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Epoxy/aluminum interphases

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Case Western Reserve University, 1992
EPOXY/ALUMINUM INTERPHASES

by

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Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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EPOXY/ALUMINUM INTERPHASES

Abstract
by
FERNANDO FONDEUR

The interactions between an epoxy/dicyandiamide adhesive and chemically treated aluminum surfaces were studied using Fourier Transform Infrared Spectroscopy (FTIR) microscopy and Nuclear Magnetic Resonance Imaging (NMRI). Applying these techniques in a concerted way provided answers to several key questions related to the phenomena of adhesion.

FT-IR was used to characterize the surfaces of Al after various chemical treatments. All of the oxide surfaces were composed of anhydrous alumina, aluminum oxyhydroxide and aluminum hydroxide. The major contaminants found in the different oxides are chemisorbed CO₂, carbonates and bi-carbonates. The chromic acid anodized surfaces (CAA) contain more hydroxyls and water than the sulfuric acid anodized surfaces (SAA). The SAA contain more alumina (Al₂O₃). The CAA surfaces have a duplex structure mainly of hydrated and oxyhydroxylated layers over a hydrated
alumina layer. The SAA surfaces have a triplex structure composed mainly of hydrate and hydroxylated layers over a oxyhydroxylated layer which is over hydrated alumina. The chemically converted surfaces by the Iridite process are made up of a duplex structure composed of a mixed organic-inorganic layer over hydrated alumina. The organic portion of the layer was identified as a carbamate species.

Microscopic reflection-absorption FTIR spectra obtained from epoxy adhesive films on treated and untreated aluminum samples showed compositional differences normal to the interphase. The epoxy on the untreated Al samples showed a large amount of the curing agent and its salt form near the surface relative to the bulk. In the case of the anodized Al surfaces, less curing agent and relatively large amounts of unreacted epoxy were found. The results indicate the surfaces induce selective adsorption depending on the surface treatment.

NMRI was used to analyze the curing behavior of epoxy adhesives in the presence of anodized and chemically treated aluminum surfaces. The proton images of the epoxy for the untreated Al samples images are
characterized by a variety of inhomogeneities (fine texture of uncured and cured domains) finely distributed throughout the sample. Large uncured domains of epoxy were found aggregated near the center of the bonded adhesive sample. Diffusion of uncured material was observed during the curing process. The anodized aluminum/epoxy samples, on the other hand, showed very small contrast and coarse texture images characteristic of phase separation phenomena. However, the onset of curing was clearly shown with increases in contrast and texture. Large amounts of uncured material were seen near the surface indicating the anodized surfaces influence the curing behavior of the adhesive near the interface. This effect was more pronounced in the CAA/epoxy samples.

FT-IR microscopic studies were made of the effect of humidity on epoxy thin films on anodized and untreated aluminum surfaces. The results showed that the anodic layer transforms to Boehmite while in the untreated aluminum/epoxy sample new oxide develops. Water attack was mostly localized. The extent of damage was larger in the untreated aluminum/adhesive sample. Carboxylate formation was seen at the air/epoxy interface away from the oxide.
DEDICATION

To my mother Ana Ventura
ACKNOWLEDGEMENTS

The author would like to thank Dr. Jack L. Koenig for his insight, support and guidance (and patience).

The author would also like to thank the members of the Macromolecular Spectroscopy Group for the time spent training on the equipment.
# TABLE OF CONTENTS

Abstract ii

Dedication v

Acknowledgements vi

Table of Contents vii

List of Figures xi

List of Tables xviii

Chapter I: Epoxy–aluminum interactions in adhesive joints. 1

I.1) Introduction 2
I.2) Oxide 3
I.3) Anodizing Process 4
I.4) The Wetting Process 10
I.5) Curing Process 14
I.6) Water Resistance 18
I.7) Conclusion 23
I.8) References 24
I.9) Figures 28

Chapter II: FT-IR Characterization Of The Surfaces Of Aluminum As A Result Of Chemical Treatment 39
II.1) Introduction 40
II.2) Experimental 42
II.2.a) Specular Reflectance 43
II.2.b) Chemical Section 44
II.3) Experimental Results And Discussion 45
II.3.a) Chromic Acid Anodized 46
II.3.b) Sulfuric Acid Anodized 49
II.3.c) Chemically Treated 50
Iridite I-14 50
II.3.d) Thermal Studies 51
II.3.e) Chemical Sectioning 52
II.3.f) Polarization Studies 55
II.4) Conclusions 58
II.5) References 59
II.6) Figures 61

Chapter III: Microscopic FT-IR Studies Of Epoxy Adhesive Films On Chemically Treated Aluminum Samples 77

III.1) Introduction 78
III.2) Experimental 80
III.2.a) Instrumentation 81
III.3) Results 82
III.3.a) Adsorption Of Epoxy on Anodized Aluminum Surfaces 82

viii
III.3.b) Composition Of Epoxy Adhesive Normal To The Anodized Surface 86

III.3.c) Curing Of Epoxy Adhesive Normal To The Surface 88

III.4) Discussion 90

III.4.a) Effect Of Surface Treatment On The Adsorption Of Epoxy Adhesives 90

III.4.b) Effect Of The Substrate Treatment On The Curing Of Epoxy-Adhesive System 91

III.5) Conclusion 92

III.6) References 93

III.7) Figures 95

Chapter IV: Nuclear Magnetic Resonance Images (NMRI) Of The Epoxy Curing Behavior In Anodized And Untreated Aluminum Bonded Joints 105

IV.1) Introduction 106

IV.2) Experimental 106

IV.2.a) Adhesive System 108

IV.2.b) Bonded Joint Samples 108

IV.2.c) NMRI Technique 108

IV.3) Results 111

IV.3.a) Cross Sectional View Of The Aluminum/Epoxy Samples As A 111
Function Of Cure

IV.3.b) Lateral NMRI Image Of The Samples As A Function Of Cure 113

IV.3.c) Histogram Curves Analysis Of The Lateral View NMRI Images 114

IV.3.d) Texture Measurements Of The Images 115

IV.4) Conclusions 118

IV.5) References 120

IV.6) Table 121

IV.7) Figures 122

Chapter V: FT-IR Microscopic studies of water ingress into aluminum-adhesive joints 136

V.1) Introduction 137

V.2) Experimental 142

V.3) Instrumentation 143

V.4) Results and Discussion 145

V.5) Conclusion 147

V.6) References 148

V.7) Figures 149

Bibliography 157
LIST OF FIGURES

Chapter I

1. Schematic diagram of the anodic film through the thickness as determined by electron microscopy techniques.  28

2. Schematic diagram of the two competing processes occurring during anodizing leading to a minima in the current density.  29

3. Schematic diagram of the non-uniform current distribution during film growth.  30

4. Average pore diameter on the surface of anodic film formed in sulfuric acid solution.  31

5. Schematic diagram of the chemical composition of the anodic films formed in A) sulfuric acid and B) chromic acid solutions.  32

6. Schematic diagram of the electric field across the anodic films formed in A) sulfuric acid and B) chromic acid solutions.  33

7. The breaking stress of epoxy/aluminum joint as a function of the hydroxyl content in the epoxy.  34

8. Schematic diagram of the interfacial structure of epoxy in epoxy/aluminum joints as obtained by acoustic microscopy.  35

10. Schematic diagram of oxide formation in adhesive/aluminum joints during exposure to humidity.

11. Schematic diagram of the processes occurring during corrosion of an adhesive/aluminum joint.
Chapter II

1a. Transmission spectra of the treated and reflection spectrum of the untreated aluminum samples.

1b. Transmission spectra of the treated and reflection spectrum of the untreated samples from the region 1800-1600 cm⁻¹.

1c. Difference spectra of the SAA and CAA oxides.

1d. OH region of the difference spectra of the anodized oxides.

2. Transmission spectrum of the CAA a) heated sample, b) room temperature sample and c) difference of a) – b).

3. Transmission spectrum of the chemically treated (Iridite) a) heated sample, b) room temperature and c) difference a) – b).

4. Specular reflectance spectra of CAA samples exposed to 2M sulfuric acid for a) two minutes, b) 4 minutes, c) 6 minutes, d) 8 minutes and e) 10 minutes.

5. Specular reflectance spectra of SAA samples exposed to 2M sulfuric acid for a) 2 minutes, b) 4 minutes, c) 6 minutes, d) 8 minutes and e) 10 minutes.

6. Specular reflectance spectra of etched samples (Iridite) to 2M sulfuric acid for a) 2 minutes, b) 4 minutes, c) 6 minutes, d) 8 minutes and e) 10 minutes.

6a. Difference spectrum of the organic layer from the inorganic layer of the Iridite treated sample.

7. Grazing angle specular reflectance spectra of CAA samples with light polarized a) no polarizer b) perpendicular to the surface and c) parallel to the
sample surface.

8. Schematic representation of the CAA surface as viewed through the thickness of the oxide.

9. Grazing angle specular reflectance spectra of SAA samples with light polarized a) no polarizer, b) perpendicular to the sample surface and c) parallel to the sample surface.

10. Schematic representation of the SAA surface as viewed through the thickness of the oxide.

11. Grazing angle specular reflectance spectra of the etched samples (Iridite) with light polarized a) no polarizer, b) perpendicular to the samples surface and c) parallel to the sample surface.

12. Schematic representation of the chemically treated aluminum surface (Iridite I-14) as viewed through the thickness of the oxide.

Chapter III

1. Infrared transmission spectrum of the adhesive system.

2. Infrared transmission spectra of the uncured and cured adhesive system.


4. Reflectance spectra of the uncured adhesive on the A) untreated aluminum, B) aluminum/CAA interface and C) CAA surface.

5. Reflectance spectra of the uncured adhesive on the A) untreated aluminum, B) aluminum/SAA interface and C) SAA surface.

6. Reflectance spectra of the uncured
nitrile band as a function of the epoxy thickness on the chromic acid anodized and untreated aluminum.

7. Intensity plot of the nitrile band as a function of the adhesive film thickness on the untreated and treated surfaces.

8. Reflectance spectra of the carbonyl band of the cured adhesive as a function of film thickness on the chromic acid anodized and untreated aluminum surface.

9. Reflectance spectra of the oxirane band after curing as a function of adhesive film thickness on the CAA anodized Al samples.

10. Intensity plot of the carbonyl band of the cured adhesive as a function of film thickness on the treated and untreated surfaces.

Chapter IV

1. Materials used in this work.

2. A cross sectional NMRI images of a CAA-epoxy sample as a function of cure time. The red color area are uncured domains and the green areas are cured domains.

3. A cross sectional NMRI image of a CAA-epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green area correspond to cured epoxy. The image has been magnified 2.5x times.

4. A cross sectional NMRI image of a untreated aluminum epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green area correspond to cured epoxy. The image has been magnified
2.5x times.

5. A cross sectional NMRI image of a chemically treated aluminum (Iridite-14)-epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green are correspond to cured epoxy. The image has been magnified 2.5x times.


7. Lateral NMRI images of the untreated aluminum-epoxy sample as a function of cure time. The red domains correspond to uncured regions and the green domains correspond to cured regions.

8. Schematic diagram of cured and uncured domains in anodized and untreated aluminum/epoxy joints.

9. Lateral NMRI images of the chemically treated aluminum (Iridite-14)-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.

10. Lateral NMRI images of the CAA-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.

11. Lateral NMRI images of the SAA-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.

12. Standard deviation values from difference statistics as a function of neighborhood size (number of pixels away from a given a pixel) for the untreated aluminum and
CAA-epoxy samples.

13. Standard deviation values from difference statistics with a 3x3 pixel window as a function of cure time for the untreated aluminum and SAA-epoxy samples.

14. Standard deviation values from difference statistics with a 3x3 pixel window as a function of cure time for the chemically treated aluminum (Iridite) and CAA-epoxy samples.

Chapter V


2. Schematic of the spatial sampling of the data on the samples. The cones represent the infrared light focused on the spot selected to form the image.

3. Three dimensional plot of the oxy-hydroxide vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area has not been exposed to humidity.

4. Three dimensional plot of the oxy-hydroxide vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.

5. Three dimensional plot of the Al-O-Al vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.
three months.

6. Three dimensional plot of the Al-OH vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.

7. Three dimensional plot of the oxyhydroxide vibrational band as a function of spatial coordinates on the sampled area of the SAA/untreated aluminum sample. The area was exposed to humidity for over three months.

8. Schematic diagram of the effect of water on anodized aluminum/adhesive joints.
LIST OF TABLE

Chapter IV

1. Tabulation of lateral view histogram 121
Chapter I

EPOXY-ALUMINUM INTERACTIONS IN ADHESIVE JOINTS
INTRODUCTION

The formation of durable and reliable adhesive joints is still a major technological problem. The main reason being the lack of understanding of bond formation, resistivity and the nature of the metal surface and adhesives used in the bonding process.

The use of atomic spectroscopic techniques have provided new insights into this problem but the information obtained from such techniques are sometimes ambiguous and do not provide a complete picture of the process¹. Further, destructive techniques such as shear, peel and tensile tests can only evaluate the integrity of the bond. On the other hand, molecular spectroscopy has been shown to successfully analyze interactions between adhesives and surfaces²,³.

This paper concentrates on the interactions and environmental resistance of epoxy and anodized aluminum alloys. The objective is to determine design factors which can improve the integrity of the adhesive bond. Eventual connection between adhesive bond formation and bond strength will be made which can lead to better adhesive bond fabrication. Emphasis is then placed on the application of modern spectroscopy techniques to the problem of adhesion phenomena.
When a fresh aluminum sample is exposed to atmospheric conditions, an oxide surface film develops quickly. The structure of the natural oxide is believed to be amorphous with a hydrated layer at the outer surface. The thickness of typical natural oxide films ranges from 1-5 nm and the films regenerate upon removal or damage. These films are under compressive stresses and are easily damaged. However, depending on the ambient humidity, repair is fast and the healing process can be either an oxygen or water reduction reaction shown below:

\[
4\text{Al} \rightarrow 4\text{Al}^{3+} + 12\text{e}^- \quad \text{anodic}
\]

\[
3\text{O}_2 + 12\text{e}^- \rightarrow 6\text{O}^{2-} \quad \text{cathodic}
\]

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2
\]

The oxygen reduction reaction yields alumina while the hydrogen evolution reaction gives hydroxylated products. There is evidence of flaws responsible for initiating film damage\(^4\). Also these flaws have been linked to poor corrosion resistance of aluminum to solutions of heavy ions\(^5\).
BII. Anodizing processes

When a current passes through the metal (anode), metal dissolution (metal ions) as well as water reduction (O and OH) occurs, the individual reactions combine to form the overall reaction products. If the reaction products are sparingly soluble in the solution and they adhere strongly to the substrate (metal), then an oxide film is formed. The oxide film can have two different morphologies one is termed, Barrier and the other porous.

Barrier films are characterized by high voltages formation and low thicknesses. Further, these films are di-electrically compact. The structure of barrier type films consists mostly of amorphous aluminum oxide and/or, depending on the electrolyte and operating conditions, \( \gamma \text{Al}_2\text{O}_3 \) (tetrahedral aluminum). Film growth reaches a steady state when the rate of formation is equal to the dissolution rate. The rate of formation is controlled by the electrolyte, operating conditions and the resistance of the film which increases with thickness. The dissolution rate is controlled by the etching strength of the solution. In any anodizing condition, film thickness is increased by high voltages and decreased by high temperatures and acidity.
The Porous type is characterized as follows:

There are conditions under which the barrier film develops with localized dissolution. These localized attacks then lead to the formation of porous structures which permits the electrolyte access to the metal. Further growth occurs below the original barrier, leaving the outer oxide exposed to the electrolyte for further attack. Thus, the final oxide consists of a thin compact di-electric film with localized depressions (See Fig.1).

The first theory of anodic oxide formation was proposed by Setoh et. al\(^6\). They suggested that the barrier film allows the passage of oxygen atoms, originating from water and oxygen reduction reactions, which then reacts with aluminum to form the oxide. The pore formation was thought to originate from the attack of anions on the oxide, a film of gaseous oxygen is believed to exit between the pore wall and the barrier which then protects the barrier from dissolution. Another theory\(^7\) suggests the formation of a gel-like substance at the barrier surface composed of negatively charged hydroxides. This gel will then repel electrolytes from the barrier film during voltage
application. Other theories\textsuperscript{8} have suggested the formation of pores due to high localized currents leading to holes. Then new oxides form below the pore base until the pore length is sufficient to decrease the electric field to the point of no oxide formation. Further, the existence of gaseous phases between the electrolyte and the oxide has been postulated which then leads to local heating effects due to electrical currents and chemical reactions. Oxygen ions are formed at the gas/solution interface. Later Schenk\textsuperscript{9} suggested that the volume increases associated with the oxygen anion were too big for the close packed barrier layer, and that the mobile unit was atomic oxygen which reacts with atomic Al at the metal/oxide interface. Thus, the pore formation is due to hydrolysis and barrier formation from atomic oxygen adsorption, diffusion and reaction with aluminum. Pore initiation can be detected electrochemically by a recovery stage in the current density-time curve (see Fig.2). The current density curve is deconvoluted into two processes one of which is due to the barrier film formation (hyperbolic curve) and the other one due to pore formation (the broad peak). The recovery effect is due water and hydroxide incorporation into the oxide which decreases the electric field. The initiation of the pore sites are believed to occur in
places where the anodic field is small or at sites of weakness such as grain boundaries or amorphous areas\(^1\). Pore initiation is believed to be associated with proton entry from the electrolyte which then leads to hydrated oxides. Another possible theory is the effect of the pre-existing aluminum texture upon the growing oxide\(^{11}\). The implication in the latter theory is that the current density is highest at the thickest part of the growing oxide due to high curvature. The high local current density is predominant in the thinnest part of the oxide leading to steady state pore development where the majority of the Al ions end up in solution (see Fig. 3). There is also a distribution of cell size of which the largest cells with films will concentrate the current to the point where metal dissolution occurs to keep the electric field constant. The concentration of current also leads to local Joule heating effects which in turn increases ionic conductance through the oxide\(^{13}\). Lateral growth of the metal base decreases the local current density which then stops other competing pores from growing. The growth process of the pores has been suggested to be catalytic in which the current passing through the pore increases the local temperature and increases the oxide dissolution\(^{14}\). This catalytic reaction shapes the growing pores into initially a
cylindrical shape with round bottoms. These cylinders then meet giving a hexagonal shape to the anodic layer. The number of pores for a given surface area decreases with applied voltage since the pore diameter increases with voltage and anodizing time (see Fig. 4). The use of point chemical analysis have shown the cell wall material to be composed of a gel like structure close to the pore wall and a solid material close to the cell outer wall. The gel like structure is rich in anions from the electrolyte. Their role is assumed to be to charge balance negatively charged colloidal particles in the gel. The solid material is composed of pure alumina which gives a dark texture in TEM. The cell wall material of sulfuric acid anodized films (SAA) is composed of acid anions (see Fig. 5). The phosphoric and oxalic acid anodized films contain both species. The chemical state of the anion incorporated in the SAA is in the sulfate and elemental sulfur state\textsuperscript{17}. The ionic transport through alumina is the rate limiting step in anodic film formation since transport through the anion rich layer is relatively fast. Electric fields are strongest in the alumina rich film (slow formation), thus CAA surfaces form slower than SAA surfaces (see Fig. 6). The acid anion rich layer contains microcrystallites rich in hydroxylated and hydrated products. This layer is active in the wetting
and interaction with epoxy. Infrared spectroscopy on anodic films has demonstrated the existence of oxyhydroxylated and hydroxylated species in the cell wall material\textsuperscript{18} and it is not clear whether these species exist in the alumina or the acid anion contaminated layer. However, the detailed work done thus far on anodic films is beginning to explain the characteristic behavior of anodized surfaces.
THE WETTING PROCESS

A droplet of liquid spreads on a solid surface until an equilibrium state is attained. Measurements of this equilibrium contact angle have been used to determine the degree of wetting of a surface by a polymer melt. The measured angle is related to the surface tension of the solid, melt, and air interfaces according to Young’s equation\(^1\):\
\[ \cos \Theta = \frac{\gamma^{ls} - \gamma^{s}}{\gamma^{l}} \]
developed from thermodynamics. This treatment requires calculation of two variables associated with the solid surface. This approach does not consider the effect of surface chemical inhomogeneity or kinetics of wetting. Shanahan\(^2\) modelled the effects of surface flaws on the measured wetting angle and proposed flaws as the cause for hysteresis effects. His derivation was based on quasi-static conditions where kinetic considerations were not addressed. Ruckenstein et. al\(^3\) modelled the flow behavior of liquids during wetting of surfaces by assuming intermolecular interactions as the possible effect for flow during wetting. Relationships between surface tension, leading angle edges and molecular interaction parameters were established. However, contact angle measurements on anodic surfaces are
difficult to obtain and only qualitative observations can be made. Arlasnov et. al\textsuperscript{22} showed, using a video camera, that polymer wetting of anodic films proceeds three different ways: spreading on smooth surfaces, over pores regions and into the pore walls. The effect of roughness have been found to be negligible while the degree of microporosity significantly affects the wetting kinetics. Further, they studied polymer flow between a convex lens and a plate and came to the following conclusions on the effect of the pore themselves on the wetting kinetics. Nonzero contact angle leads to increase time in pore filling. Increase or decrease of polymer viscosity leads to changes in the structure of the boundary layer (sorption). Compressibility as well as solubility in the polymer of trapped gases in the pores changes the curing rate and mechanical properties of the pore filled polymer. Loading pressure have been used to promote pore filling in adhesive joints. However, theoretical studies relating the size of the pore with the applied load have shown that for thin capillaries pore filling time is insensitive to loading conditions since capillary pressures are high enough for filling while for thick capillaries filling times are sensitive to loading. Pore geometry and degree of polymer filling are important because of the increase in fracture strength
of adhesive joints, over that of nontreated surfaces with anodic film thickness. The assumption is that increases in microporosity as well as pore length are responsible for the enhanced strength although there are reports indicating that the above variables do not play a role when peel tests are performed. Electron and X-ray microscopic studies of the fracture surfaces of adhesive joints indicate the presence of residual polymer on the anodic surfaces. Thus, it has been realized that the interactions between epoxy and the anodic surface, and the resulting interphase developed in the epoxy are the important variables in determining the enhanced strength as well as the weakest part of an adhesive joint.

Along with this approach, correlations between the bending strength of an anodic/adhesive joint and the hydroxyl content are linear (see Fig. 7). Molecular polarity is also thought to play a major role in wetting. Along this line, acid-base, hydrogen bonding and Van Der Waals interactions have been invoked to explain the nature of the wetting phenomena. Deposition of a multicomponent resin on a surface has been assumed to play a minor role in bond formation. Except for a few studies where it has been shown that preferential segregation of the curing agent occurs on
the substrate\textsuperscript{27,28,29}, there is a need to investigate anodic substrate effects on deposition.
CURING PROCESS

One of the first studies of the curing process of epoxy on alumina claimed the existence of chemical bonds between epoxy and the aluminum oxide\textsuperscript{30}. The conclusion was reached from the excess heat coming from the interaction. Yakobson\textsuperscript{31} also measured the excess heat due to adsorption of epoxy on alumina and further, found that dehydroxylation promoted oxirane reaction with alumina. The reaction implied was a nucleophile attack by either oxygen or aluminum ions on the oxirane molecule grafting the epoxy molecule to the surface. Yakovlev et. al\textsuperscript{32} studied the reactivity of the different aluminum oxides toward epoxy and concluded that heating above 220°C grafted epoxy with the oxide. His conclusions were based on the appearance of 1150 cm\textsuperscript{-1} and 410-390 cm\textsuperscript{-1} bands coupled with the disappearance of the 914 cm\textsuperscript{-1} band. The reaction can be written as follows:

\[
\text{AlO}_2(\text{OH}) + \underset{\text{CH}_2 - \text{CH}}{\text{CH}_2 - \text{CH}_2} \rightarrow \text{AlO}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH} \]

Other epoxide reactions have been proposed. Bell et. al\textsuperscript{33} suggested epoxide oxidation leading to carboxyl formation. Epoxide rearrangement into carbonyl or allylic groups has also been seen\textsuperscript{34}. Hydroxylation of
the oxirane group by water$^{34}$ has also been observed. Some researchers have postulated reactions between aluminum oxides and the curing agents. Protonation reaction of the amine curing agent by metal hydroxides have been seen in epoxy/aliphatic amine adhesive on aluminum$^{35}$ at room temperature. At high temperatures de-protonation of the amine curing agent by surface oxygen ions and electron transfer from nitrogen to aluminum ions have also been seen$^{36}$. Ondrus et. al$^{37}$ investigated the reactions between epoxy/anhydride adhesives and aluminum surfaces with infrared and found the anhydride reacted with the aluminum to form metal carboxylates. Boerio et. al$^{38}$ used ESCA to study the reaction between an epoxy/polyamide adhesive and 2024 aluminum surfaces. The polyamide segregated preferentially to the surface and reacted with the oxide to form metal carboxylates. Baldwin et. al$^{39}$ deposited thin films of epoxy/amine adhesive on an aluminum surface and found preferential segregation of the amine to the surface. Bolouri et. al$^{40}$ used ESCA to study thin films of epoxy/amine adhesives on anodized aluminum and found charge transfer between the amine and the surface though no surface species was identified. Affrosman et. al$^{41}$ used IETS (inelastic electron tunneling spectroscopy) to study epoxy/amine adhesives on aluminum and found condensation of the
resin and charge transfer of the amine. Only one report suggests the possibility of free radicals generated during curing interacting with the surface\textsuperscript{42}. On the other hand, there are reports suggesting the aluminum oxide inhibits epoxide curing. Commyn et al.\textsuperscript{35} use IETS to study thin films of epoxy on aluminum surfaces and found a relatively large amount of uncured epoxy at the surfaces. Janiv et al.\textsuperscript{43} used IR to study epoxy and urethane coatings curing on anodized aluminum surfaces and found no polymerization at the surface. Fin et al.\textsuperscript{44} found the curing of one component silicon rubber adhesives to be inhibited on 2024 aluminum. Along this line, suggestions of cellular structure in the epoxy/metal surfaces have been indicated by Cuthrell\textsuperscript{45} and later by Corgnard\textsuperscript{46}. The cellular structure obtained by acoustic imaging is schematically shown in (Fig. 8). The nodules are cured resin surrounded by a gel-like region. The gel-like region contains charges that make the interphase conductive in thin joints. The theory is that the aluminum oxide is thin enough for charge transfer. For anodic films this structure might exist to a lesser extent since previous studies show no metal ions since the anodic films are thick enough to shield the substrate from electrochemical reactions. The composition of the cell and nodule material must be
determined to see if the curing agent is segregating spatially during curing into islands. The most likely scenario occurring in the curing of epoxy adhesives on anodic films is that anodic films can act like molecular sieves which selectively adsorb low molecular weight. In fact, Brockmann suggested this picture to explain the TEM pictures of epoxy/anodic aluminum interfaces. It is not clear whether this phenomena is occurring, what components are absorbed, and how this polymer fractionation affects the curing rate and extent of cure.
Stability in a humid environment is an important requirement of adhesive joints. The adhesive joint is a composite of the adhesive, oxide and the interphase. The component with the poorest resistance to water will determine the durability of the joint. As already mentioned, the weakest component in aluminum-epoxy joints is the interphase. The exact mechanism of water interaction or damage with the adhesive joint is still not known precisely. The reason being the difficulty of studying the interphase nondestructively.

The hydration properties of the oxide must play a role (see Fig. 9). Venables et. al\textsuperscript{48} studied the hydration properties of anodic films and concluded that the transformations of alumina into Boehmite and then into Bayerite were responsible for the degradation of adhesive joints (see Fig. 10). On the other hand, Pesetski et. al\textsuperscript{49} found aging in humidity improved the strength of adhesive joints. The rationale given was that newly formed hydroxides interact with the epoxy increasing the net adhesive strength. Brockmann\textsuperscript{50} suggested that for thin oxide films, oxide dissolution was a consequence of humidity and this damage proceeded from the edge of the bond inwards. Support for this
theory is more evident when special inhibitors are used which prolong the lifetime of adhesive joints. The way in which hydration inhibitors work is still not clear since inhibitors can also react with the adhesive.

Another degradation theory suggests the displacement of epoxy away from the oxide surface by water. Kinloch et. al\textsuperscript{51} used a thermodynamic approach to predict epoxy debonding from the oxide by water. The modelling considered polar interactions only and it does not include other adhesion mechanisms such as chemical bonding. Thus, the approach has found little further use.

Most researchers believe the component most susceptible to water is the adhesive itself. Kerr et. al\textsuperscript{52} studied the effect of water and ethanol on the cohesive strength of the adhesive joint. It was concluded that ethanol affected significantly the cohesive strength of the adhesive while water affected more the shear strength of the adhesive joint. This indicates that water attacks the interface preferentially. Contrary to these findings, other researchers feel that the low epoxy water permeability is what determines durability. Lefebvre et. al\textsuperscript{53} studied humidity effects on adhesive joints and found that there is a critical humidity level below which
water does not degrade adhesive joints. The existence of this critical humidity level was associated with (1) a sudden increase of water solubility in the epoxy, (2) a corresponding increase in epoxy volume, and (3) large decrease in water mobility. Further, they found water irreversibly trapped by interchain hydroxyl groups reacts with uncured oxirane groups to form diols.

Su et. al\textsuperscript{54} performed fatigue tests of adhesive joints as a function of ageing and concluded that fatigue life improved with humidity while others did not. Further, the durability performance showed a close relation with the adhesive water uptake. Bowditch et. al\textsuperscript{55} studied the effect of the equilibrium water content on the mechanical properties of finely dispersed oxides in epoxy adhesives. They found that there was not a critical water content below which water does not degrade the adhesive joint, thus water affects the mechanical properties of the sample irrespective of the content. Further, the effects were found to be reversible upon removal of water and that the water was distributed between the oxide particles and the adhesive. It does appear that in adhesive joints at low water humidity, water is mostly situated in the bulk adhesive away from the interface and with increasing water content, water will ingress to the
interface. Thus, plasticization is thought to be the major effect of water at low water content but recent work now suggests hardening of the epoxy with humidity. Raveh et. al\textsuperscript{56} performed shear stress test and hardness studies of epoxy/aluminum joints as a function of aging. They concluded that the durability of adhesive joints is a competition between epoxy hardening and weakening of the epoxy/oxide interface. Which effect is occurring first is not indicated but it is most likely that epoxy/water interactions occur first.

Another mode of environmental degradation of adhesive joints is corrosion (see Fig. 11). Brockmann et. al\textsuperscript{50} argued that for thick anodic films on aluminum, durability of adhesive joints was determined by corrosion processes. His arguments were based on the observation that it takes a long time to dissolve thick oxide films and cathodic delamination of the adhesive was a possible reaction. Watts\textsuperscript{57} argued that cathodic delamination by water leads to oxide reduction, polymer saponification and interfacial debonding. He also concluded that these degradation mechanisms could be occurring simultaneously and in the case of fused bonded epoxy on steel, oxide reduction occurs first followed by interfacial delamination due to water. Oxide reduction is thought to dominate under
high cathodic potentials while interfacial delamination dominates in the unpolarized case. Dickie et al. used ESCA to investigate failure mechanisms in epoxy/dicyandiamide adhesives on cold rolled and galvanized steels. They concluded that oxide dissolution was the dominant mechanism in the absence of any applied potential. Thus, the resulting pH in the adhesive plays a role in the stability of the oxide. Aluminum oxides are unstable under basic conditions and in epoxy/dicyandiamide adhesives on anodized aluminum joints. Interfacial delamination is thought to be insignificant in epoxy adhesives on anodic aluminum due to the large surface areas associated with anodic surfaces. Thus, oxide reduction and polymer degradation are the major degradation mechanisms in epoxy adhesives/anodic aluminum joints.
CONCLUSION

In summary, there is a need to investigate spectroscopically the effect of anodized surfaces on the curing behavior of epoxy adhesive systems. Infrared microscopy combines localized spectroscopy with imaging capability. Absorbances in infrared are strictly related to the functional groups present in a molecule and thus, functional mapping of epoxy can be obtained in the present of anodized surfaces.
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Fig. 1. Schematic diagram of the anodic film through the thickness as determined by electron microscopy techniques.
Fig. 2. Schematic diagram of the two competing processes occurring during anodizing leading to a minima in the current density.
Fig. 3. Schematic diagram of the non-uniform current distribution during film growth.
Fig. 4. Average pore diameter on the surface of anodic film formed in sulfuric acid solution.
Fig. 5. Schematic diagram of the chemical composition of the anodic films formed in A) sulfuric acid and B) chromic acid solutions.
Fig. 6. Schematic diagram of the electric field across the anodic films formed in A) sulfuric acid and B) chromic acid solutions."
Fig. 7. The breaking stress of epoxy/aluminum joint as a function of the hydroxyl content in the epoxy
Fig. 8. Schematic diagram of the interfacial structure of epoxy in epoxy/aluminum joints as obtained by acoustic microscopy.
Fig. 9. The effect of surface treatment on the durability of an adhesive/aluminum joint.
Fig. 10. Schematic diagram of oxide formation in adhesive/aluminum joints during exposure to humidity.
Fig. 11. Schematic diagram of the processes occurring during corrosion of an adhesive/aluminum joint.
Chapter II

FT-IR CHARACTERIZATION OF THE SURFACES OF ALUMINUM

AS A RESULT OF CHEMICAL TREATMENT
INTRODUCTION

Anodic films of aluminum have attracted considerable attention because of their wide application in modern technology. Aluminum is usually anodized to protect the metal against corrosion, to improve its abrasive properties, to provide electrical insulation, and to improve adsorption properties in adhesive joints. There are various ways of anodizing aluminum depending on whether acidic or basic solutions AC or DC voltage are used, etc. to give different structures\(^1\).

The structures of anodized Al layers have been studied previously\(^1,2,3,4,5\). Dorsey used FT-IR to study the structure of anodic aluminum\(^6,7,8\) and concluded that the oxides are mainly composed of a barrier and porous layer. The bi-layer structure explains electrical properties. However, the barrier-porous structure used to describe anodic films is incorrect. The proper picture is a set of hollow cylinders with round bottoms composed of a passivating layer. He also found the porous layer to be mainly composed of aluminy (Al=O) and the barrier layer of hydroxides. Maeland et. al\(^4\) showed that the barrier layer was
anhydrous and the infrared band assigned to OH by Dorsey was a optical phonon due to aluminum alkoxides. Handke et. al\textsuperscript{10,11} used various FT-IR techniques and improved the correlation between the spectra of the coatings and structure. They showed that sulfuric acid anodized surfaces were composed mainly of aluminum oxide, oxy-hydroxide and hydroxides. Fin et. al\textsuperscript{13} used various spectroscopic techniques to analyze anodized layers and concluded that anionic incorporation as well as alloying elements were the differences between different anodic films. However, few studies have focused on the molecular structure of anodic films in the context of designing and developing new oxides for existing adhesive systems.

By combining FT-IR specular reflectance with chemical sectioning\textsuperscript{13}, we have investigated the molecular composition and orientation of anodic Al films. These techniques, along with transmission spectra, were used to characterize anodic films. Chemical sectioning with sulfuric acid permitted in-depth spatial analysis of the formed films. This paper demonstrates the structural and spectral differences between anodic aluminum films formed in sulfuric acid, chromic acid and films formed in an etching solution (Tridite\textsuperscript{9}).
EXPERIMENTAL

MATERIALS

Aluminum (2024-T3) coupons (1 x 1.5 inches) were mechanically polished to 3 μm roughness and then degreased with 2-butane. The coupons were then sent to a plating company to be anodized in sulfuric and chromic acid solutions according to MIL-A8625-E specifications with the following anodizing conditions:

MIL-A8625-E

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Applied

Voltage 18 Volts 40 V
Current 23 A/ft² 1.5 A/ft²
Temperature 20°C 20°C
Time 60 Min. 30 Min.
Thickness 34 μm 19 μm

Thickness measurements were done on a Permascope EWP9 by Fischer Instrument with ±2 μm uncertainty. The rest of the coupons were etched in a solution of cyano-chromic acid complex (iridite *). This treatment is widely used and little is known of the oxide structure it produces. Samples were kept in a
dessicator under vacuum after treatment. Spectroscopic studies were done as soon as possible to avoid the build up of impurities and subsequent chemical modification.

SPECULAR REFLECTANCE MEASUREMENTS

Specular reflectance measurements used an incidence angle of 74° with an aperture. All spectra were taken at a resolution of 4 cm⁻¹ and co-added with 256 scans. Polarization was done with a KRS-5 wire grid polarizer to give s-polarized light (light with electric field tangential to the sample surface) and p-polarized (light with the electric field normal to the sample surface). It is widely known that s-polarized light gives no reflection spectra on metallic surfaces at grazing angles. However, for sufficiently thick organic or inorganic films on the metallic surfaces, reflection absorbance spectra are observed. If the film is thin enough, longitudinal phonons will be optically active when p-polarized radiation is used. Longitudinal phonons are in-phase motions, normal to the sample surface, of the molecular species. On the other hand, transverse phonons are in-phase motions tangential to the sample surface. They can only be driven by s-polarized radiation. If the sample is too thin, then the large dielectric
constant of the metal will absorb the s-radiation and no transverse phonons are seen. However for thick samples, both transverse and longitudinal phonons can be seen\(^4\). For every species in the solid, there should theoretically be two resonances associated with the absorbing mode. One associated with transverse phonons and the other with longitudinal phonons. It has also been shown that phonons also occur in amorphous solids\(^6\), thus they are expected to be seen in organic as well as inorganic films. Since absorbances in organic materials are too low (compared to inorganic materials) splittings due to TO-LO (transverse and longitudinal phonons) are extremely small\(^2\), thus only single absorbances are observed with organic materials. This is not true for inorganic materials in which phonon splittings are the rule.

CHEMICAL SECTIONING

Boiling 2M sulfuric acid solutions were used to dissolve the anodic oxides on the samples. Sulfuric acid was used because it only mildly attacks the aluminum below the anodic oxide\(^{13}\). Coupons were exposed for 2 minute time intervals, rinsed in distilled water and dried in vacuum. The dissolution rate can be converted to penetration depth by weighing the coupons on a balance, using density values of 2.36
g/cm³ for SAA samples¹, 2.07 g/cm³ for CAA samples and 1.89 g/cm³ for the etched samples (iridite). The density value for the Iridite sample was supplied by the plating company. A constant exposure area was used for all the samples. This was accomplished by clapping the coupons against a socket joint containing the boiling solution. The exposure area was 5.17 cm². Infrared reflectance spectra of these samples was carried out in a Irus² microscope at incidence angles ranging from 75° with no polarizer.

EXPERIMENTAL RESULTS AND DISCUSSION

The FT-IR transmission spectra from a sample obtained by scraping the oxide off the metal surface with a Stainless steel knife are shown in the range from 4000 to 500 cm⁻¹ in Figure 1a and the expanded region from 2200 to 600 cm⁻¹ in Figure 1b for the four different Al samples (except for the untreated Al sample in which the specular reflectance spectrum is shown). The bands observed and their chemical assignments are shown in Figure 1b.
The IR spectra reflect the well-known differences in the functionality of the treated surfaces\textsuperscript{11}. The untreated Al surfaces show the simplest spectra as expected. Bands due to bulk AlO structure are observed: Al-O-Al stretching vibrations of amorphous Al\textsubscript{2}O\textsubscript{3} at 968 and 760 cm\textsuperscript{-1}. The intensities of these peaks in the untreated sample compared to the chemically treated samples reflect the greater contribution of the bulk components in the untreated samples. The reminder of the spectra of the untreated sample shows weak lines due to surface contamination and oxidation (these bands will be discussed in more detail later). The bands are weak and diffuse in the untreated sample relative to the treated samples.

A. Chromic Acid Anodized Al

The most intense lines in the chromic acid anodized (CAA) samples arise from the hydroxyl absorption in the 3600 to 3400 cm\textsuperscript{-1} region reflecting the complex distribution of hydroxyl groups on the surface of the Al. Inorganic hydroxyl groups are expected to absorb in the 3510 and 3230 cm\textsuperscript{-1} region in addition to absorbed water. The result of this multifunctionality and their interaction through
hydrogen bonding yields the broad band observed in this region. Adsorbed water is also observed at 1658 cm\(^{-1}\) and at 1625 cm\(^{-1}\) suggesting that there are several types of adsorption sites for water in the CAA treated samples. The bands due to the bulk AlO structures are weak in the CAA spectra indicating that the spectra are primarily from the treated surface. Another set of intense lines are seen between 1200 and 950 cm\(^{-1}\) reflecting the structure of the oxide on the treated surface. The bands are indicative of aluminum oxyhydroxides and hydroxides species. The broadness of the bands reflects the presence of different species. The oxyhydroxides absorb strongly near 1072 cm\(^{-1}\) and weakly near 1175 cm\(^{-1}\). This is consistent with a pseudoboehmite structure. Aluminum hydroxides absorb at 1020 cm\(^{-1}\) and 806 cm\(^{-1}\) with a band structure similar to gibbsite. The intense line near 1103 cm\(^{-1}\) is still unassigned but it either due to boehmite or to a chemisorbed water species of the form Al-OH\(_2\)\(^+\). Additional bands are observed related to the reactions and adsorption of CO\(_2\) with the CAA surface. These bands are in the 1660 and 1200 cm\(^{-1}\) region. There are chemisorbed CO\(_2\) species as noted by the bands at 1560 and 1410 cm\(^{-1}\) and unidentate carbonate species at 1384, 1360 and 830 cm\(^{-1}\). The nature of the band at 1260 cm\(^{-1}\) is still uncertain but it could be due to CH\(_3\).
groups since EDAX results showed no Si atoms. A difference spectrum of the CAA and SAA oxides between 1800 cm\(^{-1}\) and 600 cm\(^{-1}\) is shown in Fig. 1c. The difference spectrum shows a broad negative peak between 1170 – 1060 cm\(^{-1}\), a broad positive peak between 1230 – 1180 cm\(^{-1}\) and small broad positive peak between 935 cm\(^{-1}\) and 790 cm\(^{-1}\). The peak around 1100 cm\(^{-1}\) (associated with hydroxides) indicates the CAA oxide surface contains relatively more water and hydroxides than the SAA oxides. This is more clearly shown in Fig. 1d which shows the difference spectrum of the OH region between SAA and CAA oxides. The negative peak around 900 cm\(^{-1}\) associated with Al-O vibrations indicate the greater amount of backbone oxide (alumina) on the SAA oxide. The negative peak near 1180 cm\(^{-1}\) is associated with the sulfate groups trapped in this oxide. Thus, CAA oxides contain more hydroxyls and water than the SAA oxides while the latter contains more alumina (Al-O-Al).
B. Sulfuric Acid Anodized Al

The most intense bands in the sulfuric acid anodized (SAA) samples are due to water and hydroxyl groups (3600–3400 and 1620 regions). From the position, shape and intensity of these bands, similar structures are present in SAA as in the CAA treated samples. This oxide surface also contains intense bands between 1200 and 1160 cm\(^{-1}\) that are characteristic of sulfates\(^{19}\). The bands at 1200, 1160, 995 and 663 cm\(^{-1}\) are due to the \(\nu_3\), \(\nu_1\) and \(\nu_4\) vibrations of the sulfate groups\(^{19}\). Sulfate groups are also observed by other spectroscopic techniques for SAA treated samples\(^{11,20}\). Two intense bands are seen in the lower wavenumber region (532 cm\(^{-1}\) and 516 cm\(^{-1}\)), due to water. The SAA surface also contains similar bands in the region between 1130 to 950 cm\(^{-1}\) as the CAA sample. Thus, the SAA samples contain oxyhydroxides and hydroxides of the type seen in the CAA samples. The set of bands between 1600 cm\(^{-1}\) and 1200 cm\(^{-1}\) are due to contamination bands of the kind noted for the CAA samples. This is consistent with previous studies of these systems\(^{11,12}\).
C. Chemically Treated (Iridite) Al

The chemically treated sample (Iridite) spectrum is also shown in Figure 1. Bands associated with water and OH groups are the most intense bands in the spectrum for this sample treatment. The shape, intensity and location of these bands are similar to those found in the anodized samples, indicating similar water and OH structures exist in all three samples. The second most intense band is seen near 2070 cm\(^{-1}\), due to metal cyano groups. XPS work done on a similar sample showed high content of nitrogen atoms \(^2\), suggesting assignment of this band to the cyano group. Another intense band is seen at 802 cm\(^{-1}\). This band is the overlapped combination of the rocking motion of water and oxyhydroxides. The set of bands between 700 cm\(^{-1}\) and 600 cm\(^{-1}\) are due to the libration modes of lattice water (water inside the oxide). Finally the band at 540 cm\(^{-1}\) is assigned to the wagging mode of water \(^1\). Thus, this chemical treatment has nearly the same water and hydroxyl structure as the anodized layers.
D. Thermal Studies

In order to clarify some of the spectral assignments of the treated samples, thermal studies were conducted. FT-IR transmission difference spectra of the CAA treated samples heated to 180 C for 0.5 hours and evacuated are shown in Figure 2. Heating should remove water concentration from the spectra, making identification of bands associated with water easy (assuming little change occurs in the oxide structure during de-hydration).

The difference spectra reflect the bands associated with water lost during de-hydration (1620, 1120–1100, 800 and 700-500 cm\(^{-1}\)). There is a broadening and increase in the bands centered around 920 cm\(^{-1}\). This suggests the formation of Al-O-Al and hydrogen bonded OH species during heating. This result illustrates the well-known relation between de-hydration and oxide formation as follows:

\[
\text{(1) } \text{Al-OH} + \text{Al-OH} \rightarrow \text{H}_2\text{O} + \text{Al-O-Al} \\
\text{(2) } 2\text{Al-OH} \rightarrow \text{Al-OH} + \text{O-Al} + 2\text{H}_2\text{O}
\]
This has the consequence of lowering the Bronsted acidity and basicity of the treated surface. The bands at 1260 cm\(^{-1}\) and 1246 cm\(^{-1}\) decreased during de-hydration indicative that these bands are associated with water and CO\(_2\) (EDAX results showed no Si atom present in the sample). The same results were obtained for the etched samples (Iridite) as seen in Figure 3. Previous work on the interaction of water and CO\(_2\) on oxides assigned the 1246 cm\(^{-1}\) band to bi-carbonates. Thus, it is possible that such bands in our samples are also due to bi-carbonates.

E. Chemical Sectioning

In order to study the spatial distribution through the thickness of the treated surfaces, the chemical sectioning technique of the treated surfaces was done by immersing the treated samples as a function of time in a 2M solution of sulfuric acid. The specular reflectance spectra obtained at an incidence angle of 75° are shown in Figure 4 for the CAA treated samples.

The spectra reflect the chemical structure of anodized surfaces. The broad band at 1150 cm\(^{-1}\) decreases while the broad band at 950 cm\(^{-1}\) is relatively unaffected as the thicknessess of the films
decrease. The broad band at 1150 cm\(^{-1}\) is associated with the longitudinal optical phonons of the hydroxides\(^{11}\). The band at 950 cm\(^{-1}\) is associated with the longitudinal optical band of the Al-O-Al species\(^{11}\). Thus, hydroxides and water are preferentially concentrated near the surface of the treated samples while the alumina (of the kind seen in the untreated sample) is concentrated near the metal substrate. The bands associated with the contaminating species are concentrated near the surface as they are not observed after a short period of dissolution. However, the bands associated with carbonates remain after some periods of dissolution. They are either incorporated in the oxide network or they are within the pores which penetrate into the passivating oxide layer\(^{1}\). It is possible that the carbonates formed during sample exposure in air during the dissolution testing. If this is the case then carbonate formation is uniquely associated with lattice water since no carbonates are seen when the barrier oxide is at the surface. Similar results were obtained for the SAA treated samples as seen in Figure 5. However, these samples show strong hydroxyl adsorption (band near 1100 cm\(^{-1}\)) resulting from the 6 to 8 minutes exposure to sulfuric acid. This is indicative of the gradients of structures existing in anodized samples. These results are
consistent with the oxide structure developed by other workers for anodized samples\textsuperscript{11}. Thus, the SAA oxides appear to have a tri-layer structure by this anodizing process as follows;
hydrated, hydroxylated, oxyhydroxylated/
oxyhydroxylated / alumina

which is different from the CAA oxide which has a duplex structure.

The chemical sectioning of the chemically treated samples is shown in Figure 6. All of the bands decreased uniformly with time as shown in the figure. This figure also shows a gradual transition from a mixed organic-inorganic structure to hydrated alumina. By subtracting one spectrum from the other, one can isolate the organic layer and this is shown in Fig. 6a. The figure shows organic bands at 3300 cm\textsuperscript{-1}, 1640 cm\textsuperscript{-1}, 1560 cm\textsuperscript{-1} 1230 cm\textsuperscript{-1} (broad) and 800 cm\textsuperscript{-1} (broad). These bands are assigned to a carbamate structure. The bands at 2920 cm\textsuperscript{-1} and 2850 cm\textsuperscript{-1} are due to CH\textsubscript{2} groups while the band at 2079 cm\textsuperscript{-1} is due to nitrile groups covalently bonded to either chromium or iron atoms. Thus aluminum surfaces treated by the Iridite process are duplex structures composed of a mixed organic-inorganic layer (carbamates + hydroxides) above a hydrated alumina (Al\textsubscript{2}O\textsubscript{3}).
F. Polarization results

The FT-IR specular reflectance spectra obtained at an incidence angle of 75° with s and p-radiation of CAA treated samples is shown in Figure 7. The p-polarized spectrum is shown in Figure 7b. The most intense bands are from the longitudinal optical phonon vibrations of the Al-O-Al species (1114 and 987 cm\(^{-1}\)). The longitudinal phonons vibrate normal to the surface so the Al-O-Al species are normal to the surface. The rest of the bands in the p-spectrum are weak. The s-polarization reflectance spectrum is shown in Figure 7c. The most intense lines arise from the 3600 to 3400 cm\(^{-1}\) and 1620 to 1200 cm\(^{-1}\) regions. These bands are assigned to transverse optical phonon vibrations of the Al-OH, and the absorption of the H\(_2\)O and carbonate species \(^{19}\). The transverse phonon propagates tangential to the sample surface so the species associated with these phonons are preferentially tangential to the surface. Thus water, OH and carbonate species are oriented tangential to the surface. From the results of polarization and chemical sectioning, one can schematically draw the surface of CAA samples (see Figure 8).
The FT-IR reflectance spectra obtained by polarized radiation are shown in Figure 9 for the SAA sample. Band assignments are shown also in the figure.

The p-polarized spectrum is shown in Figure 9b. Since the SAA treated surfaces are virtually transparent, the spectrum shows intense birefringences (2655 and 1530 cm$^{-1}$). However, there are bands due to absorbing species not associated with the interference phenomena. These are the weak bands at 1210 cm$^{-1}$ and 1030 cm$^{-1}$ due to SO$^{2-}$ and Al-OH species. The s-polarized spectrum is shown in Figure 9c. Again the appearance of birefringence is noted at 2000 cm$^{-1}$ and 2800 cm$^{-1}$. However there are two sharp bands at 1132 and 962 cm$^{-1}$. They are assigned to the transverse phonon modes of the species mentioned above. Orientational assignment of these samples is difficult since the same species can give optical phonons in both polarization experiments$^{21}$. Thus, the SAA treated aluminum is schematically shown in figure 10.
The FT-IR reflectance spectra obtained by polarized radiation are shown in Figure 11 for the chemically treated sample. Bands assignments are also shown in the figure. The p-polarized spectrum of this sample is shown in Figure 11b. As can be seen from the figure all the bands are present with the most intense band occurring at 2090, 948 and 937 cm\(^{-1}\). These bands are assigned to metal-cyano, Al-OH and Al-O-Al longitudinal optical phonons respectively. Other set of bands are 856, 601 and 567 cm\(^{-1}\). They are assigned to the wagging, rocking and libration modes of water.

The s-polarized spectrum of this sample is shown in Figure 11c. The most intense bands arise from the region 2071 and 3600 to 3200 cm\(^{-1}\). They are due to metal-cyano, water and OH groups. Thus water, metal-cyano and OH groups are isotropically oriented in these samples. Thus its structure is different from that of the anodized samples. The chemically treated surface is schematically shown in figure 12.
CONCLUSIONS

It is shown that FT-IR reflectance is a particularly powerful technique for characterizing anodic surfaces. Identification of molecular species and their orientation with respect to the surface is possible. It is shown that the major contaminant in the different oxides are chemisorbed CO₂, carbonates and bi-carbonates. All of the oxide treatments have contributions from the anhydrous alumina, aluminum oxy-hydroxide (pseudoboehmite) and aluminum hydroxide (close to Gibbsite). CAA oxides contain more hydroxides and water than the SAA oxides while the latter contains more alumina. CAA oxides are duplex structure of hydrated and hydroxylated layers above a hydrated alumina. On the contrary, SAA oxides have a triplex structure composed of hydrated and oxyhydrated layers above an oxyhydrated layer. The chemical converted surface by the Iridite process shows a duplex structure of a mixed organic-inorganic layer above hydrated alumina. The organic portion of the layer is a carbamate species.
REFERENCES


Figure 1a. Transmission spectrum of the treated and un-treated aluminum samples.
Figure 1b. Transmission spectrum of the treated and untreated aluminum samples from the region 1800-600 cm⁻¹.
Figure 1c: Difference spectrum of the SAA and CAA oxides.
Figure 2. Transmission spectrum of the CAA oxide heated sample, b) room temperature sample and c) difference of a) - b).
Figure 3. Transmission spectrum of the etched (Iridite) a) heated sample, b) room temperature sample and c) difference (a) - b).
Figure 4. Specular reflectance spectra of CAA samples exposed to 2M sulfuric acid for a) 2 minutes, b) 4 minutes, c) 6 minutes, d) 8 minutes and e) 10 minutes.
Figure 5. Specular reflectance spectra of SAA samples exposed to 3h sulfuric acid for a) 2 minutes, b) 4 minutes, c) 6 minutes, d) 8 minutes, e) 10 minutes and f) 12 minutes.
Figure 7. Grazing angle specular reflectance spectra of CAA samples with light polarized a) no polarizer, b) perpendicular to sample surface and c) parallel to the sample surface.
Figure 8. Schematic representation of the CAA surface as viewed through the thickness of the oxide.
Figure 9. Grazing angle specular reflectance spectra of SAA sample with light polarized a) no polarizer, b) perpendicular to sample surface and c) parallel to the sample surface.
Figure 10. Schematic representation of the SAA surface as viewed through the thickness of the oxide.
Fig. 12. Schematic diagram of the chemically treated aluminum surface (Iridite I-14) as viewed through the thickness of the oxide.
Chapter III

MICROSCOPIC FT-IR STUDIES OF EPOXY ADHESIVE FILMS ON
CHEMICALLY TREATED ALUMINUM
INTRODUCTION

The formation of strong, reproducible and reliable bonds is an important technological problem. The difficulty has been the lack of information concerning the composition of the adhesive bond and the nature of its distribution through the Al interface. In this report, we investigate the adsorption of epoxy adhesives onto anodized Al surfaces.

The alumina surface has both acidic and basic groups$^1$. The hydroxyls on the alumina surface are not the only active sites for the adsorption of basic molecules. Aluminum ions, which act as Lewis acid sites, may also bind basic molecules. The aluminum ions are not found in the top layer but may be exposed by vacancies in the surface layer consisting of oxygen and hydroxyl ions$^2$. There are different Lewis acid sites with varying acidity due to the existence of different kinds of vacancies$^3$. Vacancies may differ with respect to size and nearest-neighbor configuration$^3$. Vacancies in the top layer are formed as the temperature is increased due to surface dehydroxylation$^3$. Hence, the number of hydroxy groups decreases, and the number of Lewis acid sites increases with increasing activation temperature. Not only the
number but also the strength of the Lewis acid sites may be increased by heating. The activity appears to increase continuously with increasing temperature, indicating that the Lewis acid sites are the most active binding sites for basic molecules. The relative binding strength and concentration of different adsorptions sites on solids can be probed by IR.

For an alumina surface with both alanol groups and exposed aluminum ions on the surface, adsorption of basic functional groups takes place on both types of active sites. In this case, the surface is intermediate between a fully hydroxylated and dehydroxylated rutile surface. These different structures and morphologies play a major role in determining the nature of the adsorption of the adhesive system on the surface. Additionally, the subsequent curing and adhesive bond formation could be influenced by the composition distribution in the curative in the resin. We have used reflection-adsorption FT-IR to investigate this process and the results are reported here.
EXPERIMENTAL

MATERIALS

Aluminum (2024-T3) coupons (1 x 1.5 inches$^2$) were mechanically polished to 3 $\mu$m roughness and then degreased with 2-butanone. The coupons were then sent to a plating company to be anodized in sulfuric acid solutions according to mil-A8625-E type II specifications with the following anodizing conditions:

MIL-A8625-E

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<td>60 Min.</td>
<td>30 Min.</td>
</tr>
<tr>
<td>thickness</td>
<td>34 $\mu$m</td>
<td>19 $\mu$m</td>
</tr>
</tbody>
</table>

Thickness measurements were done on a Permascope EWP9 by Fischer Instrument with $\pm 2 \mu$m uncertainty.
A dilute epoxy concentration of $3.7 \times 10^{-1}$ g/ml in DMF was prepared for thin films studies. By adding amounts of 0.02 to 0.55 ml of solution to the coupons (0.5 x 0.5 inches$^2$), thicknesses ranging from 0.4 to 11 $\mu$m were obtained (epoxy specific gravity is 1.38). The samples were then evacuated in a 35°C oven for 12 hours to drive off the solvent.

INSTRUMENTATION

All of the FTIR were performed with a rapid scanning infrared microprobe (Irus$^\circ$) with a liquid nitrogen cooled MCT detector. Spectra were obtained with a resolution of 4 cm$^{-1}$ and 512 scans. Triangular apodization was applied and interferograms were transformed with 8192 points with no zero filling.
RESULTS

I. Adsorption of epoxy resin on Anodized Al Surfaces.

The transmission infrared spectrum of the one-component epoxy resin system (epoxy and dicyandiamide) is shown in Figure 1. The band assignments are made in accordance with previously published results (5) and are given in Figure 1 as well. This spectrum is representative of the spectral features of an isotropic film of a epoxy adhesive with a dicy curative agent. Figure 2 shows the effect of curing on the spectrum of the adhesive. The bands associated with the oxirane and nitrile groups were monitored.

The deposition of the epoxy system was accomplished by spin-casting on the treated and untreated portions of the same Al sample. In order to enhance the differences, a single film was cast on an Al sample having three different spatial regions: 1) surface-untreated, 2) both untreated/treated and 3) treated. This was accomplished by taking a treated Al sample and dissolving away (using sulfuric acid solution) one portion of the sample. The result was a polished Al portion and the other half the anodized.
treated surface. A dilute solution of epoxy in dimethyl formamide was spin-coated on the entire sample and the solvent was driven off by vacuum. The microscopic FT-IR reflection-adsorption measurements allowed us to obtain spatially resolved spectra (30 μm) from three portions of the sample for the same film (Figure 3). In this way, small compositional differences within the same film on different surfaces could be easily observed.

It is clear that the intensities of the 2210 and 2160 cm\(^{-1}\) bands are greatest at the untreated Al surface (A) and decrease in going from the CAA/untreated (B) and treated portions (C) for a film of 0.1 μm thickness (Figure 4). The logarithm of the ratio of the curative agent IR band to the epoxy IR band was calculated for each area and the results are as follows; 0.42 for the untreated portion, 0.30 for the untreated/treated region, and 0.27 for the treated region. The average is 0.33 which compares to 0.34 which is the bulk result in the transmission mode (Figure 1). An average mass balance exists across the whole bonding region. Therefore, the data suggest the amount of curative in any portion depends on the nature of the absorbing Al surface.
Further, the ratio of the 2160 cm$^{-1}$ (salt form of dicyandiamide $\text{N}=\text{C}=\text{N}^+$) to the 2210 cm$^{-1}$ (nonionic form of dicyandiamide $\text{N}=\text{C}=\text{N}$) is lower for the anodized CAA surface compared to the untreated Al surface. No salt formation is expected between dicyandiamide and Al as the positions of the bands are the same as observed in the transmission spectrum (Figure 1), therefore, the distribution of other ions in the resin system or the hydroxyl system is responsible for the observed differences.

The spectra are similar for SAA anodized Al surfaces as seen in Figure 5. This result is consistent with our previous results which indicate similar oxide structures for the CAA and SAA surfaces. On this basis, corresponding adsorption behavior is expected. Again, computation of the logarithm of the ratio of the curative agent to epoxy agent IR band by area is as follows; 0.55 for the untreated region, 0.29 for the untreated/treated area, and 0.221 for the treated area. The average across the region is then 0.35 which is close to the 0.34 value obtained for the adhesive in the transmission mode.
We have also observed that the effect does not depend on the nature of the solvent as the same results were obtained with dimethyl sulfoxide and methanol as solvents.

We also investigated the effect of inhomogeneity in the plane of the Al surface as we have reported large inhomogeneities in the plane using NMR imaging (4) of cured epoxy films. In this case we used a 100 μm aperature and studied the sample at various locations within the same treatment region. The different locations did not show differences in relative intensities greater than the expected experimental error of ±5%. So the effect is not associated with inhomogeneities in the plane of the Al surface.
II. Composition of one-component epoxy resin normal to the Anodized Al Surfaces.

In order to elucidate the effect of the anodized Al surfaces on the composition of the one-component adhesive along the normal to the surfaces, studies were conducted where the thicknesses of the adhesive films were increased systematically.

It is clear that the intensities of the 2190 and 2160 cm\(^{-1}\) bands are highest closest to the surface of the untreated Al sample and decrease as you move away from it (Figure 6). In fact, there is a minima in the curative agent concentration away from the surface. This minima is perhaps a response to the high concentration of dicy near the surface to keep a mass balance locally. Further, the ratios of the 2160 cm\(^{-1}\) to the 2190 cm\(^{-1}\) bands are highest at the surface and decrease away from it. Thus, the untreated Al-adhesive interphase is rich in the curative agent. A new peak appears near 2170 cm\(^{-1}\) which is a coordinated (through the nitrogen) nitrile (6).

The opposite effect is seen in the intensity of the 2190 and 2160 cm\(^{-1}\) bands in the CAA anodized Al surface as shown in Figure 6. The intensities of the 2190 cm\(^{-1}\) and 2160 cm\(^{-1}\) bands are lowest at the surface
and reach average bulk values as you move away from the surface. Further, the ratio of 2160 to 2190 cm$^{-1}$ bands is lowest at the surface.

The effects are much the same for SAA anodized Al surfaces but to a lesser extend as seen in Figure 7. This is again consistent with our previous findings. Thus, it appears that the lack of curative agent is attributed to surface induced segregation during adsorption. The surface treatment results in the segregation of the one-component adhesive along the normal of the surfaces. Figure 7 shows the deviation of the nitrile content with respect to the epoxy as a function of the adhesive film thickness for the untreated and treated Al samples.
III. Curing of one-component epoxy resin normal to the Anodized Al Surfaces.

When the epoxy films were cured on the untreated Al sample, the intensity of the carbonyl groups at 1730 cm\(^{-1}\) (Figure 8) is highest at the surface and decreases away from it. This is consistent with the large amount of curative agent seen in the adsorption studies since the curative agent is the species generating the carbonyl group. Examination of the epoxy oxirane ring mode at 916 cm\(^{-1}\) shows that no oxirane was observed near the surface. Further, a shoulder at 1700 cm\(^{-1}\) appears, which is not seen in the anodized Al-adhesive samples, which might originate from amides (Figure 9).
In the case of the CAA anodized Al surfaces, the lowest cure (e.g. carbonyl absorbance) is seen near the surface and progressively increases away from it (Figure 8). This is again consistent with the lower amount of curative agent seen in the uncured samples. However, a large amount of unreacted oxirane groups, compared to the untreated Al samples, is seen near the surface and decreases away from it as shown in Figure 10. The effect of the surface treatment on the curing of the one-component adhesive is summarized in Fig. 10.
A. Effect of the surface treatment on the adsorption of an one-component adhesive.

It can be seen from Figure 4, that the curative agent segregates preferentially on the untreated Al sample surface but the epoxy is preferred on the anodized Al samples. This effect was reversible since wiping the adhesive with solvent and repeating the experiment gave the same results. There was no change in the results with aged samples (left overnight). The untreated Al sample is covered by an aluminum oxide film rich in aluminum atoms and is nearly depleted of Al-OH groups. Thus, it appears that the high ratio of Al atoms to oxygen atoms plays a role in the segregation of dicy at the surface.

In the case of the anodized Al samples, it is expected that the large number of Al-OH groups could be involved in hydrogen bonding with the nitrogen atoms in the curative agent. However, no spectroscopic evidence for this interaction was observed. Further, the only effect seen was the lesser amount of dicy at the anodized surface. The depletion is not as great for
the SAA anodized Al samples as for the CAA samples, probably due to the lower amount of hydroxides compared to the CAA anodized samples (7).

B. Effect of the substrate treatment on the curing of an one-component adhesive.

Upon heating the one-component adhesive on the CAA anodized Al surface, relatively large numbers of oxirane groups are left unreacted at the surface. Experiments were carried out where thin films of epoxy were deposited and heated on the CAA anodized Al samples. Little of the oxirane reacted with the surface. Thus, the existence of unreacted epoxy is due to the lack of curative agent at the surface. This is consistent with the low amount of carbonyl formed during curing. Thus, segregation plays a role in the curing process. It appears that the excess epoxy at the surface acts as a caging barrier making dicy diffusion towards the surface difficult. In the case of the untreated Al sample, the excess dicy at the surface promoted complete cure (most of the oxirane reacted) and formation of large number of carbonyl groups upon heating to 175°C.
CONCLUSIONS

The application of microscopic reflection-absorption spectroscopy is demonstrated as a useful tool to investigate thin films on treated and untreated aluminum. Compositional differences were observed across the interphase. The epoxy on untreated Al showed a large amount of curative agent in its salt form near the surface. The anodized Al surface had less curative agent and less of it in the salt form near the surface. Upon curing the one-component adhesive, the untreated Al sample cured well as indicated by the large carbonyl absorbance near the surface. Epoxy on the anodized Al samples showed less carbonyl groups at the surface consistent with less curing since the amount of curative agent is less at the surface. Further, a large amount of unreacted epoxy was found at the surface. These results indicate that the surfaces are inducing preferences in adsorption leading to differences in the composition in the cured and uncured epoxy resin. These results suggest the presence of compositional inhomogeneities in the cured epoxy adhesives. These compositional inhomogeneities certainly contribute to weak, nonreproducible and unreliable epoxy adhesive bonds.
REFERENCES

15. Kinloch, A. J., Environmental Attack at Metal-adhesive Interfaces, (Polymer Surfaces and Interfaces, Edited by W. J. Feast and H. S. Munro, John Wiley and Sons Ltd (1987)).
Fig. 1. Infrared transmission spectrum of the adhesive system.

TRANSMISSION SPECTRUM OF ADHESIVE SYSTEM

V. C-H OUT OF PLANE 700
\( \gamma \) (Cyclic Epoxyd)
\( \gamma \) C-H IN PLANE
\( \gamma \) (CH, MACROCYCLE, TWISTING)
\( \gamma \) (CH, METATHETIC DEFORMATION)
\( \gamma \) (CH, SCISSORS)
\( \gamma \) (C=H, ASYMMETRIC)
\( \gamma \) (C=H, SYMMETRIC)
\( \gamma \) (N=CH, ASYMMETRIC)
\( \gamma \) (N=CH, SYMMETRIC)
\( \gamma \) (C-H, WITH \( \gamma \) C-H, AND C-H)
\( \gamma \) (C=O, SYMMETRIC)
\( \gamma \) (C=O, ASYMMETRIC)
Fig. 2. Infrared transmission spectra of the uncured and cured adhesive system.
Fig. 3. Spatial IR sampling A: untreated. B: untreated/
treated and C: treated.
Fig. 4. Reflectance spectra of the uncured adhesive on the A) untreated aluminum, B) aluminum/CAA interface and C) CAA surface.
UNCURED DICY AS A FUNCTION OF FILM THICKNESS
FOR THE TREATED AND UNTREATED SURFACES
NITRITE BAND

Fig. 6. Reflectance spectra of the uncured nitrile band as a function of the epoxy thickness on the chromic acid anodized and untreated aluminum.
DICY CONCENTRATION FLUCTUATIONS NEAR THE SURFACE AS A FUNCTION OF ALUMINUM SURFACE TREATMENT

UNTREATED ALUMINUM  CAA ANODIZED AL SAMPLE  SAA ANODIZED AL SAMPLE

THICKNESS (MICRONS)

Fig. 7. Intensity plot of the sillite band as a function of the adhesive film thickness on the untreated and treated surfaces.
CURED ADHESIVE FILMS ON TREATED AND UNTREATED ALUMINUM SURFACES

CARBONYL BAND

Fig. 8. Reflectance spectra of the carbonyl band of the cured adhesive as a function of film thickness on the chronic acid anodized and untreated aluminum surface.
CURED ADHESIVE ON THE CAA SAMPLES
AS A FUNCTION OF FILM THICKNESS

CURED AT 175°C
OXIRANE BAND

0.3 MICRONS
0.6 MICRONS
0.8 MICRONS
1.2 MICRONS

\( \Delta R/R_0 \)

WAVENUMBER (CM⁻¹)

Fig. 9 Reflectance spectra of the oxirane band after curing as a function of adhesive film thickness on the CAA anodized Al samples.
Chapter IV

NUCLEAR MAGNETIC RESONANCE IMAGES (NMRI) OF THE EPOXY CURING BEHAVIOR IN ANODIZED AND UNTREATED ALUMINUM BONDED JOINTS
INTRODUCTION

The curing behavior of adhesive systems has been studied extensively by a number of surface techniques and considerable insight into the interfacial reactions between epoxy and metal substrates has been obtained\textsuperscript{1-4}. However, all of these techniques are limited to thin films deposited on the metal surface and to date no technique has allowed the study of the insitu adhesive curing of the epoxy between the metal substrates. NMR imaging (NMRI) can reveal the spatial aspects of cured adhesives and in this study, we report proton images of the epoxy cured between Al plates which have been anodized and chemically treated.

EXPERIMENTAL

Preparation of Substrate

Aluminum (2024-T3) coupons (0.5 x 0.5 inches\textsuperscript{2}) were mechanically polished to a 3 \textmu m roughness and then de-greased with 2-butanol. The coupons were then sent to a plating company to be anodized in sulfuric acid solutions (SAA) and Chromic acid solutions (CAA) according to mil-A8625-E specifications as follows:
<table>
<thead>
<tr>
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<th>Type I</th>
</tr>
</thead>
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<tr>
<td>solvent</td>
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<tr>
<td>Sulfuric acid</td>
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</tr>
<tr>
<td>20 wt %</td>
<td>05 wt %</td>
</tr>
<tr>
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</tr>
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</tr>
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<td>23 Amps/ft²</td>
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</tr>
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<td>20 °C</td>
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</tr>
<tr>
<td>time</td>
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<td>60 Min.</td>
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<tr>
<td>thickness</td>
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<tr>
<td>34 μm</td>
<td>19 μm</td>
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</table>

The coupons were also etched in a solution of cyanochromic acid complex (Iridite). Samples were kept in a dessicator under vacuum after treatment.
Adhesive

The epoxy resin used was bisphenol-A and the curing agent was dicyandiamide (dicy) with the composition of 7 phr. Durion was used as an accelerator to break down dicy with a composition of 1 phr. The structures of the materials are given in Figure 1.

Bonded samples

Aluminum coupons (1.2 cm x 1.2 cm) were used to make joints with 0.84 cm$^2$ adhesive area. The 0.5 mm joint thickness was obtained by using Teflon shims. Samples were cured for periods of 12 minutes at 175$^\circ$C and then imaged.

NMRI

The NMR images were obtained on a Bruker MSL 300 FT-NMR spectrometer at a proton frequency of 300 megahertz. The spectrometer was equipped with a micro-imaging accessory and a probe sample of 15 mm diameter.
The experiment was a typical Carr-Purcell\textsuperscript{7,8} spin-echo pulse sequence with a selective 90-degree pulse and a non-selective 180-degree pulse with CYCLOPS phasing. Typical duration times for the 90-degree pulse were 60 \(\mu\)seconds and 113 \(\mu\)sec for the 180-degree pulse. Repetition time was 1 seconds. A non-selective 90-degree pulse was used for proton shadowgram. Magnetic field gradients were 9-10 Gauss/cm in the in-plane space and 2-3 Gauss/cm in the z-direction. The proton of the methyl unit in the gem dimethyl was imaged. The contrast in the images are due to differences in spatial \(T_2\) originating from the different degree of cure in the sample. The intensity at a given pixel reflects the cured state of the pixel but is also contains signal from neighboring pixels due to line broadening. In our case, at 0.2 hours of cure the line width was 61 Hertz, at 0.6 hours was 172 Hertz and at 0.8 hours was 281 Hertz. These widths compare with the 244 Hertz/pixel resolution in the X-direction. Further, the intensity at a given pixel is the result of time averaging (17 minutes) the curing process at that pixel. Finally, the effects of chemical shift due to other nuclei adds shadows to the intensity in the images. We feel that the most important of the above is the line broadening effect due to the curing process and the result of this effect on the images is to
homogenize (that is to make the cured domains look bigger than they really are) the images. Nevertheless, the texture obtained early in the curing process is a fingerprint of the epoxy curing behavior.
RESULTS

A. CROSS SECTIONAL VIEW OF THE AL/EPOXY SAMPLES

A set of four NMRI images was obtained from each of the chemically treated and untreated aluminum samples. A typical set of images is shown in Figure 2 for the CAA treated sample. In the images, the red corresponds to high mobility and blue to low mobility. The cure is reflected by the small decrease in total signal.

In order to view the spatial distribution of the curing domains, enhanced images (2.5x) of the treated and untreated samples are shown in Figure 3-5. Figure 3 shows a segmented image of the uncured and cured domains in the CAA-epoxy sample. Segmentation was set from 230 to 255 for the high mobility domains (255 corresponds to red color which is the signal obtained for the uncured adhesive) and from 200 to 1 for the low mobility domain image. It clearly shows that most of the uncured epoxy (shown in red) is at the interface of the sample.
A contrasting behavior is seen for the untreated aluminum-epoxy sample cured at 175°C for 0.6 hours (see Fig. 4). The figure shows the uncured epoxy segregated at the center of the sample and away from the interface.

In the case of the chemically treated aluminum (Iridite)-epoxy sample, the image at 0.6 hours of cure (see Fig. 5) shows a more homogeneous cure of the sample and there are few domains that are uncured at this curing time. The colors in the images are referenced to the uncured adhesive.

Thus, uncured epoxy in epoxy adhesives-anodized aluminum joints is at the surface while in untreated aluminum joints is away from the surface as shown simply in Figure 6 (dark regions correspond to uncured regions).
Images were obtained through the bonded metal-epoxy-metal samples, thus showing a shadowgram or total projection of the samples. The NMRI images of the untreated aluminum-epoxy sample obtained at 0.2, 0.4, 0.6 and 0.8 hours of cure at 175°C are shown in Fig. 7. The figures show a random distribution of the cured and uncured domains. Random distribution implies low correlation between the uncured domains. That is, there is no synchronization, during curing, between neighbors leading to rough images as shown in Figure 8 (dark regions are uncured regions).
Further, there are regions, which are initially low in brightness, showing relatively high brightness at later curing times. These effects were also seen for the Iridite-epoxy samples shown in Figure 9.

Contrasting behavior was seen for the anodized samples. As shown in Figure 10, the CAA-epoxy samples shows simply connected regions (no spatial randomness, see schematic B) for the uncured domains. The same can be said for the SAA-epoxy samples shown in Figure 11.

HISTOGRAMS CURVE ANALYSIS OF THE LATERAL VIEW NMRI IMAGES

Histogram curves (numbers of pixels at a given cure state) were plotted for each sample as a function of cure time. Band shape analysis was performed on each curve and the results tabulated in table 1. The table shows values of the skewdness and kurtosis for each sample as a function of cure time. The skewdness is measure of a peak tendency to have a shoulder to the right or left of its mean. If the skewdness is positive, the peak has shoulder to the right of its mean and if negative, the peak has a shoulder to the left of its mean. The kurtosis is a measure of how sharp a peak is. If the value is less than three, the
peak is sharper than a Gaussian peak with the same width at half maximum and if greater than three is flatter than a Gaussian peak. If the kurtosis is three, then the peak is a Gaussian peak. The trend to note is the steady increase in kurtosis and skewness values as a function of cure time for the anodized samples. Contrasting behavior is seen for the untreated and chemically treated aluminum samples where the Kurtosis as well as the skewness goes through a minima. These minima are due to redistribution of signal intensities within the images.

**TEXTURE MEASUREMENTS**

The histogram calculations are sensitive to the spatial distribution of the uncured and cured domains. To classify the images (terrain classification), gray level difference statistics were performed on the images of the samples. The method is based on measuring, for a given displacement δ, the difference between the neighboring pixels at a distance δ away and the given pixel. The standard deviation calculations of the resulting difference images were obtained.
The resulting interaction between the objects distribution and size, and the statistical window (the size of the neighborhood) can be seen in Figure 12. The figure shows a plot of the gray level difference standard deviation and the neighborhoods size for the untreated and treated aluminum samples.

The untreated aluminum sample is characterized by an initial rise characteristic of very rough images and then the standard deviation reaches a steady value at a pixel neighborhood of 140 μm. The appearance of this plateau indicates a uniform distribution of objects inside the statistical window, that is, any neighborhood size bigger than 140 μm has a uniform distribution of domain size.

In contrast, the anodized samples are characterized by a very low and constant standard deviation value. This is characteristic of very coarse images where constant brightness values in large domains gives low deviations.

In order to see the effect of the surface treatment on the spatial distribution of cured and uncured domains during the curing process, the standard deviation from a neighborhood of fixed size (84 μm) was measured as a function of curing time for the treated
and untreated aluminum-epoxy samples. The images of the anodized-epoxy samples are characterized by a constant standard deviation in the early curing process and then the standard deviation value rises at the end of the cure reflecting the low NMR signal (see Fig. 13).

The images of the untreated aluminum-epoxy samples are characterized by a rise in the standard deviation in the early curing process (see Fig. 13) reflecting a domain redistribution effect. The rise in standard deviation value is probably due to diffusion of low molecular material within the sample. There is also the possibility of spatial high exotherms within the sample leading to local decreases in $T_g$ values of the material. This phenomena was also seen in the chemically treated aluminum-epoxy samples (see Fig. 14). In the anodized samples, uniform exotherms across the samples are possible since oxides are poor conductors and have high heat capacity.
CONCLUSIONS

Image analysis of NMRI pictures was used to analyze the epoxy curing process in the presence of chemically treated aluminum surfaces. The curing process was slower on the untreated and chemically treated aluminum surfaces than on the anodized aluminum surface. This was due to the limited diffusion of low molecular weight material. There was no diffusion detected in the epoxy cured anodized aluminum samples. The images in the untreated as well as in the chemically treated aluminum samples showed high texture indicative of a Gaussian image. That is, the high mobility domains were not connected in the images. This was attributed to low interactions between the untreated and chemically treated aluminum surfaces and the epoxy. In the case of the anodized surfaces, the high mobility domains were simply connected showing little texture and this was attributed to interactions between epoxy and the anodized surface. Our previous work has shown epoxy segregating preferentially to the anodized surface and this effect might occur here. A theory of the curing of epoxy has assumed diffusion
plays a role in the process especially at the late stages. For the anodized samples, the curing process is best analyzed and modelled by assuming no diffusion but rather caging effects.
REFERENCES


### Table 1. Tabulation of the lateral view histograms

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<th>CURING TIME (HOURS)</th>
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<td>43</td>
<td>34.1</td>
<td>1.51</td>
<td>6.26</td>
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MATERIAL SYSTEM

Metal: Al alloy 2024

Epoxy: \[
\begin{align*}
\text{CH}_2 \text{CH} - \text{CH}_2 - \text{O} & \left( \begin{array}{c}
\text{CH}_1 \\
\text{CH}_3 \\
\end{array} \right) \text{CH}_2 \text{CH} - \text{CH}_2 \\
\end{align*}
\]

Curing Agent: Dicyandiamide

Accelerator

Fig. 1. Materials used in this work.
Fig. 2. A cross sectional NMRI images of a CAA-epoxy sample as a function of cure time. The red color area are uncured domains and the green areas are cured domains.
Fig. 3. A cross sectional NMRI image of a CAA-epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green area correspond to cured epoxy. The image has been magnified 2.5x times. 2024
Fig. 4. A cross sectional NMRI image of a untreated aluminum-epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green area correspond to cured epoxy. The image has been magnified 2.5x times.
Fig. 5. A cross sectional NMRI image of a chemically treated aluminum (Iridite-14)-epoxy sample segmented into uncured and cured regions. The red area correspond to uncured epoxy and the green area correspond to cured epoxy. The image has been magnified 2.5x times.
Fig. 6. Schematic diagram of uncured epoxy domains in anodized and untreated aluminum/epoxy joints.
Fig. 7. Lateral NMRI images of the untreated aluminum-epoxy sample as a function of cure time. The red domains correspond to uncured regions and the green domains correspond to cured regions.
Fig. 8. Schematic diagram of cured and uncured domains in anodized and untreated aluminum/epoxy joints.
Fig. 9. Lateral NMRI images of the chemically treated aluminum (Iridite-14)-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.
Fig. 10. Lateral NMRI images of the CAA-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.
Fig. 11. Lateral NMRI images of the SAA-epoxy sample as a function of cure time. The red regions correspond to uncured domains and the green regions correspond to cured domains.
Fig. 12. Standard deviation values from difference statistics as a function of neighborhood size (number of pixels away from a given pixel) for the untreated aluminum and CAA-epoxy samples.
Fig. 13. Standard deviation values from difference statistics with a 5x5 pixel window as a function of cure time for the untreated aluminum and SAA-epoxy samples.
Fig. 14. Standard deviation values from difference statistics with a 1x1 pixel window as a function of cure time for the chemically treated aluminum (iridite) and CAA-epoxy samples.
Chapter V

FT-IR MICROSCOPY STUDIES OF WATER INGRESS
INTO ALUMINUM-ADHESIVE JOINTS
INTRODUCTION

The loss of strength due to humidity exposure limits the lifetime of adhesive joints. The mechanism by which water interacts with the adhesive joints is not known. However, several hypotheses have been proposed. Oxide dissolution by water ingress was thought to be the primary reaction in environmental exposure\textsuperscript{1}. Venables et al\textsuperscript{2} studied the hydration properties of anodized aluminum surfaces and concluded the transformation to Boehmite and consequently to Bayerite was responsible for the formation of a weak boundary layer. Support for this hypothesis is found when inhibitors are used which prolong the lifetime of adhesive joints. It is not clear whether the improvement is due to suppression of the hydration reactions or interactions between the inhibitors and the epoxy resin. Belov\textsuperscript{3} studied hydration properties of anodic films and found that the hydration of an anodic oxide depends on the coordinative ability of the corresponding anion to form bonds with the oxide surface. He also found that the chromic and sulfuric acid anodic films absorb relatively large amounts of
anions. The activation energy for oxide hydration is large for anodic films formed in acidic solutions. Brockmann\(^4\) argued that oxide dissolution is only possible in thin films but not on thicker films as obtained from anodizing conditions.

Another degradation theory suggests the displacement of epoxy away from the oxide surface by water. Kinloch et. al\(^5\) used thermodynamic approach to predict epoxy debonding from the oxide by water. His treatment does not consider forces other than polar forces involved in the adhesion phenomena. Further, the theory can not predict lifetimes of joints and the specific way in which water interacts. Thus, this approach has found very little further use.

Another possible theory suggests the adhesive itself being the most susceptible component in an adhesive joint. Kerr et. al\(^6\) studied the effect of water and ethanol on the cohesive and adhesive strength of joints. It was concluded that ethanol affected the cohesive strength while water affected the shear strength of the joint. Thus, water attacks the interface preferentially. On the contrary, others feel that the low water permeability of the adhesive is the rate determining step in the lifetime of the joint.
Lefebvre et al. studied humidity effects on adhesive joints and found that there is a critical humidity level below which water does not affect the lifetime of the joints. This critical level was associated with
(1) a sudden increase of water solubility in the epoxy,
(2) a corresponding increase in the adhesive volume and
(3) a large decrease in water mobility. Further, they found water irreversibly trapped by interchain hydroxyl groups, reacts with uncured oxirane groups to form diols.

Su et al. performed fatigue tests of adhesive joints as a function of ageing and concluded that fatigue life improved with humidity while others did not. Further, the durability performance showed a close relation with the adhesive water uptake. Bowditch et al. studied the effect of the equilibrium water content on the mechanical properties of finely dispersed oxides in epoxy adhesives. They concluded that there was not a critical humidity level below which water does not affect the adhesive joint. Thus, water affected the mechanical properties of the sample irrespective of the water content. It does appear that in adhesive joints at low humidity, water is mostly situated in the bulk adhesive away from the interface and with increasing water content, water will ingress to the interface.
Thus, plasticization is thought to be a major effect at low water content but recent work now suggests hardening of the epoxy with humidity. Raveh et. al\(^1\) performed shear stress tests and hardness studies of epoxy/alumina joints as a function of aging. They concluded that the durability of adhesive joints depends on a competition between epoxy hardening and weakening of the epoxy/oxide interface. Which effect is occurring first is not indicated but it is most likely that epoxy/water interactions occur first.

Another mode of environmental degradation of adhesive joints is corrosion. Brockmann et. al\(^1\) argued that for thick anodic films on aluminum, durability of adhesive joints was determined by corrosion processes. His arguments were based on the observation that it takes a long time to dissolve thick oxide films and cathodic delamination of the adhesive was a possible reaction. Watts\(^1\) argued that cathodic delamination by water leads to oxide reduction, polymer saponification and interfacial debonding. He also concluded that these degradation mechanisms could be occurring simultaneously and in the case of fused bonded epoxy on steel, oxide reduction occurs first followed by interfacial delamination due to water. Oxide reduction is thought to dominate under high cathodic
potentials while interfacial delamination dominates in the unpolared case. Dickie et. al\textsuperscript{12} used ESCA to investigate failure mechanisms in epoxy/dicyandiamide adhesives on cold rolled and galvanized steels. They concluded that oxide dissolution was the dominant mechanism in the absence of any applied potential. Thus, the resulting pH in the adhesive plays a role in the stability of the oxide. Aluminum oxides are unstable under basic conditions and in epoxy/dicyandiamide adhesives on anodized aluminum joints. Interfacial delamination is thought to be insignificant in epoxy adhesives on anodic aluminum due to the large surface areas associated with anodic surfaces. Thus, oxide reduction and polymer degradation are the major degradation mechanisms in epoxy adhesive/anodic aluminum joints.
MATERIALS

Aluminum (2024-T3) coupons (1 x 1.5 inches²) were mechanically polished to 3 \( \mu \text{m} \) roughness and then degreased with 2-butaneone. The coupons were then sent to a plating company to be anodized in sulfuric acid solutions according to mil-A8625-E type II specifications with the following anodizing conditions:

**MIL-A8625-E**

<table>
<thead>
<tr>
<th>solvent</th>
<th>Sulfuric acid</th>
<th>20 wt %</th>
<th>Chromic acid</th>
<th>05 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80 wt %</td>
<td></td>
<td>95 wt %</td>
<td></td>
</tr>
<tr>
<td>volts</td>
<td>18 volts</td>
<td></td>
<td>40 volts</td>
<td></td>
</tr>
<tr>
<td>current</td>
<td>23 A/ft²</td>
<td></td>
<td>01.5 A/ft²</td>
<td></td>
</tr>
<tr>
<td>temperature</td>
<td>20°C</td>
<td></td>
<td>40°C</td>
<td></td>
</tr>
<tr>
<td>time</td>
<td>60 Min.</td>
<td></td>
<td>30 Min.</td>
<td></td>
</tr>
<tr>
<td>thickness</td>
<td>34 ( \mu \text{m} )</td>
<td></td>
<td>19 ( \mu \text{m} )</td>
<td></td>
</tr>
</tbody>
</table>

Thickness measurements were done on a Permascope EWP9 by Fischer Instrument with \( \pm 2 \mu \text{m} \) uncertainty.
A dilute epoxy concentration of $3.7 \times 10^{-3}$ g/ml in DMF was prepared for thin films studies. By adding proper amount of solution to the coupons (1.0 x 1.5 inches$^2$), the film thickness ranged from 1.0 to 1.2 μm as determined by the Eddy current method. The sample were then evacuated in a 35°C oven for 12 hours to drive off the solvent. The deposition of the epoxy system was accomplished by spin-casting on the treated and untreated protons of the same Al sample (see Fig. 1). The square coupons of anodized and untreated aluminum samples were pressed against a ball socket joined to a 125 ml flask containing the saturated solution of KBr. The flask was kept to 35°C with a water bath temperature controller. The sample were then removed from the humidity chamber after appropriate exposure times for FT-IR specular reflectance studies.

INSTRUMENTATION

All of the FTIR were performed with a rapid scanning infrared microprobe (Irus®) with a liquid nitrogen cooled MCT detector. Spectra were obtained with a resolution of 4 cm$^{-1}$ and 512 scans. Triangular apodization was applied and interferograms were
transformed with 8192 points with no zero filling. Specular reflectance at grazing angle was performed. An area of 500 x 500 \( \mu m^2 \) was imaged with a round aperture of diameter equals 100 \( \mu m \) (see Fig. 2). The effective viewing window was 50 \( \mu m \) (25 files were used to imaged the square area), thus any object smaller than 50 \( \mu m \) will look bigger than the actual size. Further, the images shows the speckle effect which is a mosaic like picture where the image is collection of pixels. The images show the intensity of a given species (vibration of a molecular group) as a function of spatial position inside the imaged square. The intensities were normalized for constant thickness. The interface between the treated and untreated areas of the sample was sharp between the domains. The roughness of the oxide is smaller than the imaging window used in this experiment. The samples were imaged after 3 months and 2 weeks of a exposure to a KBr solution of double distilled water giving a 72 % relative humidity at 35\(^\circ\)C.
RESULTS AND DISCUSSION

The spatial distribution of the oxyhydroxide species on the CAA/untreated aluminum sample before exposure to humidity is shown in Figure 3. The figure shows a smooth rise in the oxyhydroxide band due to the anodic film. However, when the sample is exposed to humidity for over 3 months, changes occur on the oxide surface (see Fig. 4). The figure shows a rough image with new peaks. These peaks are not associated with surface roughness in the original sample before exposure. Thus, they are consequences of water interaction and they are assigned formation of new Boehmite. This is further supported by the fact that when the oxide group Al-O-Al is plotted there is a corresponding depression in the area where there is a lot of oxyhydroxides (see Fig. 4) and a relatively large intensity in the hydroxyl image of the same area (see Fig. 5). Thus, the effect of water on the anodic aluminum/epoxy joints is to transform the anodic film into Boehmite. In the untreated Al portion of the sample, there appears to be both oxide and oxyhydroxides formation occurring simultaneously (see
Figures 2 and 3). The same effect but to a lesser extent is seen in the SAA/untreated aluminum sample as shown in the image of the oxyhydroxide species (see Fig. 6). Although, this technique is insensitive to interfacial delamination by water because of the lack of chemical reaction in this process, it is very sensitive to chemical changes in the oxide and the adhesive itself. The damage mechanism in the untreated aluminum seems to be different from the anodized sample, that is, oxide conversion in the anodic case, and oxide and hydroxide creation in the untreated aluminum case (see Fig. 7). The extent of this transformation is higher for the untreated aluminum portion of the sample. The oxide formation in the untreated aluminum/epoxy sample may indicate that interfacial delamination of the epoxy from the aluminum surface has occurred. It is not clear whether interfacial delamination occurred in the anodized aluminum/epoxy samples. The only organic damage seen was the production of carboxylate species which were found to be at the outer surface of the epoxy film (the epoxy-air interface). The carboxylate species were completely removed upon polishing with 0.05 μ polishing cloth.
CONCLUSION

FT-IR microscopy of the effect of humidity on thin films of adhesive on anodized aluminum joints was performed in the absence of external stresses. Boehmite formation was seen in anodized aluminum/adhesive joints while newly formed oxide was seen in the untreated aluminum/adhesive joints. The extent of damage was greater in the untreated aluminum/adhesive joints. The only organic damage was the formation of carboxylates which were at the air/epoxy interface away from the oxide. The anodized aluminum/adhesive joints are more resistant than untreated aluminum/adhesive joints to humidity effects.
REFERENCES


Fig. 1. Spatial IR sampling A: untreated, B: untreated/treated and C: treated.
Fig. 2. Schematic of the spatial sampling of the data on the samples. The cones represent the infrared light focused on the spot selected to form the image.
MOISTURE ADSORPTION IN EPOXY-AL BONDS

Band at 1104 cm$^{-1}$ - Al-O-O-H

Fig. 3. Three dimensional plot of the oxyhydroxide vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area has not been exposed to humidity.
Fig. 4. Three dimensional plot of the oxyhydroxide vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.
Fig. 5 Three dimensional plot of the Al-O-Al vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.
Fig. 6 Three dimensional plot of the Al-OH vibrational band as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months.
Fig. 7 Three dimensional plot of the oxyhydroxide vibrational band as a function of spatial coordinates on the sampled area of the SAA/untreated aluminum sample. The area was exposed to humidity for over three months.
Fig. 8  Schematic diagram of the effect of water on anodized aluminum/adhesive joints.
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CHAPTER III


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CHAPTER IV


CHAPTER V


