

Effects of Thermal Cycling on Epoxy Bonded Materials

by

Michelle Burroughs

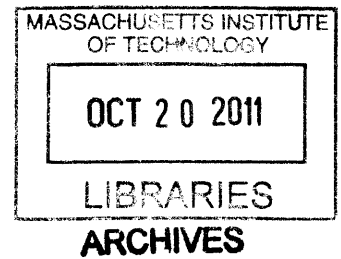
Submitted to the
Department of Mechanical Engineering
In Partial Fulfillment of the Requirements for the Degree of

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ABSTRACT

Thermal cycling is a concern to those who use epoxy as an adhesion in space applications due to the mechanical and thermal properties of both the epoxy and adhered materials. These properties include the thermal expansion coefficient, α , and the stress at which the epoxy will yield fracture. An experiment was carried out to find out if failure would occur by thermal cycling of epoxy bonded components in the propulsion components of a small satellite. Failure did not occur due to shear stress attributed to the thermal expansion coefficient but unexpectedly to the liquefaction of epoxy in 3 of the 6 samples. The samples with thicker epoxy layers failed in contrast to the thinner epoxy layer samples. Overall, thermal cycling is still a concern for failure of the epoxy bond.

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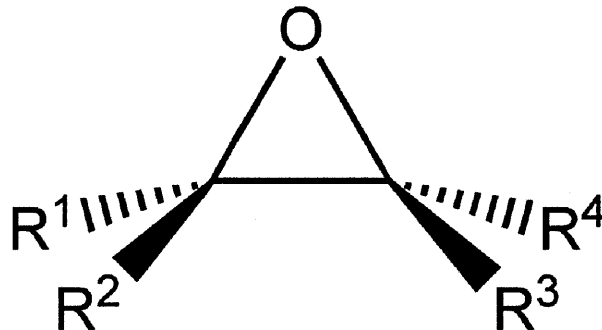
1. Introduction

Epoxy is a common adhesive for aerospace components due to its ability to withstand mechanical stress and high temperature ranges. At MIT Space Propulsion Laboratory, a satellite was developed in 2010 that utilizes electric propulsion technology, a change from traditional propulsion systems. The configuration of the propulsion system required an epoxy able to withstand compatibility with materials such as Nickel, Silicon, and Silicon Dioxide as well as changes in temperature and interaction with cleaning fluids. Of significance, thermal cycling is a concern as the different materials in the satellite respond differently to changes in temperature through a parameter called the thermal expansion coefficient. This means that one material expands more or less than that of another material in the presence in a change of temperature. In the epoxy bonded system, the bond strength may be compromised as the materials expand independently. Therefore, it is of concern to examine if the thermal cycling, -20 C to 80 C, experienced in the satellite will cause the bonds to yield to failure. This thesis serves to investigate if thermal cycling in the range experienced by the satellite disrupts the epoxy bond, and identify if the thermal expansion coefficient plays an important function.

2. Background

2.1 Chemistry

An epoxy, also called a polyepoxide, is a thermosetting polymer that is formed from the reaction of an epoxide and a polyamine.¹ The epoxide is a three ring cyclic ether, a class of organic compounds which contain R – O – R linkage with a high bond angle of 110 degrees. This means that the polarized oxygen atom (O) is highly reactive to bonding with other atoms. Figure 1 shows the generic structural model of the epoxide.



*Figure 1: A generic epoxide used as a resin in epoxies.*²

Chemically, a polyamine, also known as a hardener, is a compound which has two or more primary amino groups, NH_2 . When added to an epoxide, bonding is formed between the oxygen atom of the epoxide and a hydrogen atom of the polyamine and also between a terminal R atom of the epoxide and the nitrogen atom of the polyamine.

Figure 2 demonstrates the mechanism behind the reaction of combining the epoxide and polyamine. The result is a cross linking structure.

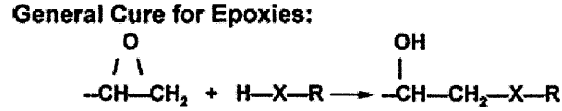


Figure 2: Reaction between the epoxide, resin, and polyamine, hardener. ³

In practice, the epoxide acts a resin, a liquid or soft plastic monomer, and the polyamine acts as the hardener, a substance that accelerates or controls the curing process. In bonding, adhesion forms between the epoxy mixture and a dry surface when the epoxy displaces the air.

2.2 History

Although many have attempted to synthesize resins as early as 1927, epoxy resin was first synthesized in 1936 by both Dr. Pierre Castan of Switzerland and Dr. S.O. Green of the United States.¹ The result of Castan's work was licensed to a Swiss company which became one of the largest suppliers of epoxy resins before it was sold to the advanced materials sector of the Huntsman Corporation, a large chemical company. Green's work went towards the Devoe-Reynolds firm, a paint and varnish manufacturing, which later become Shell Chemical.

2.3 Applications

The applications for epoxies extensively include coatings, laminations, adhesives, and composite materials such as carbon fiber and fiberglass reinforcements. The industries for these applications include electrical systems, industrial tooling, marina, wind energy, aerospace, and many others.¹ Because of the strong polar bond attraction of the epoxy, a strong bond can form underwater as well as on dry surfaces.

2.31 Space applications

The use of epoxies as an adhesive has been widely used in spacecraft as a structural adhesive and in carbon fiber reinforcements. These epoxies must exhibit many qualities unique to the industry such as high strength, thermal cycling resistance, vacuum, radiation, and have physically and chemically compatibility.

2.4 Failures

Failure is defined in this thesis as the disintegration of the bond between two solids through the epoxy. Failure can occur through tensile and shear forces, porosity, dissolving of the epoxy by incompatible fluids, vacuum incompatibility, and weakening of the epoxy structure through thermal cycle.

2.41 Failure by Stress

Tensile or shear forces can eventually cause the bond to fracture and is further complicated by the different mechanical material properties in each material. Figure 3 is a diagram of the configuration of a 3 layer composite that has unique thicknesses and material properties in each layer.

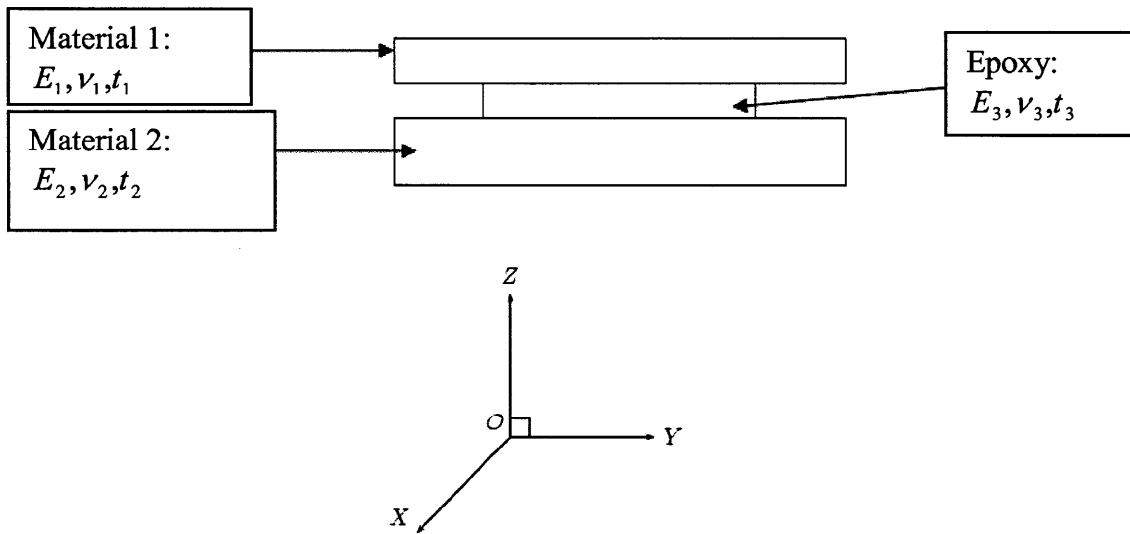


Figure 3: Diagram of the bilateral configuration showing that each layer exhibits its own material properties and thicknesses.

In tensile stress, the force would be solely in the z normal direction. In shear stress, force would be occurring between two layers pulling equal and opposite. For example, stress σ_{12} and strain ϵ of material 1 must equal the negative shear stress and strain the epoxy experiences.

Another important parameter in fracture mechanics is the stress intensity factor, K, which provides a unique measure of the amplitude of the stress singularly at the edge of a sharp

crack. G.R. Irwin identified that the stress field at the edge of a sharp crack is the highest.⁴ The reason for this is that “very near the crack edge, spatial gradients of fields in the direction parallel to the crack edge tangent are negligibly small compared to the gradients in directions normal to the edge.” Equations 1 and 2 are used to calculate the stress intensity factor K for each mode. Mode I represents the opening of the crack while Mode II represents the in-plane shear shown in figure 4. The stress intensity factor may explain how failure of an epoxy bonded system originates from cracking at edge of the epoxy rather than the center.

$$K_I = \lim_{r \rightarrow 0} \sqrt{2\pi r} \sigma_{zz}(r,0)$$

Equation 1: Mode I stress intensity factor

$$K_{II} = \lim_{r \rightarrow 0} \sqrt{2\pi r} \sigma_{xz}(r,0)$$

Equation 2: Mode II stress intensity factor

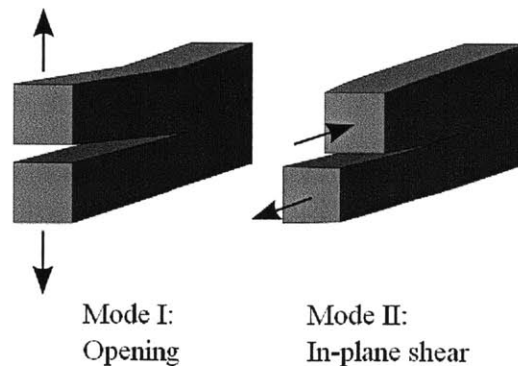


Figure 4: Visual of Mode I and Mode II of sharp edge stress⁵

2.42 Failure by Porosity

Complexity that may further weaken the epoxy bond by two solid materials can be attributed to the porous structure of these solid materials. ⁶ Porosity is defined as the fraction of void space over the total space of a material shown in equation 3. Porosity directly connected to a material's density.

$$\phi = \frac{V_v}{V_T}$$

Equation 3: Porosity is the void space over total space of a material. V_v is the volume in a substance that does not contain material. V_T is the total volume occupied by the material and void volume of a substance.

Porosity parameters also include the diameter of the pores, the depth at which fluid can penetrate the material, and the presence of either isolated or connective pores.

Porosity can mechanically change many parameters in comparison to nonporous materials such as the surface area of which a bond is formed. Also, the epoxy liquid before curing can often seep into pores connected to the surface of adhesion and thus form a plug-like bond that may change the overall force between the epoxy and the material.

Failures with the use of epoxy on spacecraft have been documented by many researchers. Of example, Grilli et al. researched the failure of bonded chromate treated aluminum revealed heterogeneous cracking associated with the chromate coating and the microstructure of the aluminum. ⁷ The experiment was carried out by using “a sample of 2219 Al alloy (Cu rich) was treated with Alodine 1200 (Henkel), a Cr(VI)-based conversion coating, in accordance with the manufacturers' recommendations.” Two

pieces of a 6000 series Al alloy (Al–Mg–Si alloy) were treated with Alodine 1200, then they were bonded together with Araldite AV 138M (an epoxy-based adhesive) and cured with hardener HV 998, both from Huntsman Speciality Chemicals. Following environmental exposure, this joint was tested in the “usual way to provide failure surfaces suitable for surface analysis.” Figure 5 shows the result SEM image of the aluminum sample with chromium coating.

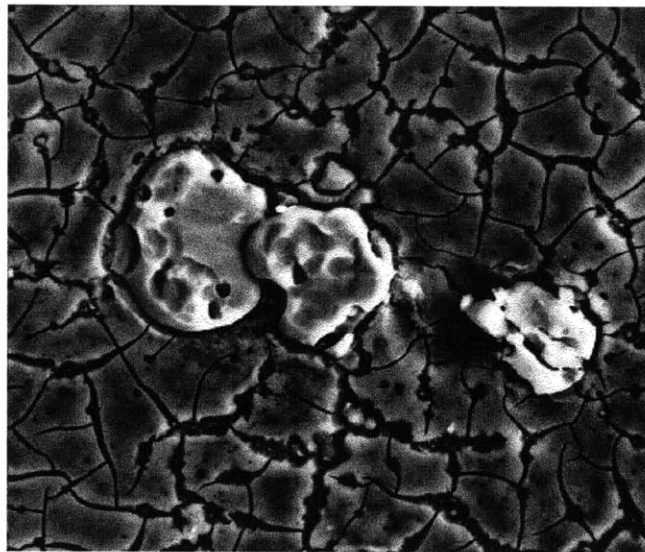


Figure 5: Porosity of Aluminum treated with Chromium Coating.

2.43 Failure by thermal cycling

Thermal cycling of materials bonded by epoxy is a complex problem as each material has its own different thermal properties. Of the most important thermal property is the thermal expansion coefficient, α . The thermal expansion coefficient is defined as the degree of expansion divided by the change of temperature. Figure 6 shows a visual of the

configuration of the materials to show that each material exhibits its own thermal expansion coefficient.

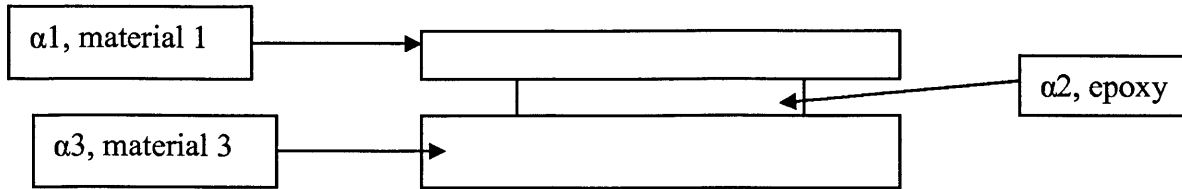


Figure 6: Bilateral adhesion between two materials with epoxy. All layers may have different thermal expansion coefficients.

The difference between the thermal expansion coefficients is significant in thermal cycling because as it heats up and each material expands at its own degree, the interfaces between material and epoxy changes and disrupts the bond. Below in table 1 is a list typical thermal expansion coefficient values of materials used in the propulsion system.

| Material | Thermal Expansion coefficient, α , ($\text{cm}/\text{cm}/^\circ\text{C} \times 10^{-6}$) |
|----------|--|
| Nickel | 13 |
| Silicon | 3 |
| Epoxy | 5.4 |

Table 1: Thermal Expansion Coefficients. ^{8,9}

The values show that epoxy has a thermal expansion coefficient small than nickel but larger than silicon. Thus, when the materials are heated, the materials bonded to the epoxy expand more outwardly than the epoxy, placing stress and strain on the bond. The result in the change of the alignment of the bonds will cause the layer of materials and epoxy to form a curvature. The problem here is finding as how much thermal cycling at

what temperatures will cause the bond lose its useful structural integrity and when does fracture occur.

2.44 Failure by chemical incompatibility

Chemical incompatibility in the satellite presents problems in two ways: the interaction with the cleaning fluids acetone and hydrochloric acid, and with exposure to the ionic liquids. Chemical incompatibility occurs because the interaction between a fluid and the epoxy dissolves the bond produced by the epoxy, causing failure.

2.5 Current predictions in thermal cycling failure

For thin, plastic films, such as epoxy, on relatively thick substrates, predictions can be made at when failure due to thermal cycling will occur. An equation for the temperature at which plastic yielding first occurs in the film is approximately equal to the temperature at which plastic flow has spread throughout the film thickness. Curvatures, k , at yield and at fully plastic response are indistinguishable for thin films and can also be calculated.

$$\overline{T}_Y = \overline{T}_{pl} = \frac{\sigma_{Yf}}{M_f(\alpha_s - \alpha_f)}$$

Equation 4: Temperature at yield. σ_{Yf} represents the yield stress of the epoxy; M_f , the elasticity of the epoxy; α_s , the thermal expansion coefficient of the material adhered to the epoxy; and α_f , the thermal expansion coefficient of the epoxy. Temperature at yield is equal to the temperature at plasticity.⁴

$$\kappa_Y = \kappa_{pl} = \frac{6\sigma_{yf}h_f}{M_s h_s^2}$$

*Equation 5: Curvature at yield. σ_{yf} represents the yield stress of the epoxy; E , the elasticity of the material adhered to the epoxy; h_f , the thickness of the epoxy layer; and h_s , the thickness of the material layer.*⁴

The epoxy used for this experiment is Epoxies Etc.'s 10-3782 one component heat cure epoxy. According to given information from the company, the operating temperature range is -50 to 180 C and the epoxy has a tensile modulus of more than 4,000 psi.¹⁰ Unfortunately, the yield tensile strength and thermal expansion coefficient are not given from the manufacturer but they state that the epoxy has Shore D hardness of 80 at 25 C and 70 at 121 C. This value comes from the Shore durometer test which is one of several measures of hardness of polymer, elastomeric, and rubber materials by measure the depth of an indentation created by a given force.¹¹ A comparable example of a material with a Shore D hardness of 80 is a hard hat. To find the tensile strength, the hardness was converted to 11.2 MPa by the following conversion equation from Shore D hardness:

$$y = e^{((x+50)*0.0235)-0.6403}$$

Equation 7: Conversion from Shore D hardness to MPa where x is the Shore D hardness

From this value, an approximate relation between hardness and yield strength is used which states that yield strength is approximately 1/3 of the hardness and is found to be 3.73 MPa.¹²

Also, in the experiment conducted for this thesis, the silicon dioxide material of the satellite will be represented by ordinary glass slides which will serve at layers above and below the epoxy. The thermal expansion coefficient is approximately $3 \times 10^{-6} /C$ for borosilicate glass, a glass common to laboratory glassware.

The last value needed in determining a prediction is the Elastic Modulus of the epoxy film. Though this can vary among epoxies and the manufacturer does not provide this value, an estimate of 2415 MPa will be used. ¹³

Using the yield strength of 3.73 MPa calculated above, the typical coefficient of expansion is $5.4 \times 10^{-6} /C$ for epoxy, the coefficient of expansion is $3.0 \times 10^{-6}/C$ for glass, and the Young's Modulus is 2415 MPa, equation 4 estimates that the temperature at plastic yielding starts is 644 C. This plastic yielding is well above the operating temperature and the thermal cycling from -20 to 80 C. The curvature prediction for an epoxy of thickness 0.001 meters and glass thickness 0.002 meters and Young's Modulus of 185 GPa is $7.66 * 10^{-6} N/m^2$ using equation 5.

3. Experimental Apparatus

The apparatus testing materials consisted of using 10-3782 one-part epoxy manufactured by Epoxies Etc. and glass slides to represent the silicon dioxide in the satellite. Six samples with various thicknesses of epoxy were applied using Kapton tape and cured between two glass slides. Each sample was cured at 120 degrees for 30 minutes. The first sample used a thickness of one layer of Kapton tape to control the thickness. One layer of Kapton tape is approximately 1.6 mm. Each other sample used an increased thickness using layers of Kapton tape from 2 layers up to 6 layers. Kapton tape was a compatible material in each sample as the tape can withstand high temperatures occurring during both curing and thermal cycling. Figure 7 shows how the Kapton tape controls the thickness of the epoxy through the curing process and is attached through the glass slides.

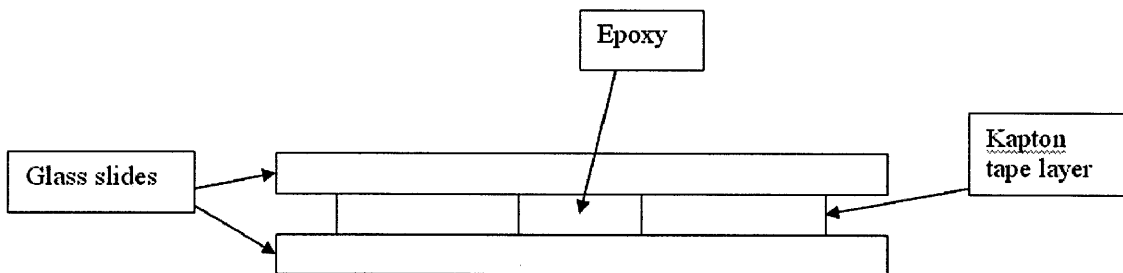


Figure 7: Sample configuration of epoxy bonded glass slides. Kapton Tape is used to control the height of epoxy.

Initially, to fully represent the accurate thermal cycling experienced in the satellite, the samples were going to be thermally cycled between -20 C and 80 C (-4 F and 176 F). To recreate a thermal cycle, a hot plate and a cold plate were utilized. The hot plate was obtained in the lab and the cold plate was obtained by filling a vessel with liquid

nitrogen. Although the hot plate's temperature is automatically controlled and stabilized, the cold plate produced by the liquid nitrogen vessel used a thermocouple to measure the temperature produced by the vessel and what changes occurred during the experiment. Because of the capacities of the liquid nitrogen in the lab environment, the cold plate initially achieved a temperature of 17 C. To accommodate the increase in temperature of the cold plate, the hot plate was set to 100 C. This gap between the cold and hot plates recreates the results expected from a similar thermal cycle with colder cold and hot plates.

To begin the experiment, all six cured samples were placed on the cold plate for 3 minutes. Immediately following the 3 minutes, all samples were placed on the hot plate for an additional 3 minutes. The total 6 minutes translated into one cycle. After each cycle, all samples were placed again on the cold plate immediately to begin another cycle. Because the cold plate was not controlled at a steady state, the hot plate increase in temperature as the cold plate increased in temperature to keep the same temperature difference between the plates. A total of 10 cycles were performed.

4. Results and Discussion

At cycle 9, samples with thickness of 3, 4, and 6 thickness layers of Kapton tape were no longer attaching the glass slides. When all 10 cycles were performed, no other samples were disassembled. With the exception of the sample with a thickness layer of 5 Kapton tape, all samples with a thinner layer of epoxy were still well intact. This relationship shows that thicker layers of epoxy are not as robust as thinner layers of epoxy.

Understanding of how the thinner layers did not fail may show that the differences in material thermal expansion coefficients in both the epoxy and glass slides were not substantial between the two temperatures. Instead of failing due to stress, the disassembled samples had all reverted back to a liquid form. The explanation for the liquid form is confusing since it had already cured and was cured in the presence of a warmer temperature than the hot plate. One possible speculation may be that the thermal cycling may have contributed by constantly exposing the samples to a hot plate after it had been cooled down by the cold plate. Another is that the thicker samples may have failed to cure and thus needed a longer curing time compared to the thinner samples.

Because none of the samples failed by shear stress between the materials, further experiments in increasing the temperature difference of the thermal cycle might indicate how close failure would occur. For instance, the temperature difference in the thermal cycle might be only a few degrees increase or may require a substantial temperature difference. Further experimentation may confirm how close the temperature difference is to a thermal cycling that will cause the epoxy to fail by stress.

As mentioned before in the experimental apparatus, the cold plate was not able to have a steady state temperature and thus the hot plate was also manually increased to keep the temperature difference. The sharp increase in temperature of the cold plate seems to be attributed to both the liquid nitrogen's exposure to room temperature and the heat transfer by conduction through the slides as it moves from the hot to cold plate. Table 2 documents the change in temperature through each cycle:

| Cycle | Cold Plate Temperature C | Hot Plate Temperature C |
|-------|-----------------------------|----------------------------|
| 1 | 17 | 100 |
| 2 | 20 | 100 |
| 3 | 23 | 100 |
| 4 | 25 | 102 |
| 5 | 26 | 104 |
| 6 | 28 | 106 |
| 7 | 29 | 107 |
| 8 | 29 | 107 |
| 9 | 30 | 108 |
| 10 | 29 | 108 |

Table 2: Temperature Measurement at each cycle

Overall, it seems that deterrence from the accurate thermal cycling seems it would minimally affect the overall experiment at the thermal expansion coefficient does not change dramatically in similar temperature ranges.

5. Conclusions

This experiment shows that the thermal cycling experienced by the propulsion system in MIT Space Propulsion Laboratory does not contribute to failure by stress but by another parameter that causes the epoxy to become liquid. Further exploration into the mechanics of thermal cycling may give light to why this happens and if it is due to solely the hot plate or the cycling between the cold and hot plates. What was also found was that thicker layers of epoxy seem to be more vulnerable to failure due to the liquefying of the epoxy, showing the thinner layers may be better in epoxy adhesion. Nevertheless, it seems that failure due to shear stress may be less important than failure due to liquefaction in thermal cycling systems.

6. Acknowledgements

I would like to thank Professor Paulo Lozano of the MIT Aeronautical and Astronautical Engineering department and Space Propulsion Laboratory for his time and efforts in helping with this thesis.

7. References

- ¹ Epoxy. Retrieved April 26, 2011, from <http://en.wikipedia.org/wiki/Epoxy>.
- ² Epoxide Generic. Retrieved April 26, 2011, from http://en.wikipedia.org/wiki/File:Epoxide_generic.png.
- ³ Petrie, Edward M. Epoxy Urethane. Handbook of Adhesives and Sealants. Retrieved April 26, 2011 from <http://www.globalspec.com/reference/13450/121073/chapter-13-3-5-epoxy-urethane>.
- ⁴ Suresh, S. Shen, Y. L. Thin Film Materials. 1995.
- ⁵ Sharp Edge Stress. Retrieved April 26, 2011, from http://upload.wikimedia.org/wikipedia/commons/e/e7/Fracture_modes_v2.svg.
- ⁶ Porosity. Retrieved on April 26, 2011, from <http://en.wikipedia.org/wiki/Porosity>.
- ⁷ Grilli R., Baker, M., Dunn, B., Watts, J. "Failure Characteristics of Adhesively Bonded Aluminum for Spacecraft Applications." Retrived April 26, 2011, from <http://onlinelibrary.wiley.com/doi/10.1002/sia.2793/pdf>.
- ⁸ Thermal Expansion. Retrieved April 26, 2011, from http://en.wikipedia.org/wiki/Thermal_expansion.
- ⁹ Typical Linear Coefficient of Expansion for Common Plastics. Retrieved April 26, 2011, from <http://www.edl-inc.com/Plastic%20expansion%20rates.htm>.
- ¹⁰ Epoxies Etc. 10-3782R One- Component Epoxy. Retrieved April 26, 2011, from <http://www.epoxies.com/tech/10-3782R.pdf>.
- ¹¹ Patton, D., "How to Convert a Durometer to Young's Modulous." Retrieved April 26, 2011, from http://www.ehow.com/how_7941189_convert-durometer-youngs-modulus.html.

¹² “Approximate Relationship Between Hardness and Tensile Strength.” Retrieved April 26, 2011, from http://www.efunda.com/forum/show_message.cfm?start=1&thread=4261&id=4358.

¹³ Epoxy. Retrieved April 26, 2011, from http://www.efunda.com/materials/polymers/properties/polymer_datasheet.cfm?MajorID=epoxy&MinorID=2.