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The University of Southern Mississippi

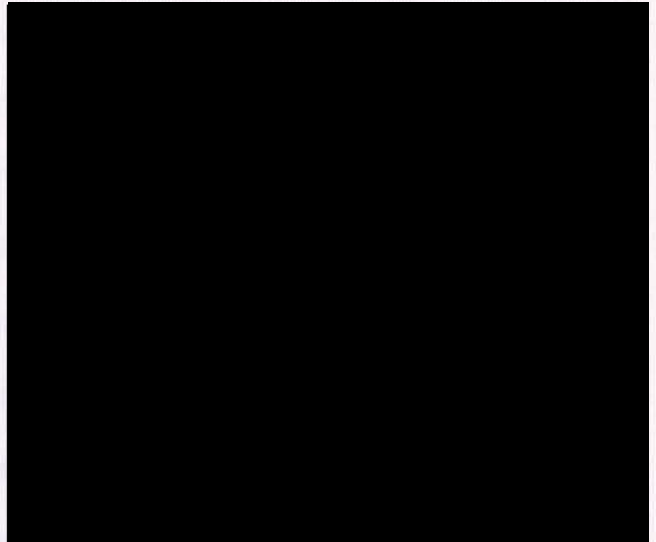
THE INFLUENCE OF EXTENDED CURE ON MECHANICAL PERFORMANCE OF AEROSPACE-GRADE FILM ADHESIVES

by

Ryan Marcus Young

A Thesis
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Master of Science

Approved:



Dean of the Graduate School

May 2013

ABSTRACT

THE INFLUENCE OF EXTENDED CURE ON MECHANICAL PERFORMANCE OF AEROSPACE-GRADE FILM ADHESIVES

by Ryan Marcus Young

May 2013

Bonded adhesive joints have seen increased usage in aircraft structures as weight and cost reductions drive manufacturers to composite designs. As the use of epoxy film adhesives become more prevalent, it is important to characterize the thermal and mechanical properties of the adhesive after exposure to various manufacturing conditions. Prior studies suggest that thermal characteristics and mechanical performance of epoxy resin formulations may be considered a function of chemical structure, cure temperature, and cure duration. It was therefore hypothesized that by controlling cure temperature and duration, the Tg, degree of cure, and mechanical performance of aerospace-grade film adhesives may be controlled.

Three epoxy film adhesives cured with three different cure cycles were thermally characterized using DSC, DMA, and rheological techniques. It was shown that increased cure duration provided increased degrees of cure and Tg of the adhesives as a result of a more developed polymer network. V-notch shear and flat-wise tensile testing at ambient dry and elevated temperature wet conditions were used to mechanically characterize the performance of the adhesives cured with three different cure cycles. Mechanical test results showed that adhesives with more aromatic chemical structures saw less degradation as a result of moisture exposure and elevated temperature testing, while the adhesive with simpler chemical structure exhibited significantly reduced performance at

elevated temperature wet conditions. It was concluded that while extended cure exposure did not provide significant gains in mechanical performance, the increased polymer network development provided increased resistance to the effects of moisture absorption and elevated temperature environments.

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LIST OF ABBREVIATIONS

ASTM: American Society for Testing and Materials

BMI: Bismaleimide

DDS: Diaminodiphenyl Sulphone

DGEBA: Diglycidyl Ether of Bisphenol-A

DGEBF Diglycidyl Ether of Bisphenol-F

DMA: Dynamic Mechanical Analysis

DP: Degree of Polymerization

DSC: Differential Scanning Calorimetry

ETW: Elevated Temperature Wet

FWT: Flat-Wise Tension

NIR: Near Infrared Spectroscopy

RTD: Room Temperature Dry

RTM: Resin Transfer Molding

Tg: Glass Transition Temperature

TMA: Thermo-Mechanical Analysis

CHAPTER I

INTRODUCTION

Thesis Organization

This thesis is organized into four chapters. Chapter I is a general introduction to the use of polymer adhesive bonding within the aerospace industry and the role various processing parameters play on the physical and mechanical properties of the cured epoxy adhesive. The advantages of adhesive bonding techniques are first introduced, and are followed by an overview of the use of epoxy-based adhesives and the polymerization process that allows for their staging as film adhesives. Next, the significance of cure temperature and cure duration as they relate to the mechanical performance of the cured epoxy adhesive is discussed. At the end of this chapter, the research goals and specific objectives of this thesis study are stated. Chapter II describes the materials, physical characterization test equipment and techniques, and mechanical test equipment and methods selected for use in this research. Chapter III comprehensively discusses the results of the physical and mechanical tests performed to characterize the adhesives under study. Finally, Chapter IV presents the conclusions of the research and future research opportunities.

Literature Review

Aerospace Adhesive Bonding

The use of adhesive bonding in the aerospace industry has seen increased usage since its development and introduction during WWII [1]. Adhesive bonding has become a popular alternative to welding, riveting, and bolting methods, especially as the composite material content in aircraft continues to rise. The use of bonding techniques

has the advantage of allowing for the joining of dissimilar materials, such as composite and aluminum, and also can help to reduce part count by eliminating the need for bolts and rivets [2]. The degradation of mechanical properties of metals associated with welding heat is also eliminated through the use of bonding techniques. Touch labor can be reduced through the use of bonded joints, as the substrates do not need to be drilled and manually fastened, but rather simply cleaned, adhesive applied, and cured. Aircraft joint designs can also be improved through the use of bonding techniques. Bonding provides an even stress distribution across the joint, as opposed to the irregular stress distribution that exists around bolts, rivets, or spot welds [3]. The even distribution of stresses present in bonded joints helps to improve fatigue performance and reduce the presence of stress concentrations that can lead to premature failure [4]. Bonded joints are also an attractive option to aircraft builders as bonded joints typically weigh less than mechanically fastened joints and can allow for a smooth external surface, improving aerolines.

One of the most common forms of bonding adhesive used in the aircraft industry is that of film adhesive. Film adhesives are comprised of a partially cured, or B-staged, thermosetting resin that allows for easier handling and control than paste or liquid resin adhesives. Although typically more expensive than two-part paste or liquid adhesives, film adhesives have the advantage of providing a precise mixture of resin and hardener and allows for a consistently controlled applied material weight. This helps to achieve repeatable bonds as the same amount of adhesive is always applied, and no manual mixing of resin components are required from part to part [2]. As the film adhesive is cured, the formulation of the adhesive allows the viscosity of the film to be reduced to a

liquid state that allows for easy flowing of the adhesive to fill any pores or voids. The crosslinking that occurs during cure then rapidly increases the viscosity of the adhesive and a solid bond between surfaces is achieved. Various carrier materials and forms may be incorporated into the film adhesive to help control the flow of the adhesive in the liquid state, which is an important characteristic that allows for the successful co-bond/co-cure of honeycomb core sandwich structures [5].

Epoxy Resins

While film adhesives can be manufactured using bismaleimide (BMI) and other resin chemistries, perhaps the most common film adhesive type is that of an epoxy resin-based adhesive. Epoxy polymers are very popular in industry and manufacturing due to their diverse base structures, wide choice of available curing agents, processing flexibility, and affordable cost. Basic epoxy resins are commonly formed by the crosslinking of two primary components, a diepoxy and a diamine, though increased levels of constituent functionality are also used [6]. Common epoxy base monomers used in aerospace applications include diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF), and phenol novolacs. Although reactive epoxide functional groups are present in all of the base monomers, differences in aromatic ring content, molecular weight, epoxide equivalent weight, and side group content result in significantly different cure kinetics, thermal performance, and mechanical properties [7].

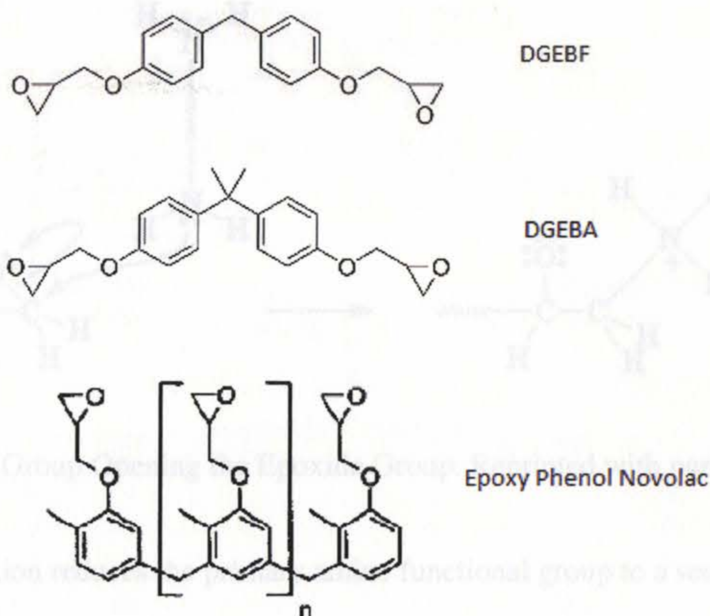

Figure 1. Common Epoxy Oligomers.

Altering the size of the epoxy oligomers will have an effect on the final cured material thermal and mechanical properties and will also affect the final polymer crosslinking density. Molecules with a higher degree of polymerization (DP) will exhibit greater molecular weight, higher epoxide equivalent weight, and a higher melting temperature. Epoxy resin molecules with a higher molecular weight will often exhibit a lower glass transition temperature (Tg) due to the lower crosslinking density [7].

The epoxy oligomers must be crosslinked to form a thermosetting resin. The crosslinking of epoxies can be accomplished with a number of different functional crosslinking agents, however this is most often accomplished in the presence of a diamine molecule. In the crosslinking process, the epoxide group will react with one of the hydrogen atoms attached to an amine. The reaction mechanism occurs via a nucleophilic attack by the amine on the epoxy group's carbon atom, followed by proton extraction by the now negatively charged oxygen ion which results in the opening of the epoxide ring.

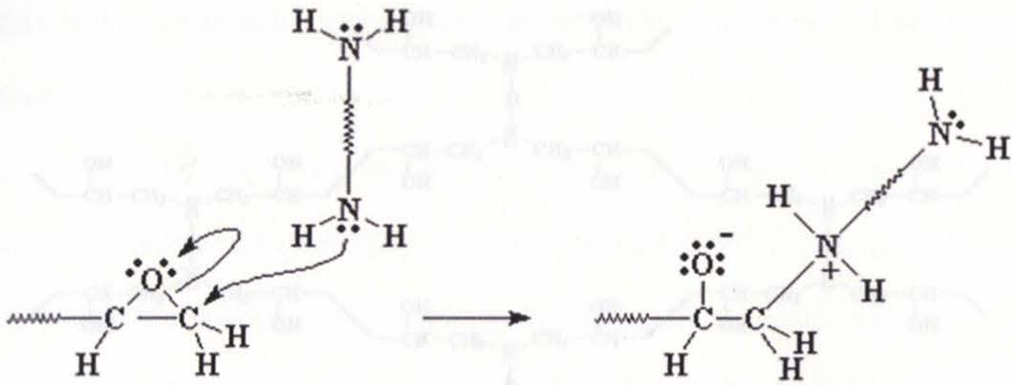

Figure 2. Amine Group Opening the Epoxide Group. Reprinted with permission from reference [8].

This reaction reduces the primary amine functional group to a secondary amine functional group that now only has one reactive hydrogen atom. The single hydrogen atom of the amine is then able to combine with an epoxide group of another diepoxy oligomer. Because the crosslinking agent is a diamine, the same reactions can occur on the other end of the molecule so that the diamine molecule is linked with four epoxy prepolymers. The remaining epoxide functional groups of the prepolymer are also able to combine with other diamines to eventually form a crosslinked network [6].

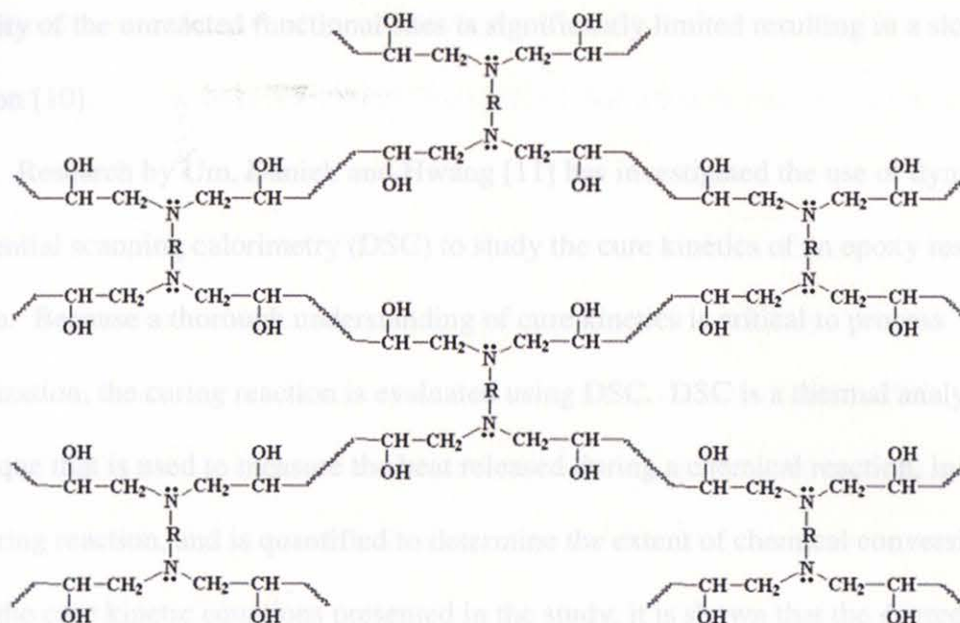

Figure 3. Amine-Cured Epoxy Crosslinked Network. Reprinted with permission from reference [8].

It has been shown that the cure kinetics of epoxy resins follow a multi-stage cure process [9]. As the epoxy and curative in stoichiometric amounts begin to crosslink, they follow a first order law until such a point that a sufficient number of functional sites become consumed in the formation of the polymer network, that the remaining functional sites are no longer in close proximity to one another. At this point, the reaction enters its second phase in which the crosslinking is now diffusion controlled, rather than stoichiometrically controlled. The diffusion controlled phase of the reaction now progresses at a much slower rate until the remaining functional sites are crosslinked, and a maximum degree of cure has been achieved. While the first order curing reaction is taking place, the network formation gradually increases the glass transition temperature (Tg) of the material. During this process, it is possible for the Tg to exceed the temperature that the material is being cured at. When the Tg exceeds the curing temperature of the resin, the material is said to have undergone vitrification, where the

mobility of the unreacted functional sites is significantly limited resulting in a slow reaction [10].

Research by Um, Daniel, and Hwang [11] has investigated the use of dynamic differential scanning calorimetry (DSC) to study the cure kinetics of an epoxy resin system. Because a thorough understanding of cure kinetics is critical to process optimization, the curing reaction is evaluated using DSC. DSC is a thermal analysis technique that is used to measure the heat released during a chemical reaction, in this case the curing reaction, and is quantified to determine the extent of chemical conversion. From the cure kinetic equations presented in the study, it is shown that the degree of cure is dependent on the thermal history, or cure profile, of the material. When conducting dynamic DSC scans, it is important to know that the degree of cure is a function of both temperature, a process controlled variable, and the rate of conversion, an inherent material property based on resin chemistry. The study by Um, Daniel, and Hwang noted that a two-phase reaction was observed, a result of the accelerated initial reaction and the eventual slowed reaction as a result of the reactive functional sites being consumed [11].

Role of Temperature on Cure

When curing epoxy film adhesives, one of the primary processing parameters that must be considered is that of cure temperature. The crosslinking reaction used to cure epoxy film adhesives is activated and controlled by thermal energy applied to the material, and as such the cure temperature must be carefully monitored and controlled to ensure the adhesive is processed to the specified cure profile. While some epoxy resin formulations are capable of curing at ambient temperatures when mixed, film adhesives require elevated temperature cures to fully crosslink and form a polymer network [12].

Most aerospace-grade epoxy film adhesives have manufacturer recommended cure temperatures ranging from 250 to 350°F based on their composition and crosslinking agents.

A study by Lapique and Redford [13] has investigated the effect of various temperatures on the curing of a two-part epoxy paste adhesive. In this study, adhesive samples were evaluated for cure behavior at curing temperatures of 23°C, 45°C, and 64°C. DSC evaluation of the resin showed a significant improvement in conversion rate and degree of cure with increased cure temperature. After 24 hours of curing, the 64°C, 45°C, and 23°C cured materials had achieved conversions (degree of cure) of 99%, 90%, and 74%, respectively. Of interest is the significant improvement in conversion rate as a function of increased cure temperature. For all temperature curing samples, the two-phase curing behavior was observed with a shift from first order to diffusion controlled reaction occurring sooner for the higher temperature curing samples. The DSC evaluation showed that a conversion of 99% was reached after only 4 hours at 64°C.

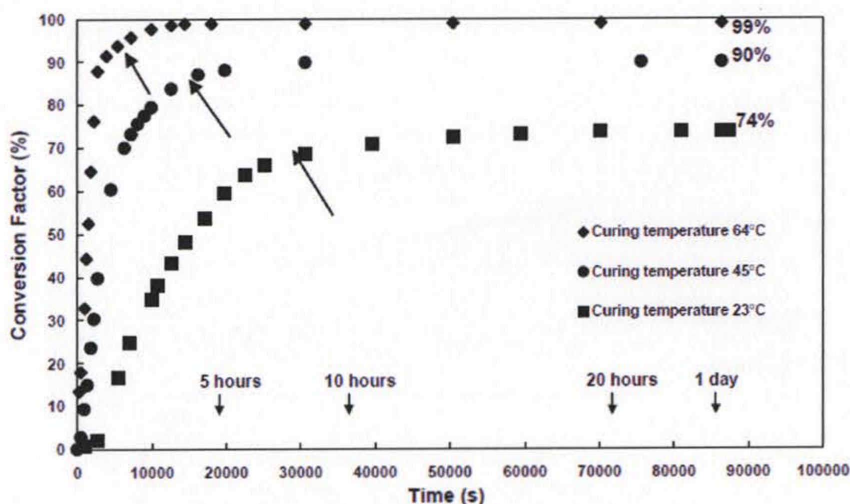

Figure 4. Conversion as a Function of Time and Cure temperature. Reprinted with permission from reference [13].

The results of mechanical tensile testing show that a cure time of 28 days at 23°C is required to achieve the same tensile strength and modulus as a sample cured for only 4 hours at 64°C. This observation is important as it demonstrates that the curing reaction indeed continues to occur after the first order reaction phase, but at a much decelerated rate. As such, the same mechanical performance resulting from a short duration, higher temperature cure was able to be achieved using a lower temperature cure profile for the epoxy resin studied when a longer duration cure was employed.

Data collected in a study by O'Brien, Mather, and White [14] also examines the role of cure temperature and time on the resultant degree of cure for a DGEBF/diethyltoluene diamine epoxy resin system. From the data, it is easy to see the transition from first order curing to diffusion controlled curing (Figure 5). For comparison, two data points from the same study are shown that were processed with a cure temperature of 145°C. As can be seen, the 145°C curing samples exhibit a 20% or greater degree of conversion than the samples cured at 110°C for equivalent cure durations (50 to 120 minutes).

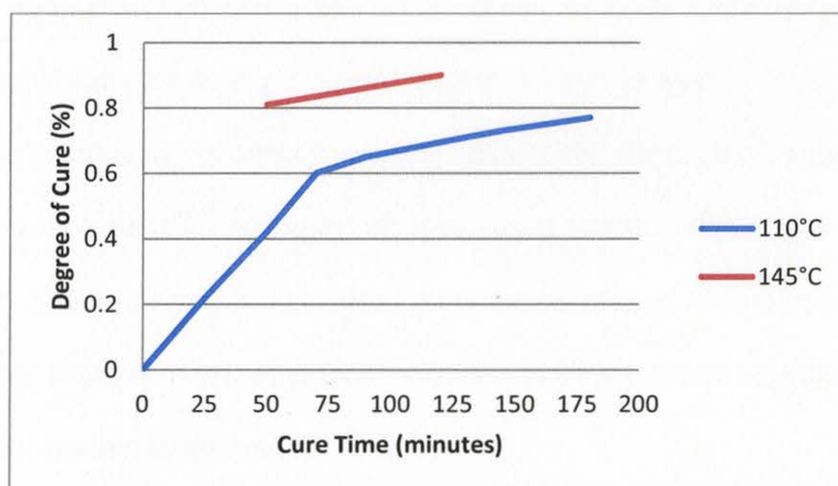

Figure 5. Degree of Cure as a Function of Cure Time and Temperature (Based on data from reference [14]).

A study by Loos and Springer [15] also noted a similar dependence of degree of cure on cure time and temperature. The curing model created and validated in this study predicted an increase in time to reach 90% conversion of 147 minutes when the cure temperature was reduced from 177°C to 135°C. The 236 minutes required to reach 90% conversion at 135°C is more than 2.5 times the 89 minutes required to reach 90% conversion with a cure temperature of 177°C. This echoes the observations made by earlier cited reports [12, 14] that elevated cure temperatures are able to achieve a faster cure rate and greater conversion than lower temperature cures of the same duration.

Sahagun and Morgan [16] have investigated the effect of cure temperature on the cure kinetics of a DGEBA epoxy resin and 3,3' diaminodiphenyl sulfone (DDS) amine curing agent. In this study, real-time near-infrared spectroscopy (NIR) was used to determine the concentration of primary amine, secondary amine, and tertiary amine as cure time progressed for cure temperatures of 90°C, 150°C, and 185°C. Results of the study showed different relationships between primary amine consumption and secondary and tertiary amine creation during the conversion reaction. Lower cure temperatures exhibited a lower rate of primary amine consumption, while the higher 185°C cure temperature yielded a much greater rate of primary amine conversion. It is also significant to note the rate of tertiary amine creation at the 185°C cure temperature, which is initially quite quick but tapers off with longer cure duration, is synonymous with the shift to a diffusion-controlled reaction. At this stage of cure, additional conversion can only be achieved through either increased post-cure temperature or prolonged cure duration at the present temperature.

Role of Cure Duration

Perhaps one of the most relevant prior works to this thesis study is the work of Chinn, Shim, and Seferis investigating the thermal and mechanical characteristics of various epoxy resin systems cured using extended cure profiles [17]. This study, based on the idea that most macroscopic mechanical properties of epoxy resins are a function of the degree of cure, examines the effect of 2, 8, and 14 hour cure holds on the Tg and three-point bend strength of resins composed of five different epoxy monomer structures including DGEBA (Epon 828), a polyfunctional epoxy phenolic novolac (DPS-155), RSL-1895 RTM resin, and two tetraglycidyl resins, HPT-1077 and HPT-1071. All resin types were cured with a stoichiometric amount of 4,4 diaminodiphenyl sulfone (DDS). To cure the samples, a two-stage process was used which involved ramping the samples at 2°C/minute to 300°F, holding at 300°F for 2 hours, ramping at 2°C/minute to 350°F, and holding for 2, 8, or 14 hours. To evaluate the degree of cure achieved using the various cure durations, DSC measurements were taken from cured and uncured resin samples. Figure 6 shows the degrees of cure observed in the study.

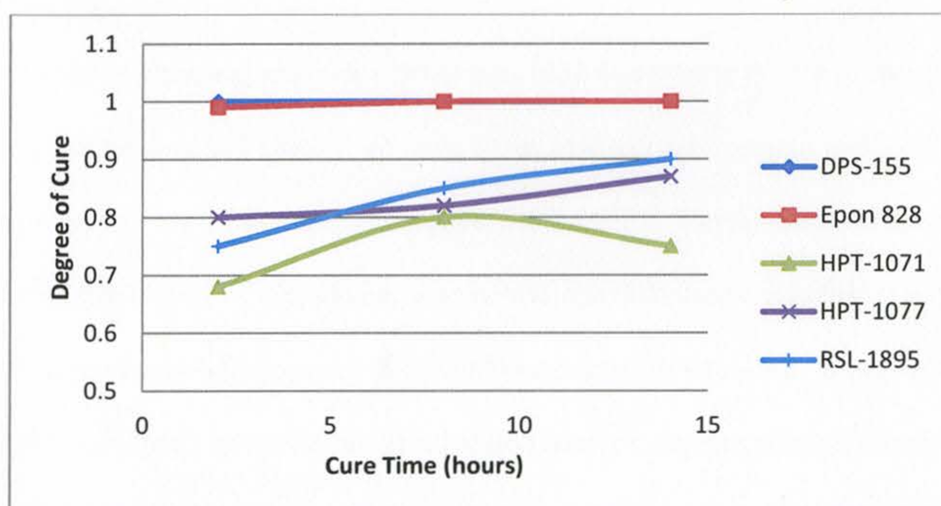

Figure 6. Degree of Cure as a Function of Cure Time (Based on data from reference [17]).

As can be seen, most resin formulations saw an improvement in conversion between 2 and 8 hours of cure, however the increase in conversion between 8 and 14 hours for most resin formulations was less significant if any improvement was observed at all. This would indicate that most of the materials have reached the diffusion controlled state of reaction and further conversion is very limited.

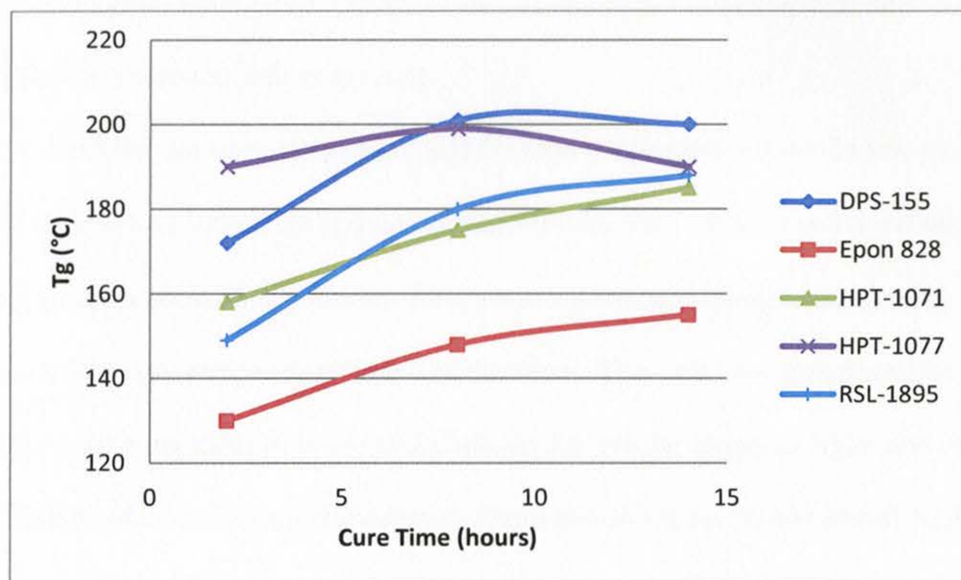

Figure 7. Glass Transition Temperature as a Function of Cure Time (Based on data from reference [17]).

Thermomechanical analysis (TMA) was used to evaluate the Tg of the epoxy resins. As can be seen in Figure 7, all resin types saw an improvement in Tg with 8 and 14 hour cures over the 2 hour cure (except for HPT-1077). These results indicate that even after a high degree of conversion is achieved, the diffusion-controlled reaction continues to rearrange and improve the crosslinked network structure. It is notable that the DGEBA and epoxy phenolic resins exhibited nearly complete conversion after only 2 hours of curing at 350°F, yet the glass transition temperatures saw improvement with extended cure times. To relate the various cure durations to mechanical performance, a

three-point flexure test was employed using methods specified in ASTM D790. Most resins showed improved yield stress with increased cure time, and all resins showed an improvement in toughness with extended cure times, with the DGEBA and epoxy phenolic resins exhibiting the largest improvement. It is concluded from this study that extended cure times can improve the degree of cure, Tg, and mechanical performance of various epoxy resin systems as a result of the increased polymer network development and improved molecular rearrangement.

A study by Stewart, Chambers, and Gordon [18] examined the degree of cure of a blend of DGEBA and DGEBF epoxies at various cure temperatures and durations. Thermal analysis showed that the resultant glass transition temperature increases with both increasing cure temperature and cure duration. This indicates that the additional thermal energy introduced to the material allows for greater chain mobility and for a greater degree of crosslinking and network formation to occur. It was observed that for the higher temperature cure, an extreme cure duration is not as effective as a longer cure duration for the lower temperature cure profile. This would imply that the higher temperature cure reaches a higher degree of cure in a short period of time, and as such less improvement is seen with increased cure duration. For a lower temperature cure profile, the extended cure duration is beneficial as the increased chain mobility as a result of the thermal exposure helps to increase the diffusion-controlled cure that results prior to vitrification. The effects of vitrification are of particular interest when discussing epoxies that cure with a temperature lower than their glass transition temperature, as the onset of vitrification leads to a significantly slower cure rate.

Effects of Cure on Mechanical Performance

The same study by Stewart, Chambers, and Gordon also examined the relationship of cohesive mechanical properties and degree of cure [18]. Mechanical testing showed a correlation between the glass transition temperature and the lap shear strength performance of the adhesive. For all specimens, a decrease in lap shear strength was observed between half hour and two hour cure durations, with an increase seen between two and four hour cure durations. The lower temperature cure specimens showed the largest improvement in lap shear strength as a function of cure duration. As such, the results of the mechanical testing support the observations made from the thermal analysis that the vitrification of lower temperature cures makes the ultimate degree of cure more dependent on extended cure durations. It is also important to note the despite achieving similar degrees of conversion with various cure temperatures and durations, significant difference in the resulting mechanical performance is evident. This is an important observation as it shows that cure temperature and duration can have a significant impact on the properties of the cured material. As such, the cure profile of an epoxy adhesive must be carefully considered if maximum properties are to be achieved, else the material must be characterized when cured using a different profile to determine the cure profile's effect on delivered mechanical properties.

The adhesive properties of a DGEBA based epoxy resin cured using various curing agents have been investigated in a study by Prolongo, Rosario, and Urena [19]. The curing agents considered in this study consisted of both imidazole initiators resulting in a homopolymerization, and the usage of amine hardeners to create a highly crosslinked epoxy-amine network. DSC analysis was used to characterize the cure kinetics of the

various resin formulations, and showed that the DDS and PAMS amine curing agents resulted in a higher degree of cure and a higher resultant Tg than the homopolymer initiators. The increase in Tg associated with the increase in degree of cure would indicate that the two characteristics are related, and that the resultant Tg of the cured epoxy is a function of the degree of cure and the degree of network crosslinking. It is also important to note that the highest Tg observed was from the resin cured with the DDS, an aromatic amine, showing the importance of the aromatic structures in achieving high temperature performance. Numerous studies have demonstrated that the phenolic adhesives achieve good durability and strength as a result of the high OH group presence in the chemical structure [19]. It should be noted that despite the high Tg and good thermal performance exhibited from aromatic amine-cured epoxy resins, the higher required curing temperatures must also be considered and could potentially limit the use of the curing agent in certain applications. From the results of the mechanical lap shear testing, it was also observed that proper adherend preparation and the use of an appropriate primer is critical to achieving the desired failure mode and improving the overall strength of the bond joint being evaluated.

A major concern when maximizing mechanical performance is desired is the degradation of a material due to solvent or moisture absorption. While the moisture absorption of polymers has been shown to follow Fickian behavior, it is believed that network polarity and free volume are primary contributors to the ultimate moisture absorption of the material [20]. A study by Jackson, et al. has shown that different network architecture and packing densities of thermosetting polymer networks exhibit differing solvent absorption rates and ultimate absorption achieved, demonstrating that

the solvent absorption characteristics, and by extension, thermal and mechanical performance, may be controlled by tailoring the network formation of an epoxy-amine polymer system.

Control of Process Parameters

For large aerospace sandwich structures, unique stepped cure cycles are often developed to ensure sufficient thermal exposure to cure the composite laminate in a co-bond/co-cure process. Such a cure cycle is shown in Figure 8. These bondment cure cycles can often significantly vary from an adhesive manufacturer's recommended cure cycle. A typical manufacturer's recommended cure cycle is shown in Figure 9. Often times in a production environment, a bondment may have to be processed through multiple cure cycles in order to cure additional bonded components or facilitate laminate repairs. Aerospace material and process specifications often specify a maximum number of cure cycles or duration at a certain thermal exposure. Often, if the maximum number of cure cycles is exceeded, a time consuming engineering review and dispositioning processes is required, with the worst case outcome being the scrapping of the bondment entirely. By demonstrating that the structural integrity of the adhesive is not degraded with a long duration or multiple cure cycle thermal exposure, the review process may be avoided, significantly reducing the as-manufactured cost of the bondment. To demonstrate that the adhesives of interest in this study are not structurally compromised with exposure to the multiple sequential cure cycles, data will be generated to compare the thermal and mechanical behavior of the cured adhesives.

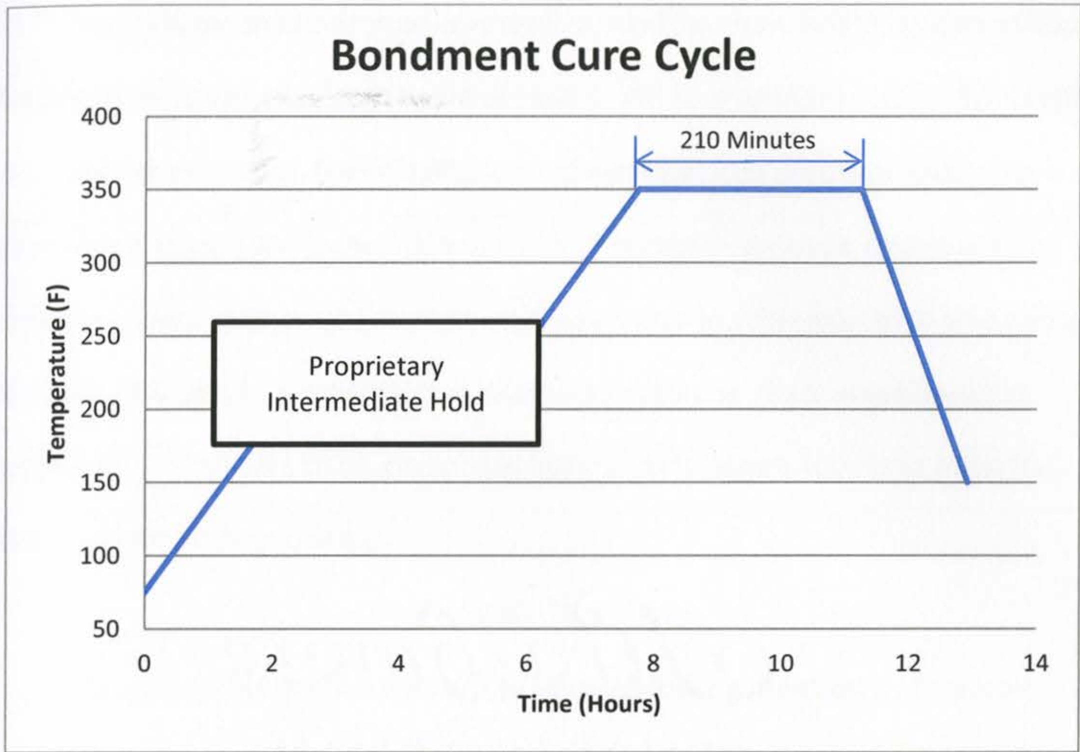

Figure 8. Long Duration Cure Cycle for Cure of a Sandwich Composite Structure.

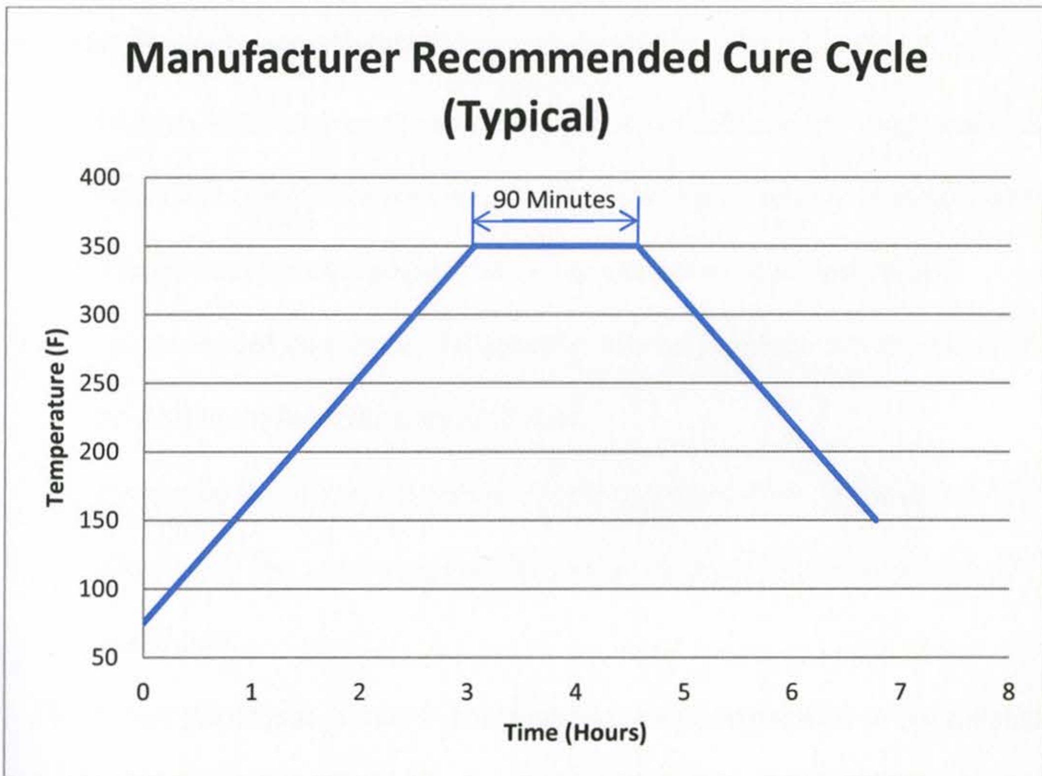

Figure 9. Typical Manufacturer Recommended Cure Cycle.

Based on the results of prior cure studies, it is hypothesized that by controlling the glass transition temperature and degree of cure, it will be possible to control the resulting cured adhesive properties. Specifically, it is believed that film adhesives exhibiting a higher degree of cure and higher Tg as a result of multiple cure cycle exposure will exhibit equivalent or improved mechanical performance to adhesives cured with a single cure cycle. It is also hypothesized that adhesives containing larger, more aromatic chemical structures will exhibit greater mechanical performance and better resist the effects of moisture degradation.

Research Objectives

The goal of this thesis research is to investigate the performance of various aerospace-grade epoxy film adhesives when cured using different levels of thermal exposure that are representative of cure cycles seen in manufacturing environments. The objectives of this study are as follows:

- Determine the degree of cure of the adhesives subjected to single and multiple bondment cure cycles for comparison to the degree of cure obtained through a shorter duration cure profile that is representative of a manufacturer recommended cure cycle. Differential scanning calorimetry techniques will be used to evaluate the degree of cure.
- Determine the wet and dry glass transition temperatures of the adhesives cured using the various cure profiles using dynamic mechanical analysis techniques.
- Relate the degree of cure to the glass transition temperature of the adhesives cured using the various duration cure profiles.

- Study the rheological performance of the adhesives during cure. Rheological performance will be evaluated through the identification of the gel point and determination of the minimum adhesive viscosity.
- Evaluate the cohesive and adhesive properties of the adhesives cured using the various duration cure profiles through V-notch shear and flat-wise tensile testing at RTD and 225F wet conditions.

CHAPTER II

EXPERIMENTAL

Materials

Three different film adhesives of similar weights and carriers were used in this study. Hysol EA 9689 epoxy film adhesive was acquired with a weight of 0.060 pounds per square foot (psf). Hysol EA 9658 epoxy film adhesive was acquired with a weight of 0.060 psf. Hexcel Redux 319 epoxy film adhesive was acquired with a knit carrier and a weight of 0.036 psf. These adhesive types and weights were chosen for their common use in bonded commercial aircraft structures and material availability. While the scope of this study did not allow for chemical analysis of the specific chemical structures, it was determine from the applicable MSDS sheets that the EA9658 adhesive is based on a polyfunctional epoxy resin cured with an aromatic polyamine, the EA9689 is a multi-component epoxy resin, and the Redux 319 is a bisphenol A based epoxy adhesive [21, 22, 23]. To prep the aluminum adherends for flatwise tensile testing, Cytec BR-127 epoxy primer was used to prime the bonded surfaces per the manufacturer's recommended procedure.

Thermal Analysis

Differential Scanning Calorimetry

DSC analysis was performed on uncured film adhesive samples with a nominal specimen weight of 12 mg using a TA Q200 or TA DSC 2920 differential scanning calorimeter. Test parameters involve a 3C/minute ramp rate over a temperature range of 50C to 250C (120F to 480F). The average heat of reaction in J/g was recorded for two specimens of each film adhesive type using methods described in ASTM E2160 [24].

Specimens cured with the short duration cure cycle shown in Figure 9, specimens cured with the bondment cure cycle of Figure 8, and specimens cured with four bondment cure cycles were tested using the same parameters as the uncured material specimens to determine the residual heat of reaction. Two samples were tested for each material and cure cycle type to determine the average residual heat of reaction.

Dynamic Mechanical Analysis

DMA testing was performed on cured film adhesive specimens using either a TA Q800 or TA DMA983 dynamic mechanical analyzer using techniques based on the methods described in ASTM D7028 [25]. Adhesive specimens of each material type were cured into a 7"x7"x0.1" plate using the two-piece mold shown in Figure 10. Plates were cured using the short duration cure cycle shown in Figure 9, the bondment cure cycle shown in Figure 8, or four bondment cure cycles. The cured adhesive plates were cut into 3.0"x0.5"x0.1" test specimens.

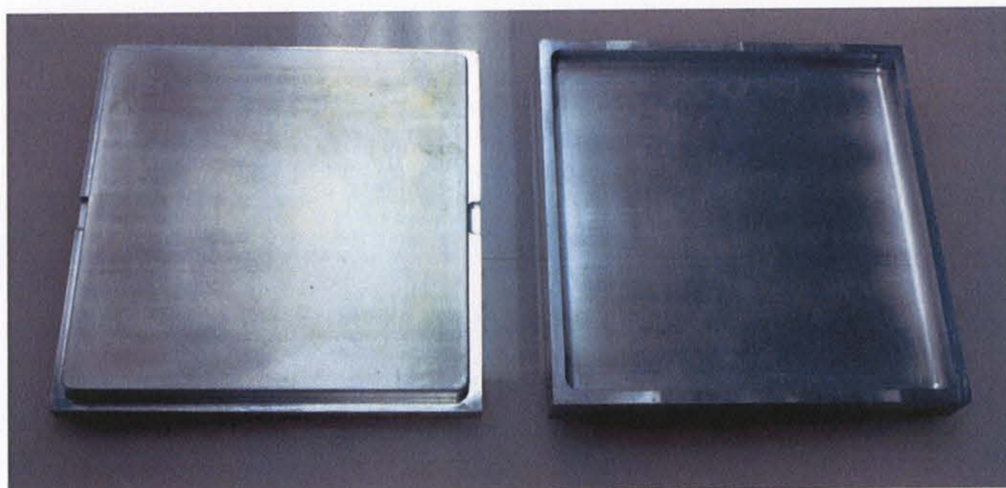

Figure 10. Adhesive Curing Mold.

All specimens were dried at 180F for a minimum of 16 hours. For each adhesive type and cure, three specimens were conditioned to a 'wet' saturated condition per

method B of ASTM D5229 [26]. Specimen weights were recorded after drying and after moisturization to determine percent moisture uptake for each specimen. Three dry specimens and three wet specimens of each material type and cure type were tested via DMA using either a dual cantilever (TA Q800) or single cantilever configuration (TA DMA983). A ramp rate of 3C/minute and a frequency of 1Hz were used to characterize each specimen. The glass transition temperature (Tg) of each sample was measured and reported as the intersection of two lines tangent to the storage modulus curve (E').

Rheology

Rheological sweeps were performed using a TA ARES dynamic rheometer. Specimens were prepared by placing an adhesive sample between two 1" diameter disposable aluminum sample plates. A dynamic scan was taken of each adhesive type by ramping the adhesive at 1C/minute to 180C (356F) to generate a plot of viscosity with respect to temperature. The temperature at which the adhesive viscosity (η^*) reached a minimum and the temperature at which η^* increased to 100 Pa-s after minimum viscosity was reached were recorded for each adhesive.

Mechanical Testing

Specimen Conditioning

After fabrication, all specimens were dried at 180F for a minimum of 16 hours. Specimens that were selected for wet conditioning were submerged in a 160F water bath until moisture uptake as determined by weight gain was equilibrated as defined by method B of ASTM D5229. Two travelers each were used to determine the moisture absorption of each adhesive and cure type. Traveler weight was recorded pre- and post-moisturization to determine the percent moisture uptake.

V-Notch Shear

To evaluate both the shear strength and shear modulus of the adhesives cured using various thermal exposures, V-notch shear specimens were fabricated and tested per ASTM D5379 [27]. For each adhesive type and cure type, 5 specimens were tested at room temperature dry (RTD) conditions and 5 specimens were tested at elevated temperature wet (ETW) conditions using an Instrumet test machine with a 11k pound capacity load cell. Testing was performed at a crosshead speed of 0.05 inches per minute. Room temperature testing was performed on dry specimens at 75F and wet conditioned specimens were tested at an elevated temperature of 225F. Failure stress and modulus were calculated for each specimen from the load at failure and the sample surface area between notches. Photos of failed specimens were examined to determine failure mode.

Flat-Wise Tension

The strength of the adhesive in an adherend to honeycomb core bond was evaluated using a flat-wise tensile test conducted per the methods of ASTM C297/C297M [28]. As the primary objective of the flat-wise tension test is to evaluate the performance of the film adhesive, aluminum adherends and honeycomb core were used to drive specimen failure into the adhesive. Specimens were prepared by fabricating a bondment using 5052 aluminum 1/4"-7.9pcf honeycomb bonded to 0.020" thick 2024-T3 bare aluminum face sheets primed with BR-127 epoxy primer. Bondments were fabricated using one of the three selected adhesives and either the short cure cycle, bondment cure cycle, or four bondment cure cycles. Cured bondments were cut into 2”x2” specimens and bonded to aluminum adherends using 0.090 psf EA9689 adhesive

with a knit carrier to control bondline thickness. This secondary bonding was performed in an oven at 270°F for a duration of two hours. This additional thermal exposure was not counted towards the total thermal history of the samples as the 270°F exposure is far below the 350°F cure temperature and the as-tested dry Tg of the adhesives, which were around 380°F. As such, it is not believed that the curing of the adhesives under study was affected by the secondary bonding cure cycle. Testing was performed at a loading rate of 0.020 inches per minute using an Instron 1127 test machine with a 10k pound load cell. For each material type and cure cycle type, 5 dry specimens were tested at room temperature (75F) and 5 moisture conditioned specimens were tested at an elevated temperature of 225F. The ultimate flat-wise tensile strength was calculated for each specimen by dividing the ultimate load at failure by the total facing area (4 in^2).

CHAPTER III

RESULTS AND DISCUSSION

Thermal Analysis

Differential Scanning Calorimetry

The total degree of cure for each adhesive/cure cycle combination was determined via DSC analysis. Results of the DSC testing of the EA9689 adhesive showed that the uncured epoxy adhesive exhibits the typical large exotherm associated with the curing reaction [29]. The cured EA9689 adhesive yielded much smaller exothermic reactions, indicating a high degree of cure from each of the three cure profiles. Table 1 shows the measured heat of reaction and degree of cure for each of the three cure profiles.

Table 1

EA9689 DSC Summary

Cure Type	Specimen	Sample Mass (mg)	Heat of Reaction (J/g)	Mean Heat of Reaction (J/g)	Degree of cure
None	1	6.4	261.9	256.2	N/A
	2	7.1	250.5		
90min	1	13.95	3.289	7.7195	96.99%
	2	13.95	12.15		
1x 210min	1	6.3	12.57	12.695	95.04%
	2	7.1	12.82		
4x 210min	1	6.6	5.64	4.69	98.17%
	2	6.7	3.74		

Similar to the results of the EA9689 adhesive, results of the DSC testing of the EA9658 adhesive showed that the uncured epoxy adhesive exhibits a large exotherm associated with the curing reaction. The cured EA9658 adhesive yields much smaller exothermic reactions, indicating a high degree of cure from each of the cure profiles.

Table 2 shows the measured heat of reaction and degree of cure for each of the three cure profiles.

Table 2

EA9658 DSC Summary

Cure Type	Specimen	Sample Mass (mg)	Heat of Reaction (J/g)	Mean Heat of Reaction (J/g)	Degree of cure
None	1	8.6	303.3	305.25	N/A
	2	9.6	307.2		
90min	1	12.67	2.312	1.973	99.35%
	2	10.47	1.634		
1x 210min	1	5.6	10.53	10.06	96.70%
	2	5	9.59		
4x 210min	1	5.7	0	0	100.00%
	2	6.2	0		

Results of the DSC testing of the Redux 319 adhesive showed that the uncured epoxy adhesive exhibits the typical large exotherm associated with the curing reaction, though the temperature range over which the reaction took place was smaller than those of the other adhesives studied. The cured Redux 319 adhesive yields much smaller exothermic reactions, indicating a high degree of cure from each of the cure profiles.

Table 3 shows the measured heat of reaction and degree of cure for each of the three cure profiles.

Table 3

Redux 319 DSC Summary

Cure Type	Specimen	Sample Mass (mg)	Heat of Reaction (J/g)	Mean Heat of Reaction (J/g)	Degree of cure
None	1	4.1	281.4	284.55	N/A
	2	5.7	287.7		
90min	1	10.13	3.401	2.984	**98.95%**
	2	14.38	2.567		
1x 210min	1	6.1	5.93	5.56	**98.05%**
	2	8.8	5.19		
4x 210min	1	5.5	0.8271	0.8005	**99.72%**
	2	6.4	0.7739		

Table 4 summarizes the mean degree of cure for each adhesive/cure cycle combination.

Table 4

DSC Results Summary: Degree of Cure

Material	90 Minute	1x210 Minute	4x210 Minute
EA9689	0.970	0.950	0.982
EA9658	0.994	0.967	1.000
Redux 319	0.990	0.981	0.997

As can be seen from Table 4, all three adhesives achieved relatively high degrees of cure during the short 90 minute cure cycle. The single bondment cure cycle exhibited a slightly lower overall degree of cure for all three adhesives, while the highest degree of cure was achieved after four bondment cure cycles for all three adhesives. These results indicate that while the short, *manufacturer recommended* cure cycle is sufficient to achieve an adequate degree of cure, there is some additional benefit to running a longer duration cure cycle. It was unexpected that the single 210 minute cure cycle would

exhibit a lower overall degree of cure than the shorter 90 minute cure cycle, though this may be attributed to the continued polymer network rearrangement facilitated by the high temperature exposure, or to the use of different DSC equipment for the 90 minute cure specimens. While 210 minutes are not sufficient to allow for full network development, the additional thermal exposure provided by additional cure cycles allows for additional post curing to occur, increasing the overall conversion. All three types of epoxy monomer structures exhibited increased conversion with extended cure durations.

Dynamic Mechanical Analysis

The glass transition temperature (Tg) of the adhesives cured using the various cure profiles was determined via DMA testing of dry and wet cured adhesive specimens. Table 5 shows the Tg onset of dry EA9689 adhesive cured using the short cure cycle, single bondment cure cycle, and four bondment cure cycles. The dry Tg of EA9689 stayed relatively constant with varying cure cycle duration, however it can be seen that the wet Tg values presented in Table 6 show the typical knockdown associated with wet conditioning. The wet Tg of the adhesive also stayed relatively consistent regardless of cure cycle duration.

Table 5

EA9689 DMA Results: Dry Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	29.03	12.69	2.71	384.5	
2	90 min	28.63	12.69	2.74	387	386.4
3	90 min	28.34	12.67	2.73	387.7	
1	1x 210min	35	12.74	2.71	382.39	
2	1x 210min	35	12.7	2.69	382.15	383.042
3	1x 210min	35	12.71	2.67	384.58	

Table 5 (continued).

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	4x 210min	35	12.72	2.75	390.56	
2	4x 210min	35	12.76	2.76	389.08	389.408
3	4x 210min	35	12.76	2.76	388.58	

Table 6

EA9689 DMA Results: Wet Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	40.82	12.86	2.72	234.4	
2	90 min	40.18	12.85	2.69	234.1	236.2
3	90 min	41	12.84	2.74	240.2	
1	1x 210min	41.46	12.84	2.76	229.1	
2	1x 210min	40.88	12.87	2.73	224.0	229.5
3	1x 210min	41.38	12.79	2.76	235.4	
1	4x 210min	40.91	12.77	2.73	237.2	
2	4x 210min	41.12	12.82	2.75	227.2	234.8
3	4x 210min	40.98	12.82	2.73	240.0	

Table 7 and Table 8 show the Tg onset of dry and wet EA9658 adhesive cured using the short cure cycle, single bondment cure cycle, and four bondment cure cycles. The dry and wet Tgs of EA9658 stayed relatively constant with varying cure cycle duration, however it can be seen that the single bondment cure cycle and four bondment cure cycle mean Tgs are slightly lower than the short cure cycle results. This trend would indicate that while the adhesive does not show additional Tg benefit from extended cure exposure, it also is not significantly degraded as a result of the exposure.

Table 7

EA9658 DMA Results: Dry Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	27.1	12.70	2.72	391.2	
2	90 min	26.41	12.69	2.69	388.9	389.83
3	90 min	25.99	12.73	2.7	389.4	
1	1x 210min	35	12.68	2.75	383.234	
2	1x 210min	35	12.72	2.76	383.018	383.108
3	1x 210min	35	12.74	2.75	383.072	
1	4x 210min	35	12.70	2.7	385.538	
2	4x 210min	35	12.73	2.71	386.132	386.20
3	4x 210min	35	12.70	2.72	386.924	

Table 8

EA9658 DMA Results: Wet Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	36.41	12.85	2.41	247.9	
2	90 min	39.64	12.85	2.64	246.5	246.0
3	90 min	39.11	12.84	2.61	243.6	
1	1x 210min	40.95	12.86	2.73	242.3	
2	1x 210min	40.53	12.80	2.7	234.5	240.4
3	1x 210min	39.54	12.78	2.63	244.3	
1	4x 210min	40.67	12.74	2.71	240.9	
2	4x 210min	40.75	12.81	2.72	248.6	244.3
3	4x 210min	40.69	12.75	2.71	243.5	

Table 9 and Table 10 show the dry and wet Tg onset of Redux 319 adhesive cured using the short cure cycle, single bondment cure cycle, and four bondment cure cycles. The dry and wet Tgs of Redux 319 show a significant improvement with extended cure duration. The increase in Tg with increasing cure duration also indicates a strong relationship between degree of cure and Tg, and that the greater degree of crosslinking

and polymer network formation resulting from a longer duration cure cycle is beneficial to resisting the detrimental effects associated with polymer moisture absorption and hydrolysis [20].

Table 9

Redux 319 DMA Results: Dry Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	41.52	12.7	2.76	254.3	
2	90 min	41.71	12.67	2.78	251.7	253.4
3	90 min	41.23	12.68	2.75	254.1	
1	1x 210min	35	12.76	2.74	284.7	
2	1x 210min	35	12.76	2.74	283.2	283.8
3	1x 210min	35	12.76	2.77	283.5	
1	4x 210min	35	12.77	2.77	288.8	
2	4x 210min	35	12.83	2.77	289.8	288.4
3	4x 210min	35	12.76	2.79	286.7	

Table 10

Redux 319 DMA Results: Wet Condition

Specimen	Cure Cycle	Length	Width	Thickness	Tg Onset (F)	Mean Tg Onset (F)
1	90 min	42.57	12.89	2.84	160.5	
2	90 min	41.67	12.85	2.79	164.5	161.8
3	90 min	42.55	12.91	2.83	160.4	
1	1x 210min	42.3	12.86	2.82	166.3	
2	1x 210min	42.5	12.86	2.83	167.1	166.8
3	1x 210min	42.03	12.89	2.80	167.0	
1	4x 210min	42.63	12.9	2.84	186.8	
2	4x 210min	42.32	12.88	2.82	184.9	185.3
3	4x 210min	42.76	12.88	2.85	184.1	

Table 11 shows a comparison of the mean dry and wet Tgs of the adhesives cured using each cure profile.

Table 11

Mean Glass Transition Temperatures (Tg)

	Dry Tg (F)			Wet Tg (F)		
Material	90 min	210 min	4x210 min	90 min	210 min	4x210 min
EA9689	386.4	383	389.4	236.2	229.5	234.8
EA9658	389.8	383.1	386.2	246.0	240.4	244.3
Redux 319	253.4	283.8	288.4	161.8	166.8	185.3

Rheology

The rheological behaviors of the uncured adhesives were evaluated via dynamic temperature ramps. Figure 11 shows the complex viscosity profiles of each adhesive, and Table 12 summarizes the results of the adhesive rheometer runs.

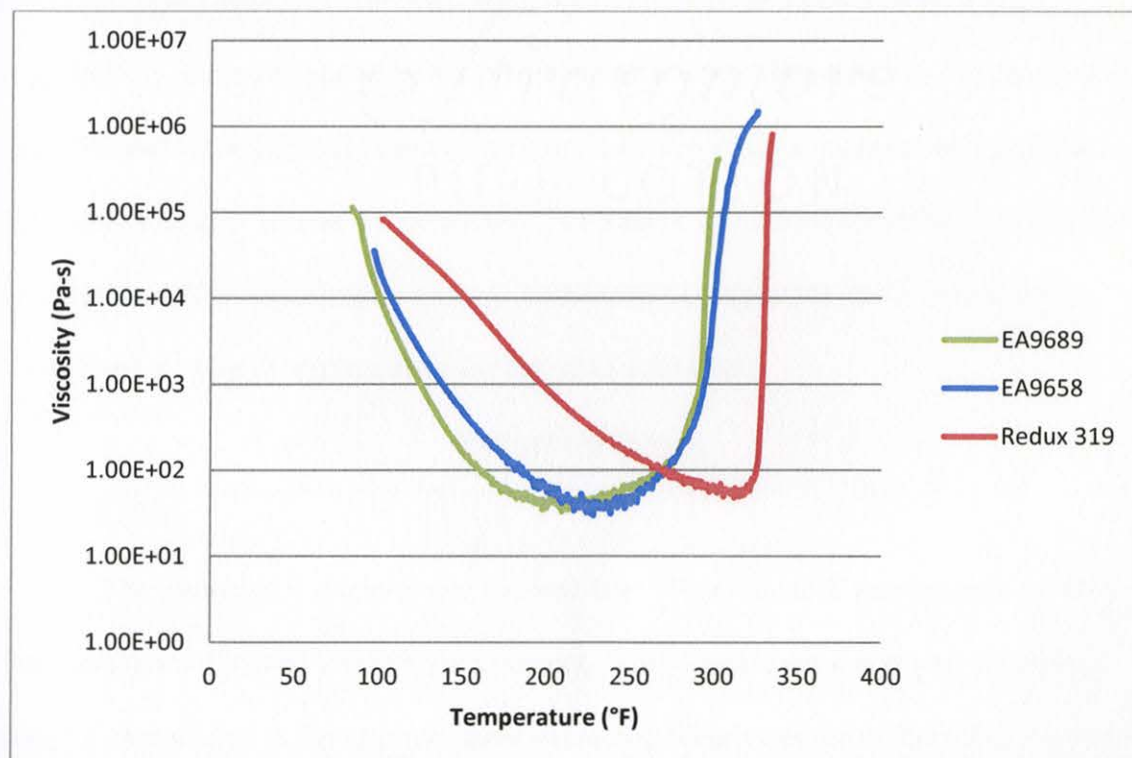

Figure 11. Adhesive complex viscosity as a function of temperature.

Table 12

Rheology Results Summary

	Minimum Viscosity, η (Pa-s)	Temperature at Minimum Viscosity (°F)	Temperature when η exceeds 100 Pa-s (°F)
EA9689	33.2	209.7	268.9
EA9658	29.7	228.4	270.4
Redux 319	48.0	305.5	325.4

It can be seen from Table 12 that the EA9689 and EA9658 adhesives exhibit the lowest minimum viscosities values, as well as the lowest temperatures at which the minimum viscosities are reached. These two adhesives also increased their viscosity to 100 Pa-s at nearly the same temperature. The Redux 319 adhesive exhibited significantly different properties, reaching a minimum viscosity of only 48.0 Pa-s. This minimum viscosity also occurred at a temperature that was 77.1°F above the next closest adhesive, EA9658. The Redux 319 increased viscosity to 100 Pa-s at 325.4°F, which is a significantly greater temperature than the other adhesives. These results indicate that the EA9689 and EA9658 would behave very similarly for a given process, and could be thermally staged at similar temperatures. The Redux 319 adhesive exhibits a viscosity profile that differs significantly enough from the other adhesives that it would not be considered a 'drop in' replacement for the other adhesives.

Mechanical Testing

V-Notch Shear

The mechanical properties of the neat film adhesives with varying cure profiles were evaluated through V-notch shear testing. The V-notch shear test was selected to allow measurement of the ultimate shear stress and shear modulus of the adhesives while minimizing test specimen size. The V-notch specimens allocated for wet testing were

soaked to equilibrium per ASTM D5229. The final percent moisture uptake at equilibrium for each adhesive and cure type are shown in Table 13. As can be seen from this table, there is not a clear relationship between cure type and moisture weight gain. While it was hypothesized that the specimens exposed to longer duration cure cycles would experience greater network formation and improved resistance to moisture absorption, the samples cured with four 210 minute cure cycles exhibited some of the highest moisture weight gain for each adhesive. The mean moisture uptake of the EA9689 adhesive cured with four 210 minute cure cycles appears to be abnormally high; this is likely a result of excessive exposed porosity on one of the measured samples.

Table 13

V-Notch Shear Mean Moisture Absorption at Equilibrium

Adhesive	Cure Type (minutes)	Mean Weight Gain (%)
EA9689	90	2.55
	1x210	3.15
	4x210	7.24
EA9658	90	2.75
	1x210	2.95
	4x210	2.79
Redux 319	90	4.23
	1x210	3.66
	4x210	4.57

EA9689 film adhesive was cured into flat panels per the previously described methods and cut into V-notch shear specimens of the dimensions specified in ASTM D5379. Table 14 and Table 15 show the results of RTD and ETW EA9689 film adhesive testing, respectively. The results show a slight decrease in mean ultimate shear strength

with increasing cure duration at room temperature test conditions and some variation in mean ultimate shear strength at ETW conditions. It should be noted that specimen number five of the wet 210 minute cure cycle group exhibited an unusually low value. If this value were to be omitted, the mean shear strength for that group would increase to 2.3 ksi and result in the trend of the wet data to match that of the dry data. Overall, there is relatively little change in ultimate shear modulus as a result of extended cure duration. Mean room temperature shear modulus remained relatively constant with varying cure duration, though a slightly higher mean was noted after four bondment cure cycles. 225F wet shear modulus data was unable to be obtained due to strain gage failure during the moisturization process.

Table 14

EA9689 RTD V-Notch Shear Results

	90 Min		210 Min		4x210 Min	
Sample	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)
1	5.09	0.5	7.50	0.5	4.37	0.4
2	5.76	0.5	5.23	0.5	4.88	0.5
3	4.80	0.4	3.52	0.4	5.46	0.5
4	5.76	0.4	4.51	0.4	-	-
5	4.26	0.5	3.89	0.5	4.09	-
Average	5.13	0.46	4.93	0.46	4.70	0.47

Table 15

EA9689 225F Wet V-Notch Shear Results

	225F Wet Ult. Shear Stress (ksi)		
Sample	90 Min	210 Min	4x210 Min
1	2.70	2.41	2.31
2	2.76	2.87	2.23
3	2.64	2.32	2.29
4	2.61	1.61	1.91
5	2.55	0.68	1.96
Average	2.65	1.98	2.14

During the test process it was observed that the test specimens were yielding somewhat atypical failure modes. The V-notch shear specimen specified in ASTM D5379 is designed to initiate failure and create a shear plane between the tips of the two notches in the specimen, allowing for repeatable failure over a measureable gage area. As shown in Figure 12, the tested adhesive V-notch shear specimens exhibited failure around, though not directly though, the gage area of the specimens. It was observed that many of the specimens exposed a relatively high degree of porosity along the failed surfaces. It is likely that this porosity, resulting from the panel manufacturing process, influenced the irregular crack path initiating from the tip of one of the V-notches. It was observed that the 225°F wet specimens exhibited similar failure modes to the RTD tested specimens.

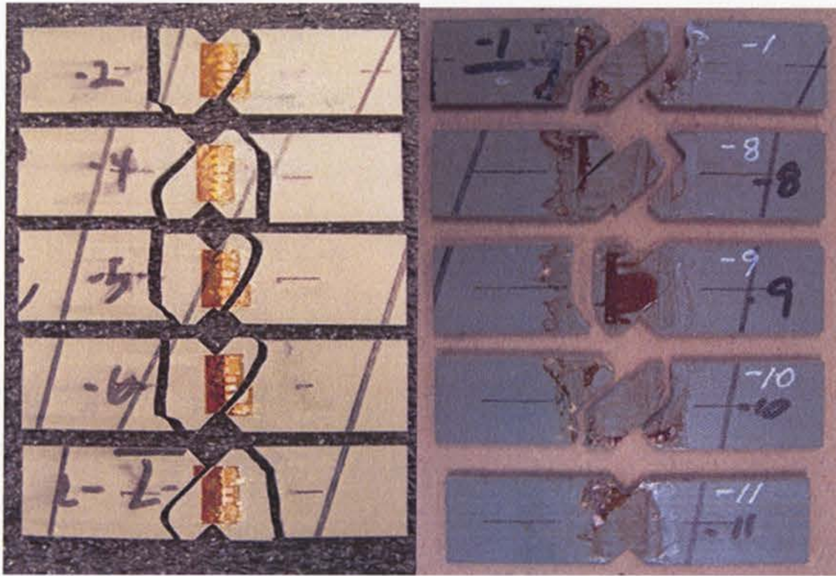

Figure 12. EA9689 V-Notch Shear Specimen Failure Modes. The left side shows specimens failed at RTD test conditions. The right side shows specimens failed at ETW conditions.

Figure 13. V-notch shear specimen porosity. Many of the V-notch shear specimens exhibited a high degree of porosity along the failure surfaces.

EA9658 film adhesive was cured into flat panels per the previously described methods and cut into V-notch shear specimens of the dimensions specified in ASTM D5379. Table 16 and Table 17 show the results of RTD and ETW EA9658 film adhesive testing, respectively. The results show relatively similar mean ultimate shear strengths at room temperature with a slight increase for samples cured with a single or four bondment

cure cycles. The ETW specimens exhibited similar behavior, with a significant improvement in strength for specimens cured with a single or four bondment cure cycles. Overall, there is relatively little change in ultimate shear modulus as a result of extended cure duration, though specimens processed with a single or four 210 minute cure cycles did show a slight increase in modulus. 225F wet shear modulus data was unable to be obtained due to strain gage failure during moisturization.

EA9658 V-notch shear specimens exhibited similar failure modes and porosity inclusions to those of the EA9689 specimens. Failure modes were similar amongst samples with different cure profiles and test conditions.

Table 16

EA9658 RTD V-Notch Shear Results

	90 Min		210 Min		4x210 Min	
Sample	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)
1	5.24	0.3	6.77	0.4	6.16	0.3
2	4.36	0.4	7.09	0.4	7.95	0.5
3	7.26	0.5	7.77	0.5	7.22	0.4
4	5.95	0.4	6.54	0.5	5.83	0.5
5	7.70	0.5	7.20	0.5	5.93	0.5
Average	6.10	0.42	7.07	0.46	6.62	0.44

Table 17

EA9658 225F Wet V-Notch Shear Results

	225F Wet Ult. Shear Stress (ksi)		
Sample	90 Min	210 Min	4x210 Min
1	1.92	2.81	2.42
2	1.50	2.46	2.79
3	1.97	3.59	2.31
4	2.22	3.75	2.61
5	2.18	2.83	2.44
Average	1.96	3.09	2.51

Redux 319 film adhesive was cured into flat panels per the previously described methods and cut into V-notch shear specimens of the dimensions specified in ASTM D5379. Table 18 and Table 19 show the results of RTD and ETW Redux 319 film adhesive testing, respectively. The results show an increase in mean ultimate shear strength at both room temperature dry and 225F wet conditions. These results indicate that for the Redux 319 adhesive, cure cycle duration appears to play an important role in the delivered shear strength of the material, with a 25% increase in mean shear strength when cure duration is increased from 90 minutes to 210 minutes, and an additional 10% increase after four 210 minute bondment cure cycles. The shear strength of samples tested at 225F wet conditions remained relatively constant with a slight increase after a 210 minute cure cycle, but slight decrease after four bondment cure cycles. Mean room temperature shear modulus showed an increase after both single and four bondment cure cycles, echoing the trend seen in the ultimate shear strength with increasing cure duration. 225F wet shear modulus data was unable to be obtained due to strain gage failure during moisturization.

Table 18

Redux 319 RTD V-Notch Shear Results

	90 Min		210 Min		4x210 Min	
Sample	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)	Ult.Shear Stress (ksi)	2% Offset Shear Modulus (Msi)
1	5.21	0.3	6.31	0.4	6.88	0.4
2	4.81	0.3	7.48	0.4	7.58	0.4
3	4.28	0.3	6.59	0.3	7.65	0.4
4	6.11	0.2	7.17	0.4	7.93	0.4
5	7.24	0.3	7.14	0.4	7.41	0.4
Average	5.53	0.28	6.94	0.38	7.49	0.4

Table 19

Redux 319 225F Wet V-Notch Shear Results

	225F Wet Ult. Shear Stress (ksi)		
Sample	90 Min	210 Min	4x210 Min
1	1.98	1.90	1.61
2	2.17	2.65	2.24
3	1.43	1.91	1.30
4	1.46	1.77	1.21
5	1.56	1.49	1.41
Average	1.72	1.95	1.55

The Redux 319 V-notch shear specimens tested at RTD conditions exhibited similar failure modes to the EA9689 and EA9658 specimens with failure initiating in the gage region of the specimens. All Redux 319 specimens tested at 225°F wet conditions, however, exhibited a failure mode of plastic deformation in the gage section of the specimens, which is shown in Figure 14. The plastic deformation failure modes of the Redux 319 specimens tested at ETW conditions agree with the results of the DMA testing of the Redux 319 adhesive after wet conditioning. With the wet Tg of the Redux 319 adhesive cured using the studied cure profiles ranging between 162-185°F, a yielding failure mode is to be expected when the adhesive is mechanically tested at a temperature above its Tg.

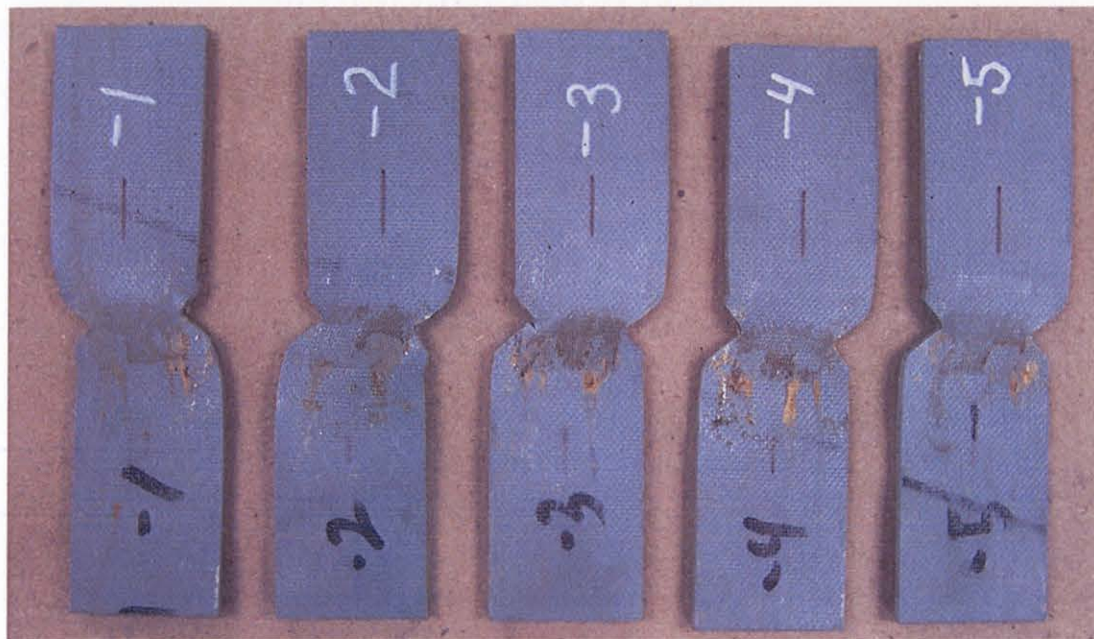

Figure 14. Redux 319 V-notch shear failure modes at ETW test conditions. Specimens cured with 90 minute cure cycle shown.

Flat-Wise Tension

To evaluate the effects of the different cure cycle durations on the adhesives as used in a composite sandwich structural bondment, flatwise tensile testing was performed. All wet conditioned specimens were conditioned to equilibrium per ASTM D5229.

Table 20 shows the mean percent weight gain of the sample travelers for each adhesive and cure type that were moisture conditioned. As can be seen from the table, there does not appear to be a clear correlation between cure duration and percent weight gain at equilibrium. It is likely that the variation in percent weight gain is a result of the amount of the adhesive exposed outside of the aluminum honeycomb core, which functions as a moisture migration barrier due to the chosen specimen configuration.

Table 20

FWT Mean Moisture Absorption at Equilibrium

Adhesive	Cure Type (minutes)	Mean Weight Gain (%)
EA9689	90	1.0166
	210	1.294
	4x210	1.008
EA9658	90	1.189
	210	1.5838
	4x210	3.272
Redux 319	90	2.491
	210	1.143
	4x210	1.364

EA9689 adhesive specimens were tested in flatwise tension at both RTD and 225°F wet conditions. Table 21 shows the results of this testing. The RTD FWT strength of the EA9689 remained relatively constant with a slight reduction in strength with extended cure durations. Despite the small reduction in strength, the RTD FWT data from specimens cured with a single or four bondment cure cycles is shown to be statistically equivalent to the short 90 minute cure cycle via a two-tailed T-test.

The 225°F wet FWT data shows a somewhat more irregular trend with the maximum FWT strength being achieved after a single bondment cure cycle. The 225°F wet FWT strength of samples show a noticeable decrease in strength with increasing cure duration, echoing the results of the RTD testing. Unlike the RTD results, the FWT results of samples cured with four 210 minute cure cycles are not statistically equivalent to the 90 minute cure cycle as determined with a two-tailed T-test.

EA9689 specimens tested at both RTD and ETW conditions all exhibited cohesive failure within the adhesive material. The failed EA9689 specimens are shown

in Figure 15 and Figure 16. The consistent failure mode within the adhesive itself indicates that the resulting test values truly evaluate the adhesive material and provide a high degree of confidence in the accuracy of the test results.

Table 21

EA9689 FWT Test Results

	FWT Ultimate Strength (psi)					
	RTD			225F Wet		
Sample	90	210	4x210	90	210	4x210
1	1330.5	1408.3	1418.8	604.5	609.3	628.0
2	1349.8	1236.3	1478.0	623.8	599.3	583.8
3	1505.0	1362.3	1153.0	641.3	605.0	534.5
4	1329.5	1391.8	1213.3	676.5	615.0	593.3
5	1439.0	1438.3	1271.5	-	642.0	572.8
Average	1390.8	1367.4	1306.9	636.5	614.1	582.5
StDev	78.17	78.28	137.38	30.60	16.63	33.86
CV	0.06	0.06	0.11	0.05	0.03	0.06

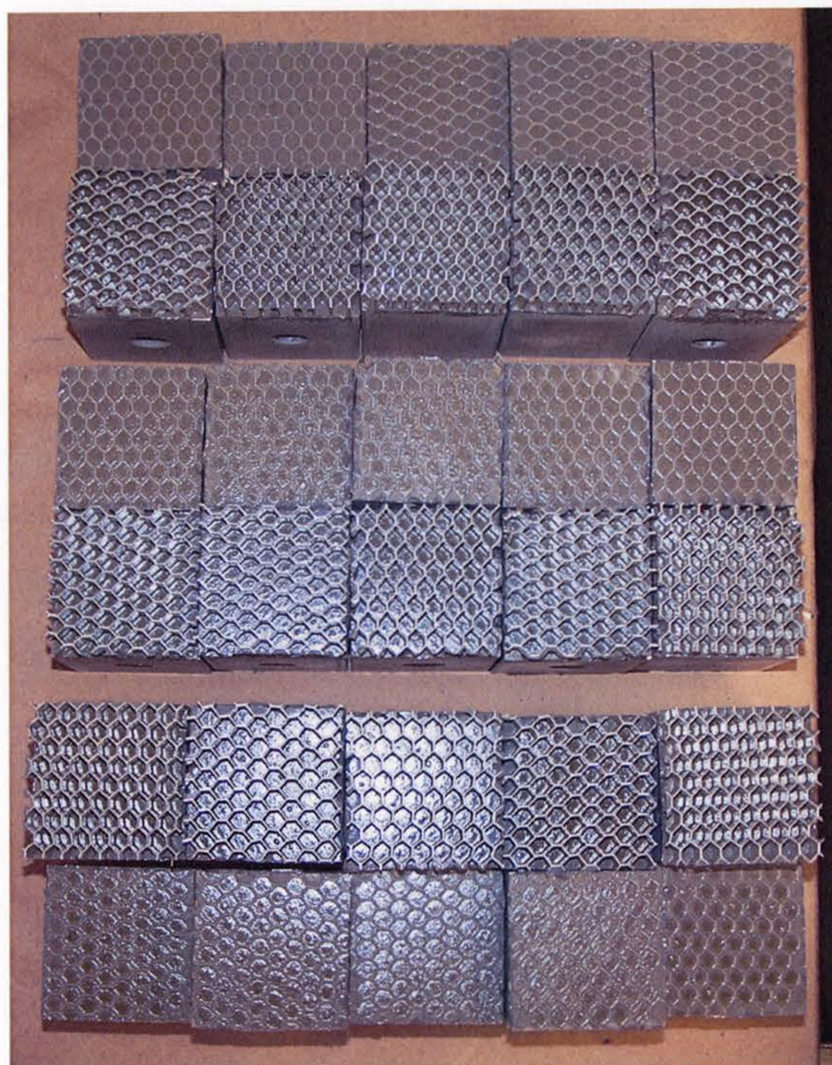

Figure 15. EA9689 FWT Failed Specimens – RTD Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

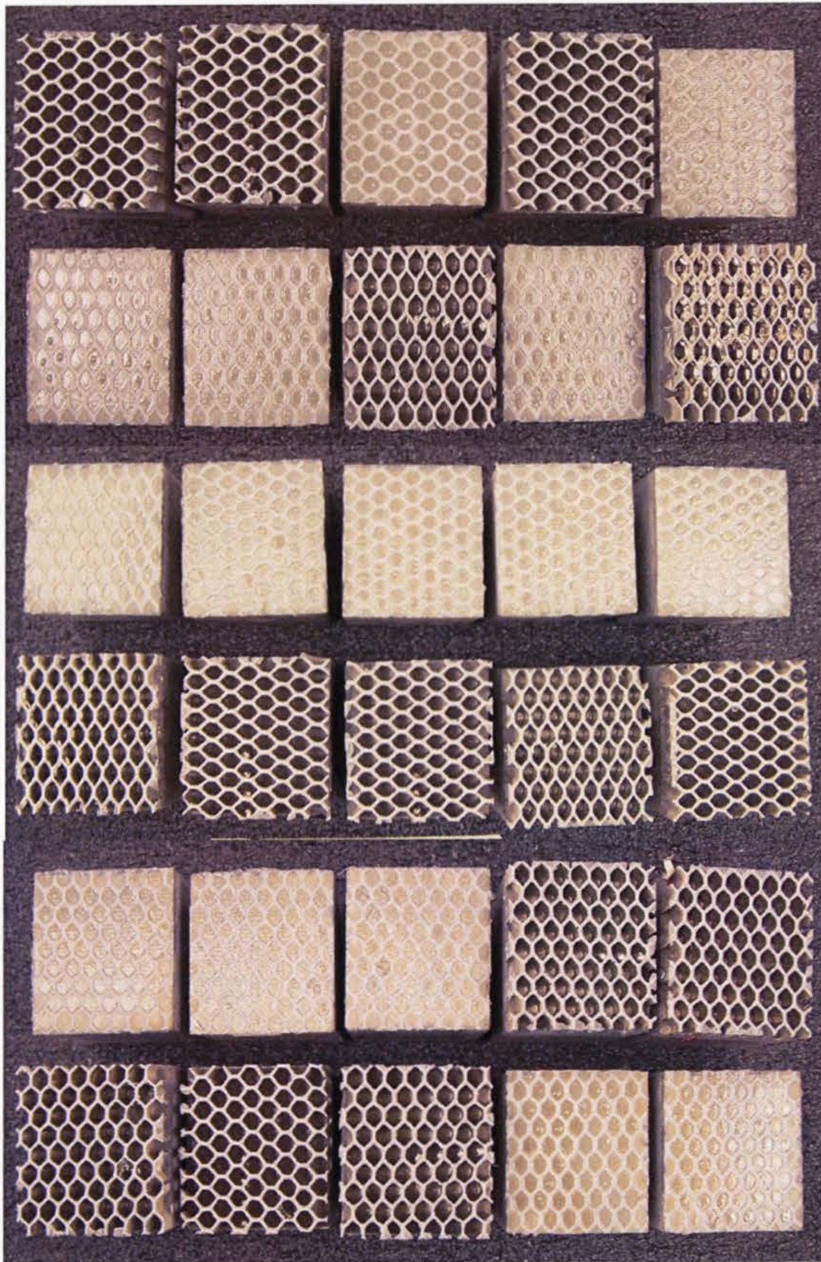

Figure 16. EA9689 FWT Failed Specimens – 225F Wet Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

EA9658 adhesive specimens were tested in flatwise tension at both RTD and 225°F wet conditions. Table 22 shows the results of this testing. The RTD FWT strength of the EA9658 remained relatively constant, however the minimum strength was observed for specimens cured with a single bondment cure cycle. Examination of the

individual single bondment cure ultimate FWT strengths show relatively consistent values with the exception of one low data point (1050 psi). If this data point is considered to be anomalous and discarded, the mean FWT strength for this cure cycle then increases to 1313 psi, which is a slight improvement over the baseline 90 minute cure cycle results. The mean RTD FWT strength of specimens cured with four bondment cure cycles showed an increase over the short 90 minute cure cycle though it is shown to be statistically equivalent to the 90 minute cure cycle via a two-tailed T-test.

The 225°F wet FWT data shows a similar trend to the RTD FWT results with the minimum FWT strength occurring after a single bondment cure cycle, while the maximum FWT performance is achieved after four bondment cure cycles. The 225°F wet FWT strength of samples cured with four bondment cure cycles also shows an increase in strength over samples cured with the short 90 minute cure cycle. This improvement in ETW FWT strength would imply that the improved network formation and greater degree of cure provided by the longer duration cure cycles allow the adhesive to exhibit improved resistance to the degrading effects associated with moisture absorption and elevated temperature exposure. While there is some improvement in FWT performance at RTD and 225F wet conditions with increased cure duration, it is most important to note that the adhesive is not degraded as a result of long-duration, multiple cure cycle exposure. The ability of the EA9658 adhesive to maintain properties with various cure exposures is a desirable quality which allows for flexibility in manufacturing with this material.

Table 22

EA9658 FWT Test Results

	FWT Ultimate Strength (psi)					
	RTD			225F Wet		
Sample	90	210	4x210	90	210	4x210
1	1291.5	1254.8	1388.0	650.3	560.8	669.3
2	1305.0	1353.8	1351.8	607.0	614.0	685.3
3	1285.0	1281.3	1400.8	713.5	680.5	589.0
4	1261.3	1049.8	1368.5	567.5	573.3	712.3
5	1378.0	1361.3	1433.8	657.8	588.5	727.5
Average	1304.2	1260.2	1388.6	639.2	603.4	676.7
StDev	44.22	126.22	31.42	55.15	47.45	54.00
CV	0.03	0.10	0.02	0.09	0.08	0.08

EA9658 specimens tested at both RTD and ETW conditions all exhibited cohesive failure within the adhesive material. The failed EA9658 specimens are shown in Figure 17 and Figure 18. The consistent failure mode within the adhesive itself indicates that the resulting test values truly evaluate the adhesive material and provide a high degree of confidence in the accuracy of the test results.

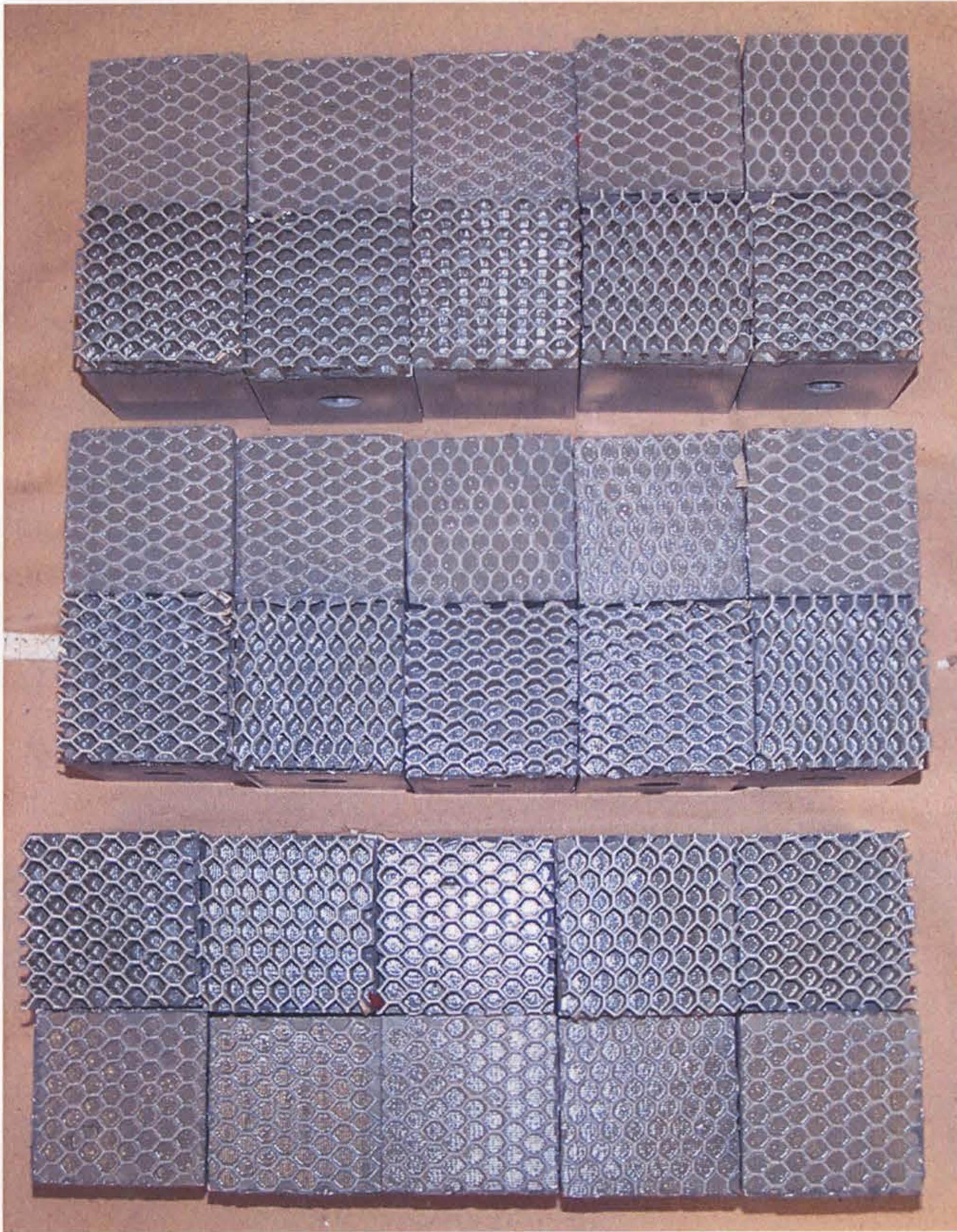

Figure 17. EA9658 FWT Failed Specimens – RTD Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

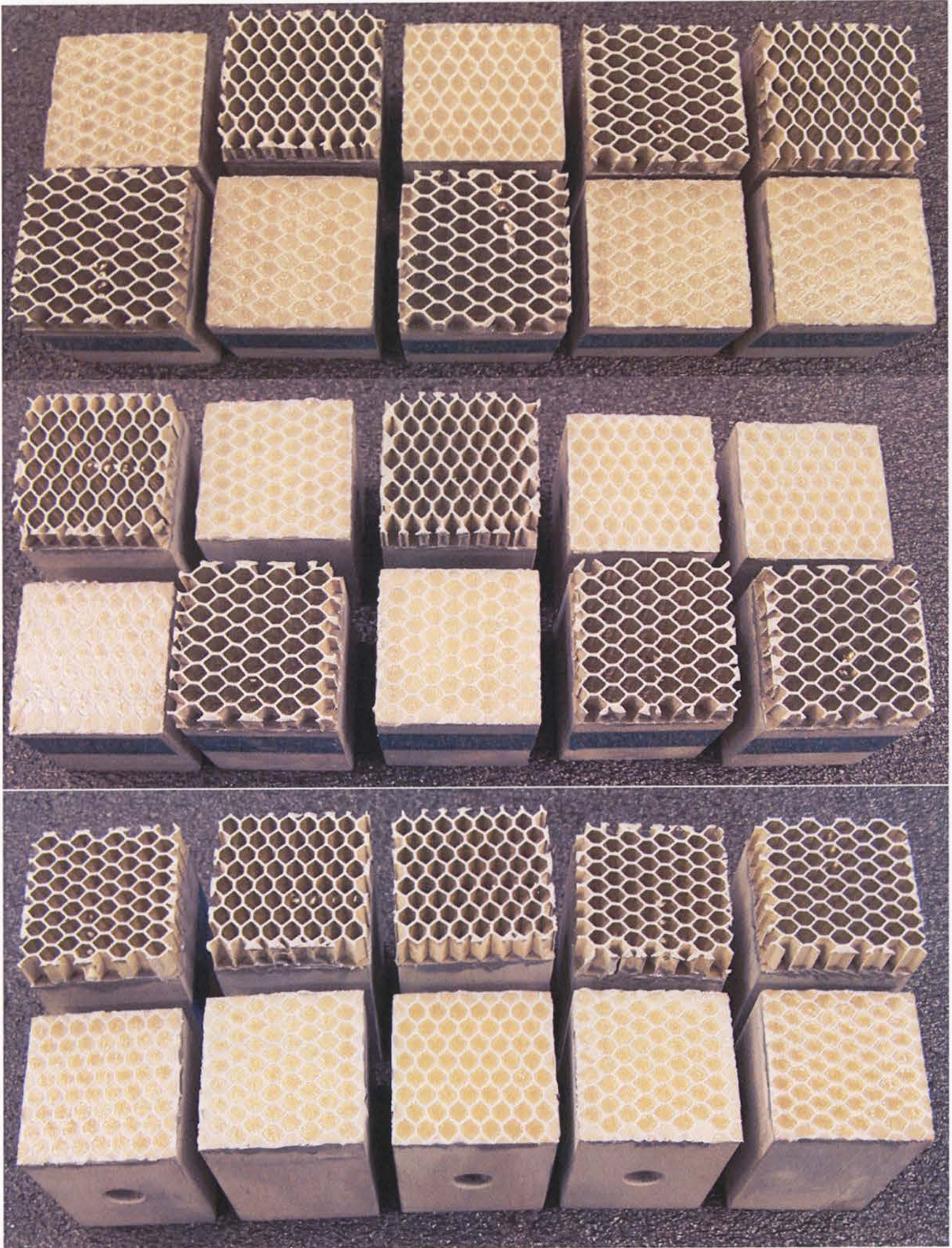

Figure 18. EA9658 FWT Failed Specimens – 225F Wet Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

Redux 319 adhesive specimens were tested in flatwise tension at both RTD and 225°F wet conditions. Table 23 shows the results of this testing. The RTD FWT strength of the Redux 319 showed a slight increase in strength from the short cure cycle to the single bondment cure cycle, however a significant reduction in strength was exhibited after four bondment cure cycles. Two of the five specimens cured with four bondment cure cycles exhibited test or fabrication errors and data was only able to be obtained for the remaining three specimens. Due to the high test error rate for the specimens cured with 4x210 minute cure cycles, the specimen prep and test methods are somewhat suspect for this particular data set.

The 225°F wet FWT specimens exhibited numerous invalid failure modes for specimens cured using both the short 90 minute cure cycle and the single bondment cure cycle. Two of the five 90 minute cure specimens and four of the five single bondment cure cycle specimens yielded a failure mode between the facesheet and the aluminum block adherend. The relatively bare aluminum that is exposed on the failed surfaces would indicate that these bonded surfaces may not have been properly prepped prior to bonding. While the numbers resulting from these specimens do not tell us the ultimate FWT strength of the adhesive at these cure and test conditions, the results do show that the material is minimally capable of achieving these strengths which provides some insight into the true performance of the material. The results of the ETW specimens cured with 4x210 minute cure cycles were able to achieve valid failure modes, and show that the reduction in strength at these test conditions is similar to the reduction in properties seen by the EA9689 and EA9658 adhesives at similar test conditions.

Table 23

Redux 319 FWT Results

	FWT Ultimate Strength (psi)					
	RTD			225F Wet		
Sample	90	210	4x210	90	210	4x210
1	1590.5	1732.3	-	425.0	-	602.8
2	1630.3	1816.5	1596.8	402.8	487.8*	884.8
3	1739.3	1759.0	1585.5	399.5	502.5*	561.0
4	1569.5	1699.8	-	447.8*	484.5*	578.0
5	1849.5	1625.0	1488.8	490.3*	436.8	600.0
Average	1675.8	1726.5	1557.0	433.1	477.9	645.3
StDev	117.10	71.08	59.37	37.40	28.51	134.94
CV	0.07	0.04	0.04	0.09	0.06	0.21

* Specimens exhibited invalid failure modes or test anomalies

Figure 19. Redux 319 FWT Failed Specimens – RTD Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

Figure 20. Redux 319 FWT Failed Specimens – 225F Wet Condition. Shown from top to bottom: 90 minute cure cycle specimens, 1x210 minute cure cycle specimens, 4x210 minute cure cycle specimens.

CHAPTER IV

GENERAL CONCLUSIONS

Conclusions

To better understand the effects of extended cure durations on the resultant physical and mechanical properties film adhesives, this thesis study investigated the degree of cure, onset of glass transition, rheological behavior, and mechanical performance of three unique aerospace-grade film adhesives.

Through differential scanning calorimetry (DSC), it was determined that the longest duration thermal exposure during cure, four cycles at 350°F for 210 minutes each, achieved an increased degree of cure over shorter duration cure exposures. This would indicate that the additional cure exposure helps to promote additional polymer network development for each type of monomer structure during the diffusion-controlled phase of the conversion reaction, though the decrease in degree of cure from the 90 minute cycle to a 210 minute cure cycle brings the accuracy of the 90 minute cure results into question due to the use of different DSC equipment.

The hypothesis that increased cure duration would yield increased glass transition temperatures was supported by the performed DMA testing. For both dry and wet conditions, all three adhesives studied exhibited equivalent or improved Tg values with the four 210 minute cure cycle exposure as compared to the 90 minute or 210 minute cure exposures. From these results, a strong relationship between degree of cure, glass transition temperature, and cure duration can be seen. The EA9658 adhesive with a polyfunctional epoxy resin and aromatic polyamine curing agent exhibited the least degraded wet Tg, indicating that the highly crosslinked, aromatic structure shows

improved resistance to moisture absorption over the less aromatic structures such as the bisphenol A epoxy resin of the Redux 319.

The rheological behaviors during a dynamic temperature ramp of the EA9689 and EA9658 adhesives were determined to be very similar as shown by their similar minimum viscosities and temperatures at which the minimum viscosities were reached. In contrast, the Redux 319 adhesive exhibited a higher minimum viscosity and much greater temperature at which the minimum viscosity was reached. This difference in rheological performance is significant, and must be taken into consideration when selecting an adhesive for use in a composite bondment material system. The more gradual increase in viscosity of the EA9689 and EA9658 adhesives may indicate the presence of multiple curing mechanisms occurring, while the sharp increase in viscosity of the Redux 319 would indicate a simpler, single cure reaction occurring at a specific temperature.

The V-notch shear properties of the adhesive as a function of cure duration were determined to be dependent on the adhesive being studied. While the EA9689 showed an overall slight decrease in ultimate shear strength with increasing cure duration, the EA9658 adhesive showed improved ultimate shear strength with the single 210 minute cure cycle and four 210 minute cure cycle exposures. The Redux 319 adhesive also showed improved shear strength with increased cure duration when tested at RTD conditions, however the performance at 225°F wet conditions suffered significantly as the test conditions were above the adhesive's glass transition temperature in the wet condition. Due to the inconsistent data of percent weight gain via moisture absorption for

the V-notch shear specimens, conclusions were not able to be made about the relationship between percent moisture uptake and mechanical performance.

The results of the flat-wise tensile (FWT) testing showed similar trends to the results of the V-notch shear testing. The EA9689 adhesive showed a small reduction in FWT strength with increasing cure exposure for both dry and wet conditions, while the EA9658 adhesive exhibited the greatest FWT strength after four 210 minute cure cycles for both dry and wet conditions. Although the Redux 319 adhesive showed an improvement in RTD FWT strength when increasing cure duration from 90 to 210 minutes, the lowest RTD FWT results were seen after four 210 minute cure cycles. The FWT testing of the Redux 319 adhesive encountered a significant number of test errors as a result of specimen fabrication, bringing the accuracy of the data into question.

From the mechanical test results, different conclusions may be drawn between the different adhesives. The results of the EA9658 adhesive best support the hypothesis that increased physical properties resulting from increased cure duration are strongly related to improved mechanical performance. The EA9689 adhesive displayed an inverse trend to the EA9658 adhesive, with the increased cure duration test specimens exhibiting some of the lowest mechanical properties. The Redux 319 adhesive exhibited a unique trend in mechanical test results, with the greatest values typically achieved with the 210 minute cure cycle, and lowest results after four 210 minute cure cycles. While the more aromatic EA9689 and EA9658 adhesives saw similar degradation as a result of moisture absorption, the bisphenol A based Redux 319 saw a much more significant degradation as a result of moisturization which would indicate the larger, more aromatic structures show a greater resistance to the degrading effects of moisture intrusion.

Future Research Considerations

Through the generation and examination of test data supporting this thesis study, numerous considerations for future research were identified. The first, and most significant area of focus would be to better characterize the chemical structure of the film adhesives under study. While the specific chemical compositions of commercial epoxy film adhesives are complex, proprietary blends, the analysis of the adhesives via FT-IR analysis would provide additional insight into the chemical structure of the B-staged epoxy. Due to mitigating circumstances, this type of testing was unable to be performed within the scope of this study.

A better understanding of the effects of extended cure duration on the mechanical properties of the adhesives may be achieved through the selection of different types of mechanical testing. While the FWT testing using aluminum honeycomb core to drive failure into the adhesive material has shown to be reliable method of generating mechanical property data (as long as proper specimen preparation is conducted), the shear properties of the adhesive might better be determined through other types of testing. While the V-notch style of shear testing was selected for this study due to the small specimen size and ability to generate modulus data through the inclusion of strain gauges, the wet conditioning process highlighted the sensitivity of the strain gauges to moisture. With the strain gauges compromised, the value of the V-notch configuration loses some of its appeal. To generate more consistent, reliable adhesive shear data, double-lap shear testing per the methods of ASTM D3528 may be employed.

Another significant consideration when characterizing a film adhesive for use in a structural composite bondment is the compatibility of the adhesive with the laminate

resin system and cure cycle. For this study, all adhesive test specimens were cured with an oven cure cycle in contrast to an autoclave cure cycle, which adds the variable of pressure into the curing process. During cure, certain adhesives can exhibit foaming or bubbling as volatiles are released when placed under vacuum. The significant porosity discovered in the V-notch shear specimens would indicate that volatile content may be a concern in a pressure-controlled autoclave cure cycle. The study of cured composite bondments would also allow for better investigation of the flow characteristics of the adhesive and the adhesive's ability to form strong, consistent fillets on the honeycomb cell walls.

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