Tools software, using Shirley background subtraction. Charging effects were corrected by setting all C-C bond energies to 284.5 eV and adjusting the difference to the other peak maxima. All prepared metal samples were analysed at 25C, 100C, 200C, 300C, 400C, and 500C. A summary of all sample preparations and analysis conducted may be found in Section 2.8.

2.3 SEM Analysis

Scanning Electron Microscopy analyses of the Natural oxide at 25C, the Boiled oxide at 25C, and the Boiled oxide at 500C were conducted on a Hitachi S – 4500 Field Emission Scanning Electron Microscope, available in the Department of Material Science Engineering at The University of Toronto.
Figure 2.1.2.1: Schematics of XPS – MS Ultra-High Vacuum System
2.4 Phenyl Isocyanate Dosing

Neat phenyl isocyanate (PIC) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) at 98% purity.

2.4.1 Controlled Phenyl Isocyanate Vapour Pressure Dosing

To control the amount of PIC vapour in contact with the oxide, a dosing chamber with high-vacuum capabilities was built and pumped by a Drytel-30 turbo molecular pump. This chamber was fitted with a “cold-finger”, a modified 0.25 inch Kovar-to-Pyrex glass adapter from Varian Vacuum Products (Lexington, MA) that holds the PIC liquid as shown in Figure 2.4.1.

The glass adapter cold-finger was custom-fitted with 0.25 inch stainless steel tubing, connected to a Swagelock (Niagara Falls, ON) quick-connect fitting. This is attached to the vacuum system with a NUPRO plug valve (Solon, OH.) With the quick-connect feature, the whole cold-finger can be removed after sample preparation and stored in the refrigerator for subsequent sample preparations.

2.4.1.2 Sample Dosing

To dose the natural and the boiled oxides, the samples were placed in a stainless steel chamber fitted to the vacuum system that was equipped with a pressure gauge and a removable glass window for sample introduction.
Figure 2.4.1: External Dosing Chamber For PIC Dosing

Pressure gauge → Valve → Valve → Intro-port → Test tube

Turbo-molecular PUMP
Drytel 30

PIC Liquid
2.4.1.3 PIC Preparation

The liquid PIC was degassed using a standard freeze-pump-thaw method. The liquid was frozen then thawed for 3 cycles, and after the final thawing the PIC was brought up to room temperature, and the valves to the dosing chamber quickly opened. The PIC pressure in the dosing chamber was allowed to equilibrate and the exposure times monitored.

2.4.1.4 Dosing Verification

To ensure that the vapour inside the external dosing chamber was PIC, the chamber was fitted with a leak valve, and connected to a UTI – 100 quadropole mass spectrometer. An analysis of the empty chamber and the atmosphere inside the chamber showed 10⁻⁷ Torr PIC. The chamber blank and the PIC-filled chamber mass spectra are shown in Figure 2.4.1.2. The mass spectrum of the PIC-filled chamber matches that of PIC.
Here, the uppermost graph is the chamber blank scan, and the bottom graph is the PIC-filled chamber. After subtraction of the background, the only remaining peaks are all consistent with PIC.
2.4.1.5 Dried Samples

To prepare the Dried samples, the foil was first prepared in the same method as the Boiled sample, then heated to 500°C for 1 hour in the UHV chamber, and quickly removed. While still hot, the sample was removed from the sample holder and placed directly into the external dosing chamber that had been heated and outgassed for over 1 hour. The chamber outgassing was conducted by wrapping the exterior with heating tape, and evacuating the chamber with the vacuum-pump. While the chamber contained the sample, it was allowed to cool to room temperature. The Dried samples were then dosed as described for the Natural and Boiled samples.

2.5 External Reflectance Fourier Transform Infra Red Analysis

The External Reflectance Infra Red (ER FTIR) analysis was conducted on a BOMEM MB Series FTIR equipped with a MCT detector. Only 2 samples were analysed by this method: the Natural oxide dosed for 24 hours, and the Boiled oxide dosed for 24 hours. The sample chamber was allowed to purge for 30 minutes with dry N₂ gas in order to remove atmospheric moisture before analysis. The samples were analysed at grazing angle of incidence, averaging 100 scans at 1 cm⁻¹ resolution. All analyses were conducted at The Ontario Photonics Research Centre, in the Department of Physics at The University of Toronto, under the supervision of Dr. T. Haslett and Dr. X. Gu.

XPS Analyses of these two samples were also conducted, as previously described in Section 2.2.
2.6 Methanol Washing of Dosed Samples

The Natural and Boiled oxides, that were dosed with PIC for 24 hours were placed in separate beakers, and rinsed twice with 20 mL high purity spectrograde methanol (Caledon Laboratories, Inc. Georgetown, ON) with continuous swirling for 5 minutes. The samples were then analysed using EX FTIR.

2.7 Temperature Programmed Desorption Mass Spectrometry Analysis

Periodic mass scans from 50 to 220 amu at 0.25C sec\(^{-1}\) from 295 to 650 K were run to verify peak positions. TPD measurements were obtained by monitoring masses 64, 91, and 119 simultaneously with a temperature ramp of 0.5C sec\(^{-1}\) from 295 to 650 K.

2.7.1 Surface Coverage Quantification

The pumping speed of the UHV system was determined by leaking 10\(^{-6}\) Torr Argon gas into the UHV chamber and monitoring the decay in the Ar mass spectrometric signal after this leak was shut off. The decay profile is illustrated in Figure 2.7.1.a. In order to determine the characteristic pumping time \(\tau\) of the system, a semi-logarithmic plot of \(\ln \text{dP(t)}\) versus \(t\) yields a straight line with a slope of \(-\tau^{-1}\). The characteristic pumping time of 3 seconds was determined, as shown in Figure 2.7.1.b.

In order to calibrate MS sensitivity for the TPD analyses, 10\(^{-7}\) Torr xenon gas was leaked into the UHV chamber, and a mass scan was taken from 1 to 145 amu. All gases were corrected for their mass spectrometer sensitivity factors, and the total was used to determine the mole fraction of Xe gas in the chamber. The Xe mole fraction was then used to convert the sample's integrated 91 amu peak to a pressure measurement. This pressure could then be expressed in terms of a molecular amount. The complete calculation can be seen in Chapter 10.
Figure 2.7.1.a: UHV Pumping 10-6 Torr Argon Decay Profile

Figure 2.7.1.b: Characteristic Pumping Speed Determination ($\tau$)
2.8 Coding System for Prepared Oxide Analysis and PIC Dosed Samples

2.8.1 XPS and SEM Analysis of Aluminum Oxides

For the XPS and SEM analyses of the prepared Al oxides, the samples will be named according to the type of oxide and annealing temperature. For example, N25C stands for the natural oxide analysed at 25°C, and B500C is the boiled oxide analysed after annealing at 500°C for 1 hour.

Table 2.8.1: List of Oxide Samples Analysed by XPS and SEM

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°C</th>
<th>100°C</th>
<th>200°C</th>
<th>300°C</th>
<th>400°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Oxide</td>
<td>N25C</td>
<td>N100C</td>
<td>N200C</td>
<td>N300C</td>
<td>N400C</td>
<td>N500C</td>
</tr>
<tr>
<td>Boiled Oxide</td>
<td>B25C</td>
<td>B100C</td>
<td>B200C</td>
<td>B300C</td>
<td>B400C</td>
<td>B500C</td>
</tr>
</tbody>
</table>

2.8.2 Coding for PIC Dosed Samples

The following 4-digit coding system will be used to label the PIC dosed samples. The first letter refers to the method of aluminum preparation

where \( N = \) Natural

\( B = \) Boiled

and \( D = \) Dried.

The following two numbers indicate the substrate’s PIC exposure time, and the last figure gives the units of the dosing time. For example,

<table>
<thead>
<tr>
<th>first letter of oxide preparation</th>
<th>numerical dosing time</th>
<th>time units</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>30</td>
<td>M</td>
</tr>
</tbody>
</table>

Hence, the sample labeled D30M refers to a 30 minute PIC exposure on Dried foil (an aluminum foil sample that was boiled in water and annealed to 500°C for 1 hour.)
Table 2.8.2 summarises the analysis procedures conducted on the appropriate PIC dosed samples.

Table 2.8.2  PIC Dosed Sample Analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS</th>
<th>ER FTIR</th>
<th>MeOH Wash</th>
<th>TPD MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>N96H</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>N24H</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>N12H</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>N01H</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>B24H</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>B02H</td>
<td></td>
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<td></td>
<td>✓</td>
</tr>
<tr>
<td>B30M</td>
<td></td>
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<td>✓</td>
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<tr>
<td>B15M</td>
<td></td>
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<td></td>
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<tr>
<td>B05M</td>
<td></td>
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<td>✓</td>
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<tr>
<td>B01M</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>B30S</td>
<td></td>
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<td></td>
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</tr>
<tr>
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<td></td>
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</tr>
</tbody>
</table>
3.0 ANALYSIS OF ALUMINUM OXIDE PREPARATION

3.1 XPS Analysis

A comparison of surface hydroxyls of the natural metal oxide and the boiled metal was conducted by annealing both surfaces from 25C to 100C, and then to 500C at 100C intervals, then analysed by XPS for the change in O 1s intensities. A summary of the samples analysed is found in Section 2.8. XPS spectra were taken for O 1s and Al 2p photoelectrons.

3.1.1 Al 2p Spectra

Figure 3.1.1 compares Al 2p peaks for the N25C and B25C. Curve-fits for the appropriate oxidation states are also included. At all temperatures, the natural oxide exhibits two oxidation states, Al\(^{0}\) appearing at 72 eV, and Al\(^{3+}\) at 75 eV, whereas the boiled oxide yields only the Al\(^{3+}\) state for all temperatures. The absence of the Al\(^{0}\) state on the B25C to the B500C indicates that the boiled oxide is much thicker than that of the natural oxide, since these photoelectrons cannot escape as the oxide thickness is greater than the escape depth.

3.1.2 O 1s Spectra

Figure 3.1.2 illustrates the N25C, B25C, N500C and the B500C O 1s spectra. The B25C and B500C samples are much broader than the N25C and N500C samples. All spectra were fit to two components, one at 530.6 eV for the O\(^{2-}\) state, and the second at 531.7 eV for the OH\(^{-}\) state, the protocol used by previous investigators\(^{14,17-21}\). The OH peak demonstrates a considerable decrease with temperature. As expected, the B25C to B500C samples shows a larger percentage OH peak than the N25C to N500C samples at room temperature and throughout the annealing process.
Figure 3.1.1: Comparison of Al 2p XPS Spectra for N25C, B25C, N500C, and B500C.
Figure 3.1.3 is a graph that compares the ratio of surface OH concentration with that of the total O 1s contribution, with annealing temperature. As expected, the Boiled surface has a consistently higher OH concentration than the Natural oxide. Both decrease linearly with increasing temperature.\textsuperscript{9,10,12,22} The binding energies are generally higher for the Boiled oxides than the Natural oxides, which increase with temperature.

Figure 3.1.3: Change in Surface OH Concentration with Annealing Temperature
The boiling process is reported to permeate the native oxide layer, consisting of approximately 14 Å of α-Al₂O₃, and hydrate it into aluminum oxy-hydroxide and aluminum hydroxide, both of which become rich in hydroxyl groups thus giving rise to H-bonding of water. Since the binding energy of the O 1s contributed by water cannot be differentiated from that of the surface hydroxyls, the contribution to the total O 1s spectrum form surface hydroxyls and from molecular water is not known.

3.2 SEM of Al Metal Oxide Preparation: Surface Morphology

It was previously found that the surface topography of Al metal changes instantly with the reaction of boiling water and aluminum where at a 60 second exposure, a fully developed hydrated oxide with cavities up to 0.1 μm diameter were detected. Even samples at 1 second exposure show a thin but densely hydrated structure. This study showed that the oxide had increased in roughness and thickness with exposure time.

Figure 3.2.1a compares the surface topography of the N25C and N500C samples, and Figure 3.2.1b compared the B25C and B500C samples. As expected, the N25C and the N500C samples are very smooth and show few surface features. The B25C and B500C samples have very rough surfaces which seems to be covered with tiny platelets, approximately 100 Å in diameter which correspond to hydroxide present as particles on the surface. The SEM of the B500C sample exhibits the same rough surface and platelet formation as the B25C sample. No change between the B25C and the B500C samples suggests that the oxide is stable to 500C for one hour. In other words, this temperature is not enough to decrease the surface area, warp the surface, or change its amorphous arrangement.

The platelets found on both the B25C and B500C samples have been shown in previous works to consist of boehmite and pseudoboehmite by XPS and SEM. It is also reported that during the reaction of Al metal and boiling water, 3 steps occur. First, an amorphous oxide is formed, then the water dissolves this oxide, and finally the hydroxide precipitates. The
hydroxide layer consisted mostly of particles also 100 Å in diameter, whose IR spectrum gave OH bands in aluminum hydroxide-like and aluminum oxy-hydroxide-like configurations. In these configurations, concentration of surface hydroxyls are reported to be 19 nm$^{-2}$.59
Figure 3.2.1a: SEM Images of N25C and N500C

**N25C**

**N500C**
Figure 3.2.1b: SEM Images of B25C and B500C

B25C

B500C
3.3 Surface Areas and Hydroxyl Concentration Determination

From the SEM pictures for B25C and B500C, the surface area was determined by assuming that every platelet is of uniform size, and each took the shape of a disc. The lower limit of the geometric surface area for the B25C sample was estimated at $2.8 \times 10^{14}$ nm$^2$ and it did not change for the B500C sample. The calculations are found in Chapter 10. Assuming that the platelets consist predominantly of boehmite and psuedo-boehmite, the hydroxyl concentration is 19 nm$^{-2}$. This would correspond to a total surface hydroxyl concentration of $5.2 \times 10^{15}$ OH cm$^{-2}$ for both B25C and B500C samples. However, the O 1s spectrum for B500C is much less than that of B25C. Therefore, the change may be attributed to the loss of water on the B500C surface. This may also be true for the change in the O 1s signal for the N25C and N500C samples as well.

3.4 Summary of Aluminum Oxide Analysis

The XPS results show that the Natural oxide has the lowest surface hydroxyl concentration and the thinnest oxide layer. The Boiled oxide showed a linear decrease in surface hydroxyl concentration with temperature, and SEM results illustrate that both the Boiled and the Dried oxides have platelet formation that do not change significantly upon heating. The increased thickness and surface roughness show that the metal treatments increase the surface area of the aluminum metal greatly.
4.0 XPS AND ER FTIR ANALYSIS OF PIC DOSED SAMPLES

For XPS and IR analysis, the N24H and B24H samples were studied to show the difference in Al surface preparation on carbamate bond formation. The high dosage times were chosen to ensure that the PIC had saturated the surface.

4.1 XPS Analysis of N24H and B24H

4.1.1 C Is, O Is and N Is Spectra

Figure 4.1.1 compares the N24H and B24H binding energies of the C 1s, N 1s and O 1s photoelectrons. Peak fitting the C 1s spectrum gave peaks at 288.8 eV, 286.7 eV, 285.5 eV +/- 0.2 eV, and 284.5 eV corresponding to aromatic C and π* shake-ups, C-N, C=O and C-H respectively. The N 1s peak for N24H and B24H samples occurred at 400 and 399.8 eV, consistent with a phenyl-N structure. The N24H O 1s spectrum shows peaks at 531.7 and 530.6 eV can be identified as organic O=C and O-C. However, looking back at the XPS spectra for the non-dosed foils (Figure 3.1.1) the same peaks are found and identified as O-H for the 531.7 eV peak, and O-Al for the 530.6 eV peak. There is no evidence of an Al-O-C bond, and thus little information about the PIC bond nature can be determined from the O1s spectra.

4.1.2 Al 2p Spectra

A comparison of Al 2p peaks for N24H and B24H and the undosed N25C and B25C are shown in Figure 4.1.2. N24H and B24H show symmetrical peaks at 74.5 and 75.1 eV, corresponding to Al\(^{3+}\). Comparing the dosed natural sample, N24H to the undosed natural sample N25C, the Al\(^{0}\) peak is present after dosing. This indicates that the PIC film on the natural oxide surface is not sufficiently thick to block Al\(^{0}\) photoelectrons from reaching the surface. The binding energies for both N24H and B24H Al\(^{3+}\) peaks are identical to those of the undosed samples, and can only be fitted with this peak. For the formation of carbamate bonds, a smaller
peak at a slightly lower binding energy than 75 eV would have to be present; as carbon is an
electron-donating atom that would lessen the O’s pull of the Al atom’s electrons. This shows
that the Al$^{3+}$ peak is definitely Al-O and shows no evidence for Al-O-C carbamate bond
formation.$^{41,43,44}$

The material formed on both the natural and boiled oxide surfaces is similar. Hence, the
difference in the surface hydroxyl concentration and surface area does not seem to affect the
overall makeup of the dosed organic material.
Figure 4.1.1: O 1s, C 1s, and N 1s XPS Comparison of N24H and B24H
Figure 4.1.2a: Comparison of N24H and N25C Al 2p XPS Spectra

Figure 4.1.2b: Comparison of B24H and B25C Al 2p XPS Spectra
4.2 ER FTIR Analysis

The next step in the surface bonding studies was to analyse both N24H and B24H using ER FTIR. The 2 spectra are compared in Figures 4.2.1.a and 4.2.1.b. Both surfaces show bands at 1237 cm\(^{-1}\), 1316 cm\(^{-1}\), 1596 cm\(^{-1}\), and 1647 cm\(^{-1}\), characteristic of O-H stretch, N-aryl bend, O=C stretch and an H vibration from a urea functionality. This suggests that the material on both surfaces is a 1,3-dipheyl urea. Present on the B24H surface were bands at 3133 cm\(^{-1}\) for the OH vibration, and 3280 cm\(^{-1}\) and 3327 cm\(^{-1}\) for an amide N-H stretch, but absent on the N24H sample. It is unknown why these bands are absent on the N24H sample, it may perhaps be too low a concentration to be detected. A summary of the frequencies and their assignments is found in Table 4.2.1.

<table>
<thead>
<tr>
<th>Band Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Band Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1084</td>
<td>Al-O-C</td>
<td>1647</td>
<td>H-N (urea)</td>
</tr>
<tr>
<td>1237</td>
<td>-O-H</td>
<td>3133</td>
<td>-O-H</td>
</tr>
<tr>
<td>1316</td>
<td>Aryl-N-H</td>
<td>3280</td>
<td>Amide-N-H</td>
</tr>
<tr>
<td>1566</td>
<td>O=C</td>
<td>3327</td>
<td>Amide-N-H</td>
</tr>
</tbody>
</table>

It is clearly seen that the intensity of the urea on the B24H sample is much greater than on the N24H. Therefore, the concentration of the urea on the B24H sample is much greater than that on the N24H sample. This is most likely due to the larger surface area and hydroxyl concentration on the B24H surface.
Figure 4.2.1.a: ER FTIR Comparison of N24H and B24H, 900 – 2100 cm⁻¹
Figure 4.2.1b: ER FTIR Comparison of N24H and B24H, 2000 – 4000 cm\(^{-1}\)
4.3 Methanol Washing of N24H and B24H

A qualitative measure of the material's bond strength to the surface is to conduct a methanol wash. Generally speaking, chemisorbed bonds are strong enough to resist dissolution, whereas physisorbed molecules, including those H-bonded to the surface, would be readily removed by a solvent rinse. This has been previously conducted to determine the bonding strength of chlorophenols to various aluminum oxide surfaces. This study indicated that chemisorbed materials have a substantially high activation barrier that cannot be easily overcome by the solvent interaction. But in the case of H-bonding, excess solvent can compete for sorption sites on the surface, thus removing adsorbed material.

Figure 4.3.1 compares the IR spectra of the methanol washed N24H with unwashed N24H, and Figure 4.3.2 compares the IR spectra of the methanol washed B24H with the unwashed B24H. The washed samples show no features that would indicate that carbamate functional groups are present.
Figure 4.3.1: ER FTIR Comparison of Washed and Unwashed N24H
Figure 4.3.2: ER FTIR Comparison of Washed and Unwashed B24H
4.4 Summary of XPS and ER FTIR Analysis of N24H and B24

The IR and XPS spectra show little evidence for carbamate bond formation. The Al 2p spectra gave no chemical shifts that indicate that Al-O-C bonds were formed. The IR spectra showed little indication of Al-O-C bonds, but the frequencies showed bands characteristic of 1,3-diphenyl urea. In addition to this, IR analysis showed that methanol washing removed the material from the surface, thus providing more evidence that carbamate bonds are not formed on the surface.

The intensities of the IR spectra are much higher for the B24H sample than for the N24H sample. This shows that the urea is more likely to form on the boiled surface than on the natural oxide, although increased surface area plays a role. Since urea is the product of phenyl isocyanate and water, the greater concentration of urea is most likely due to the larger surface area, greater hydroxyl concentration and therefore, greater concentration of water on the boiled surface. The difference in urea concentrations on the two surfaces, combined with the methanol washing results, suggest that the phenyl isocyanate vapour react only with the molecular water and not the surface hydroxyls.
5.0 TEMPERATURE PROGRAMMED DESORPTION – MASS SPECTROMETRIC ANALYSIS

5.1 Mass Spectrometric Characterisation of the Surface Material

In order to determine the mass fragmentation patterns of the desorbing material, repetition of full mass scans from 50 to 220 amu, was performed during TPD experiments. From this, the predominant masses were chosen and used for subsequent analysis. Table 5.1 gives the predominant masses with the corresponding relative peak intensity.

Table 5.1: Fragmentation Patterns of Desorbing Material from PIC Dosed Al Surface

<table>
<thead>
<tr>
<th>Mass</th>
<th>51</th>
<th>52</th>
<th>53</th>
<th>63</th>
<th>64</th>
<th>65</th>
<th>66</th>
<th>91</th>
<th>92</th>
<th>93</th>
<th>119</th>
</tr>
</thead>
<tbody>
<tr>
<td>% I</td>
<td>43</td>
<td>47</td>
<td>34</td>
<td>46</td>
<td>98</td>
<td>44</td>
<td>45</td>
<td>100</td>
<td>15</td>
<td>51</td>
<td>82</td>
</tr>
</tbody>
</table>

The same data at approximately 490 K is shown in Figure 5.1.

Figure 5.1: Mass Fragmentation Pattern of PIC Dosed Al Foil at 490 K
5.1.1 Identification

The IR and XPS data described in Chapter 4 suggest that the material on the surface was 1,3-diphenyl urea:

![1,3-diphenyl urea](image)

However, the expected mass fragmentation pattern of 1,3-diphenyl urea differs from that of the dosed samples as seen in Table 5.1.1.

<table>
<thead>
<tr>
<th>Mass</th>
<th>39</th>
<th>65</th>
<th>66</th>
<th>77</th>
<th>92</th>
<th>93</th>
<th>118</th>
<th>212</th>
</tr>
</thead>
<tbody>
<tr>
<td>% I</td>
<td>7</td>
<td>12</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>100</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

Comparing the mass fragments of the unknown and that of 1,3-diphenyl urea, it can be seen that the fragmentation patterns and the relative intensities do not agree. Both spectra contain masses 65, 66, 92, and 93 amu, but the relative intensities differ. The parent 212 amu peak of the 1,3-diphenyl urea is absent from the TPD spectrum, and the prominent 91 and 64 amu signals seen in the TPD are not present in the 1,3-diphenyl urea spectrum.
5.1.2 Thermal Decomposition

What is the material on the surface? The IR suggests that it is 1,3-diphenyl urea, but the mass spectra do not agree. The answer to this question is discovered as it was realised that 1,3-diphenyl urea does not have a set boiling point, but it decomposes to aniline and phenyl isocyanate at 260°C and at one atmosphere.

![Chemical diagram]

The mass fragmentation patterns of aniline and phenyl isocyanate are compared with that of the unknown sample in Table 5.1.3.

<table>
<thead>
<tr>
<th>PIC (m/z)</th>
<th>% I</th>
<th>Sample (m/z)</th>
<th>% I</th>
<th>Aniline (m/z)</th>
<th>% I</th>
<th>Sample (m/z)</th>
<th>% I</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>38</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>47</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>26</td>
<td>-</td>
<td>-</td>
<td>65</td>
<td>33</td>
<td>65</td>
<td>47</td>
</tr>
<tr>
<td>51</td>
<td>17</td>
<td>51</td>
<td>43</td>
<td>66</td>
<td>45</td>
<td>66</td>
<td>45</td>
</tr>
<tr>
<td>63</td>
<td>25</td>
<td>63</td>
<td>46</td>
<td>92</td>
<td>30</td>
<td>92</td>
<td>15</td>
</tr>
<tr>
<td>64</td>
<td>58</td>
<td>64</td>
<td>98</td>
<td>93</td>
<td>100</td>
<td>93</td>
<td>51</td>
</tr>
<tr>
<td>91</td>
<td>80</td>
<td>91</td>
<td>100</td>
<td>94</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>119</td>
<td>100</td>
<td>119</td>
<td>82</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

This explains the entire mass spectrum of the desorbed material with the exception of 2 peaks (52 and 53 amu.) These peaks are currently unassigned. The mass spectrum of the unknown is in good agreement with that of a mix of phenyl isocyanate and aniline, which are the thermal decomposition products of 1,3-diphenyl urea.
5.2 Surface Coverage

Once the desorbed products were identified, TPD runs were conducted monitoring only the 91, 64, and 119 amu peaks. For surface coverage determination, the 91 amu peak intensity was chosen for integration. A summary of surface coverages for all three samples is shown in Table 5.2.1.

5.2.1 Natural Oxide

A comparison of the time-exposure study for the Natural oxides is shown in Figure 5.2.1. The 1 hour and 12 hour exposure samples gave no detectable PIC adsorption, whereas the 24 and 96 hour samples gave similar coverages, $3.30 \times 10^{15}$ and $1.53 \times 10^{15}$ molecules, respectively. In accordance with the IR results in Chapter 4, these concentrations are low, again due to a low surface area, a low hydroxyl concentration and therefore a low concentration of surface water during dosing.

5.2.2 Boiled Oxide

Figure 5.2.2 compares the Boiled oxide dosing series. One main feature at a $T_{\text{max}}$ of approximately 500 K increases with increasing dosage. After 24 hours, the intensity of this feature continues to grow and, in addition, a new sharp feature appears at a temperature of 100 K lower.

5.2.3 Dried Oxide

Figure 5.2.3 compares the Dried oxide sample series. Again, one main feature appears at a $T_{\text{max}}$ of 500 K. Like the Boiled series, the surface coverages increase with PIC exposure time, with the exception of the D05M and the D24H samples. These anomalies may be a result of a decrease in water, both on the samples' surfaces and in the external-dosing chamber atmosphere.
Table 5.2.1: Table of Surface Urea Concentration with PIC Time Exposures

<table>
<thead>
<tr>
<th>Natural</th>
<th>[Urea]$_N$ (10$^{15}$)</th>
<th>Boiled</th>
<th>[Urea]$_B$ (10$^{15}$)</th>
<th>Dried</th>
<th>[Urea]$_D$ (10$^{15}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N96H$</td>
<td>1.53</td>
<td>$B24H$</td>
<td>324</td>
<td>$D24H$</td>
<td>16.4</td>
</tr>
<tr>
<td>$N24H$</td>
<td>3.30</td>
<td>$B02H$</td>
<td>10.7</td>
<td>$D02H$</td>
<td>18.4</td>
</tr>
<tr>
<td>$N12H$</td>
<td>-</td>
<td>$B30M$</td>
<td>7.36</td>
<td>$D30M$</td>
<td>8.00</td>
</tr>
<tr>
<td>$N01H$</td>
<td>-</td>
<td>$B15M$</td>
<td>1.72</td>
<td>$D15M$</td>
<td>8.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B05M$</td>
<td>1.56</td>
<td>$D05M$</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B01M$</td>
<td>0.738</td>
<td>$D01M$</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B30S$</td>
<td>0.422</td>
<td>$D30S$</td>
<td>0.135</td>
</tr>
</tbody>
</table>

*aall [Urea] concentrations are expressed as 10$^{15}$ molecules cm$^{-2}$*
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59

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UMI
Figure 5.2.1: TPD MS Time-Exposure Comparison of Natural Oxides of PIC Dosed Samples

TPD Mass Spectra for PIC Exposures at 2.8 Torr on Natural Al Oxide, m/z=91amu

![Graph showing TPD Mass Spectra for different exposures of PIC on Al Oxide.]

- N96H
- N24H
- N12H
- N01H

Temperature (K) vs. Intensity
Figure 5.2.2: TPD MS Time-Exposure Comparison of PIC Dosed Boiled Samples

TPD Mass Spectra for PIC Exposures at 2.8 Torr on Natural Oxide, 
m/z = 91 amu

Temperature (K)
Figure 5.2.2: TPD MS Time-Exposure Comparison of PIC Dosed Boiled Samples

TPD Mass Spectra for PIC Exposures at 2.8 Torr on Natural Oxide, 
m/z = 31 amu

Temperature (K)
Figure 5.2.3: TPD MS Time-Exposure Comparison of PIC Dosed Dried Samples

TPD Mass Spectra for PIC Exposures at 2.8 Torr on Natural Al Oxide, m/z = 91 amu
5.3 The Effects of Surface Coverage on $T_{\text{max}}$

The peak maxima for each of the oxide samples are also seen in Figures 5.2.1 to 5.2.3. The $T_{\text{max}}$ values for the Boiled and for the Dried oxide are generally higher than for the Natural oxides. The $T_{\text{max}}$ values are generally in good agreement, with the Natural oxide values within 1%, and the Boiled and Dried oxide values within 13%. The $T_{\text{max}}$ values do not vary with surface coverage. The $T_{\text{max}}$ values are found in Table 5.3.1.

Table 5.3.1: Temperature Values at Maximum Desorption Rate ($T_{\text{max}}$) for PIC Dosed Samples

<table>
<thead>
<tr>
<th>Natural</th>
<th>$T_{\text{max}}$ (K)</th>
<th>Boiled</th>
<th>$T_{\text{max}}$ (K)</th>
<th>Dried</th>
<th>$T_{\text{max}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N96H</td>
<td>408</td>
<td>B24H</td>
<td>402/492</td>
<td>D24H</td>
<td>524</td>
</tr>
<tr>
<td>N24H</td>
<td>410</td>
<td>B02H</td>
<td>514</td>
<td>D02H</td>
<td>496</td>
</tr>
<tr>
<td>N12H</td>
<td>-</td>
<td>B30M</td>
<td>564</td>
<td>D30M</td>
<td>513</td>
</tr>
<tr>
<td>N01H</td>
<td>-</td>
<td>B15M</td>
<td>460</td>
<td>D15M</td>
<td>493</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B05M</td>
<td>485</td>
<td>D05M</td>
<td>428</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B01M</td>
<td>482</td>
<td>D01M</td>
<td>485</td>
</tr>
<tr>
<td></td>
<td>B30S</td>
<td>485</td>
<td>D30S</td>
<td>435</td>
<td></td>
</tr>
</tbody>
</table>

All exposures gave one peak maximum except the B24H sample, which gave two peak maxima. The first $T_{\text{max}}$ occurs at 402 K, similar to that of the Natural oxides, and the second $T_{\text{max}}$ occurs at 492 K, akin to those of the Boiled and the Dried oxides. The values for $T_{\text{max}}$ for each of the Natural, Boiled, and Dried PIC exposure times are in good agreement. The exceptions include B30M and D05M. These differences may be a result of power source difficulties in the sample holder during the analysis of those particular samples. The similarity of the $T_{\text{max}}$ values with changing surface coverage indicates that desorption is a first-order desorption process.58
5.4 Summary of TPD Experiments

The TPD MS experiments have provided a wealth of information about the PIC vapour - aluminum oxide system. In summary, the mass spectra have confirmed that the material on each of the aluminum surfaces after PIC vapour dosing is 1,3-diphenyl urea, which decomposes to aniline and phenyl isocyanate upon desorption at elevated temperatures. Although the differences in oxide preparations did not affect the surface film composition, it did affect the surface coverage. The Natural oxide became saturated with urea between a 12 and 24 hour PIC dosing time at 2.8 Torr. The Dried oxide showed increasing surface coverage with exposure time, but it levelled off between an exposure of 2 and 24 hours. The Boiled oxide showed increasing surface coverage with exposure time with no upper limit of coverage. The $T_{max}$ values were considerably higher for the Boiled and the Dried samples, approximately 100 K, than for the Natural oxide. These values did not change considerably with surface coverage.
for the N24H sample is not accurate, and perhaps the XPS peak deconvolution did not properly account for carbonaceous material on the surface, thus giving an exaggerated account.

Since 1,3-diphenyl urea is the product of phenyl isocyanate and water, there must be water on the surface to form it. It follows that the amount of urea formed on the surface is proportional to the amount of water on the surface. It is well documented that the surface hydroxyls provide a hydrophilic character to the Al oxide. Therefore, the B24H sample has a larger surface area and a larger OH concentration than the N24H. The “nooks and crannies” of the surface, combined with the hydrophilic hydroxyls, allow for a much greater molecular water concentration H-bonded on the B24H surface. And it is the greater water concentration that yields the greater urea concentration.

In a similar study, Nylund and Olefjord found that when Al metal was oxidised with pure O₂ gas and then exposed to a humid environment, water molecules were found to physically adsorb to the oxide surface, to approximately 10 ML then dissociate to OH giving rise to hydration of the oxide. The corresponding stoichiometric formula is Al₂O₃ + 3H₂O → 2Al(OH)₃. The equilibrium arrows in this observation indicate that it is a reversible reaction, and that the boehmite and pseudoboehmite are susceptible to decomposition to Al₂O₃ and water under UHV conditions. They also report that the effect of heating the sample to 550°C for 5 hours neither increases nor decreases the oxide thickness.

If the water concentration is the dominant factor in urea formation, and the Dried sample should be free of physisorbed water, it is uncertain as to why the Dried samples have any urea formed on the surface at all. The answer may lie in the understanding of the amount of water trapped in the surface features. An annealing procedure of 500°C for 1 hour may not be sufficient to remove all the water that may be incorporated into the oxide structure.
6.2 Surface Coverage and Sticking Coefficient

What surface creates 1,3-diphenyl urea faster? To answer this question, one must observe the sticking probabilities of each system.

Measuring the coverage of the dosed material on the active surface allows the determining the sticking coefficient, $S$, which the gas vapour has with the respective surfaces. Sticking coefficient here is defined as the surface coverage divided by the total PIC dosage. The average sticking coefficients are shown in Table 6.2.1.

Table 6.2.1: Sticking Coefficients of PIC on Al Oxide Preparations

<table>
<thead>
<tr>
<th>Natural</th>
<th>$S_N\ (10^{-9})$</th>
<th>Boiled</th>
<th>$S_B\ (10^{-9})$</th>
<th>Dried</th>
<th>$S_D\ (10^{-11})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N96H</td>
<td>0.868</td>
<td>B24H</td>
<td>7.36</td>
<td>D24H</td>
<td>0.371</td>
</tr>
<tr>
<td>N24H</td>
<td>7.48</td>
<td>B02H</td>
<td>2.92</td>
<td>D02H</td>
<td>5.02</td>
</tr>
<tr>
<td>N12H</td>
<td>-</td>
<td>B30M</td>
<td>8.02</td>
<td>D30M</td>
<td>8.72</td>
</tr>
<tr>
<td>N01H</td>
<td>-</td>
<td>B15M</td>
<td>3.74</td>
<td>D15M</td>
<td>19.3</td>
</tr>
<tr>
<td>-</td>
<td>B05M</td>
<td></td>
<td>19.2</td>
<td></td>
<td>3.03</td>
</tr>
<tr>
<td>-</td>
<td>B01M</td>
<td></td>
<td>24.1</td>
<td></td>
<td>47.6</td>
</tr>
<tr>
<td>-</td>
<td>B30S</td>
<td></td>
<td>27.6</td>
<td></td>
<td>8.85</td>
</tr>
</tbody>
</table>

The Boiled and Dried samples have coefficients that are generally within the same order of magnitude, approximately $10^{-10}$ which indicate that only roughly one in every $10^{10}$ collisions result in adsorption. To compare the sticking coefficients of this system to those better-known, it was reported that the sticking coefficient of water to aluminum oxide is 0.1,$^71$ and that for oxygen on silver is $10^{-5}$.50 For the Natural surfaces, $S$ is approximately one order of magnitude smaller, indicating that the natural oxide is not as reactive with the PIC as either the Boiled or the Dried surfaces. The sticking coefficient for the Natural oxide samples decreases between the 24 hour and 96 hour dosing times. This suggests that the PIC hits the surface and forms urea. As the surface composition changes, the necessary surface hydroxyls and water are covered, thus preventing the build up multilayers on the surface.
6.3 Activation Energy of Desorption

The activation energy of desorption is a direct measure of the bond strength between the urea and the aluminum surface. The $T_{\text{max}}$ values, as well as the activation energies of each sample calculated by means of Redhead's Analysis are found in Table 5.4.1. The calculations are found in the Data Analysis Section, Chapter 10.

Table 6.3.1: Activation Energies of Urea on Aluminum Surfaces

<table>
<thead>
<tr>
<th>Natura l</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Boiled</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Dried</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N96H$</td>
<td>408</td>
<td>124</td>
<td>$B24H$</td>
<td>402/492</td>
<td>122/151</td>
<td>$D24H$</td>
<td>524</td>
<td>161</td>
</tr>
<tr>
<td>$N24H$</td>
<td>410</td>
<td>124</td>
<td>$B02H$</td>
<td>514</td>
<td>158</td>
<td>$D02H$</td>
<td>496</td>
<td>152</td>
</tr>
<tr>
<td>$N12H$</td>
<td>-</td>
<td>-</td>
<td>$B30M$</td>
<td>564</td>
<td>173</td>
<td>$D30M$</td>
<td>513</td>
<td>157</td>
</tr>
<tr>
<td>$N01H$</td>
<td>-</td>
<td>-</td>
<td>$B15M$</td>
<td>460</td>
<td>141</td>
<td>$D15M$</td>
<td>493</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B05M$</td>
<td>485</td>
<td>148</td>
<td>$D05M$</td>
<td>428</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B01M$</td>
<td>482</td>
<td>147</td>
<td>$D01M$</td>
<td>485</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B30S$</td>
<td>485</td>
<td>148</td>
<td>$D30S$</td>
<td>436</td>
<td>133</td>
</tr>
</tbody>
</table>

All exposures gave one peak maximum except the B24H sample, which gave two peak maxima. The first $T_{\text{max}}$ occurs at 402 K, similar to that of the Natural oxides, and the second $T_{\text{max}}$ occurs at 492 K, akin to those of the remainder of the Boiled and the Dried oxides. This suggests that the species desorbing at 402 K share the same bonding mechanism as the species on the Natural oxides, and the species desorbing at 492 K share the same bonding mechanism for the remaining Boiled and Dried oxides. As mentioned in the previous sections, the values for $T_{\text{max}}$ for each of the Natural, Boiled, and Dried PIC exposure times are in good agreement. The exceptions include B30M and D05M. These differences may be a result of poor thermocouple placement on the sample holder during the analysis of those particular samples. The consistency of the $T_{\text{max}}$ values with changing surface coverage indicate that desorption is independent of surface coverage and suggests a first-order desorption process.

If covalent bonds between the 1,3-diphenyl urea and Al formed, the bonds that are expected to break are C-O, C-N, and Al-O. However, these bond energies range from 300 to 500
kJ mol\(^{-1}\). In Chapter 4, it was suggested that the material was adsorbed to the surface by means of hydrogen bonding, yet the strength of H-bonds lay within the range of 10-50 kJ mol\(^{-1}\). Since the mass fragmentation pattern of the desorbing species tells that the 1,3-diphenyl urea decomposes and desorbs, the activation energies may be that of decomposition and breaking the H-bond to the surface. The higher energies here reveal substantial interaction with the surface and should play a significant role in adhesion phenomena.

6.4 Summary of General Discussion and Desorption Kinetics

The concentrations of urea formed on each of the three Al oxides may be directly dependent on the amount of molecular water available on the surfaces since the calculated sticking coefficients generally do not vary with coverage. The calculated sticking coefficients were quite small, \(10^{-11}\) for the Boiled and Dried oxides, and \(10^{-13}\) for the Natural oxides. The Redhead Analysis of the bond dissociation energies consistently gave energies between 120 - 150 kJmol\(^{-1}\), which are too low to represent covalent bond breaking, but are too high to signify physical bonds. Therefore, the dissociation energies may represent a combination of urea’s decomposition and subsequent desorption of the products. The first order kinetics are consistent with a decomposition-limited desorption event as well.
7.0 **IMPLICATIONS OF STUDY ON POLYURETHANE – ALUMINUM ADHESION**

7.1 **Carbamate Bonds and 1,3-Diphenyl Urea Formation**

From the IR, XPS and TPD results, there is little evidence of carbamate bond formation. The IR results show no characteristic Al-O-C stretching or vibrational bands, and the XPS spectra of the Al 2p photoelectrons gave no shift in binding energies to indicate that an Al-O-C complex was formed. The activation energies determined by TPD experiments are not within the covalent bond range. Furthermore, a methanol wash of the Al surfaces removed all traces of the urea or PIC material as tested by IR. All evidence suggests that the reaction of PIC vapour and an aluminum oxide surface yield 1,3-diphenyl urea that is bound to the surface in a poorly understood manner. Due to the high concentration of water on the oxide surfaces, the PIC vapour may react with the water found on the surfaces to form urea. The urea then hydrogen-bonds to the hydroxyl groups found on the oxides. If carbamate bonds formed at all, they are in such a minute quantity that it is below the detection limit of the instrumentation.

7.2 **Urea and the Adhesion Process**

7.2.1 **Phase Segregation**

In conventional slabstock foam, the bulk may consist of discrete hard-segment domains dispersed throughout a continuous soft-polymer phase. The term *hard-segment* refers to the product of isocyanate and water within the polyurethane reaction mixture, or urea, whereas the term *continuous soft phase* refers to the remainder of the polymer formed with a high concentration of polyol. The hard segments are known to be covalently linked throughout the soft-segment domain. However, this phase can separate from the soft-segment to form a discontinuous phase often reaching 3000 Å in thickness. This separation from the soft segment is believed to occur by means
of the symmetrical shape of the poly-urea bundles and their ability to form strong H-bonds with each other.\textsuperscript{6,62,63}

The relevance of phase segregation has been investigated as a possible contributor to the adhesion mechanism.\textsuperscript{64-66} In a study of polyurethane – silica adhesion, it was found that by adding a high concentration of phase-separated material into a poorly phase-separated polyurethane sample, the adhesion improved considerably. In other words, material that is known to form polyurea bundles was added into the regular polyurethane pre-polymer mix. When these bundles migrated to form a hard-segment domain, the adhesion between the polyurethane and the Si-OH surface improved. Here, the interphase region showed a marked change in composition and thickness.

7.2.2 \textit{The Effects of Urea Groups in Polyurethane Formation}

The urea hard-segments have also been studied for their role in the polyurethane polymerisation process.\textsuperscript{67} During the testing of polyurethane injected into mouldings, it was found that urea and urethane groups formed almost simultaneously, which lead to the investigation of urea as a catalyst for the polyurethane formation. In this case, the urea groups can catalyse polyurethane reactions by means of an H-bonded complex of the urea carbonyl group and the hydroxyl of the alcohol.\textsuperscript{68} This complex can then delocalise the isocyanate C=O electrons, which renders the isocyanate carbon prone to nucleophilic attack:

\[
\begin{align*}
\text{OH} + \text{HN-C-NH} & \leftrightarrow \text{O-H \cdots O}=C\text{N-H} \\
\text{urea} & \text{H-bonded complex} \\
\text{-NCO} + \text{O-H \cdots O}=C\text{N-H} & \rightarrow \text{HNCNH} + \text{HNCO} \\
\text{H-bonded complex} & \text{urea} \text{urethane}
\end{align*}
\]
This increases the rate of isocyanate-hydroxyl reactions which lead to faster polyurethane formation.

With an abundance of urea on the Al surface, it is feasible to argue that H-bonded complexes between the urea and the surface hydroxyls are formed. Some of these complexes can in turn react with available isocyanate to form carbamate bonds. In this case, a few covalent bonds coupled with many H-bonded complexes with the surface would provide a powerful adhesive.

7.3 Vapour Dosing Versus Liquid Application

The experiments conducted for this study were in the gas-phase. However, in “real” applications, the polyurethane foam starting mixture is a liquid, where the aluminum surfaces can be wetted. Although no covalent bonds were observed through the vapour phase dosing, covalent bonding may depend on liquid phase interactions with the oxide. A study was conducted to compare the differences of the bonding properties between dosing chlorophenol vapour on Al oxides and submerging the oxides in a dilute chlorophenol solution. Certain chlorophenols exhibited only H-bonding to the surface from a vapour dose, while chemisorption occurred with the liquid application. It was reasoned that the phenolate ion was able to dissociate in solution, which induced the stronger adsorption.

Considering the acidic properties of the surface hydroxyls and the basic nature of 1,3-diphenyl urea, it is feasible to consider ionic and electrostatic interactions of the two. Perhaps the application of a dilute urea solution on an aluminum oxide would allow the conditions necessary for dissociation that would lead to chemisorption, or covalent bond formation. An investigation of liquid phase systems, and acid-base interactions between urea and aluminum oxides would provide valuable information.
7.4 Kinetic Studies

TPD is a popular technique used in the field of heterogeneous catalysis, but it is not generally implemented in traditional adhesion studies. The TPD results obtained in this study indicate high surface coverage and activation energies of desorption higher than that of H-bonding, but lower than covalent bonds. These results can be interpreted for their relevance to the adhesion mechanism, but currently there is little TPD data on other adhesive systems that would provide a suitable comparison. TPD experiments involving both ideal surfaces, such as single crystals and other metal oxides, as well as model compounds such as polyols and poly-functional isocyanates, would provide a greater depth of understanding to the chemical kinetics of adhesive systems.
8.0 CONCLUSIONS

This thesis summarises the results of the fundamental study of the adhesion mechanism between polyurethane foam and aluminum surfaces. Here, the findings of three distinct types of analysis are listed:

8.1: XPS and SEM Analysis of Prepared Aluminum Surfaces

Three Al surfaces, the Natural oxide, the Boiled oxide and the Dried, oxide were characterised using XPS and SEM:

1. Both the Natural and Boiled oxides showed a decrease in surface oxygen and surface hydroxyl concentration with increased annealing temperatures;
2. The Boiled oxide showed a consistently higher surface oxygen and hydroxyl concentration than the natural oxide both before heating and after annealing to 500°C for 1 hour;
3. The Boiled and Dried oxides showed similar surface morphology and surface area by SEM; both have higher surface areas than the natural oxide, which showed few surface features.

8.2: ER FTIR and XPS Analysis of N24H and B24H

The natural and boiled oxides were dosed with phenyl isocyanate for 24 hours and analysed using ER FTIR and XPS:

1. The material formed on both natural and boiled oxides was characterised as 1,3-diphenyl urea;
2. The was a significantly larger amount of urea on the boiled oxide than on the natural oxide surface;
3. The urea was removed after a 10 minute methanol wash, signifying that the urea was H-bonded to the surface.
8.3: TPD MS Analysis of Time-Controlled PIC Exposures

TPD MS was used to analyse a time-controlled PIC exposure series to the natural oxide, the boiled oxide, and the boiled-then-dried oxide:

1. The mass spectra confirm the IR results that the surface material is 1,3-diphenyl urea;
2. The surface coverage for the natural oxide does not change between a 24 and a 96 hour dosage, thus saturation occurred between a 12 and 24 hour dosage;
3. Both Boiled and Dried oxides showed increasing surface coverage with PIC exposure; the Dried sample coverage did not increase after 2 hours, whereas the Boiled oxide showed no signs of levelling;
4. The sticking coefficient was found to decrease with increasing PIC time-exposure for the Boiled and Dried samples;
5. Bond desorption energies found approximately between 100 - 170 kJ mol⁻¹; which are too low for dissociation of covalent bonds, and too high for physical interactions. They are most likely representative of a combination of urea decomposition and desorption.
9.0 RECOMMENDATIONS

1. Studies of other physical properties of the PIC dosed samples, such as film-thickness, homogeneity, and uniformity, by ellipsometry and XPS would provide a greater understanding of the PIC – aluminum interaction.

2. Quantification of the water on each of the prepared surfaces, would provide an excellent comparison to the amount of urea formed on the surface, as the concentration of urea formed on the surface directly depends on the concentration of water present on the aluminum surface.

3. Desorption kinetics of PIC from other surfaces, such as single crystal aluminum oxide and other well-known catalytic surfaces, would provide an excellent comparative reference for surface interactions.

4. The adsorption of other polyurethane starting materials, such as polyether-polyol and poly-functional isocyanate, should be tested for their kinetic properties on the three prepared surfaces of this study.

5. The polymerization effects of poly-functional isocyanates on the prepared aluminum oxide surfaces should be investigated for the role of cross-linking on adhesion studies.

6. The adsorption of urea from the vapour phase should be compared with that from a dilute solution of PIC in order to test the effects of possible dissociation of PIC, urea and the hydroxylated surface on adsorption.

7. The effects of phase segregation and the role of polyurea adjacent to aluminum surfaces further investigation to elucidate their contribution in adhesion.
10.0 DATA ANALYSIS

10.1 Chapter 3: Aluminum Oxide Preparations

10.1.1 XPS Analysis

1. To quantify Al 2p peak, boiled oxide before annealing:
   Integrated area = 221 cps.eV
   R.S.F. = 0.193
   Effective peak area = integrated area / R.S.F. = 1145 cps.eV

2. Total O 1s peak, boiled oxide before annealing:
   Integrated area = 2365 cps.eV
   R.S.F. = 0.711
   Effective peak area = 3326 cps.eV

3. Deconvoluted OH peak of same sample:
   Effective peak area = 1858 cps.eV

4. \[\text{[OH]/Total O 1s before annealing} = \frac{1858}{3326} = 55.58\%\]

10.1.2 SEM Analysis of Surface Area

Boiled and Dried Surfaces:

1. For the SEM image (1480 x 2200 nm), assume surface profile as discs on top of a flat surface where:

   A: Disc area
   i) height = 266.7 nm
   ii) radius = 20 nm
   iii) area = \(2\pi rh + \pi r^2 = 34771\text{nm}^2\)

   B: With 88 discs on each surface of image, total area of disc surface = 3.06 x \(10^6\text{ nm}^2\) from discs seen on image
   Total disc area of sample = convert to 1.2 x 1.2 cm surface = 1.36 x \(10^{14}\text{ nm}^2\)

   C: Surface area unoccupied by discs:
   on image = 3.2 x \(10^6\text{ nm}^2\)
   Total area of sample unoccupied by discs = 1.42 x \(10^{14}\text{ nm}^2\)

   D: Total area of sample: 2.78 x \(10^{14}\text{ nm}^2\)
E: Total OH number on sample:
At $[\text{OH}] = 19 \text{ nm}^{-2}$,
Total OH $= 2.78 \times 10^{14} \text{ nm}^2 \times 19 \text{ nm}^{-2}$
$= 5.28 \times 10^{15}$

2. OH Number on Natural Oxide:

A: XPS $[\text{OH}]$ concentrations
at 25C, $[\text{OH}]/(\text{O 1s total})$:
Natural = 0.5103
Boiled = 0.5586

at 500C, $[\text{OH}]/(\text{O 1s total})$:
Natural = 0.2153
Boiled = 0.3930

B: SEM $[\text{OH}]$ concentration Boiled $= 5.28 \times 10^{15}$
[OH] Natural Oxide 25C $= 5.28 \times 10^{15} \times 0.5103 / 0.5586$
$= 4.82 \times 10^{15}$
[OH] Natural Oxide 500C $= 2.89 \times 10^{15}$

10.2 Chapter 4: XPS Analysis of Dosed Samples

All XPS analyses were conducted in the same manner as in Section 9.1.1.

10.3 Chapter 5: TPD Analysis of Dosed Samples

10.3.1 Surface Coverage

Xenon gas calibration, for sample B02H:

A: To find Xe partial pressure in chamber

<table>
<thead>
<tr>
<th>Mass (amu)</th>
<th>Intensity (au)</th>
<th>Assignment</th>
<th>R.S.F.</th>
<th>$I_{corr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.036</td>
<td>H$_2$O</td>
<td>1.12</td>
<td>0.0403</td>
</tr>
<tr>
<td>28</td>
<td>0.446</td>
<td>N$_2$</td>
<td>1.00</td>
<td>0.4460</td>
</tr>
<tr>
<td>44</td>
<td>0.019</td>
<td>CO$_2$</td>
<td>1.42</td>
<td>0.0269</td>
</tr>
<tr>
<td>129</td>
<td>0.032</td>
<td>Xe</td>
<td>2.87</td>
<td>0.0918</td>
</tr>
</tbody>
</table>

i) total intensity in chamber: $\Sigma I_{corr} = 0.6051 \text{ au}$

ii) mole fraction Xe: $I_{corr} \text{ Xe} / \text{total intensity in chamber} = 0.1585$

iii) total pressure in chamber: $10^{-7} \text{ Torr}$

iv) partial pressure in chamber: mole fraction Xe x total chamber pressure
$= 1.52 \times 10^{-8} \text{ Torr}$
B: Integrated PIC peak at mass 91 amu corrected to Xe pressure:

\[ PdT = \frac{RSF_{PIC} \cdot P_{Xe} \cdot I_{PIC}}{RSF_{Xe} \cdot I_{Xe}} = 153 \times 10^{-6} \text{Torr} \]

\[ \text{RSF}_{PIC} = 3.1 \quad \text{P}_{Xe} = 1.52 \times 10^{-8} \text{Torr} \]
\[ \text{RSF}_{Xe} = 2.87 \quad \text{I}_{PIC} = 2.98 \text{ K} \]

C: To find effective atmospheric exchange rate (\( \tau \)) of system

i) Volume chamber \( = 300 \text{L} \)
ii) Slope of \( \ln(dP/dP_0) = -0.3218 \)
iii) \( \tau = -\frac{1}{\tau} = 3 \text{s} \)

D: Fragmentation Ratio (FR)

i) Sum of all Xe fragment intensities = 0.236
ii) \( \frac{I_{Xe}}{I_{total}} = I_{Xe'} = 0.208 \)
iii) Sum of all PIC fragments = 0.829
iv) \( \frac{I_{PIC}}{I_{total}} = I_{PIC'} = 0.191 \)
v) \( \text{FR} = \frac{I_{Xe'}}{I_{PIC'}} = 1.09 \)

E: To convert PIC peak to number of molecules on surface area (\( N_{PIC} \))

\[ N_{PIC} = \frac{N_A \cdot V_{chamber} \cdot \text{FR} \cdot 1}{RT_{chamber} \cdot \tau} \cdot \frac{PdT = 1.07 \times 10^{15} \text{molecules}}{\beta} \]

\[ N_A = 6.022 \times 10^{23} \text{molecules} \quad V_{chamber} = 300 \text{L} \]
\[ \text{FR} = 1.09 \quad R = 62.364 \text{ Torr L mol}^{-1} \text{ K}^{-1} \]
\[ \tau = 3 \text{s} \quad \beta = 0.5 \text{ K s}^{-1} \]
\[ P = 1.53 \times 10^{-6} \text{Torr} \]

F: Number of molecules per OH surface site:

Number of molecules / OH on surface
\[ = 1.07 \times 10^{16} \text{molecules cm}^{-2} / 5.2 \times 10^{15} \text{OH cm}^{-2} \]
\[ = 2.07 \]
10.3.2 **Sticking Coefficient**

1. **Sticking coefficient (S):**

\[ S = \frac{\theta}{\Gamma} \]

\( \theta \) = surface coverage in molecules (found with Xe calibration Method)
\( \Gamma \) = collision frequency that gas molecules hit surface, defined as

\[ \Gamma = \frac{1}{4} \frac{N_o P}{R T} \sqrt{\frac{8}{3\pi}} v_{rms} = 4.82 \times 10^{22} \text{ molecules} \]

where

\( N_o \) = Avogadro's Number = 6.022 \( \times \) 10\(^{23} \) molecules
\( P \) = pressure of PIC gas in dosing chamber = 2.8 Torr = 373.3 kgm\(^{-2} \)

\[ v_{rms} = \sqrt{\frac{3RT}{M}} \]

\( R \) = gas constant = 8.314 kg m\(^2\) mol\(^{-1}\) s\(^{-2} \)
\( T \) = dosing temperature = 298 K
\( M \) = molecular mass PIC = 119 \( \times \) 10\(^{-3} \) kg mol\(^{-1} \)

10.3.3 **Activation Energy**

1. **Method I: Redhead Equation for Activation Energy of Desorption (\( E_a \))**

\[ E_a = RT_m \ln\left(\frac{\sqrt{T_m}}{\beta}\right) = 158 \text{kJmol}^{-1} \]

\( T_m \) = temperature where maximum desorption occurs = 514 K
\( \nu \) = pre-exponential factor = 10\(^{13} \) s\(^{-1} \)
\( \beta \) = sample heating \( \beta \)te = 0.5 K s\(^{-1} \)
\( R \) = 8.314 kg m\(^2\) mol\(^{-1}\) s\(^{-2} \)
10.3.4 Desorption Rate

1. First order desorption rate given by POLYANI-WGNER Equation:

\[
\text{rate} = \gamma \theta^x e^{\frac{-E_a}{RT_a}} = 4.76 \times 10^{12} \text{ s}^{-1}
\]

\(x = \text{reaction order } = 1\)
\(\theta = \text{surface coverage at max desorption } = 4.89 \times 10^{15} \text{ molecules}\)
\(E_a = \text{Activation Energy from Redhead’s Equation } = 158 \text{ kJ mol}^{-1}\)
\(v = \text{pre-exponential factor } = 10^{13} \text{ s}^{-1}\)
\(R = 8.314 \text{ kg m}^2 \text{ mol}^{-1} \text{ s}^{-2}\)

2. Rate Constant:

\[
k = v e^{\frac{-E_a}{RT}} = 9.7 \times 10^{-4} \text{ s}^{-1}
\]

\(E_a = \text{Activation Energy from Redhead’s Equation } = 158 \text{ kJ mol}^{-1}\)
\(v = \text{pre-exponential factor } = 10^{13} \text{ s}^{-1}\)
\(R = 8.314 \text{ kg m}^2 \text{ mol}^{-1} \text{ s}^{-2}\)
11.0 REFERENCES


